Tetrahedron Vol. 34, pp 419 to 424. Pergamon Press 1978. Printed in Great Britain

ESR AND ENDOR STUDIES OF PARTIALLY DEUTERATED AND CHLORINATED PHENALENYLS

NEW SYNTHETIC PATHWAYS

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(*Received in UK* 19 *May* 1977; *Accepted for publication* 11 *August* 1977)

Abstract—A variety of partially chlorinated and deuterated phenalenyl radicals has been produced by the reaction of the respective acenaphthylenes with chloroform as a carbenoid precursor and via thermal decomposition of some mercury carboxylates. By ESR and ENDOR-in-solution measurements the effectiveness of the different reaction paths to specifically substituted compounds has been investigated.

Phenalenyl 1 (Perinaphthenyl) is one of the most stable non-hetero hydrocarbon neutral radicals, and therefore is suitable for studying the electron distribution in organic doublet radicals by means of magnetic resonance methods. Compound 1 was one of the first for which negative spin densities had to be postulated.[1] ^{13}C-splittings could readily be observed in natural abundance.[2]

Due to its planarity, 1 achieves a remarkable high degree of ordering in the nematic phase of liquid crystals like *p*-azoxy-anisole and Nematic Phase IV Licristal (Merck). From ESR studies in liquid crystals of 1 fundamental contributions to the theoretical description of *g*-tensors and hfs-anisotropies in planar hydrocarbon radicals have been obtained.[3] Compound 1 has also been used as a model in studying electron and nuclear relaxation mechanisms[4] by multi resonance techniques like ENDOR (Electron Nuclear DOuble Resonance) and TRIPLE (electron nuclear nuclear TRIPLE resonance).[5] Using deuterated phenalenyls first successful measurements of deuterium quadrupole coupling constants in polyatomic doublet state molecules have very recently been performed.[6] The synthesis of the substituted and specifically deuterated phenalenyls is difficult and placing of substituents is not unequivocal. Therefore—for subsequent measurements also of heteronuclear quadrupole couplings—here we report new synthetic routes to the phenalenyl system, especially a carbenoid synthesis, which can be performed directly in the sample cell. For the elucidation of the constitution and isotopic distribution of the synthesized phenalenyls ESR and ENDOR techniques are employed.

Synthesis: As shown in the reaction scheme, the main precursors for the phenalenyl synthesis are acenaphthylenes or phenalenone respectively. The generation of 1

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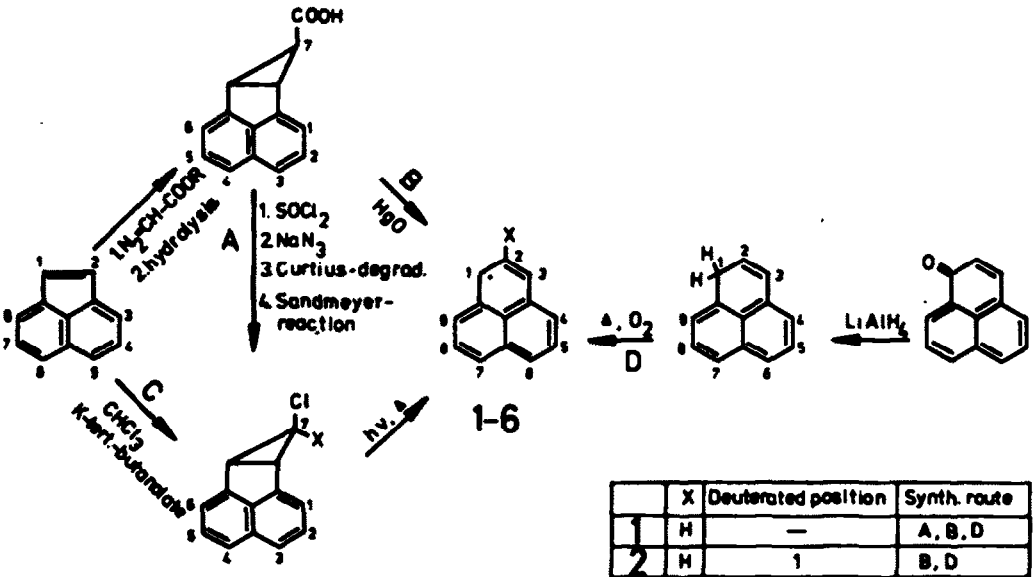

