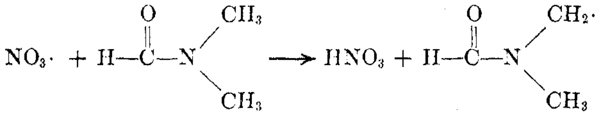
dimethylformamide demonstrate that nitrate ion is oxidized at a lower anodic potential than the amide. This conclusion is also supported by the results of cyclic voltammetric studies in acetonitrile.

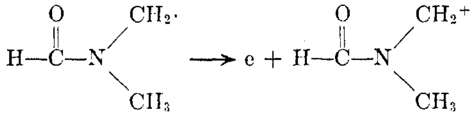
The steady-state currents at constant potentials for oxidation of nitrate ion and the amide are such that, when the ratio of the two concentrations, $C_{\mathrm{amide}}/C_{\mathrm{NO_3^-}}$, is 3, the two oxidations proceed at nearly equal rates. When the ratio is 0.3, ~90% of the charge passed goes into oxidation of nitrate ion. For 90% of the charge to go into amide oxidation, the ratio would have to be ~30.

In a controlled potential experiment, with the initial ratio, $C_{\mathrm{amide}}/C_{\mathrm{NO_3^-}}$, such that at least 85% of the charge passed was going into nitrate oxidation, the coulombic yield of *N*-methoxymethyl-*N*-methylformamide was 71.9%. It, therefore, follows that oxidation of nitrate ion can initiate a sequence of reaction steps that leads ultimately to the amide oxidation product. The first step in this sequence must necessarily be that shown in eq 2, and this reaction has also been proposed by Mann.[13] Reasonable subsequent steps are eq 3–5.

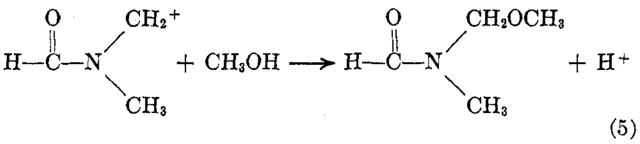
$$\mathrm{NO_3^- \longrightarrow e + NO_3\cdot} \qquad (2)$$



$$\mathrm{NO_3\cdot + HC(O)N(CH_3)_2 \longrightarrow HNO_3 + HC(O)N(CH_2\cdot)CH_3} \qquad (3)$$



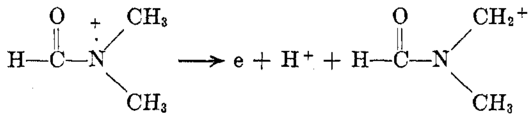
$$\mathrm{HC(O)N(CH_2\cdot)CH_3 \longrightarrow e + HC(O)N(CH_2^+)CH_3} \qquad (4)$$



$$\mathrm{HC(O)N(CH_2^+)CH_3 + CH_3OH \longrightarrow HC(O)N(CH_2OCH_3)CH_3 + H^+} \qquad (5)$$

The above sequence constitutes an over-all ECEC reaction, in which nitrate ion functions as a catalyst, which is consumed in eq 2 but regenerated in eq 3.[14]

When the initial electron transfer is from the amide, the primary step is that shown in reaction 1, and possible subsequent reactions are 6, followed by 5. The over-all sequence is EEC. Reaction 6 has been written



$$\mathrm{HC(O)\overset{+\cdot}{N}(CH_3)_2 \longrightarrow e + H^+ + HC(O)N(CH_2^+)CH_3} \qquad (6)$$

as a concerted reaction involving the simultaneous transfer of a proton to a base and an electron to the anode. It is possible that eq 6 involves two discrete steps, a proton transfer followed by a separate electron transfer, in which case the over-all sequence is ECEC.

Registry No.—*N*,*N*-Dimethylformamide, 68-12-2; methanol, 67-56-1; ethanol, 64-17-5; butanol, 71-36-3; acetic acid, 64-19-7; tetraethylammonium fluoroborate, 429-06-1; tetraethylammonium nitrate, 1941-26-0; tetra-*n*-butylammonium fluoroborate, 429-42-5; nitrate radical, 34236-35-6.

