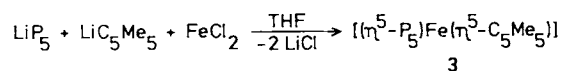
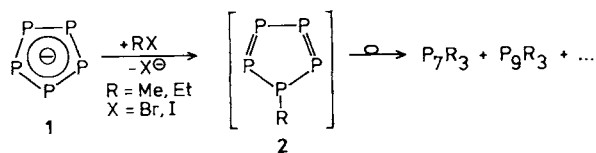


and P_9R_3 . The nonaromatic primary product **2** is apparently so unstable that it spontaneously rearranges to give the thermodynamically favored alkylpolyphosphanes. No evidence for dimers of **2** was found.



Compound **1** reacts with compounds of the transition metals Fe, Ni, Rh, Mn, Cr, or Mo to form dark brown to black solids, whose insolubility and relative nonvolatility make their characterization difficult. However, black “FeP₁₀,” formed immediately upon reaction with FeCl₂ in THF at room temperature exhibits—like **1**—an IR band at 815 cm⁻¹, which is evidence for an intact aromatic P₅ ring as structural element, since it is definitely not caused by free **1**. That a “decaphosphaferrocene” might indeed be present was further supported by direct one-pot synthesis of the mixed sandwich complex **3** (in addition to “FeP₁₀” and [(C₅Me₅)₂Fe]) from LiP₅, LiC₅Me₅, and FeCl₂; **3** is identical with the compound recently obtained by Scherer et al.^[9] by cothermolysis of [(η⁵-C₅Me₅)Fe(CO)₂]₂ and P₄.

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[3] *NaP₅ solution*: Freshly distilled white phosphorus (1.27 g, 0.041 g atom) in a mixture of THF (160 mL) and [18]crown-6 (5.04 g, 0.019 mol) was allowed to react under inert gas at reflux temperature with powdered sodium (0.44 g, 0.019 g atom) with stirring for 3.5 h. After standing for 24 h at room temperature, the reaction solution was separated from the sparingly soluble P-rich polyphosphides by siphoning off over a frit. Concentration to half of the original volume under oil-pump vacuum (bath temperature 55°C, cold trap -78°C) and renewed crystallization at -30°C followed by filtration in the cold gave a pure, ca. 10⁻² M NaP₅/[18]crown-6/THF solution. Additional NaP₅ can be extracted from the precipitate with boiling THF. Overall yield (by comparison of the intensity of the ³¹P-NMR singlet with the signal of a Ph₄PCl solution of known concentration) 0.18 g (12%, based on phosphorus).

[4] The appearance of **1** in the negative ion mass spectrum of red phosphorus at 325°C has been reported by J. T. Snodgrass, J. V. Coe, C. B. Freidhoff, K. M. McHugh, K. H. Bowen, *Chem. Phys. Lett.* 122 (1985) 352.

[5] Mass spectrometer MAT-731 (acceleration voltage 8 kV, post-acceleration 7.5 kV) equipped with an 11 NF FAB ion source (Ion Tech Ltd., Teddington; 10⁻⁵ torr Xe, 7 kV, Cu target). The sample was admitted either by a) application of a NaP₅/[18]crown-6/THF solution, concentrated to 1/6 of its volume, onto a liquid-nitrogen-cooled target followed by slow warming in the ion source accompanied by continuous recording of the spectra or b) by mixing the concentrated solution with dibenzyl ketone as matrix at 25°C.

[6] Cary 2300. The concentrations of the stock solutions (ca. 10⁻² M) were estimated from the intensity of the ³¹P-NMR singlet [3].

[7] B. O. Wagner, H. F. Ebel, *Tetrahedron* 26 (1970) 5155.

