shown in Table II is best interpreted by what Mulliken describes as "contact" charge-transfer interactions; interactions in which van der Waal forces are not contributing to bonding. The effect of absorption due to "contact" charge-transfer interference is to give a low value for the association constant while giving too high a value for the extinction coefficient. The same may be said for the effect of what Bayliss calls "solvent perturbation." If similar wave length regions are compared, it is found that, within a given series, the extinction coefficients of compounds exhibiting a dependence of association constant on wave length have the higher extinction coefficients.

It might be expected that sterically hindered donor molecules for which association constants are low should be especially susceptible to "contact" interactions. It is seen from the data in Table II that 2-*t*-butylnaphthalene exhibits this behavior. While the primary charge-transfer process necessitates a close proximity of donor and acceptor, the "contact" process should require neither a tight nor inflexible geometry. This perhaps also explains why comparable substituent effects were not observed in the spectrophotometric and partition methods for the halogenonaphthalenes. Thus, while the results of the spectrophotometric method parallel those obtained by the partition method for the stronger complexes, values for the less tightly bound halogen compounds cannot be considered a reliable indication of the extent of complexation but only of relative order of complex strength. The two iodonaphthalenes showed such a dependence of K on λ that their values were deemed unworthy of reporting.

It appears inevitable that association "constants" measured spectrophotometrically will be lower than the true association constants as a result of interactions of the type described above. Indeed, these values are association constants only to the extent that donor and acceptor species are bound by the charge-transfer energy and might best be labeled K_{c-t} if they must be expressed as association constants at all. While this method gives what is probably the lowest possible value for an association constant, the partition method must give the largest value. The latter, which sums *all* forces tending to unite donor and acceptor molecules, is technically a more accurate representation of association as the constant is mathematically defined. By the choice of method, then, one either measures association constants or studies charge-transfer spectroscopy (including environmental effects); the choice is that simple.

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AUSTIN, TEXAS

[CONTRIBUTION FROM THE DEPARTMENT OF BIOCHEMISTRY, YALE SCHOOL OF MEDICINE]

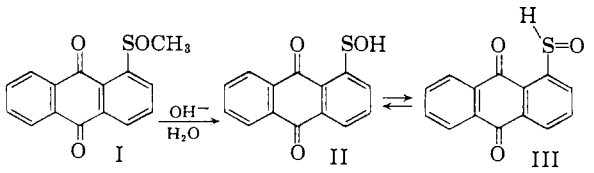
The Structure of Anthraquinone-1-sulfenic Acid (Fries' Acid) and Related Compounds

BY THOMAS C. BRUICE[1] AND ANNE B. SAYIGH

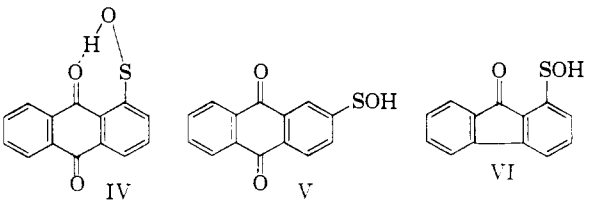
RECEIVED DECEMBER 16, 1958

Quantitative infrared spectra for the carbonyl bands of methyl anthraquinone-1-sulfenate, dimethyl anthraquinone-1,4-disulfenate and methyl fluorenone-1-sulfenate are reported and compared to those for anthrone, anthraquinone, fluorenone and the 1-hydroxy- and 1,4-dihydroxyanthraquinones. The conclusion is reached that the $-SOCH_3$ group causes splitting of the quinone absorption, because of dissymmetry, just as does the 1-hydroxy, 1- and 2-amino and the 1-dimethyl amino groups. The various postulated structures for Fries' acid (anthraquinone-1-sulfenic acid) as well as its derivatives are discussed and evaluated in view of the spectroscopic evidence. It is concluded that the original structure of Fries is correct.

