Eugen Müller (1905–1976)

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Keyword: Reminiscences

Dates and Milestones in Eugen Müller's Life

Eugen Friedrich Wilhelm Müller was born on June 21, 1905 in Merken near Düren in Rhineland as the son of the (later independent) paper merchant Friedrich Müller and wife Claire Müller, née Freiberg. Eugen Müller grew up in Berlin, where, aged 18, he completed his schooling at the Falk Realgymnasium in 1923. After initially fluctuating between further education in the fine arts as a painter and studying science, he chose chemistry. In both areas he could use careful observation, intellectual pervasiveness, and creativity. Painting remained a lifelong hobby for him. From Easter 1923 to Easter 1925 he studied chemistry at the Friedrich Wilhelm University in Berlin along with the subjects physics, technology, and philosophy, for which he completed the first collective examination with Willy Marckwald. In the summer semester of 1925, he moved to the Albert Ludwig University at Freiburg in Breisgau, but then returned to Berlin for the winter semester of 1925. There, in December 1925, Eugen Müller completed exams in chemistry with Hofrat ("court councillor") Wilhelm Schlenk, and in physical chemistry in March 1926 the second collective exam aged 21 (which would now correspond to a German "Diplom").

Between the summer semesters of 1926 and 1927 he completed his dissertation[1] in Berlin with Wilhelm Schlenk with the title "*Über neue alkaliorganische Verbindungen*" (On New Alkaliorganic Compounds), in which he described

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[‡] Translation from German into English by Dr. Stephen Horner, Darmstadt. Original, unabridged version in German: see Supporting Information.
⌨ Supporting information for this article is available on the WWW under http://www.eurjoc.org or from the author.

the addition of sodium to multinuclear aromatic hydrocarbons using an inert atmosphere and Schlenk techniques. On March 2 1928, the 23 year old completed his studies with a Dr. phil.; Max Planck was one of his examiners. His thesis was only 43 pages long, but with carefully detailed experimental work. In those days, students had to synthesize most of the starting materials themselves and had to characterize each of the products by elemental analysis and molecular mass determinations.

After completing his PhD, Eugen Müller remained at the Chemical Institute of the Berlin university from 1928 to 1929, first as an assistant and then as a scholar of the *Notgemeinschaft der Deutschen Wissenschaft* (later named Deutsche Forschungsgemeinschaft, DFG; German Scientific Support Society). There, in the Schlenk group, he met his later wife Ilse Martha Rodloff, who was born in 1903 in Jarotschin near Posen (Poland, then Prussia). Between 1909 and 1916 she attended the state *Lyceum* in Meseritz, then the Luisen school in Posen and finally, forced to move to Berlin owing to the political situation, from 1919 the Auguste Viktoria school, where she completed her *Abitur* in 1922. From 1923 to 1926, she studied chemistry in Berlin and Freiburg, and completed her PhD in 1928 also with Wilhelm Schlenk with a thesis[2] on diphenylacetaldehyde. The wedding followed in 1930. The marriage resulted in three children: daughters Heide and Renate in 1937 and 1939, and son Peter in 1941.

From 1929 to 1933, Eugen Müller worked at the Technical University in Gdansk/Danzig as a lecturer's assistant to Alfred Wohl. On his way to scientific independence, Eugen Müller showed the *cis–trans* isomerisation of azoxy compounds by UV and dipole-moment measurements after pre-

parative separation.[3] This work led to his "Habilitation" in Danzig on March 3, 1933 aged 28, with a subsequent appointment as senior assistant to Adolf Butenandt. He then concentrated, together with his wife Ilse Müller-Rodloff, on the research of organic radicals, and in particular evidence for the existence or non-existence of diradicals. Spurred on by the newly appointed Danziger inorganic chemist Wilhelm Klemm, it was shown that such compounds are paramagnetic, which was the first time that magnetic investigations had been carried out in organic chemistry with a Gouy magnetic balance.

From 1937 to 1941, Eugen Müller was active at the Friedrich Schiller University in Jena, initially as senior assistant, and then from 1939 as deputy head of department in organic chemistry. The continuation of the magnetochemical investigations resulted in a series of 24 communications.

In 1941 he received a chair in organic chemistry at the University of Frankfurt/Main and was made scientific director of the newly instigated German Research Institute for Polymer Chemistry. This institute was however destroyed by a bombing raid in 1944 a few weeks after it was opened, as was the Institute for Organic Chemistry and the family's house in the same year. Scientific research was difficult under such catastrophic circumstances, but Eugen Müller was able to successfully acquaint himself with the chemical and technical problems of polymer chemistry, such as investigating the crystallization velocity of plasticizers in the presence of polymers.[4] He held his chair until after the end of the war in 1945, when he was dismissed as a consequence of Article 52 of the Allied Military Law, as he had been a member of the Nazi party since 1935. Al-

Figure 1. Oil painting "Blühende Wiese" ("Meadow in Bloom", original size 65 × 49 cm, chromatic), Eugen Müller, 1951.

though he was regarded as a "Mitläufer ohne Maßnahmen" ("nominal member without sanctions"), he did not immediately regain a position as professor.

A difficult period in Eichtersheim near Heidelberg followed from 1945 to 1950, where he provided for his family of five as a private teacher, as scientific author (notably of his textbook, discussed below), and through his hobby as painter the sale of several paintings, such as that of the "Meadow in Bloom" shown in Figure 1. His wife Ilse also brought financial support by teaching at a secondary school in Sinsheim/Elsenz.

In 1949, Eugen Müller was asked by Otto Bayer and Hans Meerwein to become Chief Editor of the *Chemiker-Zeitung* (*Chem.-Ztg.*) and in 1950 the Editor in Charge for the newly conceived fourth edition of the Houben–Weyl Handbook "*Methods of Organic Chemistry*". He remained faithful to this task, which he initially carried out together with his wife, until his death.

In 1949, he turned down offers of chairs in organic chemistry at the universities of Leipzig and Jena, but accepted a position as guest professor at the Technical University of Stuttgart in 1950–1951.

On February 2, 1952 he took up a chair in the Chemical Technology of Synthetic Fibres at the University of Tübingen, a position which was later renamed Applied Chemistry. This professorial position was created by a foundation of the Hamburg Phrix works; a new institute building was planned, facing the old chemical institute, at a cost of two million German marks (DEM), and a monthly research grant of 10000 marks. Unfortunately the Phrix Foundation suffered financial difficulties shortly after building work had begun, so that the new building was only later built on a smaller scale with state funding as the present Lothar Meyer building. To alleviate the acute lack of space, Walter Hückel offered laboratory space in 1953 in the upper floor of the just completed new building for pharmaceutical chemistry beside the old chemical institute.

In 1957, Eugen Müller was appointed successor to Georg Wittig as the director of the chemical institute of the Eberhard Karls University in Tübingen. [*Editorial note:* an obituary to Georg Wittig by Werner Tochtermann was published in 1997 in *Liebigs Annalen* (pp. I–XXI) and is available as part of the Chemistry Society Backfile Collection in Wiley InterScience online; see http://www3.interscience.wiley.com/journal/27380/home/biog_notes1.html#lan]

The position in applied chemistry was not reappointed, and Eugen Müller held this position until his retirement.

Eugen Müller's textbook,[5] "*Neuere Anschauungen der Organischen Chemie*" ("*New Perspectives in Organic Chemistry*"), which first appeared in 1940 with 391 pages, attained great importance. A completely reworked second edition was published in 1957, with the subtitle "*Advanced Organic Chemistry*" and having 550 pages. Owing to his editorial work with Houben–Weyl, having approximately two volumes published per year, he had the means to survey the complete scope of organic chemistry of the time.

Eugen Müller's research into the chemistry of organic free radicals at carbon and in particular at oxygen (phen-

oxyls or aroxyls) is now textbook knowledge. These radicals have relevance in theoretical (spin distribution) and preparative (reactivity) aspects of organic chemistry. His investigations into diazomethane, and the first preparation of isodiazomethane, were sensational. The use of diazomethane in the BF_3-catalyzed methylation of alcohols and amines and the homologation of ketones and aromatics by copper bromide catalysis are extremely important preparative methods. Eugen Müller's Tübingen process for the photooximation of cyclohexane could be successfully developed for the production of Perlon™ (present name: PA6) via cyclohexanone oxime and subsequent rearrangement to ε-caprolactam, and thus to a technical realization in Japan (see below).

A scientific lecture tour in the USA in 1966 left many impressions on Eugen Müller, whose activity had previously been concentrated in Europe. After becoming an emeritus professor in 1973, he continued for a further two years until his successor Michael Hanack arrived in 1975. A sudden heart attack on July 26, 1976 unexpectedly ended the active working life of Eugen Müller. A manuscript for a further scientific publication lay finished on his writing desk.

The Scientific Work of Eugen Müller

In the following sections, the research areas are grouped into themes, and contain the publications that are discussed. Reviews on a theme are referenced in the section titles. Publications not directly referred to in the text are given at the end of the section, to give a thematically ordered bibliography of the complete scientific work of Eugen Müller.

Organoalkali Metal Compounds: The first scientific work from Eugen Müller and his later wife Ilse Rodloff are contained in seven publications with 18 co-workers of the Schlenk group in two volumes of *Liebigs Annalen* in 1928, with the overall theme "*Organoalkali Compounds*".[6] Eugen Müller used Schlenk techniques[7] with moisture- and oxygen-free inert gas, and came across the metal ketyls **2**, a compound class of radical anions, which was of great importance for his subsequent work on radicals. Work on organoalkali metal compounds[8–10] was also carried out in later years.

Various Initial Works: At the beginning of his scientific activity, Eugen Müller produced several results of varying themes. In analogy to the Paneth thermal decomposition of $Pb(CH_3)_4$, in Danzig lead was converted with activated hydrogen into gaseous PbH_4 and detected, upon thermal decomposition, to a lead mirror.[11] In two publications, experimental details of Perkin's synthesis were investigated.[12,13]

A progress report described the published results from 1929 to 1931 concerning alicyclic and aromatic compounds[14] and a handbook publication detailed the magnetic methods used to investigate organic compounds.[15] The introduction to a discussion conference of the German Bunsen society which Eugen Müller organized in Frankfurt

in 1942 outlined the historical development of the significant concepts of constitution[16] in organic chemistry.

