

analysis has been reported for V, but its strain energy has been estimated⁸⁷ as 46 kcal/mole.

Electronic Spectra. The only marked effect of ring strain on the ultraviolet spectra of *o*-di-*t*-butylbenzene systems is a loss of intensity and vibrational fine structure of the secondary bands between 240 and 280 m μ .^{25-31,36} Only when three *t*-butyl groups are juxtaposed^{88,89} are large bathochromic shifts comparable to

(88) E. M. Arnett and J. M. Bollinger, *Tetrahedron Letters*, 3803 (1964).

those seen in [2.2]paracyclophane and compound V observed. Assuming that equivalent assignments may be made for the bands in strained and unstrained isomers, these results simply indicate that little or no strain energy is released on going to the excited state. There are so many reasonable but unverifiable interpretations of this fact that discussion at this time is fruitless.

(89) H. G. Viehe, R. Merényi, J. F. M. Oth, and P. Valange, *Angew. Chem. Intern. Ed. Engl.*, 3, 746 (1964).

Steric and Polar Rate-Retarding Effects in the Chromic Acid Oxidation of Alcohols

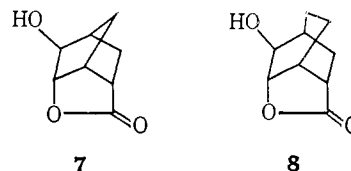
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Abstract: The rates of chromic acid oxidation of a number of cyclic, bicyclic, and bridged bicyclic alcohols have been determined. These are compared with the rates of oxidation for structurally related derivatives bearing electronegative groups. For cyclopentanol, cyclohexanol, 2-*exo*-norbornanol, 2-bicyclo[2.2.2]octanol, 2-*exo*-brendanol, and 6-oxatricyclo[3.2.2.1]decan-4 β -ol, relief of steric strain present in the ground state appears to be the dominant factor in controlling the rate of oxidation. Furthermore, for these compounds no correlation exists between the infrared carbonyl stretching frequency of the derived ketone and the rate of chromic acid oxidation of the corresponding secondary alcohol. For the bridged bicyclic and tricyclic lactone alcohol derivatives 5-*exo*,6-*endo*-dihydroxy[2.2.1]heptane-2-*endo*-carboxylic acid lactone (7), 5-*exo*,6-*endo*-dihydroxy[2.2.2]octane-2-*endo*-carboxylic acid lactone (8), and *trans*-2,3-dihydroxycyclopentaneacetic acid γ -lactone (9) very slow rates of oxidation were observed. The large rate retardations are considered to arise from electrostatic destabilization in the transition state between the developing carbonyl group and the polar lactone function.

The chromic acid oxidation of primary and secondary alcohols is well known to be subject to both polar and steric effects. Polar effects generally lead to rate retardations. Thus, the rate of oxidation of a secondary alcohol may be retarded by several orders of magnitude due to the presence within the molecules of strongly electronegative groups.^{2,3} Steric effects, on the other hand, may cause impressive rate accelerations.⁴ The steric rate acceleration in the chromic acid oxidation of secondary alcohols is believed to be due to the relief of steric strain present in the ground state of the molecule upon its conversion to the ketone. This argument assumes that the transition state for the oxidation resembles the carbonyl product. In agreement with this description, the rate of reaction increases as the number and severity of these ground-state steric interactions are increased. Kwart and Francis^{5,6} have challenged this interpretation; they point out that the above mechanistic representation requires a rate retardation in the oxidation of an alcohol leading to a strained ketone. An example which typifies their ob-

jection is found in the chromic acid oxidation of 7-norbornanol; its rate of oxidation is only slightly slower than that of 2-*exo*-norbornanol even though the respective carbonyl products differ considerably in degree of internal angular strain at the trigonal carbon atom. At present, no unequivocal example exists of steric retardation in the chromic acid oxidation of a secondary alcohol. What purported to be an example of this phenomenon was a report of the abnormally slow rate of oxidation of certain bridged hydroxy lactones in the bicycloheptane series. Crundwell and Templeton⁷ found that hydroxy lactone 7 was highly resistant to oxidation by chromic acid; in fact, they were unable to obtain any of the corresponding keto lactone 12. Further-