When methyl anthraquinone-1-sulfenate (I) is hydrolyzed under prescribed conditions, a bright red, crystalline compound forms. On the basis of the empirical formula, means of preparation, acid nature and reformation of I on treatment with methanol, Fries[2] assigned structure II to this substance noting also that the product behaved in some of its reactions as though II were in equilibrium with III. In the forty-five years since the investigations of Fries all other attempts to prepare sulfenic acids failed, although hundreds of references to sulfenic acids as postulated transitory intermediates appeared in the literature.[3]



The peculiar stability of Fries' acid was reconsidered by Kharasch,[3] who postulated a possible stabilization of the sulfenic acid group *via* hydrogen bonding, as in IV. Structure IV was proposed to account for the known instability of 2-anthraquinonesulfenic acid (V), as well as the inability



(1) Inquiries concerning this work should be sent to this author in care of the Department of Physiological Chemistry, The Johns Hopkins School of Medicine, Baltimore, Md.

(2) K. Fries, *Ber.*, **45**, 2965 (1912).

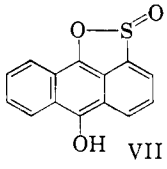
(3) N. Kharasch, S. J. Potempa and H. L. Wehrmeister, *Chem. Revs.* **39**, 276 (1946).

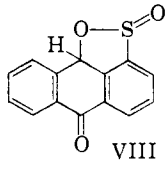
to prepare other sulfenic acids, as recorded in the total literature to that date.[3] As a test of this hypothesis, Kharasch and Bruice[4] attempted the synthesis of 1-fluorenonesulfenic acid (VI). It was shown by these workers that VI could only be logically inferred to have existed as an intermediate from the stoichiometry of the decomposition products, which were formed instantaneously on hydrolysis of the corresponding methyl ester (Ar = 1-fluorenonyl). The conclusion was then reached

$$2ArSOCH_3 + 2HOH \longrightarrow 2(ArSOH) + 2CH_3OH$$
$$2(ArSOH) \longrightarrow ArSO_2H + ArSH$$
$$2ArSH + ArSOCH_3 \longrightarrow ArSSAr + CH_3OH$$
$$3ArSOCH_3 + 2HOH \longrightarrow ArSO_2H + ArSSAr + 3CH_3OH$$

that the stability of Fries' acid, as compared to VI, could not be explained on the basis of the expected slight difference in hydrogen bonding stabilization energy between IV and VI.

Lecher[5] proposed that Fries' acid was stable because of the conversion to the phenolic lactone of anthraquinone-1-sulfenic acid (VII). On the basis of the necessity to form structures as VII the instability of V and VI could then be accounted for. However, Barltrop and Morgan[6] found structure VII to be incompatible with the qualitative infrared spectra of Fries' acid, which exhibited carbonyl as well as hydroxyl absorption. The


VII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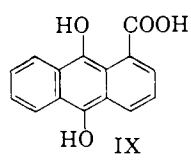
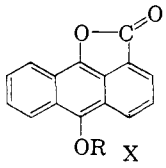

IX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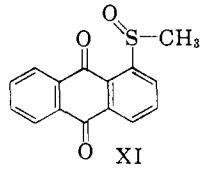
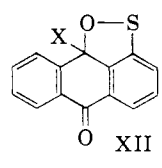

XI

possibility that Fries' acid was a mixture of the phenolic lactone of anthraquinone-1-sulfenic acid (VII) and the tautomeric oxanthrone structure VIII was eliminated by demonstrating the total absence of anthrone bands in its ultraviolet spectra, these conclusions being supported also by comparison of the ultraviolet spectra of Fries' acid to those of IX and X. A similar comparison to the spectra of XI was suggested to show that Fries' acid did not possess structure III. In the opinion of these workers, the spectral data indicated that the structure proposed by Kharasch (IV) was correct. To account for the stability of II, Barltrop and Morgan postulated that the sulfenic acid group must be attached to a particularly electronegative moiety, a suggestion which was based on the observation that the chief mode of decomposition of Fries' acid was observed to be by way of acid catalysis and it was proposed to occur *via* protonation of the sulfur atom.[7] The necessity of the sulfenic acid group being attached to an electronegative moiety for stabilization was independently suggested by Bruice and Markiw,[8] based on the known instability of V and VI, as well as the lesser stability of 4-aminoanthraquinone-1-sulfenic acid.

