[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS, AND THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE UNIVERSITY]

Anthracene Photodimers. II. The Electric Moments and Structures of the Photodimers of 9-Haloanthracenes

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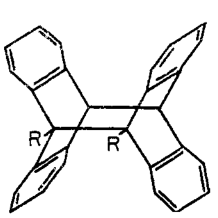
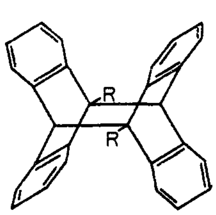
The dipole moments of the photodimers of 9-bromoanthracene and 9-chloroanthracene have been found to be zero within experimental error. It is concluded that the dimers have the "head-to-tail" or "*trans*" structure, in contrast with the "head-to-head" structures of the previously known examples of anthracene photodimers.

Introduction

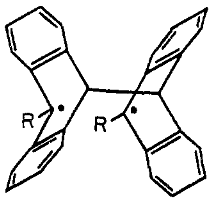
The photodimers of three 9-substituted anthracenes have been investigated chemically and found to possess the "head-to-head" structure, I.[1] The proposed explanation for the observed orientation was that an excited anthracene molecule adds to another in such a way that the positions of less stability as radicals couple most strongly in the product-determining transition state, which therefore resembles the most stable diradical (III) obtainable from a single coupling. Such a mechanism predicts head-to-head orientation whether or not the substituent R stabilizes an adjacent free radical (although the transition state would resemble III only if R stabilizes the radical).



Ia, R = CHO
Ib, R = CH$_2$OH
Ic, R = CO$_2$CH$_3$



IIa, R = Br
IIb, R = Cl



III

More recently,[2] chemical evidence has been presented in support of a head-to-tail structure (IIa) for the photodimer of 9-bromoanthracene. Since the evidence was negative in character (being primarily the failure to detect olefinic properties of the debromination product), it was deemed appropriate to obtain conclusive proof of the structure by electric moment measurement. To provide a partial test of the possibility that a steric effect was responsible for the abnormal orientation in IIa, the dimer of 9-chloroanthracene also was prepared and its electric moment measured.

Experimental

9-Chloroanthracene.—A modification of the procedure of Mikhailov and Promyslov[3] was employed. A mixture of 80 g. (0.225 mole) of anthracene, 112 g. (0.537 mole) of phosphorus pentachloride and 1000 ml. of anhydrous benzene was heated under reflux for one hour. The reaction mixture was cooled in an ice-bath and filtered to remove 23 g. of unreacted anthracene. The solvent was removed from the filtrate and the resulting residue was recrystallized from 2 l. of 95% ethanol to give 9 g. of an insoluble residue and 45 g. (65%) of 9-chloroanthracene, m.p. 93–98°. Three more recrystallizations from 95% ethanol gave material which had m.p. 98–101° (reported[3] 105–106°).

9,10'-Dichlorodianthracene (IIb).—A solution of 10 g. of 9-chloroanthracene in 90 ml. of benzene was irradiated through Pyrex in the sunlight (October–November) for 35 days. A total of 8.0 g. (4.5 g. of this in the first eight days) of IIb crystallized out, m.p. 211.5–213° dec., remelt 102–104°; flat, greenish rhombic crystals. Recrystallization from benzene gave colorless crystals, m.p. 209–210° dec., remelt 105–106°. The infrared spectrum of the recrystallized product was identical with that of the crude product.

Anal. Calcd. for $C_{28}H_{18}Cl_2$: C, 79.25; H, 4.23. Found: C, 79.52; H, 4.37.

Apparatus and Method for Dipole Moment Determinations.—The apparatus, technique, preparation of solvent and method of calculation have been described.[4] The dielectric constants and densities of five benzene solutions of the 9-bromoanthracene photodimer, ranging in mole fraction solute from 0.0003 to 0.0007, were measured at 25°. Similar measurements were made on seven solutions of the 9-chloroanthracene photodimer, ranging in mole fraction solute from 0.0002 to 0.0014 at 25°. The constants a, v_1, and b of the Halverstadt-Kumler equation are shown in Table I along with the calculated molar polarizations of the solutes, P_2; the symbols are the same as those employed previously.[4] The molar refractions of the solutes MR_D were calculated from empirical constants.[5] The probable error in P_2 is about ±5 cc.

TABLE I

EMPIRICAL CONSTANTS, MOLAR REFRACTIONS AND MOLAR POLARIZATIONS OF THE PHOTODIMERS OF 9-HALOANTHRACENES

	9-Bromoanthracene dimer	9-Chloroanthracene dimer
ϵ_1	2.2729	2.2727
v_1	1.14480	1.14472
a	2.36	2.30
b	−3.43	−2.14
P_2, cc.	130.20	129.05
MR_D	127.23	121.43
μ, Debye	0.36	0.60

Discussion

The calculated dipole moments of the photodimers of 9-bromoanthracene and 9-chloroanthracene (0.36 and 0.60 D., respectively) show that the

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(1) F. D. Greene, S. L. Misrock and J. R. Wolfe, Jr., THIS JOURNAL, **77**, 3852 (1955).

(2) D. E. Applequist, R. L. Litle, E. C. Friedrich and R. E. Wall, *ibid.*, **81**, 452 (1959).

(3) B. M. Mikhailov and M. S. Promyslov, *Zhur. Obshchei Khim.*, **20**, 338 (1950).