[8] **3**: Anhydrous FeCl₂ (60 mg, 0.47 mmol) in refluxing THF (20 mL) was stirred under inert gas until all material had gone into solution. The solution was treated at the same temperature over 10 min with a suspension of LiC₅Me₅ (67 mg, 0.47 mmol) and LiP₅ (19 mg, 0.12 mmol) [1] in 30 mL of THF. After 1 h of stirring, the solvent was completely removed under reduced pressure at room temperature. The residue was extracted three times with 30 mL of boiling dichloromethane with stirring (20 min each time). Removal of the solvent from the combined extracts and recrystallization from *n*-pentane gave 11 mg (27%) of pure **3** (³¹P-NMR, MS).

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Synthesis and Optical Properties of Terminally Substituted Conjugated Polyenes**

By Franz Effenberger,* Hubert Schlosser, Peter Bäuerle, Stefan Maier, Helmut Port, and Hans Christoph Wolf*

Dedicated to Professor Helmut Dörfel on the occasion of his 60th birthday

The mechanisms of energy transport in molecular systems have been the subject of numerous studies in recent years.^[1] Aside from investigations on the elucidation of processes involved in biological systems, e.g., in photosynthesis,^[2] increasing attention has been directed to the synthesis of compounds which are suitable for the transport and storage of information on a molecular basis.^[3]

Herein we report on the synthesis of conjugated polyenes of various lengths with terminal substituents whose spectroscopic properties differ from those of the polyene chains. The selective optical excitation of these model compounds and the possibility of an intramolecular energy transport are discussed on the basis of absorption, emission, and excitation spectra.

Starting from the polyene dialdehydes **1** and **7** we have synthesized, via Wittig reactions, numerous conjugated polyenes bearing the following terminal groups: 9-anthryl (A), 1-naphthyl (N) and 5,10,15,20-tetraphenylporphyrin-2-yl (TPP) as well as *p*-nitrophenyl, *p*-dimethylaminophenyl, ferrocenyl, alkoxy-carbonyl, carboxy, and methyl. In the present communication, however, only those compounds shown in Schemes 1 and 2 (see overleaf) and 4,8,13,17-tetramethyl-2,4,6,8,10,12,14,16,18-eicosanonaene (TMEN) used as reference compound will be discussed.^[4]

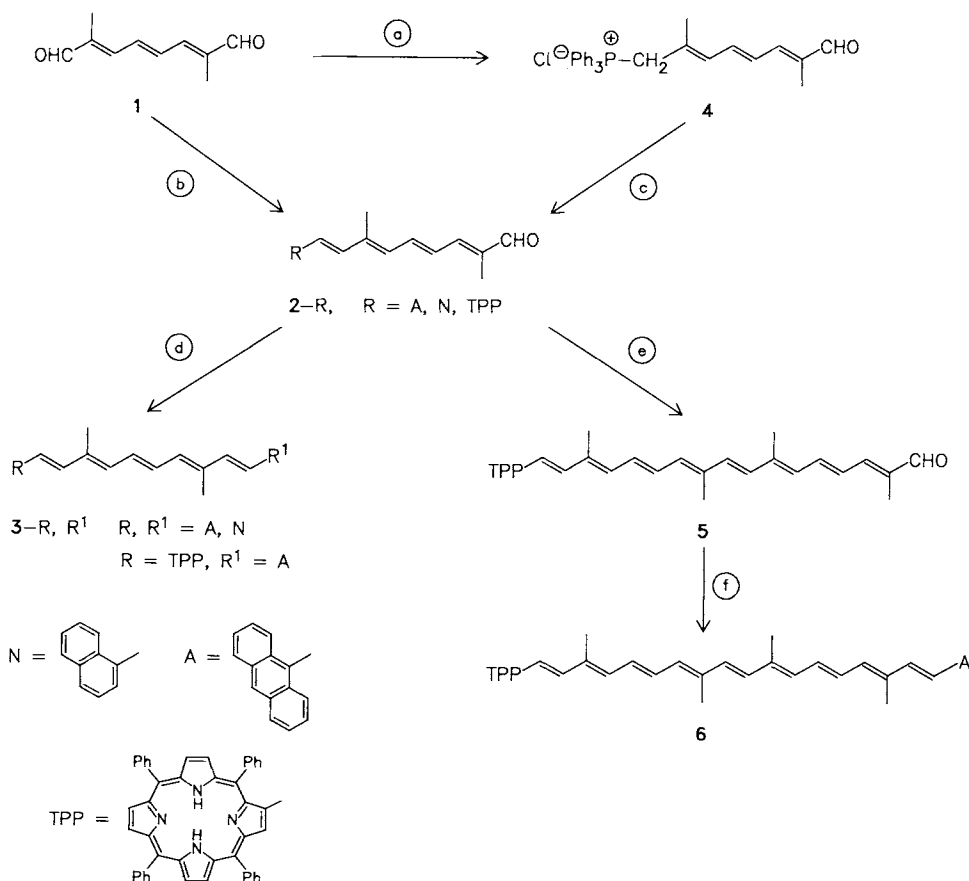
Upon Wittig reaction and purification of the products by column chromatography, the dialdehydes **1** and **7** with all-*E*-configuration initially yield *E/Z* isomeric mixtures in which the all-*E*-isomers dominate. The all-*E*-isomers can be enriched by recrystallization: for example, the compounds **2-A** and **3-A,N** are enriched to the extent of 100%, **3-A,A** and **3-N,N** to 99%, **3-A,TPP** to 95% and **6** to 70% in the all-*E*-form. The isomeric ratios were determined by HPLC and the respective isomers assigned by ¹H-NMR and UV/VIS spectroscopy.