more, this lack of reactivity appeared to be restricted to the bicycloheptane compound since the corresponding [2.2.2]bicyclooctyl hydroxy lactone 8 behaved normally toward chromic acid oxidation. Crundwell and Templeton concluded that the unreactivity of 7 represented an example of steric rate retardation due to the

(7) E. Crundwell and W. Templeton, *J. Chem. Soc.*, 1400 (1964).

(1) (a) University of Illinois at Chicago Circle, Chicago, Ill. (b) The Catholic University of America, Washington, D. C.

(2) H. Kwart and P. S. Francis, *J. Am. Chem. Soc.*, 77, 4907 (1955).

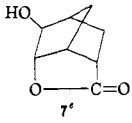
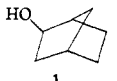
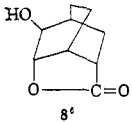
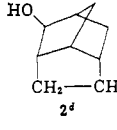
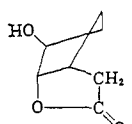
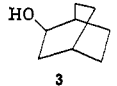
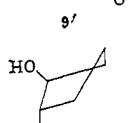
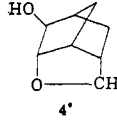
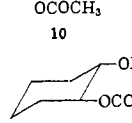
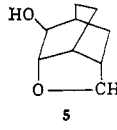
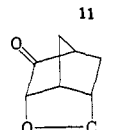
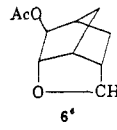
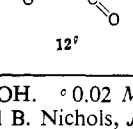
(3) J. Roček, *Collection Czech. Chem. Commun.*, 25, 1053 (1960).

(4) For a recent summary see E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Publishers, Inc., New York, N. Y., 1966, pp 81-84, 271.

(5) H. Kwart and P. S. Francis, *J. Am. Chem. Soc.*, 81, 2116 (1959).

(6) H. Kwart, *Suomen Kemistilehti*, A34, 173 (1961).

Table I. Rate Constants ($M^{-1} \text{ min}^{-1}$) for Chromic Acid Oxidations of Alcohols at $31 \pm 0.02^\circ$ in 90% Acetic Acid

| Compound | HClO_4, M | | | k_{rel}^a | Compound | HClO_4, M | | | k_{rel}^a |
|--|--------------------|-------|-------|---------------------|--|--------------------|--------------------|------|---------------------|
| | 0.0 | 0.02 | 0.05 | | | 0.0 | 0.02 | 0.05 | |
| Alcohols | | | | | Hydroxy Esters and Hydroxy Lactones | | | | |
| Cyclopentanol | 8.66 | | | | | | | | |
| Cyclohexanol | 21.96 ^b | 49.90 | | 1.00 | | | | | |
| | 5.66 | 39.24 | | 0.654 |  | | 1.07 | 1.53 | 0.0214 ^c |
|  | 7.29 | | | | | | | | |
| | 16.34 ^b | 40.70 | | 0.842 |  | | | | |
|  | 19.69 ^b | | | 0.896 ^b |  | 1.39 | 9.18 | | 0.1605 |
|  | 39.66 | | | 4.58 |  | | 2.62 | 3.84 | 0.0525 ^c |
| Hydroxy Ethers | | | | | | | | | |
|  | 2.04 | 12.72 | 20.18 | 0.235 |  | 3.825 ^b | 16.53 ^b | | 0.174 ^b |
|  | 13.85 | 63.20 | | 1.60 |  | 0.49 | 3.16 | 6.13 | 0.0565 |
|  | | 0.40 | 0.60 | 0.0080 ^c |  | | 1.36 | | 0.0273 ^c |

