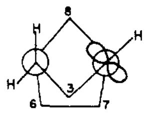
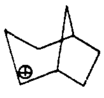
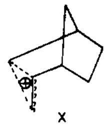
sulfonates XI, which pass through a classical intermediate before proceeding to a mesomeric cation. The relative geometry of c and d in I is roughly the same as that of Y and C.6 in XI.

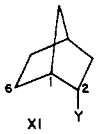


VIa


VIII


IX


X



XI

Acknowledgment.—We are indebted to the National Science Foundation (Grant No. G-11386) for support of part of this work.

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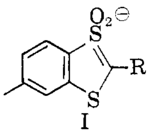
RECEIVED DECEMBER 4, 1961

STUDIES ON d-ORBITAL CONJUGATION. II. LACK OF AROMATICITY IN SYSTEMS CONTAINING A CARBANION-SULFONE DOUBLE BOND[1]

Sir:

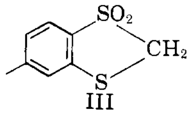
With the developing evidence[2] that the sulfone group, and other systems with strongly electronegative second row elements, can interact with adjacent unsaturated centers by a conjugation mechanism, it has become increasingly common to write structures such as I, with a double bond which (probably) involves the use of a 3-d orbital by sulfur. Among the properties of such a double bond which are of interest, its stereochemistry and its ability to conjugate seem fundamental. It has been suggested[3] that double bonds of this type can form aromatic systems if they are cyclically conjugated, but a counter view has been advanced by Dewar,[4] who suggests that the stereoelectronic properties of d-orbitals will cause pi electron nodes in the cyclic system, so that aromatic stabilization will not be observed.

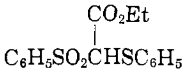

I

Several compounds are already known which are of interest in this connection. The cyclic phosphonitrilic halides have been suggested to be aromatic,[3] and Price has reported a derivative of "thiabenzene"[5] in which 10-electron sulfur is part of the cyclic system. However, no evidence for aromatic stabilization of these systems because of any special effect resulting from their cyclic conjugation is available, and the situation is also ambiguous for two known benzothiepin dioxides[6] which are d-orbital analogs of tropone.

In order to obtain evidence on this question we have examined the acidity of compounds II–V. The carbanions derived from III and V will have contributions from resonance forms of the type I, and if such a system is strongly stabilized by cyclic conjugation, as is the analogous aromatic benzothiazole system, then this should be reflected in an increased acidity of III and V. The choice of II and IV as open-chain analogs is justified by our finding[1] that the disulfones related to II–V have comparable acidities; this with the other previously reported comparisons[1] indicates that no special steric effect invalidates the comparison between II, IV and III, V.

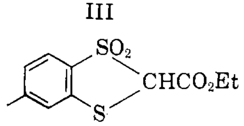
$C_6H_5SO_2CH_2SC_6H_5$
II


III



$$\overset{CO_2Et}{\overset{|}{C_6H_5SO_2CHSC_6H_5}}$$

IV


V

The sulfide sulfone (II), m.p. 55–57°,[7] was prepared by oxidation of methylene diphenyl disulfide with hydrogen peroxide in acetic acid to the corresponding sulfoxide sulfone, m.p. 67–68°,[7] and reduction of the latter to II with zinc/acetic acid. 6-Methyl-1,3-benzodithiolane 3,3-dioxide (III), m.p. 108–110°,[7] was prepared by a similar sequence. Oxidation of the benzodithiolane yielded a mixture of the two possible sulfoxide sulfones, and reduction yielded both III and the isomer, 5-methyl-1,3-benzodithiolane 3,3-dioxide, m.p. 67–69°.[7] The assignment of respective structures to these isomers was based on n.m.r. spectral studies on the aromatic hydrogens, and will be described in the full publication.