Figure 1a shows the absorption spectra of anthracene, 5,10,15,20-tetraphenylporphyrin and TMEN, while Figure 1b shows, as selected examples, those of the polyenes **3-A,TPP**, **6** and **9-A,A** (concentrations between 10⁻⁶ and 10⁻⁴ mol L⁻¹, CH₂Cl₂, T = 295 K). The shapes of the spectra are concentration-independent. The anthrylpolyenes **2-A**, **8-A**, and **10-A** all show an absorption maximum at 256 nm independent of the chain length, which is not observed in the case of **1**, **7**, and TMEN, and which corresponds to the ¹B_u state^[5] of anthracene. As expected, in the case of the bilaterally anthryl-substituted polyenes **3-A,A**, **9-A,A**, and **11-A,A**, the extinction coefficients of the absorption at 256 nm are doubled. In the absorption spectra of the mixed-substituted compounds **3-A,N**, **9-A,N**, and **11-A,N** a further band aside from that at 256 nm appears at 220 nm; this corresponds to the excitation of the ¹B_u

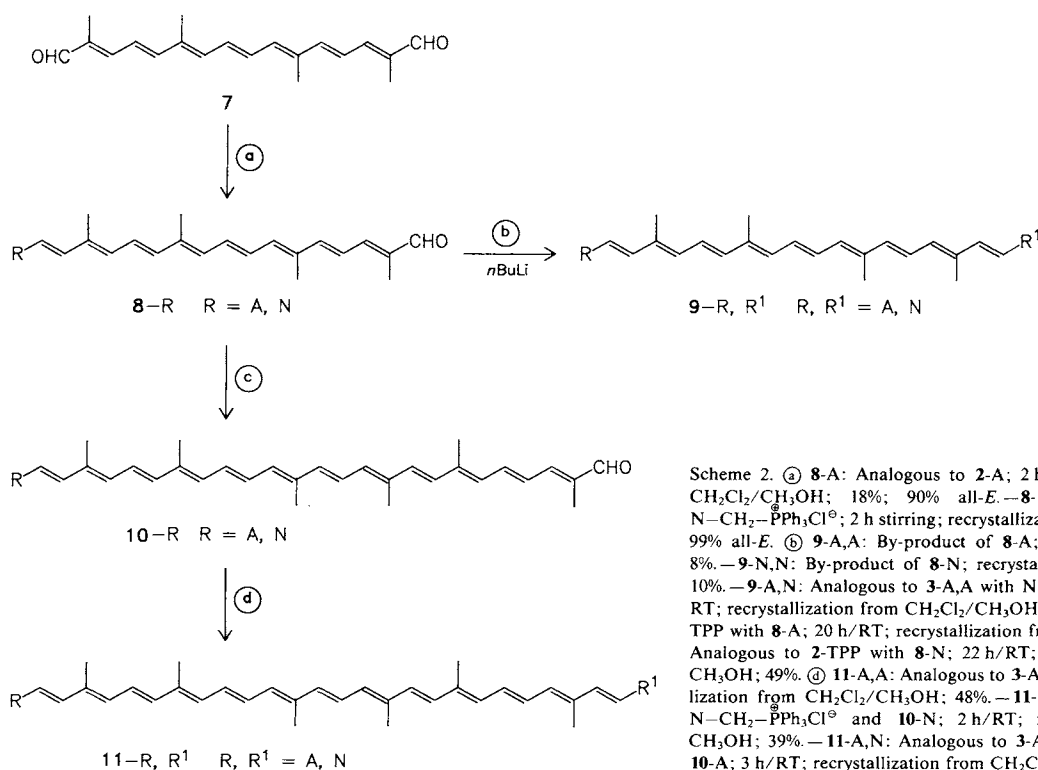
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Scheme 1. (a) 1) NaBH₄, 2) HCl, 3) PPh₃, according to [10]. (b) 2-A: A-CH₂-PPh₃⁺, *n*BuLi, Et₂O/1 h/RT; dropwise addition to 1, CH₂Cl₂/2 h/RT; 1 h stirring; chromatography on SiO₂/CH₂Cl₂; recrystallization from toluene/CH₃OH; 60%, 100% all-*E*.—2-N: analogous to 2-A with N-CH₂-PPh₃⁺; recrystallization from hexane; 21%; 97% all-*E*. (c) 2-TPP: 4, HC(OCH₃)₃, TsOH, CH₃OH/2 h/RT; pyridine; NaOCH₃/CH₃OH; TPP-CHO, CH₂Cl₂ added; 17 h/RT; chromatography on SiO₂/CH₂Cl₂; recrystallization from CH₂Cl₂/hexane; 59%, 98% all-*E*. (d) 3-A,A: A-CH₂-PPh₃⁺, *n*BuLi, Et₂O/1 h/RT; 1, CH₂Cl₂ added; 4 h/RT; chromatography on SiO₂/CH₂Cl₂; recrystallization from toluene; 40%; 99% all-*E*.