Simultaneously with the studies of Barltrop and Morgan, Rylander[9] concluded, from the finding that the integrated area under the carbonyl band of the methyl ester and chloride of Fries' acid was but half that of 1-mercaptoanthraquinone and 1-anthraquinonyl methyl sulfide, that Fries' acid possessed structure XII. Although the infrared spectra of the free sulfenic acid was not studied by Rylander, he concluded that the exhibition of a carbonyl band by the halide and ester precluded structure VII for the free acid. Thus, Rylander's conclusions of structure for Fries' acid depend on assuming that the free acid possesses the same general structural and spectral characteristics as the sulfenate and sulfenyl chloride, and also on the assumption that the measurement of area under the carbonyl band is an index of the number of carbonyl groups. Little in the infrared data of Barltrop and Morgan can be used to validate the structure proposed by Rylander, since their measurements were of a qualitative nature and apparently structure XII had not occurred to these workers.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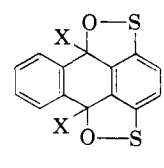
XIII

Since the studies of Lecher, Rylander and Barltrop, the synthesis of a second sulfenic acid—anthraquinone-1,4-disulfenic acid—was reported by Bruice and Markiw.[8] The existence of this substance was subsequently verified by Jenny,[10] who prepared it in an alternate way, and also synthesized the 1,5-isomer.[11] The preparation of the disulfenic acids terminated a 45-year search for analogs of Fries' acid and now allows the bringing to bear of additional data toward the evaluation of the structure of anthraquinone sulfenyl derivatives.

Structure VII was proposed by Lecher to account for the unique stability of Fries' acid. However, in the case of the 1,4- and 1,5-disulfenic acids only one of the sulfenate groups could be so stabilized, suggesting that structure VII may be disregarded.

As mentioned above, structure VIII was proposed by Rylander on the basis that the intensity of the carbonyl band of the methyl ester of Fries' acid was but half that expected for two carbonyl functions. Examination of the infrared spectra of anthraquinone (Fig. 1, A) *vs.* methyl anthraquinone-1-sulfenate (Fig. 1, E) reveals that there has been a split in the carbonyl absorption of the latter due to unsymmetrical substitution. The *a*-band for the methyl sulfenate is at almost an identical

(4) N. Kharasch and T. C. Bruice, THIS JOURNAL, **73**, 3240 (1951).
(5) H. Z. Lecher and E. M. Hardy, *J. Org. Chem.*, **20**, 475 (1955).
(6) J. A. Barltrop and E. J. Morgan, *J. Chem. Soc.*, 4245 (1956).
(7) J. A. Barltrop, unpublished data.
(8) T. C. Bruice and R. Markiw, THIS JOURNAL, **79**, 3150 (1957).
(9) P. N. Rylander, *J. Org. Chem.*, **21**, 1296 (1956).
(10) W. Jenny, *Helv. Chim. Acta*, **41**, 317 (1958).
(11) W. Jenny, *ibid.*, **41**, 326 (1958).