Reaction scheme and numbering of compounds

	X	Deuterated position	Synth. route
1	H	—	A, B, D
2	H	1	B, D
3	H	1,3,4,5,6,7,8,9	A, B
4	Cl	—	C
5	Cl	6	C
6	Cl	1,3,4,5,6,7,8,9	C

by thermal decomposition of 7-chloro-cyclopropano-acenaphthylene starts with reaction sequence A,[7] i.e. treatment of acenaphthylene with ethyl diazoacetate, followed by Curtius degradation and a modified Sandmeyer reaction as indicated. Synthetic route A does not yield definite deuterated phenalenyls nor does the reaction of phenalenone with $LiAlD_4$ (route D), giving phenalenyls deuterated not only in the original carbonyl C position. This result was also observed previously.[8] Using perdeutero acenaphthylene—made from commercially available perdeutero acenaphthene—following route A, the preparation of the acyl chloride is the last step without occurance of H/D exchange (MS, NMR). In the subsequent reaction steps the protic synthetic conditions then favor D/H scrambling. The deuterium distribution in the final product was determined by MS and NMR analysis of the 7-chloro-cyclopropano compound and by ESR and ENDOR spectroscopy of the corresponding radical 3. It turned out that 10% of the molecules show a further hydrogen in position 5 or 8 and another 20% in the equivalent positions 1, 3, 4, 6, 7 and 9. Thus, the synthesis of 3 following route A yields a product contaminated by a further hydrogen with a probability of about 30%. For this reason the intention was to find more convenient and especially aprotic synthetic pathways. The deuterated phenalenyls 2 and 3 were obtained without any by-products and with exclusively the original H/D distribution by treatment of the cyclopropano acenaphthylene carboxylic acid with mercury oxide in toluene, according to route B in the