When II was allowed to stand for several hours with dimethoxyethane/D_2O/triethylamine, the recovered starting material was completely deuterated in the methylene group, as evidenced by its n.m.r. spectrum, and III was similarly converted to the 2,2-dideuterio derivative. Treatment of this deuterated II with one mole of butyllithium in ether, addition of dimethoxyethane to effect complete solution, and addition of this solution to 2N HCl afforded recovered II with one proton in the methylene group, appearing at 5.74 τ in the n.m.r. Deuterated III was similarly converted to the monoanion by butyllithium, as revealed by the appearance, after processing as above, of one proton at 5.76 τ. When the anion of deuterated III was prepared first, and an equimolar amount of deuterio-II then was added, the resulting homogeneous solution, after quenching, gave a mixture of II and III which was analyzed by the use of n.m.r. A

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(1) For Part I, *cf.* R. Breslow and E. Mohacsi, *J. Am. Chem. Soc.*, **83**, 4100 (1961).

(2) For a review, see G. Cilento, *Chem. Rev.*, **60**, 147 (1960).

(3) D. P. Craig, *J. Chem. Soc.*, 997 (1959).

(4) M. J. S. Dewar, F. A. C. Luchen, and M. A. Whitehead, *ibid.*, 2423 (1960); *cf.* however M. J. S. Dewar and V. P. Kubba, *J. Am. Chem. Soc.*, **82**, 5685 (1960).

(5) G. Suld and C. C. Price, *ibid.*, **83**, 1770 (1961).

(6) W. Truce and F. Lotspeich, *ibid.*, **78**, 848 (1956); V. J. Traynelis and R. F. Love, *J. Org. Chem.*, **26**, 2728 (1961).

(7) These compounds gave C and H analyses within 0.3% of theoretical and their infrared and n.m.r. spectra were consistent with the assigned structures.

total of one proton had been incorporated, and was distributed equally between II and III. This result was reproducible, and the same equilibrium was obtained from the reverse order of addition of II and III, so a true equilibrium has been reached. These results show clearly that II and III have essentially the same acidity, so that the anion of III, which may be symbolized as I, has no special stability because of its cyclic conjugation, and is in that respect *not* an aromatic system.

This conclusion was confirmed by the synthesis of the esters IV and V, which were sufficiently acidic to be titratable against a glass electrode. The lithium salt of II was treated with diethyl carbonate and gave IV, b.p. (bath temp.) 190–200° (0.1 mm.).[7] This compound was soluble in 0.1 *N* NaOH, and recovered unchanged on acidification. The lithium salt of III similarly gave V, m.p. 81–83°.[7] Each of the compounds (IV) and (V) in aqueous acetonitrile solution (0.5 mmole in 9 ml. H_2O, 13.5 ml. CH_3CN) at 26° was titrated with 0.2*N* NaOH against a Beckman Model GS meter with E-2 electrode under nitrogen. The titration of IV was completely reversible with acid, and reproducibly indicated a pK_a[8] of 8.9 ± 0.1. Although V hydrolyzed more rapidly, it could be titrated reversibly over the entire curve and had pK_a[8] 11.1 ± 0.2. Thus again it is apparent that the cyclic anion has no special stability.

The anions from III and V are yellow (V with base gives a new λ_{max} at 370 mμ, $\epsilon \sim 2000$), so cyclic conjugation is spectroscopically detectable. However, it is clear that a system which would be strongly aromatically stabilized with a p-p double bond is not stabilized with a carbanion–sulfone double bond. The failure of such a double bond to complete the aromatic system probably is related to the theoretical arguments which previously have been advanced,[4] but our results demonstrate clearly that previous chemical experience with p-p double bonds cannot be extended unmodified to these new multiple bond systems.

[8] These pK_a's are not referred to pure water solution; *cf.* ref. 1.