^a From values in 90% AcOH without added HClO_4 . ^b 95% AcOH. ^c 0.02 M HClO_4 in 90% AcOH. ^d Generously supplied by Professor A. Nickon, Johns Hopkins University. ^e H. B. Henbest and B. Nichols, *J. Chem. Soc.*, 227 (1959). ^f R. K. Hill and A. G. Edwards, *Tetrahedron*, **21**, 1501 (1965). ^g R. M. Moriarty and H. Gopal, unpublished.

formation of a highly strained carbonyl compound in the rate-limiting step of the oxidation. Although they did not succeed in obtaining the keto lactone related to **7**, they noted that a similar keto derivative had an unusually high infrared carbonyl stretching frequency for the keto group, and this appeared to support the assumption that the carbonyl compound was highly strained.

Crundwell and Templeton's observation was of considerable interest because it seemed to offer the first example of a large steric rate retardation in the chromic acid oxidation of a secondary alcohol, an effect which was predicted^{5,6} but never found despite considerable effort.^{8,9}

Due to the importance of the problem of polar and steric rate acceleration, and to the fact that Crundwell and Templeton's data were based only on qualitative observations of visible changes during the reaction and on the yields of the ketonic products, we undertook a reinvestigation of some of the compounds studied by Crundwell and Templeton as well as a number of model compounds. Our intention was to obtain quantitative rate data and attempt to separate the polar and steric effects responsible for the unreactivity of the hydroxy lactones of the [2.2.1]bicycloheptane series.

The results of the kinetic study are summarized in Table I. The first part of the table contains the data

for unsubstituted alcohols. It can be seen that the oxidation rate of 2-*exo*-norbornanol (**1**) is only slightly lower than that of cyclopentanol, and is in fact higher than that of cyclohexanol. Since the position of the carbonyl stretching frequency in the infrared is related to the internal angular strain at the trigonal carbon atom, it is of particular interest to note that the carbonyl stretching frequency of the ketone produced in the oxidation is higher (1751 cm^{-1} for norbornanone¹⁰ compared with 1740 cm^{-1} for cyclopentanone¹¹).

A fairly large rate acceleration is found in 2-bicyclo[2.2.2]octane (**3**). This compound reacts about 4.6 times faster than cyclopentanol and approximately 5.5 times as rapidly as 2-*exo*-norbornanol (**1**). It is also interesting that it reacts about 7.0 times faster than cyclohexanol in spite of the fact that it produces a more strained ketone ([2.2.2]bicyclooctanone: 1731 cm^{-1} ; cyclohexanone: 1716 cm^{-1}) as judged by the value of the carbonyl stretching frequency.¹⁰ The high rate of oxidation of bicyclooctanol is obviously due to steric rate acceleration caused by the relief of strain existing in the molecule as the result of the interaction of the hydroxyl group with the C_6 hydrogen.

A similar rate acceleration has been found previously in the oxidation of 2-*endo*-norbornanol in which the hydroxyl group is in practically the same situation; two different values are available for the relative rate of the

(10) C. S. Foote, *J. Am. Chem. Soc.*, **86**, 1853 (1964).

(11) A. Nickon, H. Kwasnik, T. Schwatz, R. O. Williams, and J. B. DiGiorgio, *ibid.*, **87**, 1615 (1965).

(8) J. Roček and A. Radkowsky, unpublished.
(9) J. Roček and G. Cushmac, unpublished.

chromic acid oxidation of the *endo* compound relative to the *exo* isomer. Kwart and Francis⁵ found a value of 2.5 in 30% acetic acid, whereas Rothberg and Russo¹² recently found a value of 6.47 in 75% acetic acid.¹³

The rate of oxidation of 2-*exo*-brendanol (**2**) is particularly relevant in a discussion of the relative rate of oxidation of hydroxy lactone **8** because of the significant structural similarities which they share. The rate of oxidation of **2** is only very slightly faster than 2-*exo*-norbornanol (**1**). Thus it appears unlikely that steric factors are dominant in accounting for the unusual behavior of **8** toward oxidation. The rate of oxidation of **2** is again faster than that of cyclohexanol even though the corresponding ketone, 2-brendanone, has a higher carbonyl stretching frequency (1747 cm⁻¹) than cyclohexanone.