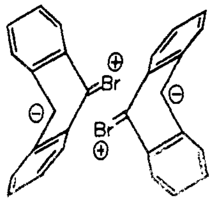
(4) M. T. Rogers, THIS JOURNAL, **77**, 3681 (1955).

(5) A. Vogel, *J. Chem. Soc.*, 1833 (1948).

molecules must be essentially non-polar. Although there is a small difference between the observed total polarization (P_2) and the calculated electronic polarization (MRD) in each case, this difference is scarcely more than experimental error. Any reasonable allowance for atomic polarization would then reduce the orientation polarization, and hence the dipole moment, to zero.

The head-to-head forms (I) of the photodimers of 9-haloanthracenes would be expected to have electric moments of about 3.8 D. (and, therefore, orientation polarizations of about 300 cc.), while the head-to-tail forms (II) should have zero moments. The two dimers studied here must, therefore, have the head-to-tail structures II.

Some modification of the proposed[1] free-radical mechanism of photodimerization appears to be required by the results reported here. It is possible that steric repulsions of the halogens would tend to stabilize the transition states for head-to-tail dimerizations, but it is improbable that this could be the only factor influencing the orientation, since steric repulsions would appear to be at least as great between two hydroxymethyl groups (which go head-to-head[1]) as between two chlorine atoms, from inspection of Fisher–Hirschfelder models. It is interesting that the substituents which give head-to-tail dimers have unshared electron pairs next to the anthracene nucleus, whereas those which do not possess such electron pairs give head-to-head dimers. This suggests that polar structures, such as IV, may contribute to the product-determining transition states. Head-to-tail orientation would certainly be promoted by such contribution. Finally, the possibility exists that head-to-tail orientation results from equilibrium control of products, whereas head-to-head orientation results from purely kinetic control. Further work on the orientation phenomena is expected to reveal the contributions of these and possibly other controlling influences.



IV

Acknowledgment.—We are indebted to Miss Claire Higham for the microanalyses and to Mr. James Brader for the infrared spectra.

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[CONTRIBUTION FROM THE NAVAL STORES STATION, U. S. DEPARTMENT OF AGRICULTURE[1]]

Preparation of 6-Hydroxydehydroabietic Acid from the Photoperoxide of Levopimaric Acid

BY R. N. MOORE AND RAY V. LAWRENCE

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A peroxide obtained from levopimaric acid by a photosensitized air oxidation process and tentatively formulated as 6,14-peroxy-$\Delta^{7(8)}$-dihydroabietic acid, was rearranged readily in alkaline medium to a hydroxy-enone. Dehydration of the hydroxy-enone gave 6-hydroxydehydroabietic acid and a dienone presumed to be 6-ketoabietic acid, on the basis of its ultraviolet absorption. The presence of the alcoholic hydroxyl group in the hydroxy-enone was shown by the hydroxyl stretching band at 2.9 μ in the infrared spectrum of its methyl ester, and a tertiary, α,β-unsaturated location was indicated by its ease of dehydration. The hydroxy-enone was therefore formulated as 6-keto-14-hydroxy-$\Delta^{7(8)}$-dihydroabietic acid. The phenolic dehydration product was reduced by $LiAlH_4$ to 6-hydroxydehydroabietinol.

A peroxide, obtained from levopimaric acid by a process of photosensitized air oxidation,[2] has been formulated tentatively as the product of 1,4 addition of oxygen to the homoannular dienic grouping in levopimaric acid, that is, 6,14-peroxy-$\Delta^{7(8)}$-dihydroabietic acid (I). This formulation of the peroxide was supported by the absence of selective ultraviolet absorption in the region of 220–320 mμ, the absence of any new Grignard-reactive hydrogen, the neutralization equivalent, elemental analysis, its instability in alkaline medium and by the fact that one mole of oxygen per mole of levopimaric acid was absorbed during its formation.

It is known that the decomposition of certain hydroperoxides and dialkyl peroxides is catalyzed by base, to yield alcohols and ketones. It has been pointed out that only those dialkyl peroxides and alkyl hydroperoxides having a hydrogen on the carbon attached to the peroxide linkage will undergo base-catalyzed decomposition, and a mechanism has been proposed which involves abstraction of this hydrogen as the primary step.[3] Extension of this mechanism to an intramolecular peroxide such as I predicts molecular rearrangement to a hydroxy-enone, rather than decomposition. The predicted product, 6-keto-14-hydroxy-$\Delta^{7(8)}$-dihydroabietic acid (II), having a tertiary, α,β-unsaturated hydroxyl group, should be readily dehydrated to either 6-ketoabietic acid (III) or 6-hydroxy-dehydroabietic acid (IV) or a mixture of the two. The dienone III also should be isomerizable to IV. A similar rearrangement recently has been employed for the preparation of a corticosteroid intermediate.[4] Reinvestigation of the

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(1) One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture. Article not copyrighted.

(2) R. N. Moore and Ray V. Lawrence, THIS JOURNAL, **80**, 1438 (1958).

(3) N. Kornblum and H. E. De La Mare, *ibid.*, **73**, 880 (1951).

(4) G. D. Laubach, E. C. Schreiber, E. J. Agnello, E. N. Lightfoot and K. J. Brunings, *ibid.*, **75**, 1514 (1953).