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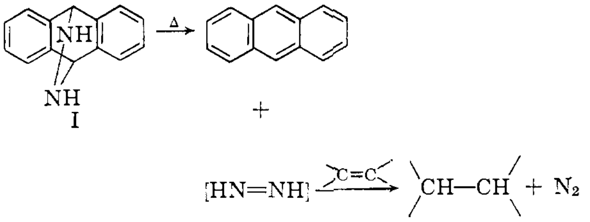
Received January 15, 1962

CHEMISTRY OF DIIMIDE. III. HYDROGEN TRANSFER TO MULTIPLE BONDS BY DISSOCIATION OF THE DIIMIDE-ANTHRACENE ADDUCT, ANTHRACENE-9,10-BIIMINE

Sir:

The stereospecific *cis* hydrogenation[1,2] of multiple bonds by a variety of species related to hydrazine can be interpreted most readily in terms of diimide [HN=NH] as the active reducing agent. The systems known to effect such reduction include (1) hydrazine in combination with various oxidizing agents,[2-4] (2) potassium azodiformate[3,5] and (3) p-toluenesulfonylhydrazine.[2,6] To this list may now be added anthracene-9,10-biimine (I) which appears to act according to the equation


I

As is the case with the previously described systems the diimide precursor I is an effective reductant for azo and mono- and disubstituted olefinic linkages. These examples are illustrative:

Azobenzene ⟶ Hydrazobenzene (2, 99%)
trans-Cinnamic acid ⟶ β-Phenylpropionic acid (3, 81%)
cis-4-Cyclohexene-1,2-dicarboxylic acid ⟶
cis-Cyclohexane-1,2-dicarboxylic acid (5, 45%)
Sclareol ⟶ Dihydrosclareol (6, 80%)[7]
3α-Hydroxy-$\Delta^{11,12}$-cholenic acid ⟶
Lithocholic acid (8, 79%)
cis-1,4-Dihydroxy-2-butene dibenzoate ⟶
1,4-Dihydroxybutane dibenzoate (8, 38%)
Maleic acid ⟶ Succinic acid (3, 87%)
Fumaric acid ⟶ Succinic acid (3, 80%)

The figures in parentheses refer to the number of equivalents of I employed in the reaction and the yield of isolated product. Although no acetylenic substrates were tested, it seems quite likely that the triple bond can be reduced readily.

The reagent I was prepared by careful hydrolysis of the anthracene–diethyl azodiformate adduct[8] in excess 2 *M* sodium hydroxide in ethanol[9] under nitrogen at 25° for 20 hours, then concentration *in vacuo*, dilution with water, acidification with hydrochloric acid, filtration (to remove insoluble impurities) and basification to precipitate I (all operations must be carried out in the cold, yield 78%). The product was obtained as a fine white powder, found: C, 80.46; H, 5.69; N, 13.38, dec. *ca.* 100° with evolution of gas but without melting to give a solid residue of anthracene, identified by mixed m.p. and infrared absorption. In the temperature range of its thermal stability the diimide adduct I is ineffective as a reducing agent for multiple bonds, but at higher temperatures where the rate of dissociation is appreciable reduction of unsaturated linkages occurs. In general the reductions using I as a diimide precursor can be carried out at 50–90° in various solvents; use of ethanol at reflux has proven to be quite satisfactory as a standard technique.

Deuteriation of maleic and fumaric acids was accomplished using I in deuterium oxide–dioxane solution at *ca.* 85° to give stereospecifically *meso*- and *dl*-2,3-dideuteriosuccinic acids, respectively

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[1] E. J. Corey, D. J. Pasto and W. L. Mock, *J. Am. Chem. Soc.*, **83**, 2957 (1961).

[2] S. Hünig, H. Müller and W. Thier, *Tetrahedron Letters*, **11**, 353 (1961).

[3] E. J. Corey, W. L. Mock and D. J. Pasto, *ibid.*, **11**, 347 (1961).

[4] F. Aylward and M. Sawistowska, *Chem. and Ind.*, 404, 433 (1961).

[5] E. E. van Tamelen, R. S. Dewey and R. J. Timmons, *J. Am. Chem. Soc.*, **83**, 3725 (1961).

[6] R. S. Dewey and E. E. van Tamelen, *ibid.*, **83**, 3729 (1961).

[7] M. M. Janot, *Compt. rend.*, **191**, 847 (1930); **192**, 845 (1931).

[8] O. Diels, S. Schmidt and W. Witte, *Chem. Ber.*, **71**, 1186 (1938).

[9] Prepared by addition of water to ethanolic sodium ethoxide.