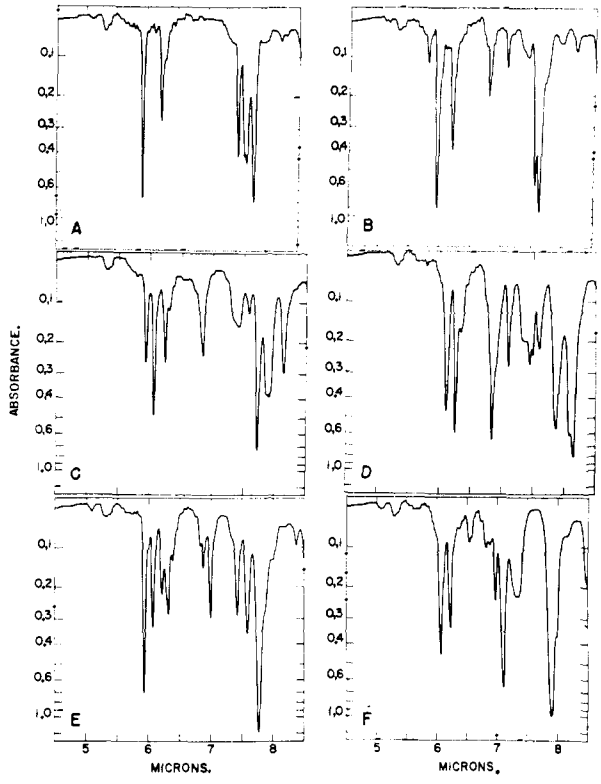

Fig. 1.—The infrared absorption (tetrachloroethylene solvent) in the 5–8μ range for: (A) anthraquinone, 8.55×10^{-3} mole $l.^{-1}$; (B) anthrone, 17.2×10^{-3} mole $l.^{-1}$; (C) 1-hydroxyanthraquinone, 8.21×10^{-3} mole $l.^{-1}$; (D) 1,4-dihydroxyanthraquinone, 8.83×10^{-3} mole $l.^{-1}$; (E) methyl anthraquinone-1-sulfenate, 14.4×10^{-3} mole $l.^{-1}$; and (F) dimethyl anthraquinone-1,4-disulfenate, 12.5×10^{-3} mole $l.^{-1}$.

position to the *a*-band of anthraquinone (5.94 *vs.* 5.93 μ) but as observed by Rylander is only of about one-half the intensity (44.4 *vs.* 75.4). Unfortunately, Rylander did not observe this most interesting split in the quinone absorption because he overlooked the significance of the "small satellite" bands "associated with the carbonyl band."

Unsymmetrical monosubstitution of anthraquinone has not previously been noted to give rise to the splitting of the carbonyl bands of anthraquinone except in the case of the substitution of the hydroxy or dimethylamino groups in the 1-position or the amino group into the 1- or 2-position.[12] In the case of 1-hydroxyanthraquinone there is ample evidence in the OH stretching region that there is a strong hydrogen bond formed between the hydroxyl and carbonyl groups, but by similar observations in the N–H region there appears to be little interaction of the amino group with the adjacent carbonyl function in 1-aminoanthraquinone.[12] The splitting of the carbonyl absorption would, therefore, appear to be predominantly the result of electronic dissymmetry, rather than hydrogen bonding. This is strongly supported by the splitting observed in 2-aminoanthraquinone and 1-dimethylaminoanthraquinone, where intramolecular hydrogen bonding cannot occur, and in the observations of Rasmussen, Tunnicliff and Brattain[13] that the position of the carbonyl group is not greatly affected by hydrogen bonding. The similarity between the carbonyl absorption of the 1-OH and 1-$SOCH_3$ substituted anthraquinones (Fig. 1, C and E) suggests that the methyl sulfenate group is capable of strong resonance interaction with the 9-carbonyl group (XIV and XV). It should be noted in this regard that the extinction coefficients of the visible absorption

XIV XV

Y = –OH, $-SOCH_3$, $-NH_2$, $-NMC_2$

of 1-substituted anthraquinones follow an order[8] [NH_2 > OH = ($SOCH_3$) > OCH_3 > (SOH) > CH_3 > Cl > CN > NO_2] of decreasing electron release and that the position of the methyl sulfenate group in this series also suggests strong resonance interaction with the carbonyl group of position 9. For 1,4-disubstituted anthraquinones, the width of the visible absorption band widens with increasing electron release by the substituents and, finally, in 1,4-diaminoanthraquinone splits into two bands. This splitting of the visible band of anthraquinone is also caused by the 1,4-dimethyl sulfenate substituents,[8] again supporting the strong electronic releasing nature of the $SOCH_3$ group. By the same comparative criteria the –SOH group may be said to be intermediate, in electron displacement, between the methyl and methoxyl groups. Examination of the infrared spectra of 1-hydroxyanthraquinone and anthraquinone-1-methyl sulfenate (Fig. 1, C and E, respectively) shows that their *a* and *b* carbonyl bands are located in identical positions (5.94 and 6.07 *vs.* 5.94 and 6.08). The *a*-bands, then, represent absorption by the 9-carbonyl group and the *b*-bands by the 10-carbonyl group.

