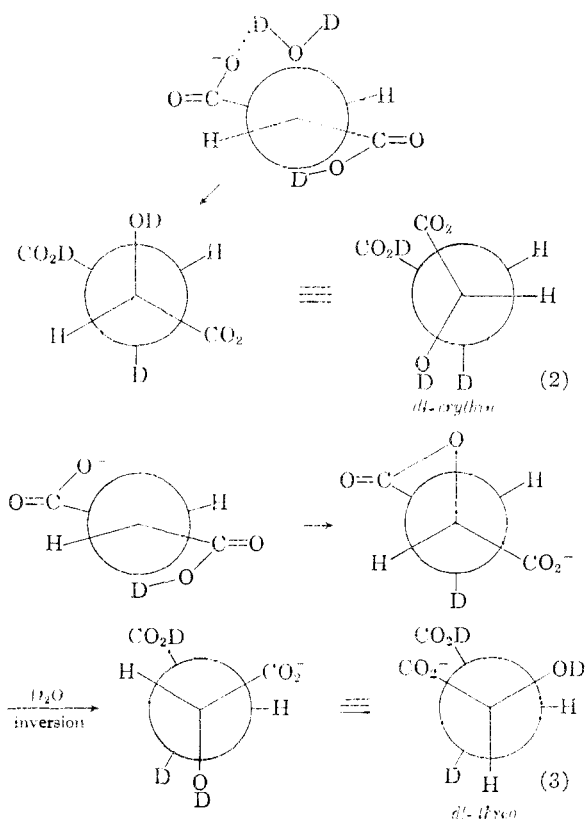


Neither the un-ionized nor the doubly-ionized form of the acid appears to undergo an uncatalyzed reaction, while the singly-ionized form, containing both a  $-\text{COOH}$  and a  $-\text{COO}^-$  group in the molecule, does. Therefore these two groups may be necessary for this uncatalyzed reaction to occur. One may postulate either that the presence of these groups in the molecule allows the spontaneous reaction to proceed (a substituent effect), or alternatively that the carboxylic acid and carboxylate ion groups actively participate in the reaction. The latter possibility seems the more likely one.<sup>13</sup> Two mechanisms may be written in which these groups act in concert. One involves an intramolecular general acid-general base catalysis, the elements of water being included in the transition state (eq. 2). The other mechanism can be described as a general acid-nucleophile catalyzed reaction, with the carboxylate ion attacking carbon to form an intermediate lactone, which then hydrolyzes to give malic acid (eq. 3).



Equations 2 and 3 imply the formation of stereochemically different products when the hydration is carried out in deuterium oxide: *dl*-erythro-monodeuteriomalic acid (*trans* addition) and *dl*-threo-monodeuteriomalic acid (over-all *cis* addition),<sup>14</sup> respectively. However, it has not been possible to observe the stereochemistry predicted by either Eq. 2 or 3, even though the nuclear magnetic resonance spectra of both of these acids

(13) At pH 4.5 the rate is increased by a factor of  $3 \times 10^4$  over that to be expected if the monoanion does not undergo reaction.

(14) H. N. K. Rørdam, *J. Chem. Soc.*, 2931 (1932); A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed., Chap. 12, J. Wiley and Sons, Inc., New York, N. Y., 1961.

have been recorded,<sup>15,16</sup> since the monodeuteriomalic acid formed at pH 4.0 and  $175^\circ$  apparently exchanges its methylene proton with the solvent to yield 3,3-dideuterio-malic acid. Therefore it is not possible to decide whether Eq. 2 or 3 describes the course of the hydration reaction, or indeed to show that the reaction is stereospecific.

The reaction described in this communication appears to be the first observed non-enzymatic olefinic hydration under neutral conditions (at  $175^\circ$  neutrality is at pH 5.77). The rate of the reaction is far too small to permit a serious comparison with that of the fumarase-catalyzed hydration of fumaric acid. However, its occurrence demonstrates a new mechanism of olefin hydration and provides some support for a hypothesis of enzymatic catalysis involving the simultaneous functioning of both an acidic and a basic group.

(15) R. A. Alberty and P. Bender, *J. Am. Chem. Soc.*, **81**, 542 (1959).

(16) F. A. L. Anet, *ibid.*, **82**, 994 (1960).

