

imino ether hydrochloride intermediate.⁸ In most preparations the presence of some free carboxylic acid was shown by infrared spectroscopy; hence the product mixture was esterified with methanol and thionyl chloride. The yield of the dicarboxylic ester (4d) was about 90%.

The dicarboxylic ester (4d) was converted (63%) to the next higher homolog, dimethyl (4*S*:5*S*)-4,5-dimethoxy-suberate (5d), by the same sequence of reactions used for the transformation of 3 to 4d. Under the conditions of the acyloin condensation⁹ the dicarboxylic ester (5d) did not yield any of the desired (5*S*:6*S*)-2-hydroxy-*trans*-5,6-dimethoxycyclooctanone. The major product isolated (31% yield), (4*S*:5*S*)-2-carbomethoxy-*trans*-4,5-dimethoxycycloheptanone, resulted from a Dieckmann condensation.

Hydrolysis of (4*S*:5*S*)-2-carbomethoxy-*trans*-4,5-dimethoxycycloheptanone gave (4*S*:5*S*)-4,5-dimethoxycycloheptanone (6). However, a better yield (57%) of the cycloheptanone (6) was obtained by Thorpe-Ziegler cyclization¹⁰ of the dinitrile (5c) followed by hydrolysis with 30% aqueous sulfuric acid.

The cycloheptanone (6) was converted to the cyanohydrin which was hydrogenated catalytically. The resulting amino alcohol on treatment with sodium nitrite and acetic acid yielded (4*S*:5*S*)-4,5-dimethoxycyclooctanone (7, 23% from ketone 6).¹¹

Wolff-Kishner reduction¹² of the cyclooctanone (7) gave (1*S*:2*S*)-1,2-dimethoxycyclooctane (8) [$[\alpha]^{31,3D} +50.3^\circ$ (*c* 4.63, CHCl₃)].¹³

The identical diether (8) having $[\alpha]^{31D} +49.5^\circ$ (*c* 4.337, CHCl₃) was obtained from (–)-*trans*-cyclooctene, by treatment of the olefin with osmium tetroxide yielding (+)-*trans*-1,2-cyclooctanediol¹⁴ followed by methylation.¹⁵

Thus, (2*R*:3*R*)-tartaric acid (2) has been related to (–)-*trans*-cyclooctene and the only assumption in assignment of the (*R*)-configuration to the olefin is that osmium tetroxide attacks from the side of the double bond not hindered by the ring methylene groups. In the osmium tetroxide oxidation of 5 α ,22 α -spirost-2-ene it has been reported¹⁶ that the product is the 2 α ,3 α -diol which results from the approach of the reagent to the $\Delta^{2,3}$ -bond from the less hindered α -side of the steroidal nucleus.

During the course of this work, Moscowitz and Mislow¹⁷ reported on the basis of theoretical considerations that (–)-*trans*-cyclooctene has the (*S*)-configuration, contrary to these results.

(8) The method was similar to that of W. Davey and D. J. Tivey [*J. Chem. Soc.*, 1230 (1958)].

(9) The procedure was similar to that of N. L. Allinger [*Org. Syn.*, **36**, 79 (1956)].

(10) Carried out essentially according to the method of N. L. Allinger, M. Nakazaki, and V. Zalkov [*J. Am. Chem. Soc.*, **81**, 4074 (1959)] for the preparation of *cis*-bicyclo[5.2.0]nonan-4-one.

(11) The cyanohydrin was prepared according to the procedure of G. C. Ayerst and K. Schofield [*J. Chem. Soc.*, 3445 (1960)] but was not isolated pure. The subsequent steps followed essentially the method of C. D. Gutsche [*J. Am. Chem. Soc.*, **71**, 3513 (1949)].

(12) Huang-Minlon, *ibid.*, **68**, 2487 (1946).

(13) Optical rotations were determined with a Zeiss photoelectric polarimeter which gave values at 546.1 and 577.8 m μ and the value at the sodium D-line (589.2 m μ) was calculated by extrapolation using the first approximation of Drude's formula for normal rotation dispersion.

(14) A. C. Cope, R. A. Pike, and C. F. Spencer, *J. Am. Chem. Soc.*, **75**, 3212 (1953).

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(16) C. Djerassi, L. B. High, T. T. Grossnickle, R. Ehrlich, J. A. Moore, and R. B. Scott, *Chem. Ind. (London)*, 474 (1955).

(17) A. Moscowitz and K. Mislow, *J. Am. Chem. Soc.*, **84**, 4605 (1962).