From these considerations, it would be expected that for the 1,4-dimethyl sulfenate and 1,4-dihydroxyanthraquinone there would only be *b*-band absorption (XV). This is borne out in Fig. 1, D and F. However, on the basis of Rylander's postulation, there should be no carbonyl absorption by the 1,4-anthraquinone disulfenate (XIII). The establishment of *b*-band absorption by the 1,4-disulfenate thus precludes the need to invoke structure XII to explain the stability of Fries' acid.

The instability of 1-fluorenone sulfenic acid (VI) as compared to 1-anthraquinone sulfenic acid has been suggested to be due to less resonance interaction of the carbonyl and sulfenate groups in the former.[8] That this may be so is seen in a comparison of the infrared spectra of fluorenone and methyl-1-fluorenone sulfenate (Fig. 2) to anthraquinone-1,4-dimethyl sulfenate (Fig. 1, F). In the former there is a shift of 0.07 μ on substitution

(12) Mt. St. C. Flett, *J. Chem. Soc.*, 1445 (1948).

(13) R. S. Rasmussen, D. D. Tunnicliff and R. R. Brattain, THIS JOURNAL, **71**, 1068 (1949).

of the methyl sulfenate group, whereas in the latter the shift is double (0.15 μ).

TABLE I

EFFECT OF STRUCTURE AND SUBSTITUTION ON CARBONYL ABSORPTION

Compound	Position, μ a	b	Base line density a	b
Anthrone	5.96		41.9	
Anthraquinone	5.93		75.4	
Anthraquinone -1-OH	5.94	6.07	25.0	50.5
Anthraquinone -1-$SOCH_3$	5.94	6.08	44.4	18.4
Anthraquinone -1,4-$(OH)_2$		6.11		46.4
Anthraquinone -1,4-$(SOCH_3)_2$		6.08		31.2
Fluorenone	5.78		57.4	
Fluorenone -1-$SOCH_3$		5.85		41.1

In Table I are presented the base line densities of the *a* and *b* carbonyl bands for the compounds considered. It can be seen from Table I that the *a*-band for anthraquinone is essentially double that of anthrone and that, therefore, the base line density, in this case, indicates the number of carbonyl groups. For 1-hydroxyanthraquinone, the sum of the densities of the *a*- and *b*-bands are identical to the *a*-band intensity of anthraquinone, which again supports the view that the total absorbance of the carbonyl bands relates to the number of carbonyl groups.[14] This criterion holds fairly well for methyl anthraquinone-1-sulfenate, where the total base line densities are 85% that of anthraquinone or the 1-hydroxyl substituted anthraquinone. However, for the 1,4-dihydroxy and dimethyl sulfenates the *b*-band intensities are but one-half that of the *a*-band intensity of anthraquinone.

In conclusion, it can be stated that, of those structures proposed for Fries' acid and its methyl ester, only the more or less equivalent structures II and IV agree with existing spectral data. Furthermore, the $-SOCH_3$ group appears to be capable of strong resonance interaction with electronegative groups such as the carbonyl groups of anthraquinone.

Acknowledgment.—This work was supported by grant A-980 from the National Institutes of Arthritis and Metabolic Diseases, National Institutes of Health. We should like to thank Dr. Adnan Sayigh and the Carwin Co., North Haven, Conn., for the prolonged use of their infrared equipment. We should also like to thank Dr. N. Kharasch for his interest in this research.