—3-N,N: by-product of 2-N; recrystallization from toluene/CH₃OH; 13%; 99% all-*E*.—3-A,N: analogous to 3-A,A with N-CH₂-PPh₃⁺ and 2-A; 2 h/RT; recrystallization from toluene/CH₃OH; 72%; 100% all-*E*.—3-TPP,A: analogous to 3-A,A with 2-TPP; 5 h/RT; recrystallization from CH₂Cl₂/CH₃OH; 26%, 95% all-*E*. (e) 5: analogous to 2-TPP with 2-TPP; 49%; 99% all-*E*. (f) 6: analogous to 3-A,A with 5; 22 h/RT; recrystallization from CH₂Cl₂/CH₃OH; 18%; 70% all-*E*.



Scheme 2. (a) 8-A: Analogous to 2-A; 2 h stirring; recrystallization from CH₂Cl₂/CH₃OH; 18%; 90% all-*E*.—8-N: Analogous to 2-A with N-CH₂-PPh₃⁺; 2 h stirring; recrystallization from CH₂Cl₂/hexane; 18%; 99% all-*E*. (b) 9-A,A: By-product of 8-A; recrystallization from CH₂Cl₂; 8%.—9-N,N: By-product of 8-N; recrystallization from CH₂Cl₂/CH₃OH; 10%.—9-A,N: Analogous to 3-A,A with N-CH₂-PPh₃⁺ and 8-A; 15 h/RT; recrystallization from CH₂Cl₂/CH₃OH; 88%. (c) 10-A: Analogous to 2-TPP with 8-A; 20 h/RT; recrystallization from CH₂Cl₂/Et₂O; 45%.—10-N: Analogous to 2-TPP with 8-N; 22 h/RT; recrystallization from CH₂Cl₂/CH₃OH; 49%. (d) 11-A,A: Analogous to 3-A,A with 10-A; 2 h/RT; recrystallization from CH₂Cl₂/CH₃OH; 48%.—11-N,N: Analogous to 3-A,A with N-CH₂-PPh₃⁺ and 10-N; 2 h/RT; recrystallization from CH₂Cl₂/CH₃OH; 39%.—11-A,N: Analogous to 3-A,A with N-CH₂-PPh₃⁺ and 10-A; 3 h/RT; recrystallization from CH₂Cl₂/MeOH; 58%.