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[13] R. R. Rao, S. B. Mulliken, S. L. Robinson, and C. K. Mann, *Anal. Chem.*, **42**, 1076 (1970).

[14] G. Cauquis and D. Serve [*C. R. Akad. Sci., Ser. C*, **262**, 1516 (1966)] have proposed the electrochemical oxidation of nitrate ion to give the nitronium ion. The nitronium ion could abstract a hydride ion from the methyl

$$\mathrm{NO_3^- \rightarrow e + NO_2^+ + {}^1/_2O_2\cdot}$$

group of the amide and thus lead to the observed *N*-methoxymethyl-*N*-methylformamide. A corollary of this mechanism is that oxidation of the amide is accompanied by conversion of the quaternary ammonium nitrate to a nitrite. Since the nitrate can be recovered unchanged from the present reactions, this mechanism is eliminated.

The Crystal and Molecular Structure and Absolute Configuration of *d*-Spiro[3.3]heptane-2,6-dicarboxylic Acid at −160°

L. A. Hulshof, Aafje Vos,*[1] and Hans Wynberg

Laboratorium voor Structuurchemie and Department of Organic Chemistry, The University, Groningen, The Netherlands

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The crystal and molecular structure of *d*-spiro[3.3]heptane-2,6-dicarboxylic acid or *d*-Fecht acid, $C_9H_{12}O_4$, at −160° has been solved by conventional X-ray diffraction methods. The dimensions of the monoclinic cell are a = 8.486, b = 7.609, c = 6.928 Å; β = 93.25°; space group $C2$, Z = 2. The structure was refined by least-squares techniques, R = 0.056 and R_w = 0.062 for 2314 independent reflections. From a determination of the absolute configuration by use of the anomalous scattering of oxygen and carbon, a strong indication was obtained that *d*-Fecht acid has the R configuration shown in Figure 1. The molecules have twofold symmetry. The four-membered rings are puckered with a dihedral angle of 152.6°, resulting in an approximate equatorial position of the carboxylic acid groups. The bond lengths and angles in the ring range from 1.539 to 1.564 (0.0013) Å and from 88.0 to 88.9 (0.08)°, respectively. The C–C–C angles at the central spiro carbon atom vary from 114.8 to 126.2°.

The isolation and identification of *dl*-spiro[3.3]heptane-2,6-dicarboxylic acid or Fecht acid was first reported by Fecht[2a] in 1907. The resolution of the acid in its optical antipodes was achieved by Backer and Schurink[2b] in 1928 by fractional crystallization of the brucine salts.

Recently the acid has aroused interest as a suitable starting material for the synthesis of optically active 2,6-disubstituted spiro[3.3]heptane derivatives.[3] A knowledge of the absolute configuration of Fecht acid would establish the absolute configuration of this whole series of compounds. Wynberg and Houbiers[3] on the basis of ORD and CD measurements and making use of the application of Lowe's rule[4] to the spiro[3.3]-

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[1] Laboratorium voor Structuurchemie, Zernikelaan, Paddepoel, Groningen, The Netherlands.

[2] (a) H. Fecht, *Chem. Ber.*, **40**, 3888 (1907); (b) H. J. Backer and H. B. J. Schurink, *Proc. Kon. Ned. Akad. Wetensch.*, **37**, 384 (1928); *Recl. Trav. Chim. Pays-Bas*, **50**, 921 (1931).

[3] H. Wynberg and J. P. M. Houbiers, *J. Org. Chem.*, **36**, 834 (1971).

[4] G. Lowe, *Chem. Commun.*, 411 (1965).

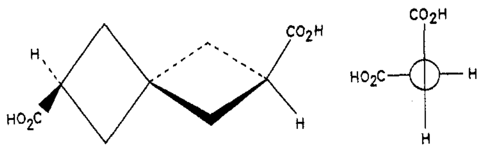

Figure 1.—*R*-(+)-Spiro[3.3]heptane-2,6-dicarboxylic acid with the notation of R. S. Cahn, C. K. Ingold, and V. Prelog, *Experientia* **12**, 81 (1956); *Angew. Chem.*, **78**, 417 (1966).

heptane system assigned the *R* configuration (see Figure 1) to the dextrorotatory Fecht acid. Wynberg and Hulshof[5] in later work confirmed this assignment using ORD and CD spectra in concentrated sulfuric acid.