The results then clearly indicate that no steric rate retardation operates in bicyclic and tricyclic alcohols at least as long as no polar group is introduced into the molecule. They also demonstrate the lack of correlation between oxidation rates of alcohols which do not have polar substituents and strain in the resulting ketone as measured by the value of the carbonyl stretching frequency.¹⁴

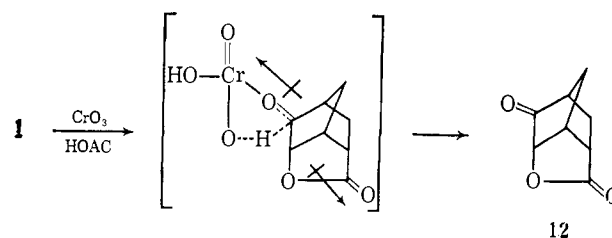
Now turning to the compounds bearing neighboring polar substituents, one finds that the introduction of an ether oxygen has a considerable rate-retarding effect. It reduces the rate of oxidation in the [2.2.2]bicyclooctane series by a factor of 2.9, in the [2.2.1]bicycloheptanol by a factor of 3.6.¹⁶ The fact that the rate decrease for the bicycloheptane compound is somewhat higher could indicate the operation of a mild steric rate-inhibiting effect. However, the difference is by no means significant enough to justify definite conclusions to be made, particularly in view of the fact that an even larger effect has been observed in simple aliphatic compounds. 2-Methoxyethanol is oxidized about 8.6 times slower than ethanol.³

The introduction of a lactone group has a much stronger rate-retarding effect than that of an ether group. Again, the effect is most pronounced in the [2.2.1]bicycloheptane series where the introduction of the lactone bridge results in a rate reduction by a factor of 38.2. The oxidation rate of the bicyclooctanol lactone is similarly reduced by a factor of 28.5 and that of the cyclopentanol lactone derivative itself is slowed by a factor of 19.0.

It is interesting to note that an acetoxy group exerts a considerably smaller effect on the oxidation rate of the hydroxyl group (cf. $k_{rel} = 5.25$ for **9** and $k_{rel} = 17.4$ for **10**). The reason probably lies in the higher electro-

negativity of the lactone ring, which, unlike the ester group, cannot be oriented so as to partially compensate the polar contributions of the C-O-C and the C=O groups. The difference in the polarity of the lactone and the ester group is clearly brought out by the much higher dipole moment of the lactone group. Butyrolactone has a dipole moment of $\mu = 4.12$ D. as compared with the dipole moment of $\mu = 1.70$ D. for ethyl acetate.¹⁷

We propose that the rate of retardation observed in the oxidation for **7**, **8**, and **9** is due to the incursion of a severe dipolar electrostatic interaction in the transition state for formation of the ketonic carbonyl group.



The observation that the rate-retarding effect follows the order bicycloheptane > bicyclooctane > cyclopentane leaves room for the possibility of some steric rate retardation. However, in view of the small magnitude of these differences, it seems safer to assume that the polar effects of the lactone group increase with the rigidity of the molecule and this precludes any minimization of the dipolar interactions in the transition state by deformation of the molecule.

Comparing directly the oxidation rates of **7** and **8** we find, of course, a rather large difference in reactivity even though by far not as large as implied by Crundwell and Templeton.⁷ However, this direct comparison fails to take into account that all rates in the [2.2.2]-bicyclooctane series are enhanced by steric acceleration which is absent in the 2-*exo*-bicyclo[2.2.1]heptanols. The relatively higher reactivity of **8** is therefore due to a partial compensation of the polar rate retardation by a steric rate acceleration.¹⁸

We conclude from the results presented in this study that no steric rate retardation can be unambiguously demonstrated in the oxidation of 5-*exo*,6-*endo*-dihydroxybicyclo[2.2.1]heptane-2-*endo*-carboxylic acid. Even though small effects of this nature cannot be ruled out, most if not all of the rate retardation can clearly be identified with polar rate effects.