Experimental[15]

Materials.—Anthraquinone, m.p. 286–287°, was sublimed at 200° (3 mm.), giving material of the same melting point (reported 275°,[16] 285–286°[17]). **Anthrone** (Eastman Kodak Co.), m.p. 158–159° (reported 151.5°,[18] 154°,[19,20] 161°,[21] 163–170°,[22] 154–155°,[23] 163–165°,[24] 163–164°,[25] 158°[26]) and **fluorenone** (Eastman Kodak Co.), m.p. 82–83.5° (reported 83.5–84°,[27] 83°,[28] 84°,[29] 83–84°,[30] 85–86°[31]) were employed without further purification.

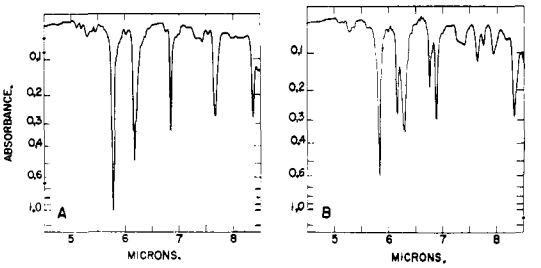

Fig. 2.—The infrared absorption (tetrachloroethylene) in the 5–8 μ range for: (A) fluorenone 8.3×10^{-3} mole $l.^{-1}$; and (B) methyl 1-fluorenonesulfenate, 13.5×10^{-3} mole $l.^{-1}$.

Dimethyl 1,4-anthraquinonedisulfenate was that of a previous study[8] and was recrystallized from benzene and methanol, m.p. 186–189° (reported[3] 189–190°).

Methyl 1-anthraquinonesulfenate was prepared according to Fries[3] and recrystallized from methanol, m.p. 188–190° (reported[3] 189°).

1-Hydroxyanthraquinone.—Several attempts to prepare this substance by literature procedures proved unsatisfactory. The following method was employed. 1-Aminoanthraquinone (10 g., 0.045 mole) was dissolved in 100 ml. of concentrated sulfuric acid at 70°. After cooling, 750 g. of cracked ice was added followed over a 30-min. period (0–3°) by a solution of 4.0 g. of sodium nitrite (0.047 mole) in 25 ml. of water. After stirring at 0–3° for 20 min. the solution of the diazotized amine was poured slowly into 500 ml. of boiling 10% aqueous sulfuric acid. Boiling was continued for 30 min. followed by chilling and collection of the solid product. Extraction of the latter four times with 750-ml. aliquots of 2% potassium hydroxide solution followed by acidification of the extract yielded the 1-hydroxyanthraquinone which after collection, washing with water and recrystallization from benzene with *n*-heptane (charcoaling) amounted to 7.15 g. (71.5%), m.p. 196–197° (reported 190°,[32,33] 191°,[34] 193°,[35–37] 200°[38]).

1,4-Dihydroxyanthraquinone (Carwin Co.) was crystallized three times from glacial acetic acid, m.p. 197.5–199° (reported 194–195°,[39] 200–202°).[40]

Methyl 1-Fluorenonesulfenate.—An 8-year old sample of 1-fluorenonesulfenyl chloride was found to have decomposed to 1-fluorenonyl disulfide. After recrystallization from hot nitrobenzene, it melted at 335° with decomposition (reported[4] 335–336° dec.), and a mixed m.p. with a pure sample was not depressed. Methyl 1-fluorenonesulfenate was synthesized from the disulfide according to the procedure of Kharasch and Bruice.[4] The disulfide was reduced to the sodium salt of the thiol, from which the free thiol was collected on acidification. The thiol was converted to 1-fluorenonesulfenyl chloride which gave methyl 1-fluorenonesulfenate after treatment with sodium methoxide. The yellow crystals of the ester melted at 79–80° (reported[4] 79–80°).