Azoxybenzenes:[3] The first independent investigations[17–21] between 1932 and 1935 on the way to his habilitation involved evidence for the *cis–trans* isomerisation of azoxybenzene and its ring-substituted derivatives. This was achieved after separation and isolation of the isomers by very modern physical methods of the time, namely UV spectroscopy and dipole moment measurements.

The melting point and dipole moment μ of the stable *trans*(*Z*) isomer (**1a**) and the unstable *cis*(*E*) isomer (**1b**) are very different. The chemistry of azoxy compounds was summarized in 1936 in a monograph[3] which was no doubt based on his habilitation Thesis, which has not survived.

1a: *trans* (*Z*)
m.p. 36 °C; μ = 1.7 D

1b: *cis* (*E*)
m.p. 84 °C; μ = 4.67 D
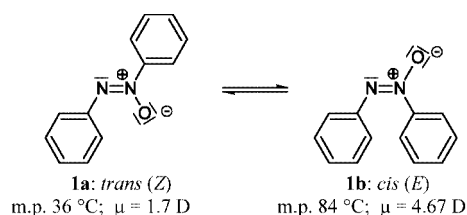
The thermal decomposition of phenylhydroxylamine leads, after disproportionation, to the intermediates nitrosobenzene and aniline, which condense to the final products azobenzene and water.[22]

Magnetochemistry of Organic Radicals[23–30]

The principal work of Eugen Müller between 1934 and 1945 was the magnetochemistry of organic compounds. In a series of 24 publications with the general title "*Magnetochemical Investigations of Organic Substances*",[40] the use of a Gouy balance to determine temperature-dependent paramagnetic susceptibility of radical compounds was described. The results were summarised in several reviews noted above and the methods later again critically examined.[31,32]

Research themes that were investigated in particular were: free carbon radicals, for example the temperature-dependent cleavage of hexaphenylethane to the triphenylmethyl radical,[33–36] an account of the pentaphenylcyclopentadienyl radical,[35] the stability of nitrogen radicals,[33,37] the possible existence of diradicals,[38–42] and the radical character of metal ketyls[43–45] compared to the potassium salts of 1,2-diketones.[46]

[The crystalline dimerisation product of the triphenylmethyl (trityl) radical does not exist as hexaphenylethane, but was shown by NMR spectroscopy to be 1-diphenylmethylene-4-trityl-2,5-cyclohexadiene: H. Lankamp, W. T. Nauta, C. MacLean, *Tetrahedron Lett.* **1968**, 249–254; H. A. Staab, H. Bretschneider, H. Brunner, *Chem. Ber.* **1970**, *103*, 1101–1106.]

Metal ketyls in the form of radical anions **2** are obtained by the addition of alkali metals to non-enolisable ketones. In general, various ketones reacting with metallic potassium give, depending on the structure, dimeric diamagnetic pinaconates **3**, such as 2,6-dimethyl-γ-pyrone,[43] partially para-

magnetic as meriradical compounds, such as benzil potassium[46] **4**, which was obtained according to Eugen Müller as a quinhydrone-like π-complexed mixture comprising benzil potassium (**4a**), stilbenediol potassium (**4b**) and benzil (**4c**), or genuine paramagnetic monomeric radical metal ketyls, such as potassium benzophenone (**2**) with two mesomeric limiting structures **2a** and **2b** and a radical content which was experimentally determined to be 80%.[45]


2a **2b** **3**

4a **4b** **4c**
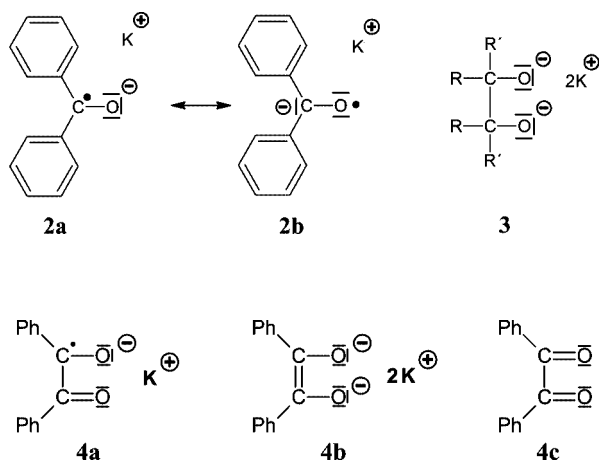
A central question was experimental evidence for the existence of reputed[39,41,42] or genuine[47–50] carbon diradicals. Their nonexistence, now shown experimentally, was explained with the then advanced mesomer theory, with a delocalisation and coupling of the diradical electrons with antiparallel spins to a diamagnetic quinoid system. The verified presence of parallel electron spins in verifiably genuine diradicals occurs with steric or positional hindrance of conjugation.


5a **5b**
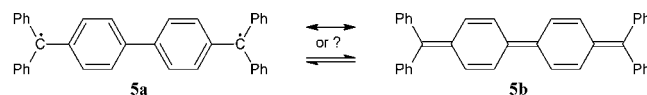
This situation was first clarified by Eugen Müller with the following systems. The Chichibabin hydrocarbon **5** was long thought to have two unpaired radical electrons with parallel spins (**5a**). Müller's magnetochemical investigation[39] showed that **5** is however diamagnetic, so that the quinoid structure **5b** must be responsible. Similarly, for Thiele's tetraphenyl-*p*-xylylene[41] **6b** and the N-heterocycle[39] with structure **7a** were found to be diamagnetic. Compound **7a** can comproportionate with the diamagnetic dipyridinium dichloride **7b** to a paramagnetic dipyridinium subchloride **7c**.[51] In contrast, for *meta*-substituted Schlenk hydrocarbon **8**, a genuine diradical is present (6% in a benzene solution at 74 °C).[39]

If the conjugation between the biphenyl rings of hydrocarbon **5** is prevented by bulky *ortho*-substituents, a genuine diradical also arises, as for example in **9a** (30% radical character in an orange-red 2.5% benzene solution at 80 °C).[47] Variation of the structure by multiple biphenylyl substitution[48] to **9b** increases the diradical character to 75% in 2% benzene solution at 80 °C.

6a   or ?   6b

7a   +   7b

7c

8   9a : R =   9b : R =
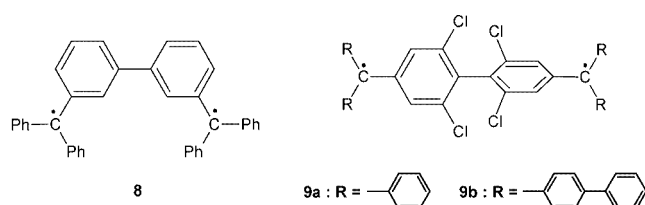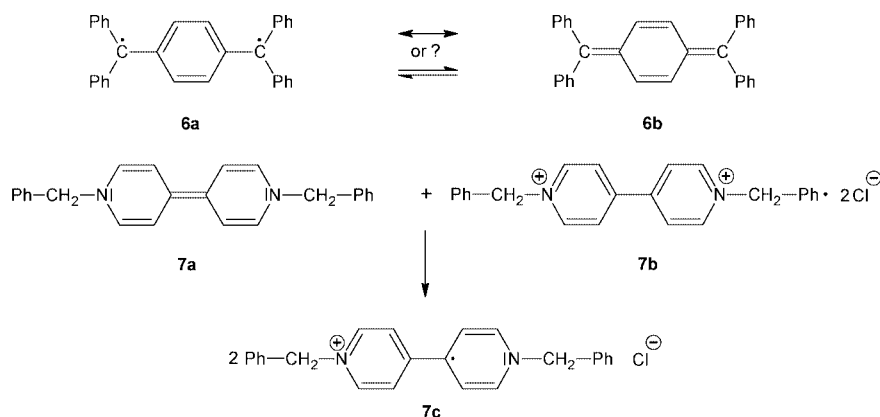
If the distance between the two radical centres is increased by insertion of a phenyl ring to terphenyl derivative[52,53] **10** or to quaterphenyl compound[54] **11**, the diradical character decreases in 2 % benzene solution at 80 °C to 40–55 %. These compounds were described by Eugen Müller as being diradicaloids,[26] as parallel and antiparallel spins can be found together in thermal equilibrium.

10

11
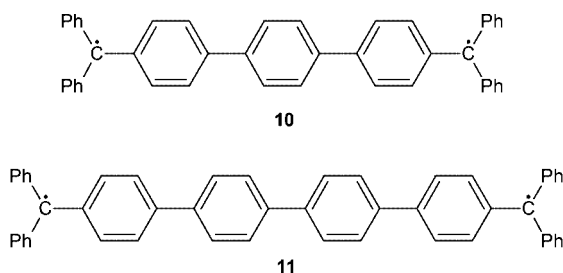
For hydrocarbon **5**, Eugen Müller investigated the magnetic influence of a pairwise symmetrical substitution with methyl groups in positions A to D in the potential diradicals **12**.[55] Only methyl group substitution in the sterically relevant *ortho* and *meta* positions (A,A′ and B,B′) of the biphenyl unit lead to paramagnetism, with 27 % diradical character for **12a** and 43 % for **12b** in 2 % benzene solution

12
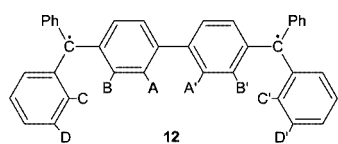
12a: A = A′ = CH₃: diradical content: 27 %
12c: C = C′ = CH₃: diamagnetic
12d: D = D′ = CH₃: diamagnetic
**12b**: B = B′ = CH₃: diradical content: 43 %

at 80 °C. **12c** and **12d** are in contrast diamagnetic with undisturbed quinoid conjugation. Further magnetochemical investigations can be found in ref.[56–60]

Oxygen Free Radicals (Aroxyls)[61,62]

In Tübingen, Eugen Müller's investigations into radicals moved into a new area from 1953 with the synthesis of stable oxygen radicals, the aroxyls[63–65] or phenoxyls, leading to about 50 publications. At almost the same time and independently, Cook[66] described in a publication of August 25, 1952 the oxidation of 2,4,6-tri-*tert*-butylphenol **14**,[67] which had been known of since 1945, with PbO₂ to give a phenoxy radical, which is blue in solution. As the first publication from Eugen Müller[63] was received on November 25, 1953 and cited Cook's work, the latter has the right of discovery. However, Eugen Müller had isolated the so-called "blue" aroxyl **13** in crystalline form and had thoroughly investigated the properties of the new class of compound.[64] The prototypical compound **13** can be obtained by oxidation of the phenol **14** or by bromine elimination with metallic silver from **15**.