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F¹⁹ Magnetic Resonance Determination of σ -Constants for the –ICl₂ Functional Group

Sir:

Iodobenzene dichloride and its derivatives have been the subject of several recent publications by Keefer and Andrews.^{1–11} They have reported the effect of substituents and solvents on the rates and equilibria of dissociation of substituted iodobenzene dichlorides into chlorine and substituted iodobenzenes^{1–6} and the behavior of the complex as a chlorinating agent.^{7–11} Little information has been obtained concerning the effect of the –ICl₂ functional group on the chemical or physical properties of aromatic compounds. We have obtained the F¹⁹ n.m.r. spectra of *m*-fluoriodobenzene dichloride and *p*-fluoriodobenzene dichloride and have utilized Taft's correlations of F¹⁹ chemical shifts in *m*- and *p*-substituted fluorobenzenes with σ -constants^{12–16} to determine these parameters for the –ICl₂ group.

Fluorine-19 magnetic resonance spectra were obtained at 56.4 Mc./sec. using a Varian HR-60 spectrometer and associated equipment on dilute solutions of the substituted fluorobenzenes in carbon tetrachloride in 15-mm. tubes. *p*-Difluorobenzene was employed as an internal reference and chemical shifts were obtained by the standard side-band technique. The chemical shifts are presented in Table I in p.p.m. with respect to fluorobenzene. Similar but less precise shifts were obtained using fluorobenzene as an external reference.

TABLE I

F¹⁹ CHEMICAL SHIFTS

Compound	Conditions	Chemical shifts, p.p.m. with respect to fluorobenzene
<i>p</i> -Fluoriodobenzene dichloride	<i>a</i>	–7.1
<i>p</i> -Fluoriodobenzene dichloride	<i>b</i>	–7.0
<i>m</i> -Fluoriodobenzene dichloride	<i>a</i>	–7.2
<i>m</i> -Fluoriodobenzene dichloride	<i>b</i>	–7.2
<i>p</i> -Fluoriodobenzene	<i>c</i>	+1.6
<i>m</i> -Fluoriodobenzene	<i>c</i>	–2.4

^a Spectra obtained on supernatant liquids above the solid formed by treatment of 2% solution of ArI in CCl₄ with chlorine gas. ^b Spectra obtained on saturated CCl₄ solutions prepared from the washed solid referred to in *a*. ^c Spectra obtained on 2% solutions in CCl₄.

The shifts listed for *m*- and *p*-fluoriodobenzene in Table I are in good agreement with the values reported elsewhere.^{13,16} When carbon tetrachloride solutions of these compounds were treated with chlorine, the F¹⁹

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- (2) R. M. Keefer and L. J. Andrews, *ibid.*, **80**, 5350 (1958).
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- (4) L. J. Andrews and R. M. Keefer, *ibid.*, **81**, 4218 (1959).
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- (6) L. J. Andrews and R. M. Keefer, *ibid.*, **82**, 3059 (1960).
- (7) R. M. Keefer and L. J. Andrews, *ibid.*, **79**, 4348 (1957).
- (8) R. M. Keefer and L. J. Andrews, *ibid.*, **82**, 4547 (1960).
- (9) L. J. Andrews and R. M. Keefer, *ibid.*, **82**, 5823 (1960).
- (10) R. M. Keefer and L. J. Andrews, *ibid.*, **83**, 376 (1961).
- (11) J. L. Cotter, L. J. Andrews, and R. M. Keefer, *ibid.*, **84**, 793 (1962).
- (12) R. W. Taft, Jr., *ibid.*, **79**, 1045 (1957).
- (13) R. W. Taft, Jr., S. Ehrenson, I. C. Lewis, and R. E. Glick, *ibid.*, **81**, 5352 (1959).
- (14) R. W. Taft, Jr., E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *ibid.*, **85**, 709 (1963).
- (15) R. W. Taft, Jr., E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *ibid.*, **85**, 3146 (1963).
- (16) R. W. Taft, Jr., *J. Phys. Chem.*, **65**, 1805 (1960).

resonance peaks corresponding to the starting materials were replaced by new peaks with chemical shift of -7.1 ± 0.1 p.p.m., and light yellow solids were formed. These peaks are assigned to *m*- and *p*-fluoriodobenzene dichloride and were the only peaks observed in saturated solutions prepared by dissolving washed samples of the solids in carbon tetrachloride. The chlorine analyses of the solids showed 24.5% for the *para* isomer and 23.5% for the *meta* isomer, compared to a calculated value of 24.2%.