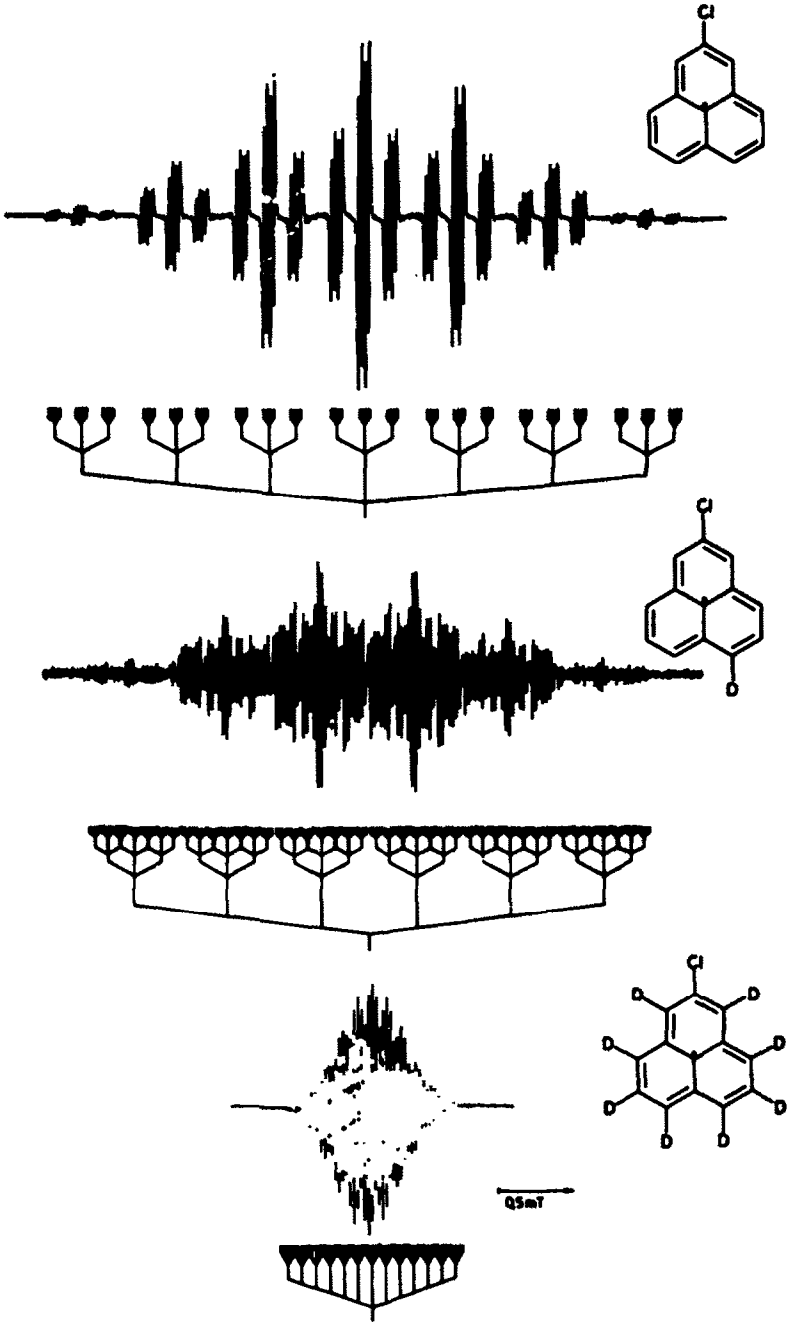

Fig. 1(a).

