

AN INTRAMOLECULAR CHLOROALKYLATION REACTION

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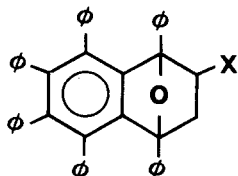
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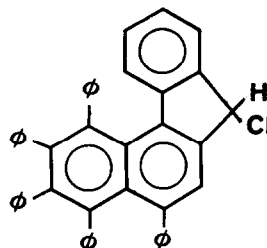
Treatment of an acetic acid suspension of 1,4,5,6,7,8-hexaphenyl-1,4-oxido-1,2,3,4-tetrahydro-2-naphthaldehyde (1a, the Diels-Alder adduct of hexaphenylisobenzofuran¹ with acrolein) with gaseous hydrogen chloride at ambient temperature yields moderately soluble 2-phenyl-3,4-(tetraphenylbenzo)-9-chlorofluorene (2, melting point 193° dec.)² in about 50% yield.



1a: X = CHO

1b: X = COCH₃

1c: X = CN



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The structure of 2 was established from the following evidence:

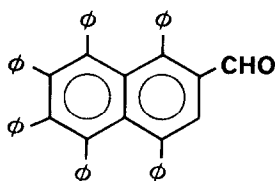
- Elemental analysis (recrystallized from benzene-ethanol). Found: C, 89.40; H, 5.09; Cl, 5.65. Calculated for C₄₇H₃₁Cl: C, 89.43; H, 4.95; Cl, 5.62.
- Lability of chlorine (positive reaction with silver nitrate).
- NMR spectrum³ (carbon disulfide solution): singlet at 5.83 δ and complex multiplet at

6.4 to 7.6 μ in approximately the correct ratio (1 to 30).

d) U.V. spectrum: λ_{max} (ethanol): 243, 277, 370 $m\mu$. (Low solubility in ethanol precluded an accurate determination of the extinction coefficients, but $\log \epsilon$'s were estimated to be between 4 and 5).

The infrared spectrum was inconclusive due to the complexity in the 600 - 800 cm^{-1} region, although 2 exhibited a strong band at 742 cm^{-1} (o-disubstituted benzene ?) absent in the spectrum of 1a.

Analogous reactions have been reported for the Diels-Alder adducts of acrolein with 1,3-diphenylisobenzofuran⁴ and 1,3,4,7-tetraphenylisobenzofuran⁵ although in neither instance was the structure of the chlorinated product established. In the latter case, 2-chloro-1,4,5,8-tetraphenylnaphthalene was suggested⁵ as a possible structure on the basis of satisfactory elemental analysis and UV spectrum identical to that of 1,4,5,8-tetraphenylnaphthalene; however, both analysis and spectrum are also consistent with the fluorene derivative. In both of these cases^{4,5}, the corresponding phenylated 2-naphthaldehydes were also isolated, but we have been unable, thus far, to prepare the analogous 1,4,5,6,7,8-hexaphenyl-2-naphthaldehyde (3).



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Preparation of the fluorene derivative, 2, is an example of an extremely facile intramolecular haloalkylation reaction⁶. The fact that previous workers^{4,5} were able to isolate the phenyl-substituted 2-naphthaldehydes as well as the chloroalkylated compounds indicates that aromatization precedes ring closure. Our failure to isolate the aromatized aldehyde, 3, could be the result of extra crowding caused by the phenyls at positions 6 and 7 pushing the phenyl group at position 1 into closer proximity with the aldehyde group.

Attempts to make the hexaphenylisobenzofuran - methyl vinyl ketone adduct (1b) undergo

a similar chloroalkylation reaction failed, as did attempts to make the acrylonitrile adduct (1c) undergo an intramolecular Hoesch acylation reaction⁷ (using hydrogen chloride with or without added zinc chloride) to form the fluorenone derivative. In fact, both 1b and 1c failed even to aromatize under these conditions^{8,9}.

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References and Footnotes

1. W. Ried and K.H. Bonnighausen, *Ann.*, 639, 61 (1960).
2. Compound 2 appears to decompose with evolution of HCl. This possible thermal α -elimination reaction is under investigation.
3. The benzylic proton of diphenylmethyl chloride absorbs at 6.12 δ in deuteriochloroform. (N.S. Bhacca, L.F. Johnson, and J.N. Schoolery, *High Resolution NMR Spectra Catalog*, Vol. 1, Varian Associates, 1962, Spectrum No. 176).
4. A. Etienne, A. Spire, and E. Toromanoff, *Bull. Soc. Chim. France*, 750 (1952).
5. E.D. Bergmann, Sh. Blumberg, P. Bracha, and Sh. Epstein, *Tetrahedron*, 20, 195 (1964).
6. Haloalkylations are usually run in the presence of Friedel-Crafts catalysts, particularly zinc chloride. See, for example, R.C. Fuson and C.H. McKeever, *Organic Reactions*, 1, 63 (1942); G.A. Olah and W.S. Tolgyesi in G.A. Olah, "Friedel-Crafts and Related Reactions", Interscience, New York, 1963-4, Vol. 2, pp. 659-784.
7. P.E. Spierri and A.S. DuBois, *Organic Reactions*, 5, 387 (1949).
8. Bergmann and coworkers (Ref. 5) were also unable to aromatize the methyl vinyl ketone and acrylonitrile Diels-Alder adducts of 1,3,4,7-tetraphenylisobenzofuran, but Etienne and coworkers (Ref. 4) did aromatize the methyl vinyl ketone-1,3-diphenylisobenzofuran adduct with gaseous hydrogen chloride; the aromatized methyl ketone did not, however, undergo chloroalkylation.

9. The failure of 1c to undergo the intramolecular acylation reaction is apparently not due to its inability to aromatize since 2,3,4,5-tetraphenylbenzotrile¹⁰ was also found to be unreactive under conditions of the Hoesch reaction. Similar conclusions may be drawn about 1b (see footnote 8).
10. R.F. Doering, R.S. Miner, Jr., L. Rothman, and E.I. Becker, J. Org. Chem., 23, 520 (1958).