In order to obtain additional physical evidence in support of this conclusion and to determine the conformation of the acid, its crystal structure has been determined by means of X-ray diffraction.

Experimental Section

Crystals were grown from a solution of analytically pure *d*-spiro[3.3]heptane-2,6-dicarboxylic acid in acetone, optical purity of the compound 90%, $[\Phi]_{578}$ +7.8°. The geometry of the crystals (monoclinic sphenoidal) and their Weissenberg photographs showed the compound to be monoclinic. The space group was unequivocally found to be *C*2 (no. 5 in International Tables[6]) from the systematic absences (*hkl* absent for $h + k \neq 2n$) and the fact that the compound exhibits optical activity and a piezoelectric effect. The unit cell dimensions were obtained from zero layer line Weissenberg photographs taken at −160°, calibrated at room temperature with NaCl reflection spots [$\lambda(\text{Cu K}\alpha_1) = 1.54051$, $\lambda(\text{Cu K}\alpha_2) = 1.54433$, a (NaCl) = 5.6396 Å]. The crystallographic data are $a = 8.486$ (2) Å, $b = 7.609$ (3) Å, $c = 6.928$ (2) Å; $\beta = 93.25$ (2)°; unit cell volume 446.7 Å^3; $Z = 2$, μ (Mo Kα) = 1.16 cm^{-1}; $\rho_{\text{exptl}} = 1.35$ g cm^{-3} (flotation); $\rho_{\text{calcd}} = 1.37$ g cm^{-3}.

The intensities of *d*-Fecht acid were collected at low temperature (−160°) with an automatic Nonius single-crystal diffractometer (Zr filtered Mo radiation), the θ–2θ scan method being used. Deviations from linearity of the scintillation counting equipment were kept below 1% by the use of attenuation filters. For 2314 independent reflections (out of the 2441 measured up to $\sin \theta/\lambda = 1.0778$ Å^{-1}), the measured intensity was larger than zero. Corrections were made for intensity changes in the primary beam (by use of reference intensities), for the Lorentz and polarization effects, and for absorption. The latter corrections were calculated according to the Busing and Levy scheme.[7]

From the fact that the general position in *C*2 is fourfold and $Z = 2$, it could be concluded that the molecules have to lie at the twofold axes in the crystal. First the approximate arrangement of the carbon and oxygen atoms in the centrosymmetrical [010] projection was found from a three-dimensional Patterson synthesis sharpened according to the method of Jacobson, Wunderlich, and Lipscomb.[8] After refinement of this projection the *y* coordinates of the "heavy" atoms could be deduced from the Patterson map.

The positions and anisotropic temperature factors of the "heavy" atoms were refined with a least-squares program working in block diagonal approximation.[9] After some cycles the hydrogen atoms could be found from a difference Fourier map (hydrogen not included in F_c). In the final cycles of the refinement each hydrogen atom was given a fixed position at 1.00 or 1.08 Å, respectively, from its neighboring oxygen or carbon atom, the directions of O–H and C–H being taken from the previous refinement cycles. Isotropic refinement was used for their temperature factors. The weighting scheme $w = [w_o^{-1} + 0.0009|F_o|^2]^{-1}$ was applied, w_o being the weight based on counting statistics. Corrections for extinction were not necessary. The scattering factors for carbon and oxygen were taken from Doyle and Turner[10] and that of hydrogen from Stewart, Davidson, and Simpson.[11]