(14) R. N. Jones, D. A. Ramsay, D. E. Kein and K. Dobriner, THIS JOURNAL, **74**, 80 (1952); D. A. Ramsay, *ibid.*, **74**, 72 (1952).
(15) All melting points are corrected.
(16) A. Kekule, *Ber.*, **5**, 908 (1872).
(17) E. Phillipi, *Monats.*, **33**, 373 (1912).
(18) A. Bezdzik and P. Friedlander, *ibid.*, **30**, 875 (1909).
(19) K. Lagodzinski, *Ber.*, **38**, 2304 (1905).
(20) E. B. Barnett and M. E. Matthews, *J. Chem. Soc.*, **123**, 390 (1923).
(21) J. Meisenheimer and E. Connerade, *Ann.*, **330**, 144, 166 (1904).
(22) C. Liebermann, *Ber.*, **9**, 1201 (1876); *Ann.*, **212**, 6 (1882).
(23) K. H. Meyer, *Ann.*, **379**, 55 (1911); "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 52.
(24) L. Braun and O. Bayer, *Ber.*, **58**, 2675 (1925).
(25) W. Minajew and B. Fedorow, *ibid.*, **62**, 2492 (1929).
(26) F. Mayer and W. Fischbach, *ibid.*, **58**, 1252 (1925).
(27) R. Fittig and E. Ostermayer, *Ann.*, **166**, 374 (1873).
(28) W. Wislicenus and M. Waldmuller, *Ber.*, **41**, 3339 (1908).
(29) H. Staudinger and N. Kon, *Ann.*, **384**, 133 (1911).
(30) H. Stobbe, *Ber.*, **44**, 1482 (1911).
(31) A. Sieglitz, *ibid.*, **57**, 317 (1924).
(32) v. Pechmann, *ibid.*, **12**, 2127 (1879).
(33) C. Liebermann, *ibid.*, **10**, 611 (1877).
(34) C. Liebermann, *Ann.*, **212**, 20 (1882).
(35) W. Birukoff, *Ber.*, **20**, 2438 (1887).
(36) P. Pfeiffer, *Ann.*, **398**, 176 (1913).
(37) F. Ullmann and A. Conzetti, *Ber.*, **53**, 829 (1920).
(38) F. Blicke and O. Weinkauff, THIS JOURNAL, **54**, 333 (1932).
(39) F. Grimm, *Ber.*, **6**, 508 (1873).
(40) L. Bigelow and F. Reynolds, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1932, p. 464.

Apparatus and Method.—A Perkin–Elmer model 21 double beam spectrometer was employed for the spectra determinations. A 1.0-mm. microcell with sodium chloride windows was used for the sample solutions and a 1.0-mm. cell with sodium chloride windows was used as the reference cell. The solvent used in the spectra, tetrachloroethylene, was of spectral grade (courtesy Carwin Co.), b.p. 121°. After calibration and checking the I_0 line, solvent was run against solvent; no observable uncompensated absorption took place in the region of carbonyl absorption. The spectra of the compound was then scanned slowly (concentrations ranged from 0.0082 *M* to 0.0183 *M*, see legend of Figs. 1 and 2) with the resolution set at 960. Spectra were also taken with changed gear ratios; an attempt was made to measure the area of the expanded curves by use of a planimeter but in several cases overlapping bands made the determinations questionable. This method was therefore abandoned and the "base-line" density method was employed to determine the intensity of the carbonyl absorption bands. In practice, a base-line was drawn as nearly parallel to the I_0 line (*i.e.*, solvent *vs.* solvent) as possible; the difference between the absorbance at the band maximum and absorbance at the point where a vertical line through the maximum crosses the base-line was determined. This figure was divided by the molar concentrations (given in Figs. 1 and 2) to give the base line density (intensity/mole). The base line densities so determined are recorded in Table I.

NEW HAVEN, CONN.