The triple ring substitution with bulky *tert*-butyl substituents is utilised to prevent dimerisation of the oxygen radicals to give a peroxide by the two *ortho tert*-butyl substituents and to also block dimerisation by O–C bonds in the mesomeric radical *ortho* or *para* positions. In 1957, K. Dimroth[68,69] synthesised the structurally related, stable 2,4,6-triphenylphenoxyl radical. This compound is sterically and mesomerically stabilised and in solution is found to have a temperature- and concentration-dependent equilibrium with the peroxide.

The phenoxyl or aroxyl **13** can be obtained as a dark blue, crystalline paramagnetic solid. The unpaired radical electron at the oxygen atom in form **13a** can be delocalised to the *o*- and *p*-ring positions, as shown in structures **13b**. Furthermore, zwitterionic structures **13c** with polarised C=O bonds and the structures **13d** with radical spin density in the *meta* position, which is allylically stabilised by 1,3-delocalisation, also participate. The ionic structures **13d** are additionally stabilised by the inductive effect of the *tert*-butyl groups and an allylic 1,3-charge localisation. The
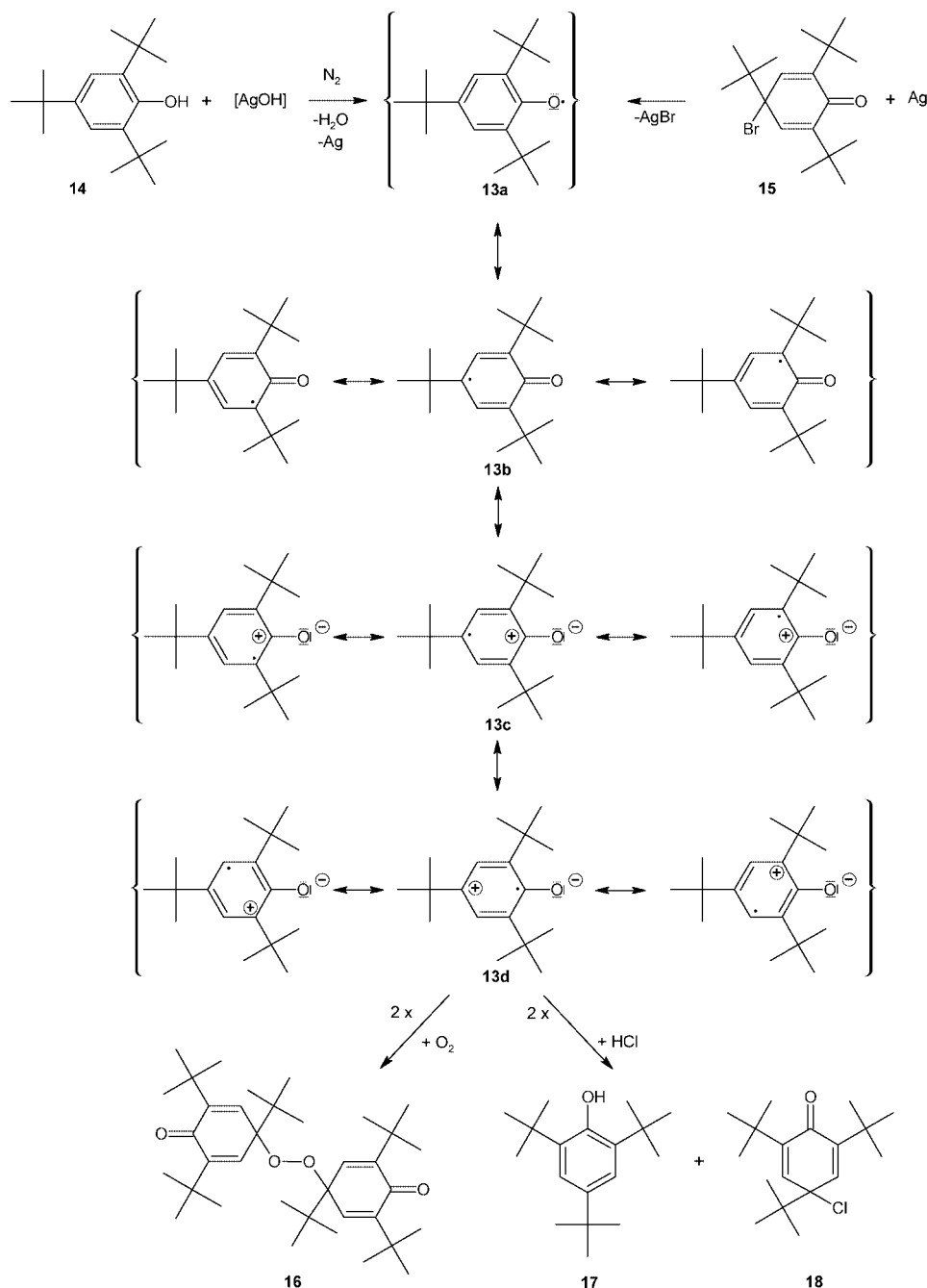
complete picture of the delocalised electron structure characterisable by the mesomeric structures **13a–d** of the aroxyls was described by Müller as being a special $5\pi^+$ resonance system.[70] The aroxyl **13** is highly sensitive to oxygen and acids. Reaction with O_2 in solution leads to peroxide[64] **16** by addition in the *para* position, and HCl gives rise to disproportionation to **17** and **18**.[71]

The earlier magnetochemical measurements on radicals was complemented by the then new, much more sensitive and informative ESR spectroscopy.[72–74] This method allowed, in addition to evidence for paramagnetism, information on the spin density distribution in the ring system.[75] For this purpose, also ^{13}C isotope substitution was

carried out.[76] The Institute for Organic Chemistry in Tübingen was one of the first in Germany that had an ESR spectrometer before the end of the 1950s.

The substitution pattern of the aroxyles was varied with methoxy,[77] *tert*-butoxy,[78,79] triphenylmethyl,[80] phenyl,[81,82] or cyano[83,84] substituents in the 4- or 2-position. Polyhalogen substitution of the ring[85] also led to aroxyls.

Aroxyls can be used preparatively in the synthesis of aryl alkyl ethers from hydrocarbons, of aryl esters from aldehydes, and of quinol ethers from phenols,[86] and in the synthesis of thioquinol ethers.[87] The dehydrogenation of phenols with aroxyls was also investigated.[88,89]

Further reactions of the oxygen radicals that were studied were the nitration[90] of **13**, several studies on the dehydrogenation with phenoxyls,[91–96] the reaction of aroxyls with Grignard reagents[97] and other organometallic compounds,[98] and with isonitriles[99] and diazoalkanes.[100–102] In one work, the possibility that organolead radicals form thermally was discounted by ESR spectroscopy.[103]

New Heteroatom-Substituted Radicals: Expansion of the concept of free aroxyls led to ESR investigations of structurally analogous radicals with heteroatom substituents, such as sulfur,[104,105] selenium,[106] phosphorus,[107–109] and arsenic[110,111] in the *para* position. The spin density distribution determined by ESR spectroscopy in the aroxyl ring served as an aid to the determination of the degree of mesomeric bond involvement of these *para* heteroatom substituents.[112]

The sesquixanthydryl system **19** forms a planaritised triphenylmethyl radical[113] through the *ortho* bridging via oxygen. Stable *ortho*-semiquinone salts, such as **20**, can also be formed.[114,115] Compound **21** was synthesised[116] and is a stable oxygen diradical. Relatively unstable aroxyls form from alkyl or carbinol substitution in the *para* position.[117]

Further work on aroxyls can be found in ref.[118–121] The properties of free radicals, and their applications and limits of the magnetic methods in radical chemistry are described in reviews.[122,123]


19

20: M = Li, Na or K

21
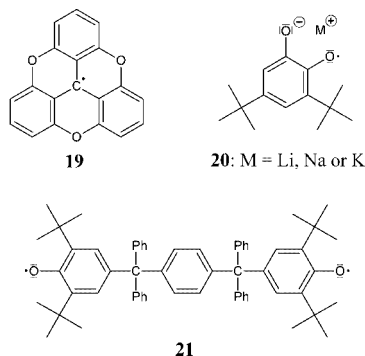
Aliphatic Diazo Compounds

Isodiazomethane: Diazomethane is a compound that accompanied Eugen Müller from the start of his scientific endeavours,[124–126] and between 1954 and 1969 led to a series of 28 investigations into diazomethane.[127–129] Starting with the sensational preparation of isodiazomethane[127] in 1954, and peaked with the definitive description of its structure in 1968 as fulminic amide.[129,130]

$$CH_2N_2 + H_3C-Li \longrightarrow [CHN_2]^{\ominus} Li^{\oplus} + CH_4$$

22
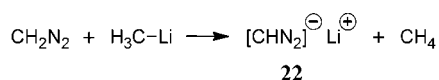
Lithiation of Diazomethane: In the reaction of methyllithium with diazomethane[131–134] in diethyl ether, methane is formed along with a precipitate of the lithium salt **22**, which explodes in the air when dry.

Careful protonation of **22** with aqueous ammonium chloride solution at –15 °C in diethyl ether results in a pale yellow ether phase, and in the aqueous phase formyl hydrazine and hydrazine can be detected. Removal of the dried ether at –50 °C gave a yellow liquid that decomposed by release of dinitrogen when warmed above 15 °C, and which exploded above 35–40 °C. This isodiazomethane was initially thought, as was hydrogen azide (HN_3), to be the symmetrically protonated compound[135] **23**. With solid KOH, it rearranges to its tautomer, the starting compound diazomethane.