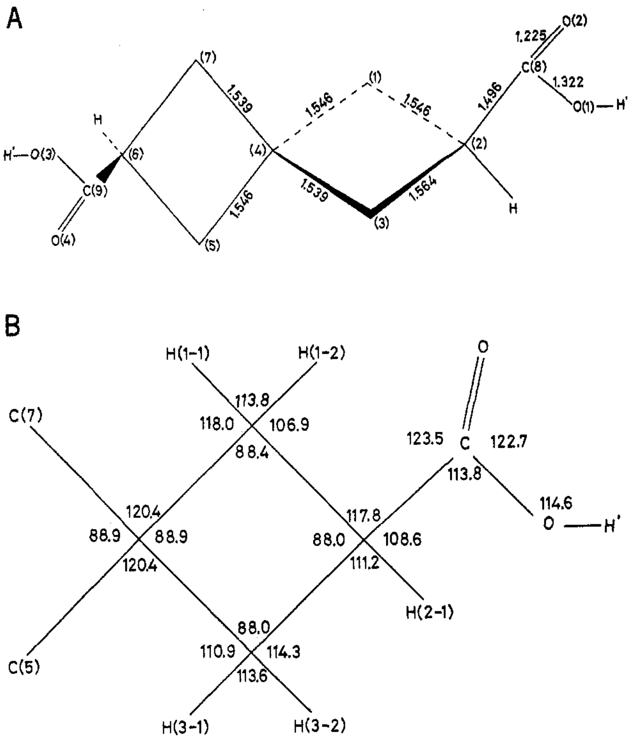

Figure 2.—Molecular geometry. The molecule has twofold symmetry. C(1) is related to C(5), C(3) to C(7), etc. A, bond lengths, standard deviation 0.0013 Å; B, bond angles, standard deviation for angles not involving hydrogen 0.08°. The bond angles omitted in the figure are C(4)–C(1)–H(1–2) = 109.9°, C(2)–(C3)–H(3–1) = 108.5°, C(2)–C(1)–H(1–1) = 116.9°, C(4)–C(3)–H(3–2) = 118.7°, C(1)–C(2)–H(2–1) = 113.5°, C(3)–C(4)–C(7) = 126.2°, C(3)–(C2)–C(8) = 116.7°, C(1)–C(4)–C(5) = 114.8°.

At the end of the refinement $\langle w|\Delta F|^2\rangle$ did not show systematic variations with $|F|$. The index $R = [\Sigma|\Delta F|^2/\Sigma|F|^2]^{1/2}$ and the corresponding weighted index R_w decreased to 0.056 and 0.062, respectively. The final atomic parameters[12] have been calculated with the standard deviations by the least-squares program. Analysis of the thermal parameters[12] according to Cruickshank[13] showed that the molecule is not a rigid body. The bond lengths and angles given in Figure 2 and Table I (B) are therefore not corrected for libration effects.

Discussion

Absolute Configuration.—The molecule given in Figure 2 (for coordinates, see ref 12) has the *R* configuration proposed by Wynberg and Houbiers[3] for *d*-Fecht acid. To check whether this configuration is correct, Weissenberg photographs about the c axis were taken with both Cu (layers 0, 1, and 2) and Cr (layers 0, 1, 2, and 3) radiation. A nice cylindrical crystal with a diameter of 0.2 mm was used. For

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(5) H. Wynberg and L. A. Hulshof, unpublished results.

(6) "International Tables for X-Ray Crystallography," Vol. I, Kynoch Press, Birmingham, England, 1952, p 81.

(7) W. R. Busing and H. A. Levy, *Acta Crystallogr.*, **10**, 180 (1957).

(8) R. A. Jacobson, J. A. Wunderlich, and W. N. Lipscomb, *ibid.*, **14**, 598 (1961).

(9) D. W. J. Cruickshank in "Computing Methods and the Phase Problem in X-Ray Crystal Analysis," Pergamon Press, Oxford, 1961.

(10) P. A. Doyle and P. S. Turner, *Acta Crystallogr., Sect. A*, **24**, 390 (1968).

(11) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(12) Listings of structure factors, atomic coordinates, and anisotropic temperature factors will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JOC-72-1767. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

(13) D. W. J. Cruickshank, *Acta Crystallogr.*, **9**, 757 (1956).

Table I

Results of the CNDO/2 Calculations

A. Models Used

	α, deg	β, deg	Energy, eV
Model 1	114.8	127.3	0
Model 2	120.0	120.0	1.38
Model 3	108.0	132.0	1.59

B. Calculated Bond Orders and Observed Bond Lengths

Bond	$\Sigma P\sigma$	$\Sigma P\pi$	Length, Å
C(1)–C(2)	1.777	0.267	1.546
C(2)–C(3)	1.777	0.265	1.564
C(3)–C(4)	1.773	0.249	1.539
C(4)–C(1)	1.765	0.243	1.546

some weak reflections there appeared to be very small differences between the intensities of the Bijvoet pairs[14] *hkl* and $\bar{h}\bar{k}\bar{l}$. The crystal used (weight *ca.* 0.007 mg) was definitely proved to consist of the *d* form by dissolving it in concentrated sulfuric acid (0.018 ml) and by measuring its CD spectrum. The spectrum was found to be the same as that observed for *d*-Fecht acid in the same solvent[5] ($[\theta]_{188}$ −3000, $[\theta]_{212}$ + 1050, Dichrographe II, Jouen).