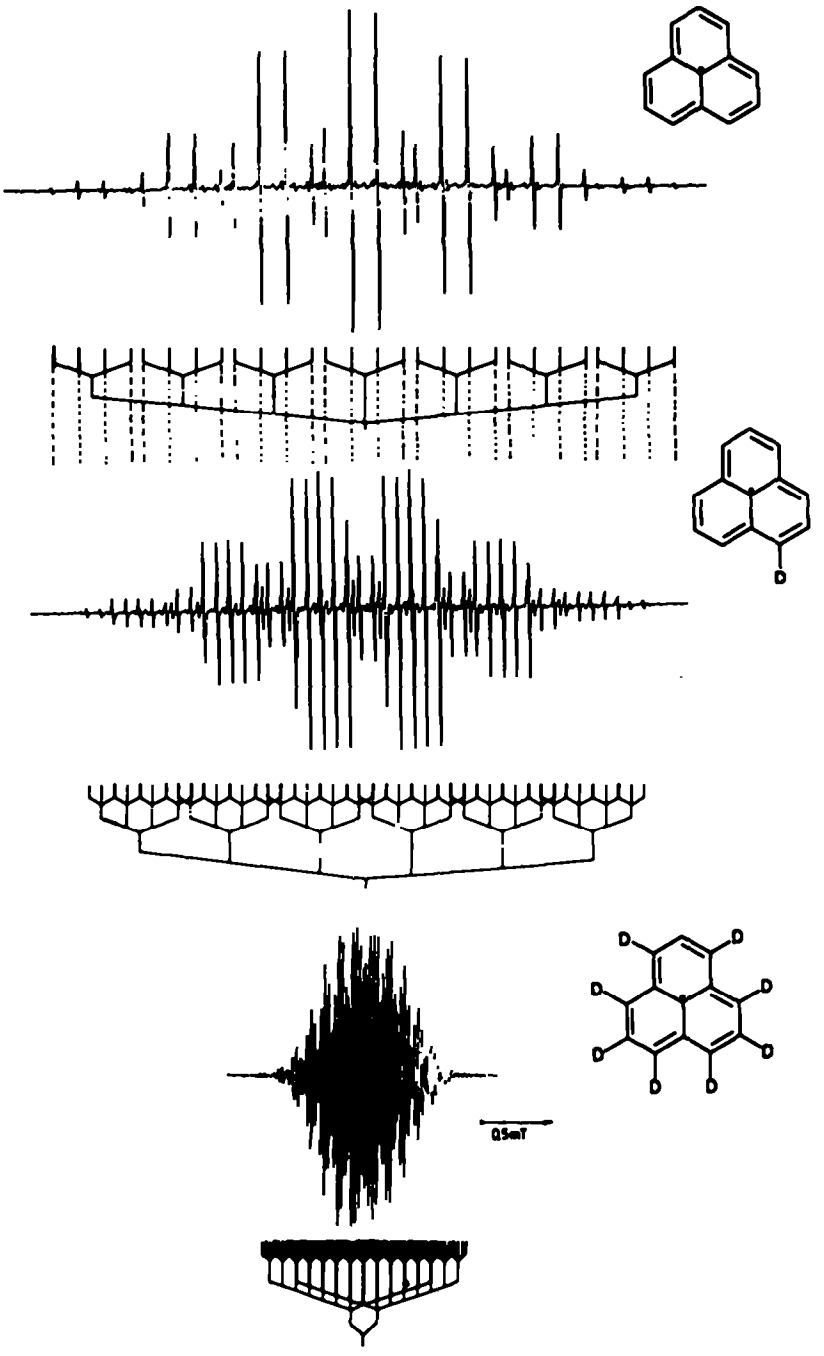

Fig. 1(b).

Fig. 1. ESR spectra of phenalenyls 1–3 (route B) and 4–6 (route D); toluene, – 10°C. The spectrum of 2 indicates 4% contamination by 1, see experimental.

reaction scheme (Fig. 1). This synthesis was also performed by preparing the mercury carboxylate from the acid and HgO, and isolating the salt before its thermolysis. The pure silver carboxylate could also be converted to the phenalenyl radical by thermal decomposition, but in this reaction a partial H/D exchange took place, probably during the preparation of the silver salt. Furthermore a paramagnetic phenalenyl-like by-product was obtained with no hydrogen—or deuterium respectively—at the 2-position. This unidentified radical has also been observed repeating the already known[9] pyrolysis of acenaphthylene to phenalenyl. The direct Hunsdiecker reaction was unsuccessful so far.

The most interesting novel phenalenyl synthesis is the carbenoid reaction of acenaphthylene with chloroform and potassium *t*-butanolate in toluene (route C). No isotopic exchanges take place, and without isolation of the plausible intermediate 7,7 - dichlorocycloprop[a]acenaphthylene the 2-chlorinated phenalenyls are formed (Fig. 1). With regard to compound

4 it is evident that route C is also successful with hexachloroacetone/K-*t*-butanolate or with sodium trichloroacetate as carbene deliverers. However, route C only allows a 2-chlorine substitution up to now. Attempts to use methylenchloride, bromoforme, benzyl-chloride and other carbene sources failed, further work in this field is in progress.

RESULTS AND DISCUSSION

An unambiguous assignment of the deuterated and/or chlorinated positions of the phenalenyls discussed was achieved by measuring the isotropic H, D and Cl hyperfine coupling constants using ESR- and ENDOR-techniques. Figure 1 illustrates the resolution obtained in the ESR spectra for the substituted phenalenyls. Except for the less resolved spectrum of 6 a complete interpretation of the spectra is possible. Thereby we made use of the fact,[8] that for odd alternant radicals like phenalenyl deuterium substitution does not affect the π-spin density distribution.[10] Table 1 demonstrates the expected reduction of hyperfine splittings when replacing H by D. The ratio of the corresponding hfs constants is approximately equal to the quotient of the magnetogyric ratios of the two nuclei $\gamma_H/\gamma_D = 6{,}514$. Small deviations from this value can be interpreted by different magnitudes of the CH and CD out-of-plane vibrations and orbital following[12] contributing to the hyperfine interaction.[8]

As indicated in Table 1 the experimentally determined widths of the spectra are in good agreement with the calculated values—assuming a specific and total H/D exchange and a reduction of the proton constants by γ_D/γ_H.