23

24
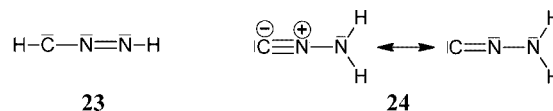
In 1968 however, it was shown by IR and ^1H NMR spectroscopy that for isodiazomethane, not structure **23**, but rather its tautomeric structure, the amide of fulminic acid (CNOH) or *N*-isocyanamine **24** is correct.[129,130] An investigation of the reactivity of **24** involved saccharin and thiosaccharin.[136]

A new diazomethane synthesis was given by the reaction of dinitrogen monoxide with methyllithium.[137,138] This reaction produces methane, lithium hydroxide, and diazomethyllithium **22**, which by alkaline hydrolysis gives diazomethane, and through careful protic hydrolysis isodiazomethane **24**. The reaction of methylamine with nitrosyl chloride is a further diazomethane synthesis[139,140] which could find technical application. Kinetic studies of the photolytic and thermal decomposition of diazomethane in the presence of cyclohexane and cyclohexene give evidence for the rate-determining formation of methylene, which inserts into all C–H bonds and adds to the double bond.[141]

BF3-Catalysed Methylation of Alcohols and Amines with Diazomethane:[142] The most important preparative reaction of diazomethane is the methylation of substrates with acidic protons to give methyl derivatives, for example from carboxylic acids to methyl esters. Eugen Müller extended the reaction by Lewis acid catalysis. BF3 catalysis allows alcohols[143,144] and amines[145,146] to be methylated with diazomethane. $AlCl_3$ can also be used as catalyst for this purpose.[147]

Catalytic Homologation with Diazoalkanes:[142] As a further important reaction, Eugen Müller introduced the Lewis acid catalysed methylene homologation of cyclic compounds with diazomethane. He demonstrated this with cyclic ketones;[148–151] large ring ketones are of importance in the aroma industry as musk-like substances. Spiroalkanones,[152] steroid hormones[153,154] and steroid ketones[155–157] were also reacted.

Aromatic compounds can undergo a carbene addition (cyclopropanisation) or ring expansion by CH2 insertion with diazomethane using CuBr as catalyst.[160] Benzene[161,162] or toluene[163] thus lead to tropylidene derivatives **25**. Hexamethyl Dewar benzene[164] reacts to give **26a** and **b**, although a thermal ring opening of **26a** to **26c** takes

place only above 180 °C. Naphthaline[165] gives the products **27a**–**c**. The thermal ring opening of **27a** to **27b** only occurs above 260 °C. Anthracene can be homologised to the three compounds **75a**–**c**.[166] Phenanthrene[165,167] forms the adducts **28a**–**c**, and pyrene[168] reacts to give **29**. The five-membered-ring heteroaromatics[169] furan and thiophene give the products **30a** and **c** in yields of 50% and 22%, respectively, and **30a** reacts with an excess of diazomethane to give **30b** in 5% yield. Further publications on diazomethane can be found in ref.[170–174]

Diazotates and Azo Compounds: The potassium methyl-diazotate[175] **31**, which is obtained by action of NOCl on methylamine in the presence of potassium methoxide, can be stored as a stabilised and stable diazomethane and then used in reactions. The anion can be described by two mesomeric structures, the diazotate form **31a** and the nitroso form **31b**. An X-ray structural analysis[176] shows a not completely flat *cis*-(*syn*) arrangement regarding the N–N and the N–O bond, and almost symmetric orientation of the potassium cation to atoms O and N1. In water, protonation occurs to give the tautomeric structures **32a** and **b**. These forms are unstable and decompose by various paths to diazomethane and water, or to methanol and nitrogen.
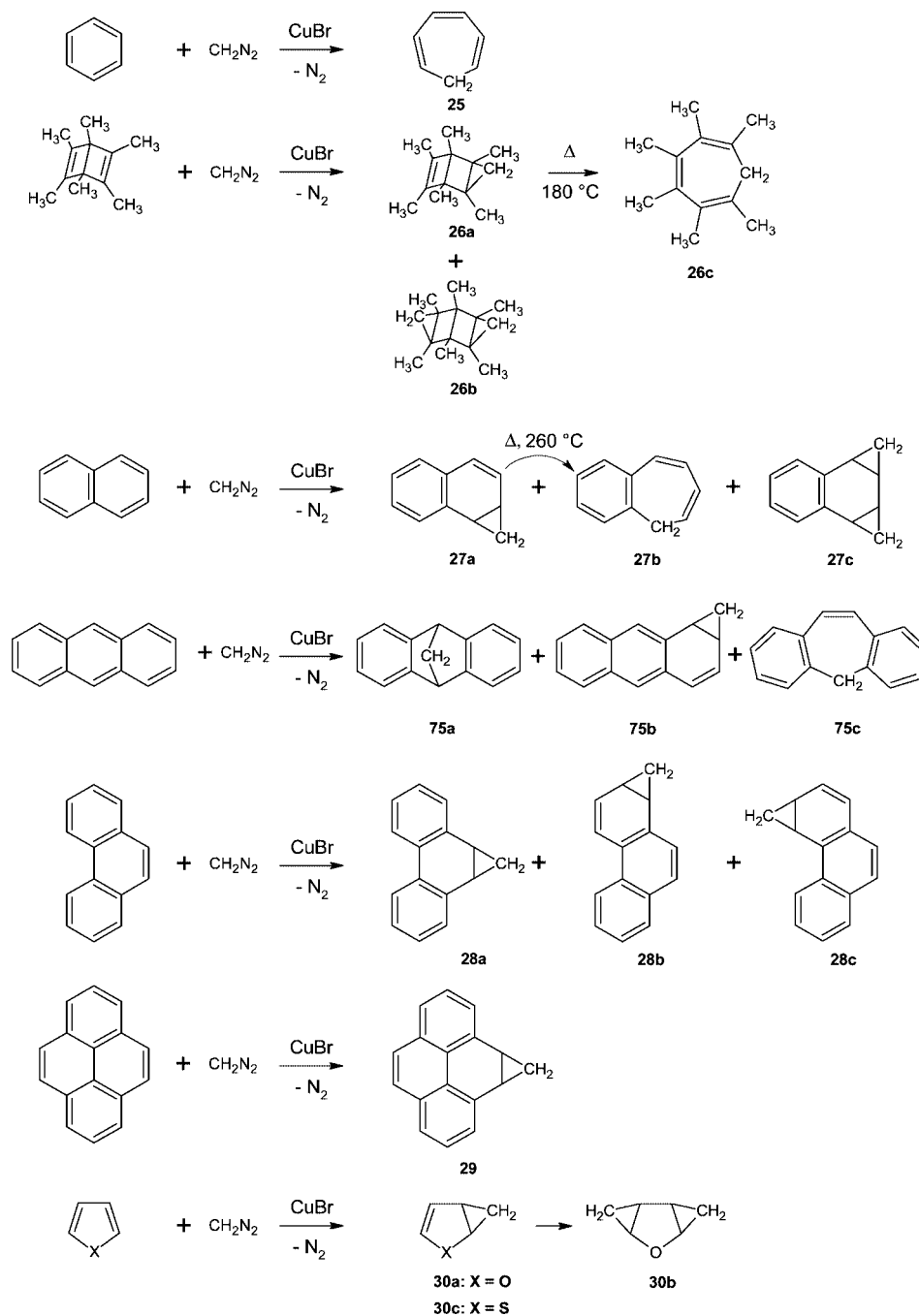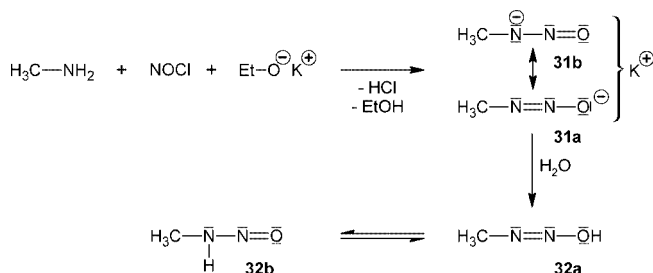
Eugen Müller's path from the aliphatic diazotates leads to the aromatic diazotates **33**. In 1963, he was able to obtain IR spectroscopic[177] evidence that the *syn* and *anti* diazotates formulated by Hantzsch are *cis* and *trans* isomers **33a** and **b**.

*syn (cis)-n-*diazotate   *anti (trans)-n-*diazotate
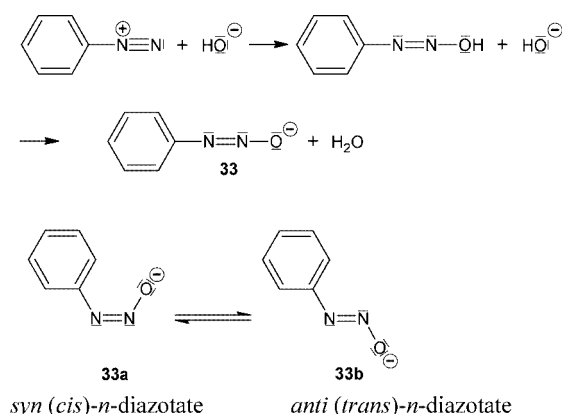
The difference between *n*- and iso-diazotates, for which the oxygen atom is either terminal or bound to the central nitrogen atom, was also investigated.[178] A diethyl ether solution of nitrosyl chloride and primary aromatic amines give at low temperature (–70 °C) primary aromatic nitrosamines, as shown by UV spectroscopy. Their reaction with potassium ethanolate in diethyl ether gave a precipitate of potassium isodiazotate, which is stabilised by electron withdrawing groups, such as NO_2, $COCH_3$, and COPh. At elevated temperatures, a rearrangement to the much more unstable *n*-diazotates **33** occurs, which are stabilised by electron-donating groups (Cl, CH_3, OCH_3) and undergo a rapid azocoupling with β-naphthol.

In contrast to aromatic azobenene, alphatic azo compounds can tautomerise by proton migration. This is shown by the azomethane **34a**,[179] which lies in equilibrium with formaldehyde methylhydrazone **34b**.

Nitroso Compounds: Between 1954 and 1968, Eugen Müller published a series of 19 articles with the series title "*On Nitroso Compounds.*"[180–198] These publications can be described as accompanying scientific investigations to his technical photooximisation[182,201] (see below), as primary aliphatic nitroso compounds tautomerise easily to oximes,

and these can be subjected to a Beckmann rearrangement to amides (see Scheme 2).