Starting from the coordinates and thermal parameters[12] and using the anomalous scattering factors given by Cromer and Liberman[15] for the carbon and oxygen atoms, we calculated the intensities of the reflections *hkl* and $\bar{h}\bar{k}\bar{l}$. For five pairs obtained with Cr radiation and three pairs obtained with Cu radiation the difference was calculated to be larger than 3%. Visual estimations made by different persons showed that for 75% of the cases the observed intensity order corresponded with the calculated one. It can thus be concluded that the present X-ray work gives a reasonable support for the earlier proposed *R* configuration for *d*-Fecht acid.

Conformation.—This first X-ray diffraction structure determination of a simple spiran type compound shows that the four-membered rings of the molecules are not planar. The molecule is shown in Figure 2. The observed dihedral angle between the planes of C(1)-C(2)-C(3) and C(1)-C(4)-C(3) is 152.6°. This value lies close to the value of 147° observed for cyclobutane in the gaseous phase[16] (for a further discussion of four-membered rings observed in crystal structures, see Greenberg and Post[17] and Adman and Margulis[18,19]). Due to the nonplanarity the atoms C(2), C(4), and C(6) of the spiro system show a left-handed helicity for the observed *R* configuration, as could be seen from a Newman projection. The bending of the planes is such that the carbon atoms of the carboxyl groups are in a more equatorial position than for a planar four-membered ring. The angle between the plane through the carboxyl group and the best plane through the four-membered ring is 64.4°, while the angle between the planes through the carboxyl groups at the 2 and 6 position of the spiro[3.3]heptane system is 32.9°. It is further noteworthy that the angles C(1)–C(4)–C(5) (α = 114.8°) and C(3)–C(4)–C(7) (β = 126.2°) differ considerably. Smaller differences are observed between the C–C bond lengths in the four-membered ring (see Figure 2).

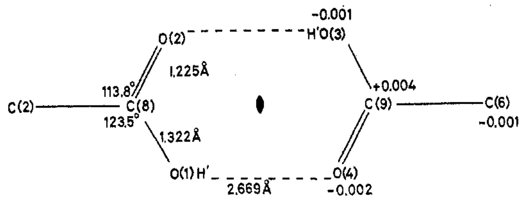

Figure 3.—The hydrogen bonding system viewed along the *b* axis. The asymmetric position of the hydrogen atoms was clearly shown by the $[F_o - F_c(\mathrm{C, O})]$ map. Each of the CCOOH groups lies in a plane, which makes an angle of 73.6° with the twofold axis. For distances to the plane, see the right-hand side of the figure.

By using the stereochemical information given above, for *d*-Fecht acid the *R* configuration is predicted by Klyne's sector rule for carboxylic acids.[20,21] This indicates that in this particular case the conformation in the crystals will not differ too much from that in solution, where the optical activity is measured. It should be noted, however, that in other cases (see, *e.g.*, Adman and Margulis[19]) the conformation of four-membered rings can be influenced to a considerable extent by the intermolecular interactions in the crystals.

Packing of the Molecules.—The structure in [010] projection (Figure 4)[12] shows that the carboxyl groups of successive molecules are linked by asymmetric hydrogen bridges, in such a way that linear arrays of molecules along [101] are formed. The geometry of the hydrogen bonding system is given in Figure 3. The neighboring carboxyl groups in Figure 3 are related by a twofold axis. As far as we know this has not been observed before for similar hydrogen bonding systems. The general rule that the carboxyl groups are related by an inversion center or pseudoinversion center cannot be obeyed by the present crystal because of the optical activity of the molecules.