state^[5] of naphthalene. The intensity ratios of the anthryl and naphthyl bands (2 : 1) of these polyenes approximately correspond to those of the free arenes anthracene and naphthalene. The spectra of 3-A,TPP and 6 show the typical anthryl band at 256 nm, in addition to the Q bands (500–650 nm) as well as the intense Soret band (425 nm)^[6] of the TPP group. The TPP bands are more or less largely superimposed by the polyene absorptions.

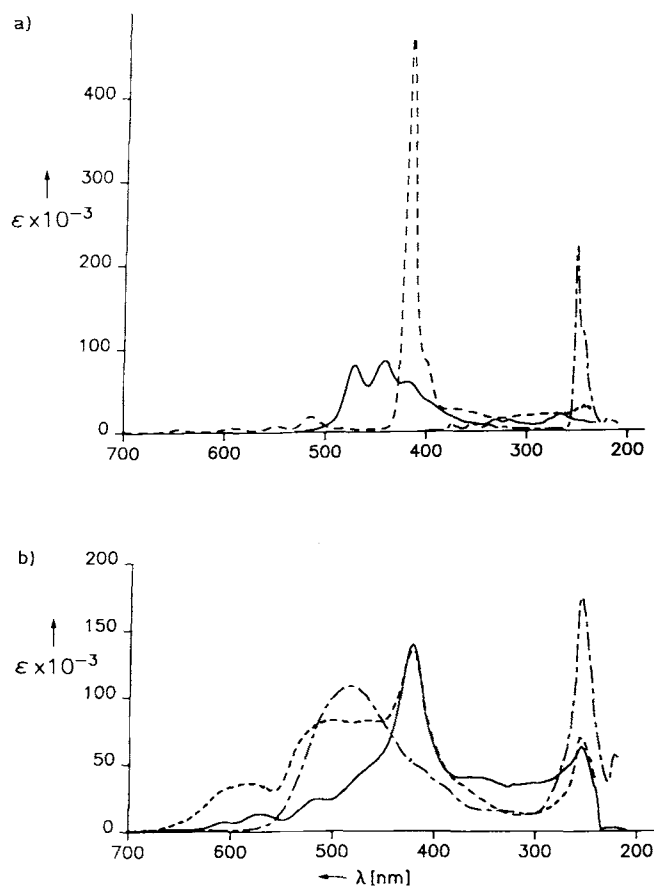


Fig. 1. Absorption spectra (CH_2Cl_2 , $T=295\text{ K}$) of a) TMEN (—), anthracene (---), and 5,10,15,20-tetraphenylporphyrin (· · ·), and of b) 3-A,TPP (—), 6 (---), and 9-A,A (· · ·).

Evaluation of the absorption spectra accordingly reveals the not fully expected but important finding, especially as regards an application in the sense alluded to in the introduction, that a localized excitation of terminal groups is possible in the conjugated π -systems mentioned here.

In order to check whether an energy transport from an electronically excited terminal group via the conjugated polyene to another terminal group is possible we chose the compounds 3-A,TPP and 6, in which the absorption and emission bands of the relevant molecular moieties are adequately separated. Figures 2a and 2b show the corrected emission spectra^[7] of anthracene and tetraphenylporphyrin and of 3-A,TPP, respectively (*n*-hexane, $T=180\text{ K}$, excitation at 257 nm). Compared to the emission spectrum of the anthracene-tetraphenylporphyrin mixture, the emission spectrum of 3-A,TPP shows a decrease in the anthryl emission with concomitant increase in the tetraphenylporphyrin emission.