Photochemistry:[199–201] Reactions using irradiation – "chemistry with light as reaction partner" – allow alternative reaction paths with excited states. The photochemistry was a central theme of Eugen Müller's work in the area of technical chemistry. In 13 publications between 1963 and 1975, he described photochemical reactions of saturated, linear, or cyclic hydrocarbons in cyanation,[202–203] sulfenechlorination,[204–206] phosphonylation,[207] and as principal reaction of the Tübingen photooximation[201] of saturated hydrocarbons with nitrosyl chloride or nitrogen monoxide (NO) and elemental chlorine with radiation using a high-pressure mercury lamp.[188,191,208,209] The mechanism of this reaction was proposed in 1968,[210] and is shown in Scheme 1. This radical reaction does not involve a radical chain mechanism. The cyclohexyl radical as intermediate is trapped by NO to an oxime without further radical formation, so that the initial chlorine atom must be continuously regenerated by irradiation. The quantum yield and wavelength dependency of the photooximation of cyclohexane was experimentally determined[198] and the influence of deuteration investigated.[181,211,212]
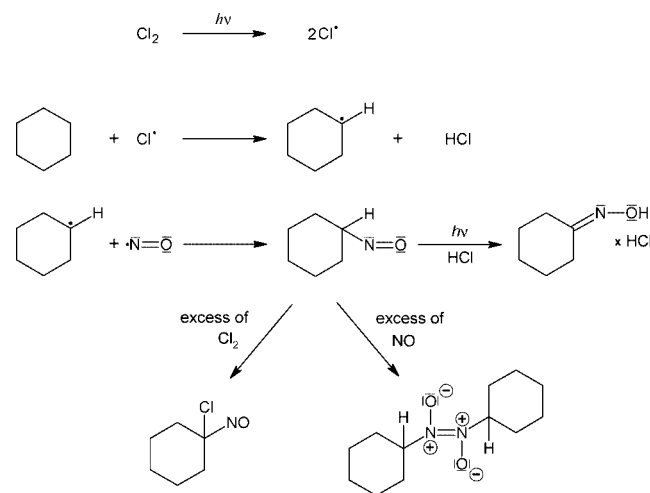
Scheme 1. Mechanism of the Tübingen photooximation.

Phthaloyl-protected amino ketenes could be obtained by photochemical Wolff rearrangement of *N,N*-phthaloyl-α-diazoamides. Trapping reactions with alcohols to give esters or in a [2+2] cycloadditions with *N*-benzylideneaniline to unusual amino-substituted β-lactams.[213,214] The photochemistry of alkynes in the presence of metal carbonyls was investigated concurrently.[215]

Technical Chemistry, Polymers, and Patents: As mentioned already, in 1952, Eugen Müller was appointed to a chair in "Technical Chemistry of Synthetic Fibres," which, under the title Applied Chemistry, he had until he reached emeritus status.

Early publications dealt with the properties of plastisizers[4] and the chemical processes that lead to the formation of synthetic fibres.[216] Many results are described in patents. A CAS database search in the years 1951 to 1971

shows about 50 German and other patents that are not described in Eugen Müller's own publication list. Patents from the Tübingen era dealt with polymeric vinyl ether,[217,218] plastic putties[219] and pastes,[220] water-repelling fibres,[221] various copolymers,[222–224] the synthesis of halogen-free dimers[225] or polymers[226] from halogenated organic compounds, and stain removers[227] from urea or thiourea containing toluene or isooctane (K2R).

Further patents dealt with special compounds for the *N*-methylation of amines,[228] the synthesis of NOCl,[229] (surprisingly) diazomethane[230] and its stable storage form metal methyldiazotate,[231] various ketones[232,233] and nitriles,[234–236] various chlorosulfanes,[237] cycloalkenylglyoxylamides[238] and alkapolyenes.[239] Patents were also lodged relating to acenchinone pigments,[240] naphthacenequinone[241] and pentadiyn-1-one derivatives.[242]

A central theme of Eugen Müller's technical work was the Tübingen photooximation process.[201] The mechanism of the formation of cyclohexanone oxime,[243] which can rearrange to ε-caprolactam, is described in Scheme 1. This compound is of great importance industrially,[244] as it can be polymerised to a valuable synthetic polyamide fibre (Perlon™, PA6 or Nylon 6, see Scheme 2), as the Hoechst chemist Paul Schlack showed in 1938. Müller's photooximation delivered ε-caprolactam from cyclohexane in only two steps and in high purity. In Japan, the Perlon™ synthesis using this method was realised industrially by the Toray company as the PNC process; however Eugen Müller received no licence payments as no patent protection for that country was present.
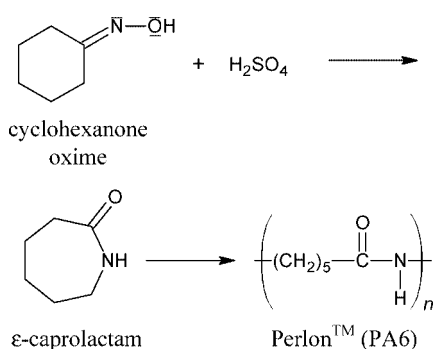
Scheme 2. From cyclohexanone oxime to Perlon™.

The photooximation can also be used successfully to obtain other ketoximes, which is documented in a series of patents.[245–255]

Reactivity of Aromatic *ortho*-Bis(acetylene) Derivatives

The Synthesis of Verdene.[256] From 1966 until after his emeritation, Eugen Müller started on a completely new late area of research, the reactivity of *o*-bis(ethynyl)benzene and analogous aromatic compounds in a series of 43 publications[257,258] with the series titles "*Bis(acetylene) Compounds*" or "*Diyne Reactions*". Starting with thoughts on a possible synthesis of cyclobutadiene derivatives,[257,259,260]

he described the reaction of *o*-bis(phenylethynyl)benzene (**35**, with R = Ph) under irradiation (photochemical),[261–263] by heating (thermal),[263] and in the presence of coordinating transition metals.[264–266]
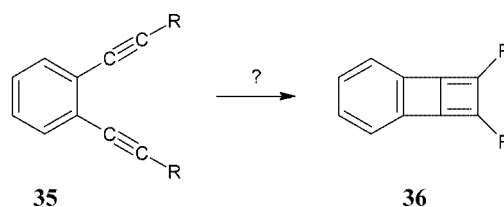
The desired cyclobutadiene derivative **36** could however not be obtained. Instead a dimeric green hydrocarbon was isolated after irradiation, which Eugen Müller named "verdene".[267] The original suggestion for the structure of verdene as bis(azulene) **37** was corrected, through an X-ray structural analysis,[268] to structure **38** as an alkyne-substituted monoazulene[269] in 1971.

Irradiation of structurally related *o*-bis(ethynyl)benzene (**35**, with R = H) gave two positional isomers[262] similar to structure **38**, and the *o*-bis(phenylethynyl)cyclohexene led to a tetrahydroazulene derivative[270] with a hydrocarbon skeleton that is analogous to **38**.
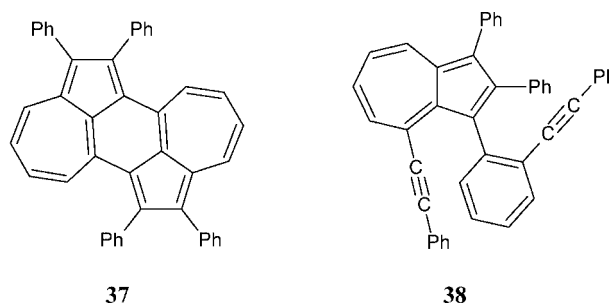
A photochemical control reaction with the vinyl system of *o*-distyrylbenzene leads to a dibenzocyclooctadiene[271] **39** by a dimerisation reaction with condensed four-membered rings arising from a [2+2] cycloaddition.
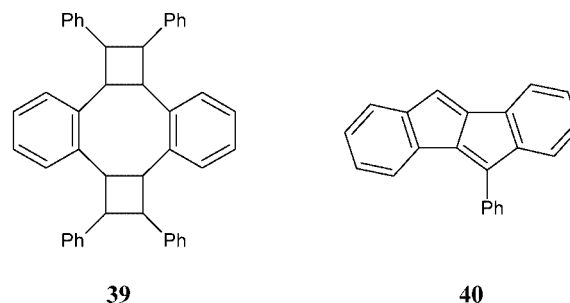
PtCl$_4$ reacts with **35** via an unstable intermediate to form the dibenzopentalene derivative[264–266] **40**. Analogously, in the reaction of 1,2,4,5-tetrakis(phenylethylyl)benzene with PtCl$_4$, three isomeric products with a pentalene structure[272] are obtained and two isomers with a double indenoidene skeleton.

Aromatic diyne systems[263] that were investigated are **41**, which gives **42** thermally, isomers **42** and **43** photochemically, and by complexation with PtCl₄ forms the phenylindenoperinaphthene **44**. Analogously, the diyne **45** gives **47a** thermally and photochemically, but forms phenyltribenzoazulene **47b** with PtCl₄.
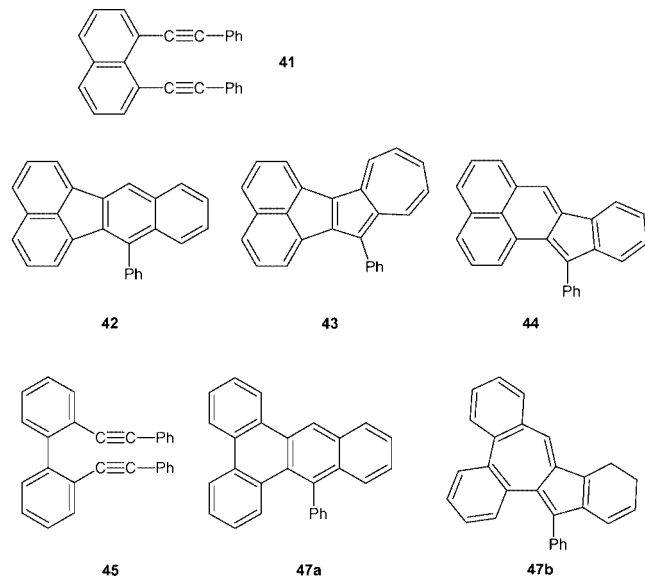
Changing the transition metal to rhodium lead to highly successful complex chemistry. With tris(triphenylphosphane)rhodium(I) chloride, compounds **41** and **45** gave the stable, isolatable complexes **41a** and **45a**, in which the metal is part of metallacycles[273] which allow characteristic alkyne additions to benzene derivatives or with chalcogens form oxygen, sulfur, selenium, or tellurium five-membered heterocycles (see below).

