

INTERMEDIATES IN NUCLEOPHILIC AROMATIC SUBSTITUTION. PART II (1).

SPIRO MEISENHEIMER COMPLEXES DERIVED FROM 1-(β -HYDROXYETHOXY)-2,4-DINITROARENES

C. E. Griffin, E. J. Fendler (2), W. E. Byrne

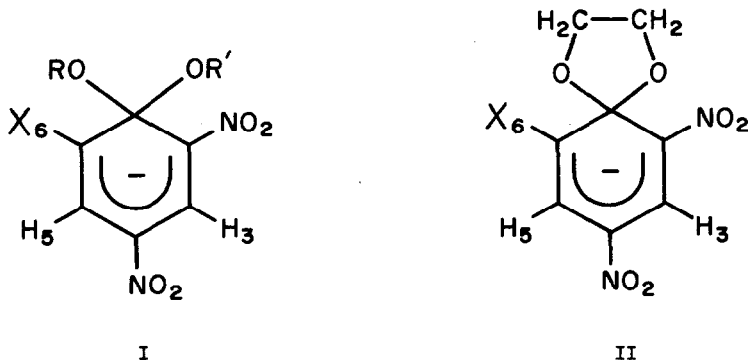
Department of Chemistry, University of Pittsburgh
Pittsburgh, Pennsylvania 15213

J. H. Fendler

Radiation Research Laboratories, Mellon Institute, Carnegie-Mellon University
Pittsburgh, Pennsylvania 15213

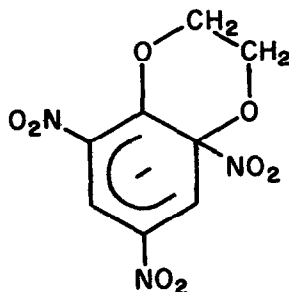
(Received in U.S.A. 19 July 1967)

In recent years, the application of PMR spectroscopy, in conjunction with infrared and ultraviolet studies, has substantiated the covalent nature of Meisenheimer complexes (3), particularly those (I) formed by the attack of alkoxide ion on nitroaryl ethers (1, 4-7), and has effectively eliminated the alternative charge-transfer formulations (3).



The covalent structure (I) requires sp^3 hybridization at C-1 of the cyclohexadienylidene system, a requirement met by the PMR identity of R and R' in symmetrical (e.g. R = R' = CH_3) complexes (1, 4-7). A particularly convincing demonstration of this hybridization is provided by the formation of spiro complexes (II) by the attack of base on the nitroaryl ethers of glycol (5-7). The spectral characteristics of the product (II, X = NO_2) formed by the action of either sodium glycolate or hydroxide on the picryl ether are in accord with the postulated structure (5, 7, 8). However, because of the symmetry of this system, the structural proof is not unequivocal, i.e. the observed methylene equivalence is consistent with both non-cyclic and

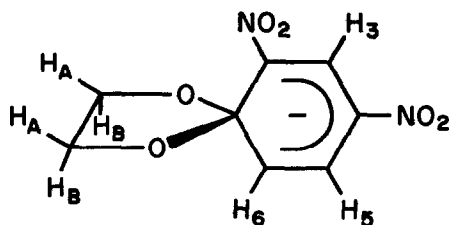
and dimeric structures, as well as the spiro structure. The identity of chemical shifts for the methylene protons and for H-3 and H-5 conclusively eliminates the isomeric structure (III). Sim-



III

ilar considerations hold for the complex formed from the corresponding 2,6-dinitrophenyl ether (6).

A more appropriate spiro compound for PMR studies and the demonstration of C-1 sp^3 hybridization is that (IV) derived from 1-(8-hydroxyethoxy)-2,4-dinitrobenzene (V). The



IV

lower degree of symmetry of IV should lead to the observation of an A_2B_2 spectrum (9) for the methylene protons in the spiro configuration, while non-cyclic or dimeric structures should result in either methylene equivalence or A_2X_2 spectra. Pollitt and Saunders (10) postulated the formation of IV on the basis of the ultraviolet spectra of alkaline solutions of V. More recently, the PMR spectrum of IV generated, but not isolated, by the action of methoxide ion on V has been reported (6); the chemical shifts, multiplicities and coupling constants reported for H-3, H-5 and H-6 were consistent with structure IV but, contrary to expectation, methylene equivalence was reported. This latter observation made the assignment of structure IV to this product questionable in view of the previously cited considerations (11). Since a confirmation of the structure of this spiro complex appeared to be essential in the general context of Meisenheimer complex chemistry, we have reinvestigated the preparation and PMR spectral characteristics of IV.