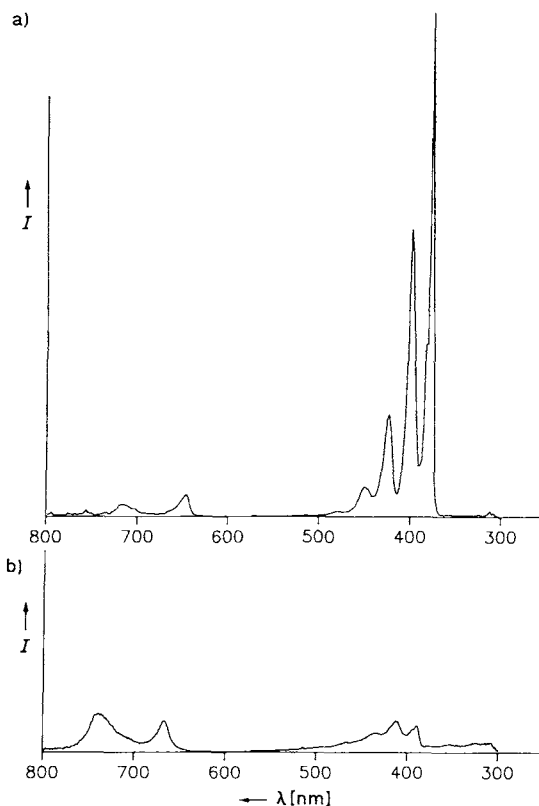


Fig. 2. Emission spectra (*n*-hexane, $T=180\text{ K}$, excitation at 257 nm) of a) anthracene/5,10,15,20-tetraphenylporphyrin (1/1), concentration $10^{-6}\text{ mol L}^{-1}$ (the spectrum corresponds to a superposition of the individual spectra) and of b) 3-A,TPP, concentration $2 \times 10^{-5}\text{ mol L}^{-1}$ (the origin of the weak emission between 300 and 380 nm is still unknown).

From the corrected excitation spectra of the compounds 3-A,TPP and 6 shown in Figure 3 it clearly follows that, depending upon the excitation wavelength, the emission intensity of the TPP terminal group at 665 nm shows a

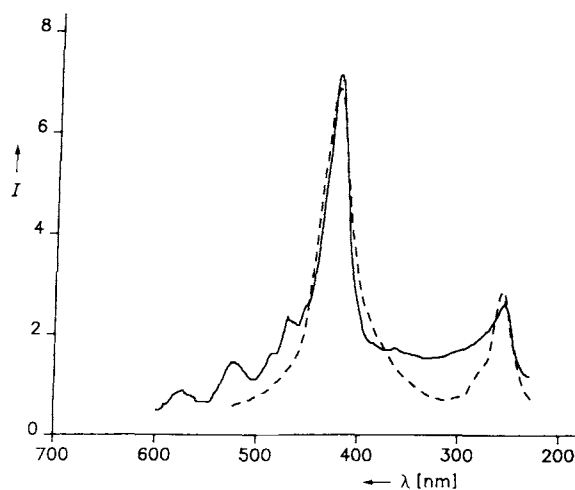


Fig. 3. Excitation spectra at $T=295\text{ K}$. Detection at 665 nm. 3-A,TPP (—) and 6 (---).

maximum upon excitation with 256 nm, corresponding to the absorption band of the anthryl substituent. A TPP emission is not observed upon excitation in the range of

the polyene absorption of the compound **6** (at ca. 500 nm).

The time resolved measurements of the emission (picosecond laser pulse excitation, single-photon counting detection) gave no significant changes of the time constants for the growth and decay behavior of the coupled systems **3-A**, **TPP** and **6** compared to anthracene and tetraphenylporphyrin. The time constants for the growth are in all cases <25 ps, while those for the decay lie between 3.6 and 5.5 ns.