An interesting starting material is the cyclobutadiyne **46**, which can be reacted with alkynes by the rhodium complex **46a** to give highly substituted naphthalenes[274] **46b**. A thermal valence isomerisation of **46** forms benzocyclobutadiene **46c**, which reacts with benzyne to phenanthrene **46d**.[275]
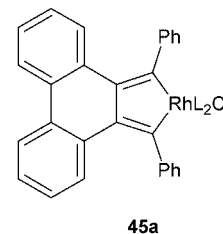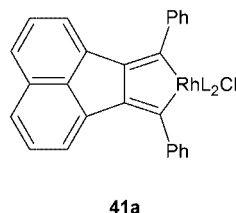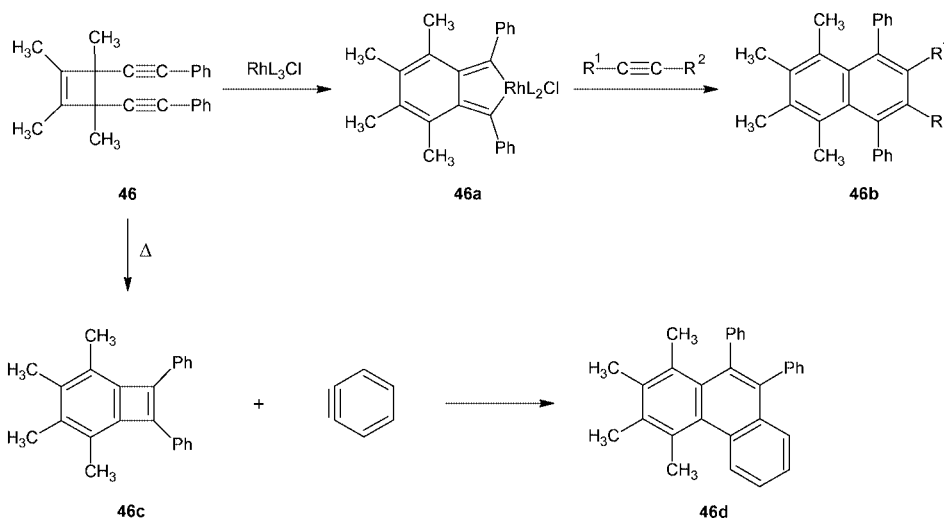
Seven-membered ring systems form with the acyclic diynes **47**, **48**, and **49** by the rhodium complexes **47a** to **49a** after alkyne addition to tribenzotropone[276] **47b**, the silepinene[276] **48b**, or the thiepinoxidene[277] **49b**. In contrast, compounds **48** and **49** react with PdCl₂ to form heterocyclic seven-ring systems with condensed azulene systems[278] **48c** and **49c**.

Complexation of ortho-Bis(propinoyl)arenes:[279,280] Variation of the diyne structure to ketoalkyne systems proved to be very fruitful, for instance, with *ortho*-bis(arylpropynoyl) arenes.[281]

The aromatic compounds **50–54**, the acyclic 1,7-diphenyl-1,6-diyn-4,4-heptane-3,5-dione[282] **55**, and the 1,8-diphenyl-1,7-diyn-4-*cis*-octen-3,5-dione[283] **56** were used for complexation studies.

With [RhL₃Cl], the diketo alkynes **50–56** were converted into isolatable rhodium complexes having the form **50a**, as for the diynes **41a** and **45a**. Their rhodium five-membered-ring structure was confirmed by an X-ray structure determination.[284] This result contradicts a previously thought alternative formulation[280] as the cyclobutadiene π complex **50a′** (Figure 2).

The first keto alkyne system to be converted into the new rhodium complex **51a** was 2,3-bis(phenylpropynoyl)naphthalene[285] **51**. With iridium, completely analogous complexes form,[286] whereas ruthenium and osmium salts lead to decarbonylation.[286]

Reactions of the Rhodium Complexes with Alkynes: All rhodium complexes that were synthesised react with numerous alkynes, forming a benzene unit from the metallacycle

47: Y = C=O   47a: Y = C=O   47b: Y = C=O

48: Y = Si(CH$_3$)$_2$ 48a: Y = Si(CH$_3$)$_2$ 48b: Y = Si(CH$_3$)$_2$ 48c: Y = Si(CH$_3$)$_2$

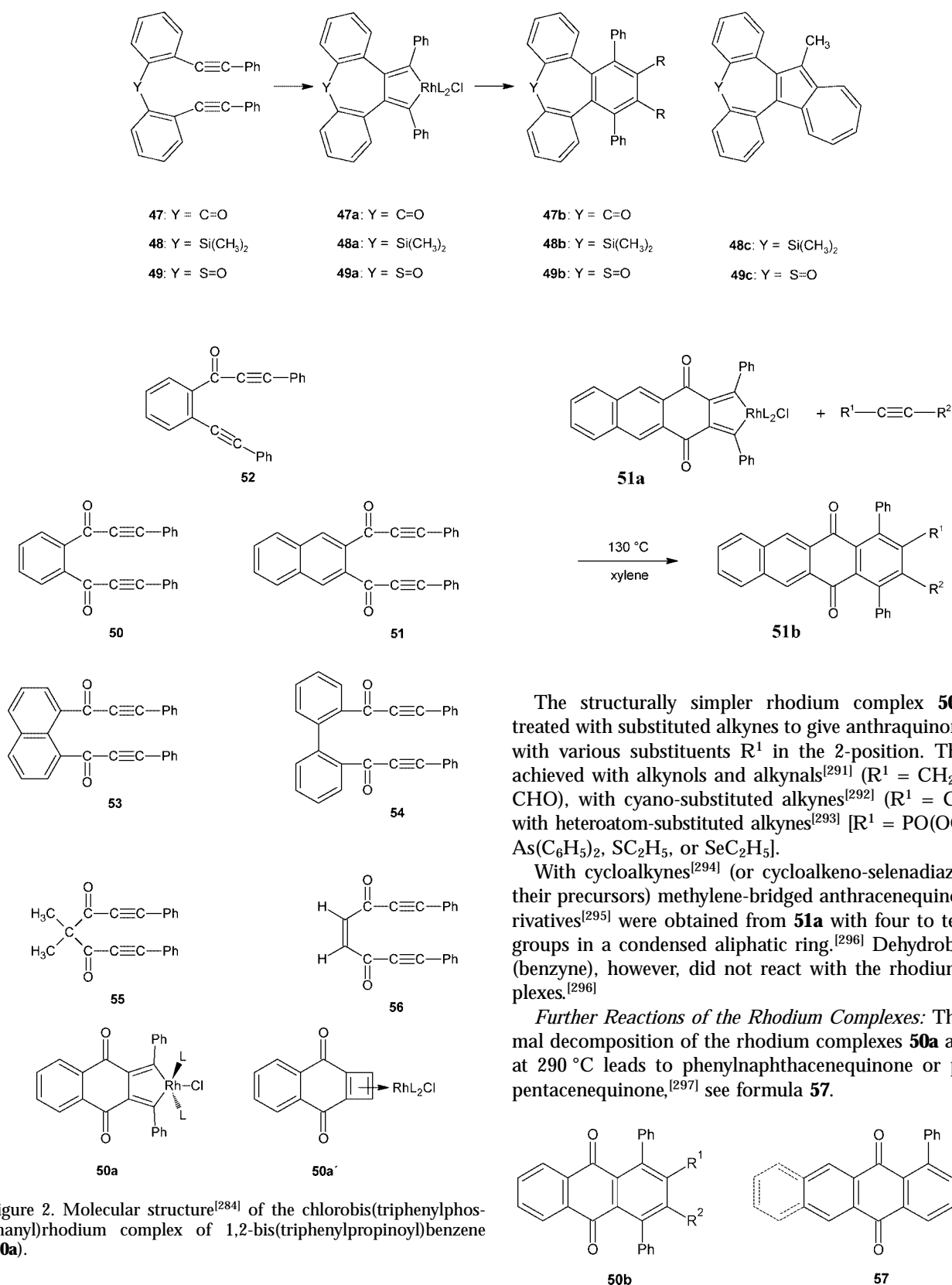49: Y = S=O   49a: Y = S=O   49b: Y = S=O   49c: Y = S=O

Figure 2. Molecular structure[284] of the chlorobis(triphenylphosphanyl)rhodium complex of 1,2-bis(triphenylpropinoyl)benzene (**50a**).

neighbouring a *p*-quinone ring.[287] In the review from Eugen Müller,[256] a table lists around 40 different alkynes which were used in the diyne reaction with rhodium complexes. For example, from **51a**, substituted naphthacenequinones[287–290] **51b** could be obtained.

The structurally simpler rhodium complex **50a** was treated with substituted alkynes to give anthraquinones **50b** with various substituents R^1 in the 2-position. This was achieved with alkynols and alkynals[291] (R^1 = CH$_2$OH or CHO), with cyano-substituted alkynes[292] (R^1 = CN), or with heteroatom-substituted alkynes[293] [R^1 = PO(OC$_2$H$_5$)$_2$, As(C$_6$H$_5$)$_2$, SC$_2$H$_5$, or SeC$_2$H$_5$].