[CONTRIBUTION FROM THE INSTITUTE OF SCIENTIFIC AND INDUSTRIAL RESEARCH, OSAKA UNIVERSITY]

The Effect of Conformation on Reactivity. I. Acetolysis of the *trans*-Decalyl *p*-Toluenesulfonates; 1,3-Diaxial Interactions as a Factor in the Chemical Behavior of Decalyl Derivatives

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The rates of acetolysis of 1-axial, 1-equatorial, 2-axial and 2-equatorial *trans*-decalyl tosylates were measured in order to determine the effects of the conformations on the reactivities of these compounds. The relative reactivity was observed to decrease in the order: 1-axial $\gg$2-axial > 2-equatorial > 1-equatorial. The increased rate of solvolysis of the 2-axial to the 2-equatorial derivative, 3:1, is attributed to 1,3-diaxial interactions. The larger effect observed in comparing the 1-axial to the 2-axial, 9:1, is attributed to increased 1,3-diaxial interactions. The rates of solvolysis of the tosylates correlate well with earlier data on the rates of hydrolysis of the corresponding decalyl hydrogen succinates. It is concluded that the fixed conformation of the decalyl system provides a valuable tool for quantitative studies of the effect of conformation on chemical behavior.

It is of considerable interest to correlate the reactivity of cyclohexane derivatives with their conformations. Since the electronic effects of both axial and equatorial bonds in such molecules should be quite similar, significant differences in reactivity must arise from conformational effects.[1] Detailed knowledge of the relationship between conformation and reactivity is important for the full understanding of the chemical behavior of many natural products, such as the steroids and triterpenes, whose structures are based on the cyclohexane system.

A major difficulty in studying relative reactivities of isolated axial and equatorial bonds in simple cyclohexane derivatives is the ready interconversion of the two types of bonds in these compounds. For example, according to Kojima and Yoshino[2] and Larnaudie,[3] *trans*-1,2-dichloro- and *trans*-1,4-dibromocyclohexane are present in solution as an equilibrium mixture of the equatorial–equatorial and axial–axial conformations.

Recently, Winstein and Holness[4] have attempted to circumvent this difficulty by working with the *cis*- and *trans*-4-*t*-butylcyclohexyl *p*-toluenesulfonates. They postulate that in these derivatives the bulky *t*-butyl group would prefer to occupy the equatorial position and thereby prevents the interconversion of the cyclohexane ring into the alternate conformation. The observed rate ratio of *cis*- to *trans*-4-*t*-butylcyclohexyl *p*-toluenesulfonate, 2.7, has been attributed to the steric strain arising from the axial conformation of the tosyl group in the *cis* derivative.

The *trans*- decalin system appears to possess real advantages for the study of conformational effects. In this system the two rings cannot be joined through axial–axial bonds. Consequently, no rotary isomerization can occur and the conformations can be assigned on the basis of the structure of the molecules. Hückel observed differences in the reactivities of the *trans*-1- and 2-decalyl *p*-toluenesulfonates.[5] Accordingly, we undertook to obtain precise quantitative data on the acetolysis of these derivatives.

Results

The rate of acetolysis were determined at several temperatures following the procedure described by Winstein and co-workers.[6]

The reactions followed first-order kinetics. Data for a typical kinetic study are shown in Table I. In the case of the *trans-trans*-1- and *trans-trans*-2-derivatives it was noted that the reaction rate is not influenced by the presence of potassium acetate.

The rate constants at several temperatures gave excellent plots of log k vs. $1/T$. Heats and entropies of activation were calculated using the equation given by Eyring.[7] The results are summarized in Table II.

The solvolysis of *trans-cis*-1-decalyl tosylate pro-

(1) D. H. R. Barton, *Experientia*, **6**, 316 (1950).
(2) K. Kojima and T. Yoshino, THIS JOURNAL, **75**, 166 (1953).
(3) M. Larnaudie, *Compt. rend.*, **236**, 909 (1953).
(4) S. Winstein and N. J. Holness, THIS JOURNAL, **77**, 5562 (1955).
(5) W. Hückel, *Ber.*, **77**, 805 (1944).
(6) S. Winstein, E. Grunwald and L. L. Ingraham, THIS JOURNAL, **70**, 812, 821 (1948).
(7) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw–Hill Book Co., Inc., New York, N. Y., 1941, p. 196