(17) R. J. B. Marden and L. E. Sutton, *J. Chem. Soc.*, 1383 (1936).

(18) The fact that Crundwell and Templeton⁷ were unable to synthesize keto lactone **12** by oxidation of alcohol **7** is undoubtedly due not only to the slow rate of oxidation of **7** but also due to the high reactivity of the keto lactone under the reaction conditions. Thus, synthesis of **12** presents an isolation problem rather than one depending upon any unfavorable kinetic phenomena. We have found that keto lactone **12** can be made in excellent yield by means of ruthenium tetroxide oxidation of **7** (unpublished result with H. Gopal). The ketonic carbonyl group displays an unusually high stretching frequency (1800 cm⁻¹), and it is rapidly (5 min) and completely converted to the hemiketal by dissolving it at room temperature in methanol. Under the reaction conditions or in subsequent work-up procedures, such addition reaction to the carbonyl group could initiate ring-opening processes to yield rather highly water-soluble products which might escape isolation. Furthermore, the possibility exists that these cleavage products could undergo further oxidation. In fact, we have found that the rate of oxidation of the keto lactone **12** is actually faster than that of the hydroxy lactone **7**. The ratio of rates is 1.39. The products of oxidation have not been identified but they may derive from solvolysis of the lactone ring and subsequent rapid oxidation of the vicinal hydroxy ketone.

(12) I. Rothberg and R. V. Russo, *J. Org. Chem.*, **32**, 2003 (1967).

(13) Rothberg and Russo¹² also found a further large increase in rate if the carbon-hydrogen bond in the 6 position was replaced by a carbon-carbon bond. *endo*-5,6-Trimethylene-*endo*-2-norbornanol reacted 311 times faster than *exo*-2-norbornanol.

(14) It is interesting to note that the equilibrium measurements of Wilcox, Sexton, and Wilcox¹⁵ suggest that *endo*-norbornanol is strained by about 1 kcal as compared with the *exo* isomer. The maximum rate acceleration which one could expect on this basis at 31° is by a factor of about 7; hence a considerable part of the strain must be released in the transition state.

(15) C. F. Wilcox, Jr., M. Sexton, and M. F. Wilcox, *J. Org. Chem.*, **28**, 1079 (1963).

(16) The 6-oxatricyclo[3.2.1.1]nonan-4 β -ol acetate (**6**) has been included in the table to demonstrate that the reaction being measured is indeed the oxidation of the hydroxyl function in **4** and not the oxidation of a particularly activated C-H bond in an α position to the ether oxygen.

Experimental Section

Acetic Acid. Fisher reagent ACS, 99.7%, was diluted to 90 and 95% (w/w) aqueous solutions, respectively.

Chromic Acid. The solutions were made from chromium trioxide by weighing and the concentrations were checked by determining molar absorptivity at 350 μ . Solutions of higher concentrations were normally prepared and diluted to kinetic conditions. The solutions were stored in the cold.

Perchloric Acid. Baker reagent HClO_4 (70%) was diluted to 1 *M* aqueous solution and standardized against standard NaOH to methyl red indicator end point. This solution was then diluted with 99.7% acetic acid to stock solutions in 90 or 95% acetic acid. Solutions were checked for 100% transmission at 350 μ ; they had no absorption compared to solvents as blank.

Alcohols. Cyclopentanol, cyclohexanol, and *trans*-2-acetoxycyclohexanol-1 were purified by preparative gas-liquid partition chromatography (10% Carbowax, 100° and 10% diethylene glycol succinate, 110°, respectively) until a purity of at least 98% was achieved.