CNDO Calculation.—To check whether the observed differences between the angles α and β, and between the C–C bond lengths of the four-membered ring, can be expected for a free Fecht acid molecule, CNDO/2 calculations[22] have been done. A standard CNDO/2 program was modified for this work by Dr. D. Kracht. Because of memory restrictions of the TR-4 computer the carboxyl groups of Fecht acid were replaced by hydroxyl groups, C–O(H) = 1.427 Å. The shape of the four-membered rings was slightly changed in order to give all C–C bonds a length of 1.5457 Å. With these rings three models were constructed, having twofold symmetry and the values for α and β mentioned in Table I (A). The CNDO/2 calculations showed that the value for α, 114.2°, for which the energy is minimal, −0.01 eV, lies surprisingly close to the experimental value of 114.8°. The $\Sigma P\sigma$ and $\Sigma P\pi$ bond orders of the C–C bonds, calculated for model 1, are compared with the observed bond lengths in Table I(B). We see that the differences in the bond orders are very small and not consistent with the observed bond lengths, although it is interesting to notice that there is a qualitative agreement for the bonds C(3)–C(4) and C(4)–

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[14] J. M. Bijvoet, A. F. Peerdeman, and A. J. van Bommel, *Nature (London)*, **168**, 271 (1951).

[15] D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).

[16] A. Almenningen, O. Bastiansen, and P. N. Skancke, *Acta Chem. Scand.*, **15**, 711 (1970).

[17] B. Greenberg and B. Post, *Acta Crystallogr., Sect. B*, **24**, 918 (1968).

[18] E. Adman and T. N. Margulis, *J. Amer. Chem. Soc.*, **90**, 4517 (1968).

[19] E. Adman and T. N. Margulis, *J. Phys. Chem.*, **73**, 1480 (1969).

[20] J. D. Renwick and P. M. Scopes, *J. Chem. Soc. C*, 1949 (1968).

[21] Reference 17 cited in ref 3.

[22] J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **44**, 3289 (1966).

C(1). Further attempts to explain the differences between the bond lengths will be made.

Registry No.—(+)-*R*-Spiro[3.3]heptane-2,6-dicarboxylic acid, 27259-78-5.

Acknowledgment.—The authors are greatly indebted to Mr. J. F. Kleibeuker of the Department of Physical Chemistry, Rijksuniversiteit, Groningen, for the CD measurements, Dr. D. Kracht for his contribution to the CNDO calculations, Dr. J. L. de Boer for his valuable comments, Dr. J. P. M. Houbiers of the Department of Organic Chemistry, Rijksuniversiteit, Groningen, for the preparation of the *d*-Fecht acid used in this work, and Dr. G. J. Visser for his considerable contribution to this work.

Electrophilic Bromination of Aromatic Conjugated Olefins. I. Evaluation of a Competitive Path Mechanism in Bromination of Trans-Monosubstituted Stilbenes[1a]

MARIE-FRANÇOISE RUASSE AND JACQUES-EMILE DUBOIS*

Laboratoire de Chimie Organique Physique de l'Université Paris VII, associé au CNRS, Paris 5°, France

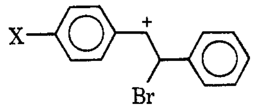
Received October 27, 1971

The bromine addition to monosubstituted stilbenes, $XC_6H_4C_xH{=}C_yHC_6H_5$, is treated as a reaction that can take place at two discrete centers C_x and C_y passing *via* C_x^+ and C_y^+ carbonium ion intermediates. The free-energy relationship for stilbenes whose substituents vary from *p*-hydroxy to *p*-nitro, and whose rate constants cover six powers of ten, is markedly curved. It corresponds to the equation, $\log (k/k_0) = \log [(k_x + k_y)/k_0] = \log (10^{\rho_\alpha \sigma^+} + 10^{\rho_\beta \sigma})$, where ρ_α is the reaction constant when the incipient carbonium center is C_x in the α position with respect to the substituted ring and ρ_β for the C_y center and where ρ_α and ρ_β are -5.0 and -1.5, respectively. It is shown that the bromination of *p*-methoxy- and *p*-hydroxystilbenes proceeds exclusively *via* the C_x path, whereas *p*-methyl, *m*-methyl, and *p*-chloro compounds involve this path only to the extent of 95, 65, and 35%, respectively. For *m*-chloro to *p*-nitro derivatives, only the C_y path is significant. These results are consistent with the regioselectivity of the nucleophilic attack of the solvent on the intermediates. The intermediate of the C_x path is clearly the free carbonium ion C_x^+, whereas in the intermediate of the C_y path, bromine participation cannot be excluded on the basis of kinetic data alone. The stereochemical and regiochemical analysis does not provide conclusive evidence either. Nevertheless, these latter data suggest that a free carbonium ion structure is the more likely.