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#### STUDIES ON d-ORBITAL CONJUGATION. I. THE ABSENCE OF A THROUGH-CONJUGATION EFFECT IN SOME SULFONE CARBANIONS

Sir:

In a classic theoretical paper on the conjugative properties of sulfones Koch and Moffitt<sup>1</sup> pointed out that a carbon 2-p orbital may adopt two extreme orientations with respect to an adjacent sulfone group, *viz.*, it may lie in the C-S-C plane ("Case II" conjugation) or perpendicular to that plane ("Case I" conjugation). They concluded, from a treatment involving chiefly symmetry arguments, that Case I conjugation would be better than Case II, and also that either Case I or Case II conjugation would be weak unless *both* substituents on the sulfone group were unsaturated. This treatment has been criticized by Jaffé,<sup>2</sup> who with an explicit consideration of the form of the d orbitals has concluded that potentially conjugating groups attached to a d-orbital element, far from reinforcing each other's conjugation, will in fact compete for the d-orbital. We have examined this point and wish to report that in a clear example of Case I conjugation there is no evidence for Koch and Moffitt's predicted through-conjugation effect.

The species selected for examination were the enolate ions derived from the disulfone esters I-IV. The ester group guarantees that the carbanion will be  $\text{sp}^2\text{-p}$  hybridized, which need not otherwise be true,<sup>3</sup> and the geometry of the cyclic anions derived from II and IV is such that only Case I conjugation is possible. Compound I

(1) H. P. Koch and W. E. Moffitt, *Trans. Faraday Soc.*, **47**, 7 (1951). This work has been discussed by G. Cilento, *Chem. Rev.*, **60**, 147 (1960).

(2) H. H. Jaffé, *J. Phys. Chem.*, **58**, 185 (1954).

(3) Cf. W. E. Doering and L. K. Levy, *J. Am. Chem. Soc.*, **77**, 509 (1955); H. E. Zimmerman and B. S. Thyagarajan, *ibid.*, **82**, 2505 (1960); D. J. Cram, W. D. Nielsen and B. Rickborn, *ibid.*, **82**, 6415 (1960); E. J. Corey and E. T. Kaiser, *ibid.*, **83**, 490 (1961).

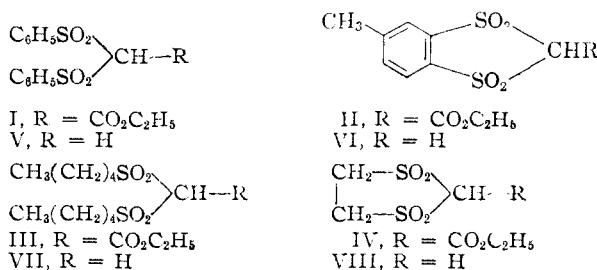
m.p. 140–142° (C, 52.22; H, 4.28) was prepared by oxidation of the corresponding dithioacetal, while II–IV were obtained by carbethoxylation of the related methylene disulfones VI–VIII with sodium hydride and ethyl chlorocarbonate: II, m.p. 153–154° (C, 43.49; H, 4.11) from VI, m.p. 166–167° (C, 41.61; H, 3.54); III, m.p. 187–189° (C, 46.88; H, 8.29) from VII, m.p. 110–111° (C, 46.65; H, 8.65); IV, m.p. 90–91° (C, 29.85; H, 4.25) from VIII, m.p. 210–211° (reptd.<sup>4</sup> 204°). The  $pK_a$ 's<sup>5</sup> of I–IV are listed in Table I. Comparison

TABLE I

Compound	I	II	III	IV
$pK_a$ <sup>5</sup>	4.60	3.35	5.75	4.00

of II and IV shows that no significant effect results from the presence of the unsaturated substituent in II; only a small effect is apparent in the comparison of I and III as well, although here Case I conjugation is not geometrically required.

Furthermore, the comparison of III with IV, and perhaps of I with II, show that there is no large energetic disadvantage to the restriction of the cyclic compounds to Case I conjugation, so if the open-chain compounds utilize the Case II mode at least the preference cannot be large. Finally the  $pK_a$  of II shows that no particular effect attends the formation of a cyclic conjugated anion, so that apparently a new aromatic system has not been formed.



It is interesting that we find the  $pK_a$  of V to be 11.5 while that of VI is greater than 13. Thus the order of stability of these systems is reversed when the carbethoxyl group is missing. This may reflect a changed hybridization at carbon when the substituent no longer demands  $sp^2$ - $p$  hybridization, and we are further investigating systems of this type. However, it is clear from our results that a large extra conjugation effect, such as was predicted from the Koch and Moffitt treatment of Case I interaction between a carbon  $2p$  orbital and the sulfone hybrid orbitals, is not found experimentally.

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(4) E. Baumann and G. Walter, *Ber.*, **26**, 1124 (1893).