The ESR spectrum of 4 can be simulated satisfactorily by superposition of the spectra of radical species containing Cl-35 and Cl-37 respectively, taking into account the different magnetogyric ratios and natural abundances and assuming constant line widths.[13]

Previously it could be shown that the absolute sign of π-spin densities can be deduced from the shift of the electronic g-factor.[14] Substituting a proton in the 2-position by chlorine (for which the spin orbit coupling is larger) in the phenalenyl system to give 4, a reduction of the g-factor by $(140 \pm 10).10^{-6}$ was determined as compared to 1. Hence, the π-spin density in the 2-position of phenalenyl has a negative sign being in agreement with theoretical considerations,[3d] work in liquid crystals[3a,b] and TRIPLE resonance data,[3b] *vide supra*.

Recently, D-ENDOR-in-solution has been observed for partially deuterated ion radicals.[15] Deuterium resonances are also detectable for the deuterated phenalenyl radicals. As shown in Fig. 2 the ENDOR spectrum of 3 exhibits two pairs of lines centered around the free deuterium frequency $\nu_D = 2.154$ MHz and one proton line pair equally spaced around $\nu_H = 14.035$ MHz. The increase of deuterium ENDOR amplitudes to higher frequencies is due to the hfs-enhancement,[8] which defines the effective field at a nucleus to be proportional to $\nu_{ENDOR}/\nu_{free\ nucleus}$. This effect influences protons as well as deuterons, but in the case of the protons it is not so pronounced because of NMR saturation. The rf field being constant, saturation is not achieved for the deuterons because of the smaller magnetic moment.

Chlorine ENDOR signals could not be detected up to now, probably due to the effective quadrupole relaxation diminishing the ENDOR effect. The determination of chlorine quadrupole couplings using ENDOR in liquid crystals may be quite interesting, since these couplings in a radical are expected to be different from those measured for diamagnetic systems by NMR.[16]

From the high resolution ESR and ENDOR spectra of compounds 2–6 it turns out that 2-substitution by deuterium and/or chlorine does not affect the equivalence of positions compared to the symmetry of 1. The influence

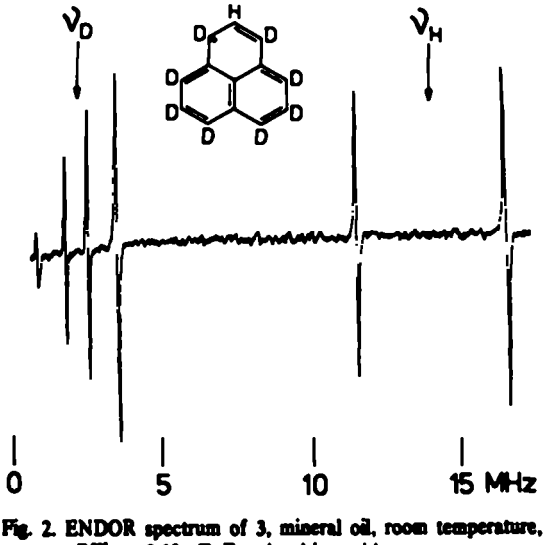

Fig. 2. ENDOR spectrum of 3, mineral oil, room temperature, $B_{NMR}^{rms} = 0.65$ mT. For signal intensities see text.