With cycloalkynes[294] (or cycloalkeno-selenadiazoles as their precursors) methylene-bridged anthracenequinone derivatives[295] were obtained from **51a** with four to ten CH$_2$ groups in a condensed aliphatic ring.[296] Dehydrobenzene (benzyne), however, did not react with the rhodium complexes.[296]

Further Reactions of the Rhodium Complexes: The thermal decomposition of the rhodium complexes **50a** and **51a** at 290 °C leads to phenylnaphthacenequinone or phenylpentacenequinone,[297] see formula **57**.
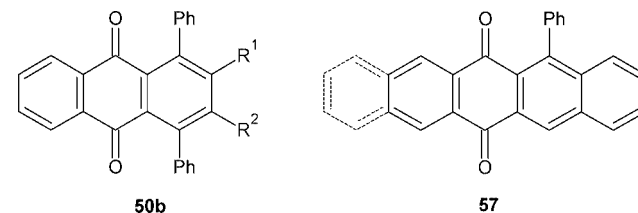
The acyclic diynone system **58** undergoes a shift of the carbonyl groups to the end of the chain[298] upon reaction with PtCl$_4$ to give **59**. With [RhL$_3$Cl] however, an elimination of the carbonyl group occurs to give conjugated di-

yne[299] **60**. This carbonyl elimination was also observed by mass spectrometry.[300]
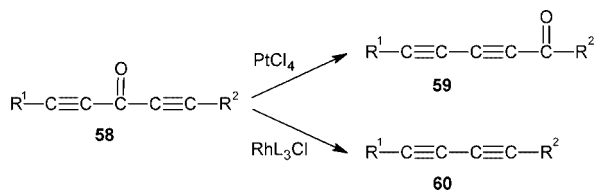
Reaction of the Rhodium Complexes to Heterocycles: Of great importance is the formation of five-membered heterocyclic rings from the rhodium complexes by reaction with chalcogens which replace the rhodium metal by heteroatoms. With O_2 or H_2O_2, furans[301] form, with sulfur thiophenes,[301] with selenium selenophenes,[301] and with tellurium tellurophenes;[302] these are heterocondensated benzoquinones of the form **61a**. With CO cyclopentadienones[273,303] are formed from the rhodium complexes, with phenylazide pyrroles,[304] and with 2,6-dimethylphenylisonitrile ketimines[305] of the form **61b** are obtained.
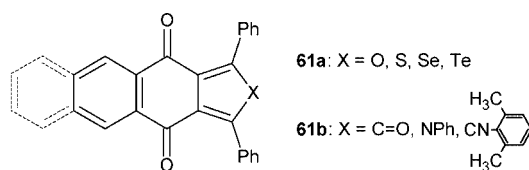
Interesting rhodium complexes can also be formed from 1,2-keto diynes which already contain a heterocycle. Such rhodium complexes **62a** and **63a** react for example by cycloadditions to heterocondesated isofuranobenzoquinones[304] **62b** and isoindolquinones[306] **63b**, along with all the chalcogen additions described above. This leads to a plethora of bisheterocycles of the form **62c** as furan derivatives[304] or pyrroles[306] **63c**.

All the bis(heterocyclic) systems can be described by the general formula **64**, in which X in **64a** stands for the rhodium complex, in **64b** for the benzene system (via alkynes), in **64c** for the chalcogens O to Te, and in **64d** for the double-bond systems shown. The heterocyclic ring systems **64** given by A are furans[304] **62**, pyrroles[306] **63**, triazoles[307] **65**, thiophenes[308] **66**, and benzothiophenes[309] **67**.
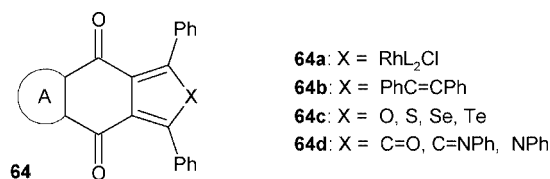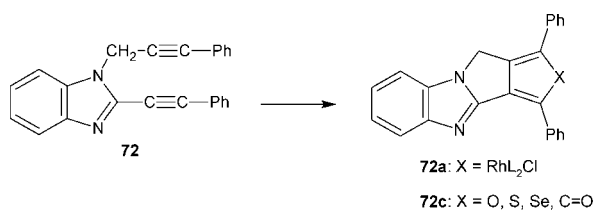
Further heterocycles that are presented are the indenone systems[310] **68a–c** and the heterobenzoquinones[311] **69c** (from **56**), the isobenzoheterocycles[312] **70c**, and (from **71**) the dihydroisofuran systems[313] **71a–c**.
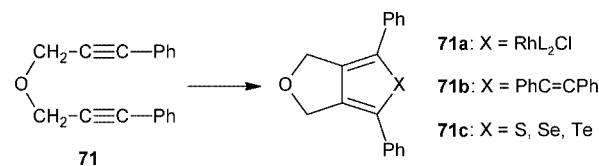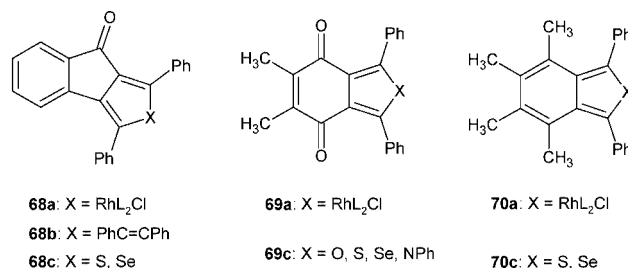
From the heterocycle[314] **72** without a carbonyl functional group, the benzimidazole systems **72c** form via the complex **72a**.

72a: X = RhL₂Cl

72c: X = O, S, Se, C=O
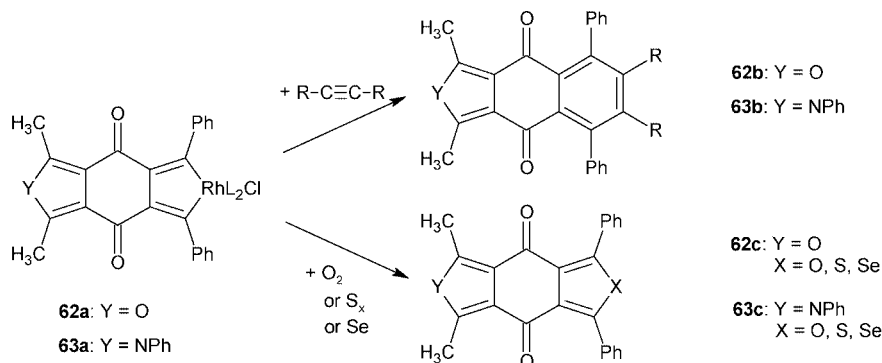
Furthermore, thermal and photochemical reactions of α-oxoacetylenes with cobalt, nickel, and iron carbonyl compounds were carried out.[315] Tetracarbonylnickel induces a [4+2] cycloaddition or a dimerisation to a cyclooctatetraene system, and dicarbonylbis(triphenylphophane)nickel leads to quinone syntheses in good yields.[316] A further work deals with the thermal and photochemical reaction of cyclooctyne with pentacarbonyliron.[317]

Both the last publications of the Eugen Müller group to be referenced in the Chem. Abstr. Service (CAS), the 42nd and 43rd communication on diyne reactions, were posthumously compiled by his last PhD student, Jürgen Hambrecht, when he had begun employment with BASF. These publications describe the formation of substituted 1,4-naphthoquinones[318] and 1,2,4,5-tetrakis(phenylpropynoyl)benzene[258] **73** along with its reaction to the dirhodium complex **73a**.

73

73a
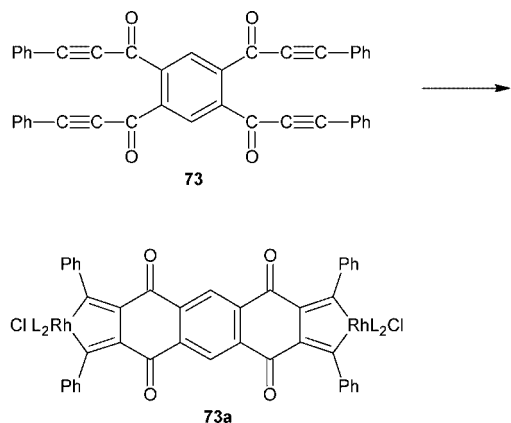
Synthetic Organic Chemistry: Separate publications from Eugen Müller describe syntheses starting from alkyne-substituted cyclooctatetraenes[319,320] and their valence isomerisation[321] or an oxidative trimerisation of substituted phenols[322] with potassium hexacyanoferrate. An interesting early reaction is the elimination of water from cyclic α,β-unsaturated ketones with phosphoryl chloride and pyridine, forming 1,3,5-trienes.[323] In the steroid series, these regents could be used to phosphorylate the hydroxy group at C17 of testosterone[324] with subsequent methylation of the phosphoric acid with diazomethane to the ester.

Further work dealt with the synthesis of benzyne[325] from 1,2-dihalobenzenes and tetraphenylethane disodium salt, with variations of the Wurtz reaction,[9,326] and a comparison of the effectiveness of reductions according to Clemmensen or Wolff–Kishner with mid-sized ring ketones with six to twelve carbon atoms.[327] The Huang–Minlon

modification of the Wolff–Kishner reduction gave the best yields. Eugen Müller described the synthesis of *N*-nitrosoethyleneimine,[328] on new brenzcatechines and *o*-quinones,[329] and from demethylated carotinoids[330] from a Grignard reaction of dibromobenzocyclobutene.

The synthesis of 1,2,3-thiadiazol 2-oxide[331] and of 2,5-diphenyltellurophenedicarbaldehyde[332] and its reaction with *o*-phenylenediamine or C–H acidic compounds to complex tellurium heterocycles[333] were reported as special heterocycle syntheses. Furthermore, the ring-opening of 2,5-diphenyltellurophene with *n*-butyllithium leading to 1,4-substituted butadienes,[334] the synthesis of triazolylmercury compounds,[335] and the synthesis of imidazoles from lithium aldimines with oxygen[336] were described.

A tautomeric mixture of pyrazoldicarbaldehydes were *N*-methylated and the methyl derivatives were separated preparatively and identified by IR and ¹H NMR spectroscopy.[337] These compounds and the 1,2,3-triazol-4,5-dicarbaldehyde[338] were important as starting materials for the synthesis of the above-mentioned heterocyclic diyne ketones.

