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RADICAL DECARBONYLATION REACTIONS I.

DECARBONYLATION OF 9-PHENYL-9-FLUORENYLACETALDEHYDE

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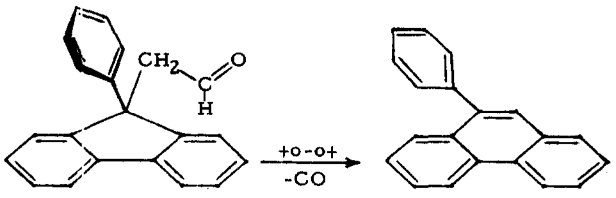
Free radical rearrangement reactions have been the subject of a number of publications in recent years. Of the many reports that appear in the literature, few describe uncomplicated radical migrations that involve simultaneous ring expansion.[*1] We have examined the peroxide initiated decarbonylation of 9-phenyl-9-fluorenylacetaldehyde (I) and found that the decarbonylation was accompanied by a rather smooth conversion to 9-phenylphenanthrene (II).

[*1] During the latter stages of the preparation of this paper we learned that Brother H. Philip, F.S.C., Lewis College, Lockport, Illinois was also working on these systems. (Eighth Annual Report on Research Sponsored by the Petroleum Research Fund for the period ending August 31, 1963). In a private communication Brother Philip stated that he obtained substantially the same results as we did. Another reaction similar to the one described in this paper is the decarbonylation of (1-methylindanyl)acetaldehyde under free radical conditions to give 1,1-dimethylindane and 2-methyltetralin [J. W. Wilt and C. A. Schneider, J. Org. Chem. 26, 4196 (1961)].

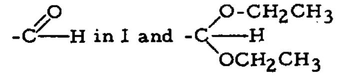


I II

The aldehyde[*2], I, m.p. 114-115°, (aqueous ethanol), DNP m.p. 179-180°, was prepared in 64% yield from 9-chloro-9-phenylfluorene and chloromercuriacetaldehyde by a procedure similar to one used by Curtin and Hurwitz for the synthesis of β,β,β-triphenylpropionaldehyde (1). Both infrared and nuclear magnetic resonance (n.m.r.) analyses support the assigned structure of I; IR 1720 cm.$^{-1}$ (C=O), 2740 cm.$^{-1}$ (aldehydic C-H); n.m.r. a triplet at 1.2τ (1 proton), multiplets at 2.34 and 2.85 τ (13 protons) and a doublet at 6.62 τ (2 protons).[*3]

[*2] All new compounds gave satisfactory microanalyses. The microanalyses were performed by Micro-Analysis, Inc., Wilmington, Del. The infrared spectra were obtained in potassium bromide on a Baird-Atomic KM-1 recording spectrophotometer. The n.m.r. spectra were taken on a Varian Associates recording spectrometer (A-60) at 60 Mc in deuterated chloroform using tetramethylsilane as the internal standard.

[*3] One notes that the chemical shifts for all non-aromatic type protons in both I and III are displaced from their normal positions. This can be explained if one considers the magnetic anisotropy of rings A, B, and B'. The methylene group of I lies essentially in the plane of the average position of ring A and therefore would experience a reinforcement of the applied field at this point which would result in a shift of its proton resonances to lower field. Similarly all protons on carbons beyond the methylene group, i. e.



$-\overset{O}{\overset{/\!/}{C}}-H$ in I and $-\underset{OCH_2CH_3}{\overset{O\text{-}CH_2CH_3}{C}}-H$

in III, lie above the plane of rings B and B'. The induced fields in these rings would shield these protons and cause their resonances to shift to higher field. This topic will be discussed further in another publication.

The reaction was run at 135-140° using di-t-butylperoxide as the initiator. The amount of carbon monoxide evolved corresponded to approximately 49% decarbonylation.

The reaction mixture was a liquid which crystallized on standing overnight at room temperature. From the crystalline mass was isolated starting material (55% recovery)[*4], 9-phenylphenanthrene (II)[*5], m.p. 104-105°, (alcohol-water), (45% yield)[*6], picrate m.p. 114.5-115.5°, and a substance, III, m.p. 75-76°, which had a molecular weight of 358 as determined by mass spectrometry.[*7] Elemental analysis and infrared and n.m.r. spectroscopy indicate III to be the diethyl acetal of I (7.9% yield)[*6]; I.R. 1601 w, 1500 w, 1445 m, 1373 ms, 1139 ms, 1108 ms, 1055 ms, 1023 ms, 770 w, 754 ms, 746 ms, 736 s, and 697 cm.$^{-1}$ ms; n.m.r. multiplets at 2.31 and 2.82 τ (13 protons), a triplet at 6.32 τ (1 proton), a multiplet at 6.97 τ (6 protons) and a triplet at 9.2 τ (3 protons).[*3] The formation of III could conceivably have been spontaneous from I when ethanol was added to induce the crystallization of II.