All the emission and excitation spectroscopic findings are consistent with an intramolecular energy transport from the excited anthryl group via the polyene chain to the TPP substituent, which then emits in competition with the anthryl group. Other known energy transfer mechanisms such as reabsorption,^[8] Förster mechanism^[9] or light-induced electron transfer^[11] are not involved. The independence of the emission spectra on the concentration and the short growth times of the TPP emission rule out reabsorption and an intermolecular energy transfer by Förster mechanism. In the case of an intramolecular energy transfer by long distance interactions as described by Förster a shortening of the anthryl emission decay time should be observed, as also in the case of an electron transfer from the anthryl- to the TPP-substituent.

For an explanation of the observed energy transport we must therefore assume that the energy absorbed in the anthryl substituent leads only to partial relaxation into the anthryl S₁ state, which then emits. Occupation of an energy state delocalized over the molecule competes with this; after relaxation into the first excited singlet state of the TPP group the corresponding emission finally takes place.

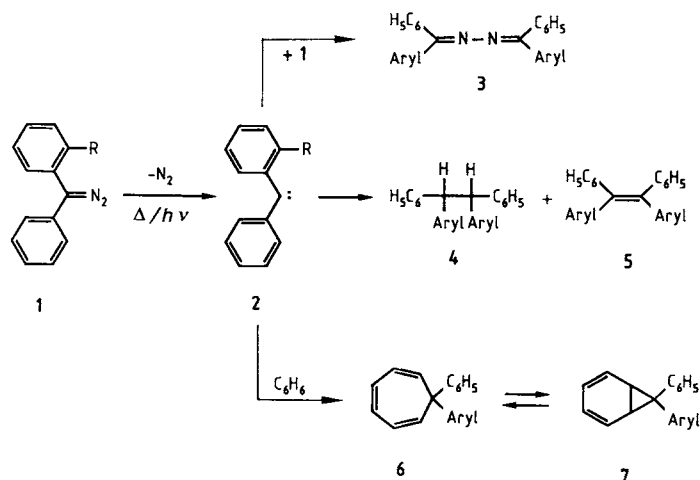
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Formation of Cycloheptatriene/Norcaradiene Systems in the Decomposition of Diaryldiazomethanes in Benzene**

By Klaus Hannemann*

Whereas numerous carbenes are known to react with benzene to form cycloheptatriene/norcaradiene systems,^[1] to our knowledge this reaction has hitherto not been observed with diphenylcarbene. Benzophenone azine **3a** and small amounts of tetraphenylethane **4a** and tetraphenylethene **5a** were mainly obtained as products of the thermal and photochemical decomposition of diphenyldiazomethane **1a** (Scheme 1).^[2] We have now been able to observe addition of the corresponding carbenes **2** to benzene in the thermal decomposition of diphenyldiazomethane **1a** and its *ortho*-methyl derivative **1b** and to isolate the previously unknown cycloheptatriene/norcaradiene systems **6/7** in substantial yields.^[3,4]



Scheme 1. Aryl = C₆H₄R; a, R = H; b, R = CH₃.

When the diazomethanes **1** are decomposed in boiling benzene the product composition strongly depends on the concentration of the starting material. At high concentrations of **1** the reaction of the carbene **2** with its precursor **1** dominates.^[2] At greater dilution, reactions of **2** with the solvent and with traces of impurities such as water and oxygen predominate.

In the thermolysis of **1b** in boiling benzene (on a preparative scale, high dilution, complete absence of moisture and oxygen) an addition product of **2b** and benzene could be isolated in 31% yield.^[5] Diphenylcarbene **2a** is less reactive: under the same conditions, only 8% of the addition products **6a/7a** were obtained. The same compounds are also formed on photolysis, but the yields are lower.^[6]

The NMR spectra of the compounds are consistent with a cycloheptatriene/norcaradiene equilibrium.^[7] The chemical shifts of the 1,6 H and C atoms of pure cyclohepta-

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