For the bromination of styrenes, linear free-energy relationships, $\log k/k_0 = \rho\sigma^+$, were reported by Dubois, *et al.*, for electron-releasing substituents[1b,c] and by Yates, *et al.*, for electron attractors.[2] The value of ρ, -4.3 in methanol, -4.5 in acetic acid, compared with that of *tert*-cumyl chlorides,[3] -4.8, indicates that the benzylic carbon atom bears the charge in the transition state and neither the β carbon nor the bromine is concerned in the delocalization of the charge. The absence of bromine bridging in the transition state and consequently in the intermediate would lead to the absence of stereoselectivity in these solvents. However, in acetic acid, some stereoselectivity is observed in the bromination of the *cis*- and *trans*-β-methylstyrenes. This was explained[2] not by bromine bridging but by hindrance to free rotation in the carbonium ion, due to association with a bromine anion in an intimate ion pair. Thus, even when the ring bears a strongly electron-withdrawing substituent, the intermediate is an α-arylcarbonium ion, rather than a β-arylcarbonium or a bromonium ion where the destabilizing influence of the substituent would be minimized.[4]

It was, therefore, interesting to examine a system in which any carbonium ion formed would necessarily have both α- and β-aryl substituents. The charge distribution might then be expected to depend markedly on the electron-donating or electron-attracting character of the substituent. The present kinetic analysis[6] of the bromination of planar trans stilbenes was undertaken with this problem in mind.

The bromination of an unsymmetrical trans stilbene could generate three limiting intermediates, **1**, **2**, and **3**,



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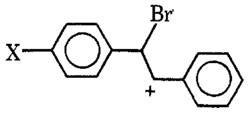

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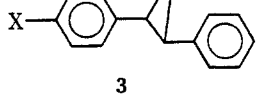

3

in which the charge is located on the α-aryl, the β-aryl carbon, or the bromine, respectively. For each one, there is a corresponding transition state, resembling each intermediate rather closely, since for bromination[7], the transition state structure has been shown to be nearer the intermediate than the ground state. Then the kinetic effect of X would be expected to be

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[1] (a) Also regarded as part XXX of "Reactivity of Ethylenic Compounds: Bromination." Part XXIX: E. Bienvenue-Goetz, J. E. Dubois, D. W. Pearson, and D. L. H. Williams, *J. Chem. Soc. B*, 1275 (1970). (b) J. E. Dubois and A. Schwarcz, *Tetrahedron Lett.*, 2167 (1964). (c) M. Ropars, Ph.D. Thesis, CNRS, No. AO 2640, 1968, Paris.

[2] J. H. Rolston and K. Yates, *J. Amer. Chem. Soc.*, **91**, 1469 (1969); J. A. Pincock and K. Yates, *Can. J. Chem.*, **48**, 2944 (1970).

[3] Y. Okamoto, T. Inukai, and H. C. Brown, *J. Amer. Chem. Soc.*, **80**, 4972 (1958).

[4] In bromination of nonplanar 1,1-diphenylethylenes,[5] where two rings exert their influence on the same olefinic carbon, a dependence between the ring orientation and the electronic character of the substituent is observed; the more electron-releasing ring lies preferentially in the plane of the incipient carbonium ion, the other being turned out of this plane.

[5] E. D. Bergmann, J. E. Dubois, and A. F. Hegarty, *Chem. Commun.*, 1616 (1968).

[6] Preliminary communication: M. F. Ruasse and J. E. Dubois, *Tetrahedron Lett.*, 1163 (1970).

[7] F. Garnier, R. H. Donnay, and J. E. Dubois, *J. Chem. Soc. D*, 829 (1971).