Table 1. Hfs constants from ESR, total splittings of the ESR spectra and ratio of proton to deuteron coupling constant at equivalent positions; toluene, −10°C

Radical	hfs constants [mT] (±0.001)					spectrum width [mT]		ratio
	a_{H_1}	a_{H_2}	a_{D_1}	a_{D_2}	a_{Cl}	exp.	calc.†	a_H/a_D
1	0.631	0.181	—	—	—	4.33	4.33	—
2	0.631	0.191	0.095	—	—	3.86‡	3.89	6.64
3	—	0.179	0.096	0.027	—	1.45	1.45	6.62
	—	0.180§	0.096§	0.027§	—			
4	0.630	0.183	—	—	0.023	4.24	4.22	—
5	0.633	0.181	0.093	—	0.023	3.83	3.78	6.81
6	—	—	0.095	0.026	—	1.31	1.32	—
	—	—	0.097§	0.027§				

†See text.
‡Taken solely from the absorption of 2.
§Coupling constant from ENDOR, mineral oil, room temperature.

of substitution on hyperfine splittings in the phenalenyl systems in general will be the subject of a more distinct ENDOR investigation.

Whereas in synthetic route A, the phenalenyl precursor is the well known 7-chloro-cyclopropano acenaphthylene, in route C (to the 2-chloro-phenalenyls) an analogous 7, 7-dichloro intermediate may be formulated. As pointed out by the experimental results, radicals are more easily generated, i.e. at lower temperatures, from the 7, 7-dichloro than from the 7-monochloro compound, the latter being only converted to phenalenyl at temperatures higher than 80°.[17]

Assuming a hypothetic equivalence of the chlorine substituents, statistics will induce a smaller stability of the disubstituted molecule. Furthermore the formation of the 2-chloro-phenalenyl can be rationalized in terms of the cyclopropyl/allyl rearrangement mechanism concerned with separation of a chlorine radical; the reaction is to be considered as an electrocyclic free radical rearrangement, following the disrotatory rule for steric reasons.[18] Provided that this mechanism is valid and taking into account the concept of 'anchimeric assistance', the cleavage of the *endo* substituent is preferred, since this is the only possibility to dissolve the σ-bond, see ref.[19] Therefore the 7-monosubstituted cyclopropano compound is unfavored for the rearrangement reaction because the halogen is in the *exo*-position—as could be shown from NMR investigations.[20] In the 7, 7-dichloro compound the *endo* oriented one of the substituents may easily leave the molecule. Corresponding to this mechanism postulated, the formation of highly energetic derivatives of the cyclopropyl radical may be evaded along the reaction coordinate. Since ionic mechanisms cannot be excluded, further experimental work must be done to clarify the applicability of the suggested mechanism.

CONCLUSION

The scope of these new types of phenalenyl formation is not restricted only to introduction of deuterium but reveals a good chance for ^{13}C-labelling of this radical, hence giving rise to further investigation of the magnetic properties of these isotopes. In the meantime we obtained 2-chlorinated phenalenyl ^{13}C-labelled in the 2-position (using route C), as could be deduced from the ESR experiments.[21] Furthermore we succeeded in measuring the deuterium nuclear quadrupole coupling constants in partially deuterated phenalenyls using ENDOR in liquid crystals.[6] Finally, the chlorine substituted phenalenyls may serve for studying the chlorine hyperfine interaction since only a few chlorine containing radicals exhibiting well resolved hyperfine structure are known.[22] Further experimental work is required in order to obtain chlorine ENDOR resonances and chlorine quadrupole couplings from ENDOR in liquid crystals.

EXPERIMENTAL

The ESR measurements were performed in toluene at −10°, using an AEG-12X-ESR- spectrometer (125 kHz field modulation). The ENDOR spectra were observed with a broad band ENDOR spectrometer built in our laboratory,[5b] using Shell Ondina G 17 mineral oil as solvent at 285K. Mass spectra were recorded on a VARIAN CH5D.