The nearly zero difference between the chemical shifts of the *p*- and *m*-dichlorides indicates a negligible resonance contribution to the reactivity constant, σ . This conclusion is based on Taft's rather precise correlation¹⁵

$$\int_{\text{H}}^{\text{p-X}} - \int_{\text{H}}^{\text{m-X}} = (-29.5)\sigma_{\text{R}}^0$$

where $\int_{\text{H}}^{\text{p-X}}$ and $\int_{\text{H}}^{\text{m-X}}$ are the fluorine chemical shift of *p*- and *m*-substituted fluorobenzenes, respectively, in p.p.m. (Table I) defined in the usual manner with respect to fluorobenzene. The substituent constant σ^0 is defined by Taft as the sum of σ_{R}^0 and σ_{I} , the resonance and inductive contributions, respectively, to the constant σ^0 . His complementary correlation¹⁵

$$\int_{\text{H}}^{\text{m-H}} = -7.1\sigma_{\text{I}} + 0.60$$

predicts $\sigma_{\text{I}} = +1.1$. Then, on the basis of the equations

$$\sigma_{\text{p}}^0 = \sigma_{\text{I}} + \sigma_{\text{R}}^0$$

and

$$\sigma_{\text{m}}^0 = \sigma_{\text{I}} + 0.5\sigma_{\text{R}}^0 (\textit{para})$$

where σ_{p}^0 and σ_{m}^0 refer to *para* and *meta* substituents respectively, we estimate $\sigma_{\text{p}}^0 \cong \sigma_{\text{m}}^0 \cong \sigma_{\text{I}} \cong 1.1$. Similar conclusions can be drawn on the basis of Taft's alternative relationships¹²

$$- \int_{\text{H}}^{\text{m-X}} = 5.83\sigma_{\text{I}} - 0.2$$

and

$$- \int_{\text{H}}^{\text{p-X}} = 5.83\sigma_{\text{I}} + 18.80\sigma_{\text{R}} - 0.8$$

where $\sigma \equiv \sigma_{\text{R}} + \sigma_{\text{I}}$. With the present data, these equations lead to a negligible σ_{R} -value and $\sigma_{\text{m}} \cong \sigma_{\text{p}} \cong \sigma_{\text{I}} \cong 1.3$ for the $-\text{ICl}_2$ substituent.

Thus, all our results indicate that the $-\text{ICl}_2$ functional group in aromatic molecules exerts a profound inductive effect of electron withdrawal and a negligible resonance effect. This inability to interact by resonance is consistent with the small effect which *para* substituents have on the rates and equilibria for dissociation of derivatives of iodobenzene dichloride.¹

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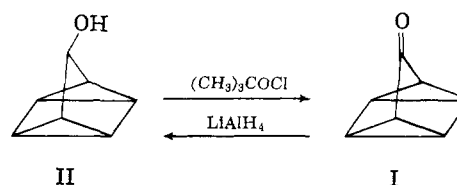
GARY E. MACIEL

RECEIVED OCTOBER 26, 1963

7-Quadricyclo[2.2.1.0^{2,6}.0^{3,5}]heptanone (Quadricyclanone)

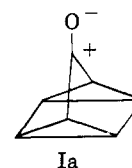
Sir:

We wish to record the synthesis and some of the properties of a rather unusual tetracyclic ketone, 7-quadricyclo[2.2.1.0^{2,6}.0^{3,5}]heptanone (I). Oxidation of 7-quadricyclo[2.2.1.0^{2,6}.0^{3,5}]heptanol (II) with *t*-butyl hypochlorite produces quadricyclanone (I) in 14% yield. The ketone (I) is reduced nearly quantitatively to quadricyclanol (II) with lithium aluminum hydride.



This highly strained ketone (I) is of interest because of its relation to the 7-quadricyclic carbonium ion¹ and because it is potentially the key intermediate in the synthesis of other 7-quadricyclic and 7-norbornadienyl derivatives, important to the understanding of bonding in these strained systems. The photochemistry of I is also potentially of considerable interest.

The stability of the 7-quadricyclic carbonium ion¹ would make it seem likely that the ionic structure Ia would contribute appreciably to the resonance hybrid. That this is the case is reflected in the apparently



large dipole moment of quadricyclanone (I). For example, the retention time of I is greater than that of the alcohol (II) on polar g.p.c. columns and the boiling point of I is also slightly higher than that of II. Although quadricyclanone (I) did not appear to be particularly deliquescent as reported for norbornadienyl derivatives,² it is quite water-soluble. Water solutions of I were found to be very weakly basic. Presumably water solubility could also be explained by hydration of I to a *gem*-diol, since formation of such a diol would be expected to result in considerable relief of the strain imposed by the trigonal carbonyl structure. We have examined the ultraviolet and n.m.r. spectra of I in water, however, and can find no positive evidence for the existence or absence of a *gem*-diol. The ultraviolet spectrum of I in water exhibited end absorption and a maximum at 293 m μ (ϵ 84). In ethanol the maximum was observed at 296 m μ (ϵ 66) and in cyclohexane at 297 m μ (ϵ 40). Obviously, the carbonyl is not completely hydrated to a diol.

The 60 Mc. n.m.r. spectrum of I in 97% deuterium oxide (0.4 M) consisted of a four hydrogen doublet 143 c.p.s. upfield from the water signal, which we have assigned to the β -hydrogens, and a two hydrogen triplet, 216 c.p.s. upfield from the water signal, assigned to the α -hydrogens. Some fine structure was visible in both multiplets. In carbon tetrachloride the

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