Compound IV has been obtained in a stable crystalline form by the action of potassium methoxide and ethoxide in dioxane and potassium methoxide in benzene on V, following established procedures (1), as well as by the action of metallic sodium on V in toluene. The products formed by each of these methods are identical, with the exception of differences due to solvent (dioxane, benzene) of crystallization (1); the formation of IV by the action of sodium in the absence of alkoxide clearly eliminates the possibility of a mixed complex of type I (11). The 60 MHz spectrum of crystalline IV dissolved in DMSO- d_6 showed the aromatic resonances established (1) as characteristic of I (X = H): $\tau_3 = 1.45$, $\tau_5 = 3.17$, $\tau_6 = 4.70$ p.p.m.; $J_{35} = 2.7$, $J_{56} = 10.7$ Hz. These parameters are essentially identical to those reported by Foster *et al.* (6). However, the methylene resonances were observed as a complex multiplet centered at $\tau = 5.92$ p.p.m. with a total multiplet width of ca. 30 Hz, clearly indicative of methylene non-equivalence. Eighteen of the twenty-four transitions expected for an A_2B_2 spectrum (9) in a 50 Hz sweep width spectrum were observed (12). The spectrum was analyzed following the procedure of Abraham (9) to yield the following parameters: $J_{cis} = 7.2$, $J_{trans} = 6.1$, $J_{gem} = 7.6$ Hz and $\tau_A = 5.87$, $\tau_B = 5.97$ p.p.m. A computer generated spectrum was in good agreement with the experimental spectrum and the assignments were verified by recording the spectrum at 100 MHz. These parameters are quite similar to those calculated for 2-methyl-1,3-dioxolane (9). The relative ease of spiro Meisenheimer complex formation was illustrated by the generation and isolation of the corresponding complex (VI) formed by the attack of methoxide ion on 1-(β -hydroxyethoxy)-2,4-dinitronaphthalene; molecular models indicate VI to be highly crowded due to *peri* interactions. The aromatic proton resonances of VI were similar to those of 1,1-dialkoxy Meisenheimer complexes of 2,4-dinitronaphthalene systems (13); methylene non-equivalence similar to those of IV was observed.

The observation of the A_2B_2 spectrum for the methylene protons of IV confirms the structure of this complex and the close similarity of the PMR parameters for these protons to those of the dioxolane (9) are only consistent with the postulated spiro geometry and sp^3 hybridization at C-1 (14). The observed spectrum is clearly incompatible with other formulations for this Meisenheimer complex and, by analogy, for other complexes of type I.

Acknowledgement. This study was supported in part by the U. S. Atomic Energy Commission and by a grant from Merck Sharp and Dohme Research Laboratories. A portion of the PMR studies utilized instrumentation provided by a grant (FR 00292) from the National Institutes of Health.

REFERENCES

1. Part I: W. E. Byrne, E. J. Fendler, J. H. Fendler and C. E. Griffin, J. Org. Chem., in press.
2. NASA Postdoctoral Fellow, 1966-1967.
3. For a recent review, see R. Foster and C. A. Fyfe, Rev. Pure Applied Chem., 16, 61 (1966).
4. M. R. Crampton and V. Gold, J. Chem. Soc., 4293 (1964); R. Foster and C. A. Fyfe, Tetrahedron, 21, 3363 (1965); M. R. Crampton and V. Gold, J. Chem. Soc. (B), 893 (1966); K. L. Servis, J. Am. Chem. Soc., 89, 1508 (1967).
5. R. Foster, C. A. Fyfe and J. W. Morris, Rec. trav. chim., 84, 516 (1965).
6. R. Foster, C. A. Fyfe, P. H. Emslie and M. I. Foreman, Tetrahedron, 23, 227 (1967).
7. P. Caveng, P. B. Fischer, E. Heilbronner, A. L. Miller and H. Zollinger, Helv. Chim. Acta, 50, 848 (1967).
8. J. Murto, Suomen Kem., B38, 255 (1965).
9. R. J. Abraham, J. Chem. Soc., 256 (1965).
10. R. J. Pollitt and B. C. Saunders, ibid, 1132 (1964); for an earlier misinterpreted observation, see S. S. Gitis and A. Y. Kaminski, J. Gen. Chem. USSR, 30, 3771 (1960).
11. The observed PMR (6) and ultraviolet (10) spectra of IV are consistent with a mixed 1,1-complex (I, R = -CH₂CH₂OH, R' = -CH₃ or H, X = H), a feasible product from the action of methoxide or hydroxide ion on V.
12. As in the case reported by Abraham (9), two sets of transitions (8, 11, 12 and 9, 10) are unresolved.
13. J. H. Fendler, E. J. Fendler, W. E. Byrne and C. E. Griffin, to be published.
14. The structure is also supported by the observation of infrared and ultraviolet spectra characteristic of I (X = H), e.g. typical (1) ketal absorptions were shown by IV at 1075 and 1025 cm.⁻¹