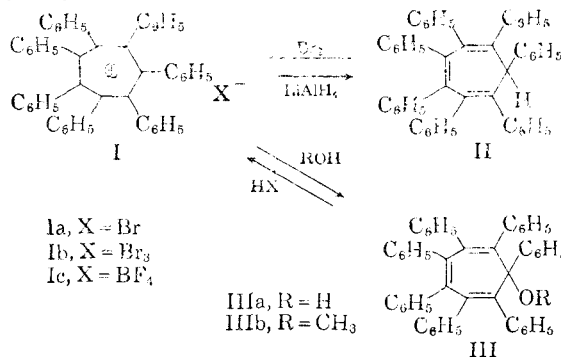
(5) The  $pK_a$ 's were determined in a standard fashion. An accurately weighed sample of the compound (0.5 mmole) was dissolved in 13.5 ml. of acetonitrile, 9 ml. of water was added, and the titration was performed at 26° under nitrogen by adding 0.206 *N* aqueous sodium hydroxide and observing the pH with a Beckmann model G pH meter and E-2 glass electrode. Smooth classical titration curves were obtained. Duplicate runs agreed within 0.03 pH unit, and back titration with hydrochloric acid and recovery of the unchanged starting materials establish the reversibility of the titrations. Of course, these  $pK$ 's cannot be referred directly to dilute aqueous solution.

## SALTS OF THE HEPTAPHENYLTROPYLIUM ION AND THEIR STABILITY

Sir:

In a recently reported study,<sup>1</sup> Breslow and co-workers investigated the effect of phenyl substituents on the stabilities of the triphenyl- and diphenylcyclopropenyl cations. Unfortunately, in this series a direct comparison with the as yet unknown, unsubstituted cyclopropenyl cation is not possible. In the tropilidene series, however, the stabilities of various aryl or alkyl substituted tropylium ions may be conveniently related to the stable tropylium ion.<sup>2</sup> Consequently, phenyl substituted tropylium ions have immediate interest in connection with the effect of phenyl groups on stable carbonium ions, and in this Communication we wish to report our observations on the synthesis and stability of heptaphenyltropylium bromide (Ia), tribromide (Ib), and fluoroborate (Ic), the first reported persubstituted tropylium salts.

The treatment of a carbon tetrachloride solution of heptaphenyltropilidene (II),<sup>3</sup> obtained from the Diels–Alder reaction of tetraphenylcyclopentadienone and triphenylcyclopropene, with a slight excess of bromine resulted in the slow liberation of hydrogen bromide and the formation of an amor-



phous yellow solid (mainly the tribromide Ib), m.p. ca. 270° (dec.),  $\lambda_{max}^{MeCN}$  (log  $\epsilon$ ), 250 (4.96), 268 (4.67)  $m\mu$ . Digestion of this solid in acetonitrile, containing a few per cent. of acetone to remove positive bromine, converted the amorphous material to bright red needles of the bromide Ia, m.p. 265–270° (dec.), slightly soluble in acetonitrile and chloroform, insoluble in benzene, ether, acetone and water,  $\lambda_{max}^{MeCN}$ , 250 (4.96), 284 (sh.) (4.22)  $m\mu$ . *Anal.* Calcd. for C<sub>49</sub>H<sub>35</sub>Br: C, 83.63; H, 5.01; Br, 11.36. Found: C, 83.78; H, 4.75; Br, 11.53. When a 5:1 mole excess of bromine was used, with recrystallization of the yellow product from chloroform–acetonitrile, reddish–orange prisms were obtained, m.p. 270–272° (dec.) ( $\lambda_{max}^{MeCN}$ , 250 (4.96), 268 (4.82)  $m\mu$ ). *Anal.* Calcd. for C<sub>49</sub>H<sub>35</sub>Br<sub>3</sub>: C, 68.15; H, 4.08; Br, 27.77. Found: C, 68.26; H, 4.29; Br, 27.71), whose analysis and spectral properties<sup>4</sup> confirm its tribromide structure Ib.

(1) R. Breslow, J. Lockhart and H. W. Chang, *J. Am. Chem. Soc.*, **83**, 2375 (1961).

(2) W. v. E. Doering and L. H. Knox, *ibid.*, **76**, 3203 (1954).

(3) M. A. Battiste, *Chemistry and Industry*, 550 (1961).

(4) Popov and Swenson (*J. Am. Chem. Soc.*, **77**, 3724 (1955)) have found the ultraviolet absorption maximum for the tribromide ion (as tetra-*n*-butylammonium tribromide) at 269  $m\mu$  (log  $\epsilon$  4.74) in acetonitrile solvent.