Acenaphthene-5-d was prepared by treating 5-bromo-acenaphthene[23] with $LiAlD_4$ in THF under reflux over a period of 10 days, according to ref.[24] The mixture was hydrolyzed by dropwise addition of THF/D_2O (1:1); after ether extraction and solvent evaporation the product was dried over P_2O_5 *in vacuo*. GC analysis: 100%, MS see acenaphthylene-5-d. There were two runs, (i) 3.5 g (0.015 mol) bromoacenaphthene, 2.52 g (0.06 mol) $LiAlD_4$ in 60 ml THF, yielding 2.25 g (96.8%), m.p. 92–93.5°C, (ii) 9.32 g (0.04 mol)/6.72 g (0.16 mol)/160 ml, yielding 6.1 g (98.4%), m.p. 92–93°.

Acenaphthylene-5-d and acenaphthylene-d_8 were prepared according to ref.[25] from the corresponding acenaphthenes (acenaphthene-d_{10} from CEA, France) by 15 hr reflux in benzene with 2, 3-dichloro-5, 6-dicyano-*p*-benzoquinone. After addition of ether, the mixture was washed thoroughly with 10% NaOH and with water; the solvent was removed and the crude product purified by column chromatography (neutral Al_2O_3/benzene), yielding 43–50%. Deuterium contents (MS): acenaphthylene-5-d from run (i), used for carbenoid reaction route C, 97.5%, from run (ii), used for preparation of the carboxylic acid and route B, 96% acenaphthylene-d_8 99.6%.

7-Carboxy-6b, 7a-dihydro-7H-cycloprop [a] *acenaphthylene* and the corresponding deuterated compound were prepared by refluxing the acenaphthylenes in toluene with ethyl diazoacetate according to ref.[7b] The carboxylic ester was hydrolyzed with NaOH (10%), the remaining Na-salt was thoroughly triturated with norite. The soln was acidified with conc HCl, the ppt was collected, washed with cold water, and dried over P_2O_5 *in vacuo*, yield 22% (monodeutero carboxylic acid: m.p. 193–6°C, deuterium content (MS) 96%; octadeutero carboxylic acid: m.p. 194–6°, 99.6% deuterium content).

Generation of radicals

2-Chloro-phenalenyls 4–6 (carbenoid reaction, route C). In the ESR sample cell 50 mg (0.5 mmol) K.-t-butanolate were added to a soln of 8 mg (0.05 mmol) acenaphthylene in 2 ml toluene. Purified and dried N_2 was bubbled continuously through the suspension. After addition of 0.12 g (1.0 mmol) $CHCl_3$, the heterogenous reaction was allowed to take place by N_2 mixing for 15 min, yielding an amount of radicals sufficient for spectroscopy. In this mixture the radicals remained stable for about one day.

Phenalenyls 1–3 (decomposition of the mercury carboxylates, route B). In the ESR sample cell the suspension of 5 mg (0.025 mmol) carboxylic acid, dissolved in 2 ml toluene, and 3 mg (0.015 mmol) well ground HgO, was kept at 85° for 5 hr, being mixed by an N_2 stream; a browaish ppt and phenalenyl radical was generated. The isolated mercury carboxylate, prepared from the acid and HgO in toluene at room temp, had also been decomposed by 5 hr heating to 80–85° in toluene in the ESR cell. Excluding O_2, the radicals may be stored in this mixtures for about one week. For ENDOR measurements at room temp., the solvent toluene had to be replaced by mineral oil.

Acknowledgements—The authors are indebted to Mrs. E. Brinkhaus for collaboration and to assistant professor Dr. J. Reusch for many stimulating discussions. H. K. wants to thank the Deutsche Forschungsgemeinschaft and Fonds der Chemischen Industrie for financial support. Part of this work was done with the support of "Sonderforschungsbereich 161" at the Institut für Molekülphysik, FU Berlin.

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