Several publications dealt with the reactions of isonitriles.[99,339–341] The ring-opening reactions of bicyclo[4.2.0]octa-2,4-dienes[342] were investigated. The reaction of substituted cyclobutenediones with various Grignard reagents was described in later publications.[343,344]
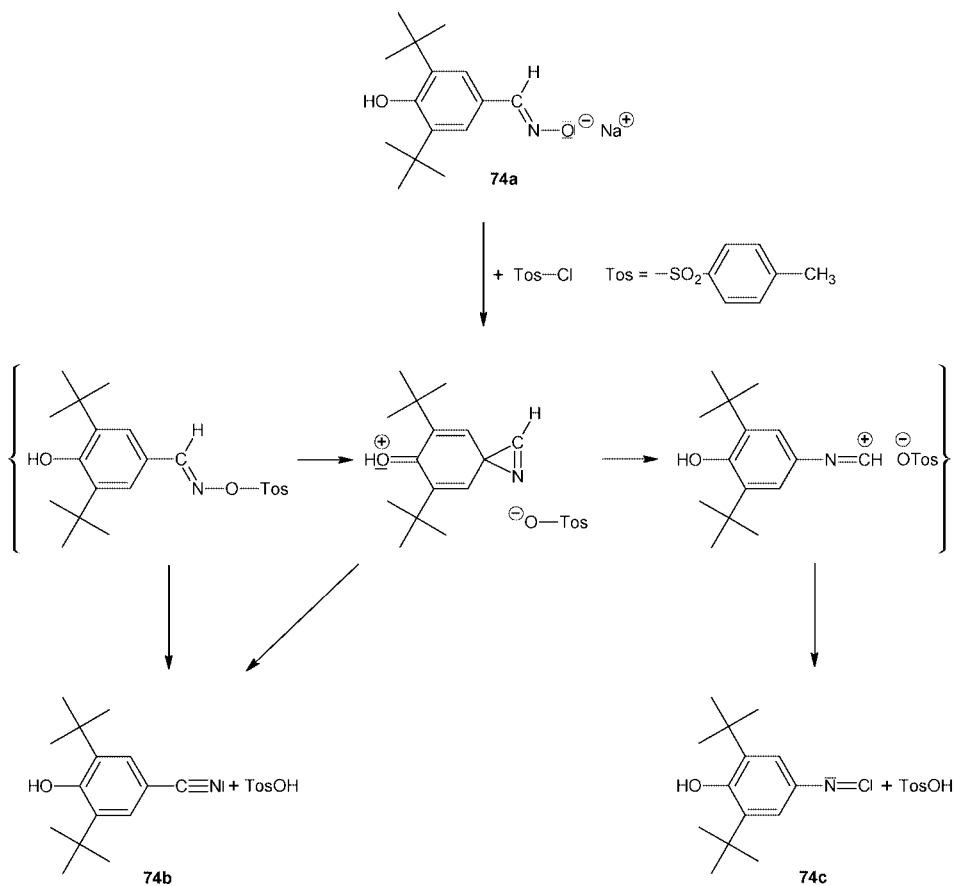
The detailed procedure for the demonstration of the dangerous explosiveness of chloroform with sodium/potassium alloy arose from the organic experimental lecture.[345]

Mechanistic Studies: A series of mechanistic studies are also of relevance, starting in 1972 with investigations into the valence isomerisation related to the Woodward–Hoffmann rules for diethynyl-substituted tetramethylcyclobutene[346–350] and related systems[351] (see for example compound **46**).[275]

The mechanism of the Wolff rearrangement of diazoketones was investigated,[352,353] and ¹³C labelling showed that thermally the carbonyl carbon atom is retained, but photochemically, a rearrangement via an oxirene takes place, and the labelled carbon is scrambled. This rearrangement can also be initiated and detected by mass spectrometry.[354] A related reaction that was investigated was the electron-impact-induced fragmentation of 1,2,3-thiadiazoles.[355]

The Beckmann rearrangement of aldehydoxime **74a** does not, as would normally be the case for aldehydes, lead to the nitrile **74b**, but forms the isocyanide[356] **74c** by ring substitution.

Application of New Methods: Eugen Müller was always open to new experimental methods. His important ESR investigations have already been discussed above.[72–76,104–106,108,357] Thin-layer chromatographic separation of polynuclear aromatic compounds by complexation on an absorption layer half-coated with picric acid[358] should also be mentioned, or polarographic investigations of heteroacenquinones[359,360] from the diyne reaction, where a relationship was found between the half-wave potential of the first one-electron reduction step and the Ham-

mett substituent constants. As simple determination of oxygen in the air, Eugen Müller developed a colorimetric method which involves a reaction of oxygen with the Chichibabin hydrocarbon.[361]

^{1}H NMR spectroscopic investigations dealt with alkylcycloheptatrienes[362] and the Mills–Nixon effect,[363] which was also studied by ionisation energies of benzene derivatives.[364] The fragmentation of 1,2,3-thiadiazoles[355,365] in comparison to the photchemical behaviour[366,367] of this class of compound was studied by mass spectrometry.[368]

Lecture Reports: In Eugen Müller's publication list, many lectures are compiled.[369–375] One manuscript on wood-pulping with 1,4-butanediol fell victim to the Second World War.[376]

Eugen Müller as an Academic

Activity as Author: i. The textbook "New Perspectives in Organic Chemistry": As mentioned above, in 1940, in the series "Organic Chemistry in Monographs" supervised by Eugen Müller, his monograph[5] with the title "New Perspectives in Organic Chemistry" was published as the first volume by Springer, and completely reworked in the second edition in 1957 with the addition "Advanced Organic Chemistry".
ii. Houben–Weyl: Handbook of Organic Chemistry:[377] Eugen Müller gained particular credit as the editor of the fourth edition of the handbook "*Houben–Weyl: Methods of Organic Chemistry*". This work was founded by the German chemist Theodor Weyl in 1909 and 1911 in two volumes. The second edition, expanded to four volumes; was worked on by Heinrich J. Houben between 1921 and 1924. A third edition of Houben–Weyl, also in four volumes, was produced between 1924 and 1941. The re-worked comprehensive fourth edition,[378] produced between 1952 and 1975, consisted of 45 volumes in total, with Eugen Müller as the editor together with Otto Bayer (1902–1982, Leverkusen), Hans Meerwein (1879–1965, Marburg), and Karl Ziegler (1898–1973, Mülheim an der Ruhr). Ten contributions were from Eugen Müller and his co-workers and are given in his publication list.[379–388] The work was continued until 1986 by Heinz Kropf (Hamburg) and Hans-Gerd Padeken (Stuttgart; a student of Eugen Müller) with a total of 67 text volumes and 3 index volumes. The successful series was then further updated, from 1990 with English as the publication language, with 89 supplementary volumes.

Since 2000, the fifth edition[377] of Houben–Weyl has been published as "*Science of Synthesis*" in printed and electronic form. The decade-long success of Houben–Weyl lay in the comprehensive description of preparative methods in unchanged characteristic style with it own classification system of reaction types and critical presentation by experienced experts. Through is editorial activity, Eugen Müller had a comprehensive knowledge of the entire area of organic chemistry at his fingertips, much to the dismay of many examination candidates, who had to suffer his preference for historical aspects and name reactions.

Eugen Müller was also on the editorial boards of "*Synthesis*" and "*Chemiker-Zeitung*".

Students of Eugen Müller: Eugen Müller supervised approximately 100 PhD students, of which a significant number became university professors or industrial chemists in Tübingen or elsewhere. The names of the numerous students of Eugen Müller can be found as co-authors in the list of publications.

Professors active elsewhere include Herbert Meier, Horst Kessler, Werner Winter, Henner Straub, and Willy Dilger. Müller students who became professors in Tübingen are (or were) Anton Rieker, Hartmut B. Stegmann, Klaus Scheffler, Harald Suhr, Wolfgang Rundel, and Klaus-Peter Zeller.

Lectures: After receiving the chair in chemistry as successor to Georg Wittig, Eugen Müller held the experimental lecture in organic chemistry from 1957 for beginners of all scientific fields and medicine. Eugen Müller's experimental chemistry lecture was linguistically polished and could inspire many students to study organic chemistry. He celebrated the lecture and it was brought about with much effort experimentally and personally. A Ph.D. graduate lecturer's assistant and two laboratory assistants were available for preparation and carrying out the elaborate and memorable experiments. Owing to the large number of students attending, the lecture had to be held in the largest lecture theatre of the university, and equipment and chemicals had to be transported in trolleys 500 m along Wilhelmstrasse from the old institute of chemistry to the main university building.

Apparatus and Personnel of the Institute of Organic Chemistry at the University of Tübingen: In the 1950's, concerning physical apparatus the Tübingen Institute of Organic Chemistry was one of the best equipped chemical institutes in Germany. IR and UV spectrometers and a magnetic balance were standard, and ESR, MS, and ^{1}H NMR instruments were also available before 1960 in Tübingen. For each of these instruments, Eugen Müller could win experienced specialists: Klaus Scheffler and Hartmut B. Stegmann for ESR spectroscopy, Harald Suhr for NMR spectroscopy, and Klaus-Peter Zeller for mass spectrometry.

The Person

Eugen Müller was without doubt one of the most significant organic chemistry researcher in post-war Germany. It is difficult to describe his personality satisfactorily, as he had many contradictory sides. Eugen Müller was a stately, imposing person with a strong charisma; a grand seigneur. He could be described as a monolith with edges and corners on which one could catch oneself. Outside Tübingen he was seen as a difficult person by the scientific community. Under a brusque and abrasive exterior was hidden a great sensibility. He could motivate his numerous co-workers to research accomplishments by his own example. The following quote is characteristic of Müller: "*Those who don't have the guts to graduate under me are not capable as chemists.*" In scientific activity, a single-mindedness and systematic handling of new research areas each with 20 to 30 communications is typical. Eugen Müller worked on a series of meaningful new systems and results that today belong to standard textbook knowledge. It was important to him to acknowledge and work on interrelationships. His editorial activity for Houben–Weyl meant that he had an active overview of preparative organic chemistry which he could also influence.

Alongside a large scientific workload, Eugen Müller had little time later to relax as hobby painter, although after the war he had partially financed his family with it.

Bibliographical Information: Apart from the entries in Poggendorff's "*Biographical Literary Dictionary*",[390] there has been no compilation of the scientific publications of Eugen Müller, and only a few appraisals of his life in the scientific literature. On November 10, 2005, his last PhD student, Jürgen Hambrecht, Chairman of the Board of BASF, held a lecture celebrating the one-hundred-year anniversary of Eugen Müller in the German Chemical Society (GDCh) symposium.[404]

The references are taken from Chemical Abstracts using SciFinder Scholar, from 1928 to 1961 under "Muller, Eugen" and from 1955 to 1977 under "Mueller, Eugen" and cross-checked with his publication list that was later acquired.

Supporting Information (see also the footnote on the first page of this article): Original, unabridged version of this article in German written by Prof. G. Häfelinger (Tübingen). The complete list of references is included.

[1–404] For the complete list of references see the footnote on the first page of this article (Supporting Information).