If the mechanism of this reaction is like that proposed by Winstein and Seubold (2) for the chain decarbonylation of aldehydes, then 9-phenyl-9,10-dihydrophenanthrene (VI) should have formed in this reaction

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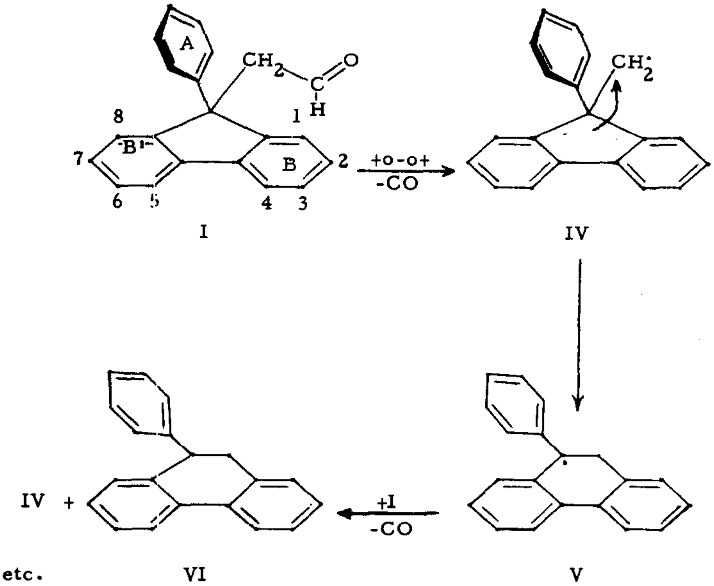
*4. The per cent recovery is based on the total amount of aldehyde (I) used in the reaction.

*5. The infrared spectrum of II is superimposable on one of 9-phenylphenanthrene supplied to us by Brother H. Philip.

*6. This yield is based on the amount of aldehyde (I) that reacted or 45 per cent of the total aldehyde used in the reaction.

*7. The mass spectrum was determined by Mr. Maurice Bazinet, Analytical Laboratory, U. S. Army Natick Laboratories, Natick, Mass.

according to the following scheme.



Disproportionation of intermediate V would also seem a likely process leading to VI. None of the dihydro-compound could, however, be detected among the reaction products. The failure to detect VI does not preclude its formation in the reaction since it is likely that the presence of oxygen could result in the oxidation of V to II.

It is interesting to note that phenyl (ring A) migration was not observed. The failure of this migration to occur may be explained if one considers the transition states of the two possible migrations. The rate at which rings A or B will migrate is determined to a great extent by the degree of overlap that may be attained in the transition state between the p-orbital of the methylene group and that of the migrating carbon, maximum overlap occurring when these orbitals are coplanar. An examination of molecular models reveals that ring A experiences considerable restriction to rotation due to the interaction of its *ortho*-hydrogens with those on C-1 and C-8. This would result in an increase in the activation energy for ring A migration and consequently would lower the tendency for this group to migrate.[*8] Furthermore, the migration of ring B would tend to relieve the strain at C-9 of the 5-membered ring of fluorene while simultaneously forming the rather stable radical V. The migration of ring B through a bridged intermediate is not likely since this would involve a high energy spirane-type structure.

Work is now in progress in this laboratory on several reactions of this type and additional reports are forthcoming.

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REFERENCES

(1) D. Y. Curtin and M. J. Hurwitz, J. Amer. Chem. Soc. **74**, 5381 (1952).

(2) S. Winstein and F. H. Seubold, J. Amer. Chem. Soc. **69**, 2916 (1946).

[*8] A similar effect was noted by J. W. Wilt and Brother H. Philip, F.S.C. (J. Org. Chem. **25**, 891 (1960)) who observed that the rate of migration of the phenyl group in 1-phenylcyclohexylacetaldehyde was greater than that in 1-phenylcyclopentylacetaldehyde.