Kinetic Measurements. The reaction rates were followed spectrophotometrically in a thermostated cell holder of a Carl Zeiss PMQ spectrophotometer at 350 μ at $31 \pm 0.02^\circ$. The cells were placed in the cell compartment at least 15 min before the start of the run in order to assure full temperature equilibration. The solvent was checked for stability. The reaction of the acetic acid solvent with chromic acid was negligibly slow in the absence of perchloric acid, but was measurable in solutions containing HClO_4 . All rate constants were therefore corrected for solvent oxidation. The corrections were very low for reactive alcohols (e.g., 0.2% of the rate constant for cyclopentanol in 0.02 *M* HClO_4), but could not be neglected for the least reactive compound (9% correction for hydroxy lactone 7).

The concentration of chromic acid in all kinetic runs was about 5×10^{-4} *M*. A 20-fold excess of the organic substrate was generally used. Good straight-line plots of $\log A$ vs. time were obtained and used for the determination of first-order rate constants. The second-order rate constants (obtained from the first-order rate constants and the initial alcohol concentrations) showed good reproducibility, usually within $\pm 5\%$; for the most reactive alcohol (bicyclooctanol) the variation was somewhat greater ($\pm 10\%$). The values given in Table I are averages from at least two measurements.

6-Oxatricyclo[3.2.1.1^{3,8}]nonan-4 β -ol (4) was prepared according to the method of Henbest and Nichols¹⁹ and had mp 114–115° (lit.¹⁹ 115°).

6-Oxatricyclo[3.2.1.1^{3,8}]nonan-4 β -ol acetate (6) was prepared by acetylation of 4 and had mp 50–51° (lit.¹⁹ 50–52°).

6-Oxatricyclo[3.2.2.1]decan-4 β -ol (5). A 4-g portion (0.029 mole) of the 2-*endo*-hydroxymethylbicyclo[2.2.2]octene-5²⁰ was treated with 4.0 g (0.029 mole) of perbenzoic acid in chloroform at 0°. The reaction mixture was left overnight in a refrigerator and then tested for excess perbenzoic acid by means of starch-iodide paper. The mixture was washed successively with potassium iodide, sodium thiosulfate, potassium carbonate, and water, dried over anhydrous magnesium sulfate, and then evaporated to dryness. The residue left was distilled *in vacuo*, and the distillate, bp 110–115° (1.3 mm), was collected as a hygroscopic solid (mp 110–120°), yield 1.8 g (40%).

Anal. Calcd for $\text{C}_9\text{H}_{14}\text{O}_2$: C, 70.10; H, 9.15. Found: C, 69.83; H, 8.98.

5-*exo*,6-*endo*-Dihydroxy[2.2.1]heptane-2-*endo*-carboxylic acid lactone (7) was prepared according to the method of Henbest and Nichols¹⁹ and had mp 155–157° (lit.¹⁹ 160°).

5-*exo*,6-*endo*-Dihydroxy[2.2.2]octane-2-*endo*-carboxylic acid lactone (8) was prepared according to the method of Crundwell and Templeton⁷ and had mp 230–233° (lit.⁷ 235–237°).

***trans*-2,3-Dihydroxy-1-cyclopentylacetic acid γ -lactone (9)** was prepared according to the method of Hill and Edwards²¹ and had bp 123–124° (0.4 mm).

***trans*-1,2-Dihydroxycyclohexane monoacetate (10)** was prepared according to the method of Auwers and Dersch²² and had bp 123° (0.14 mm).

Acknowledgments. The support of this work by grants of the National Science Foundation (GP 737) (J. R.) and of the U. S. Army Research Office, Durham (AROD-31-124-G871) (J. R.), is gratefully acknowledged. Syntheses of many of the compounds used in this study were carried out by H. Gopal of this laboratory.

(19) H. B. Henbest and B. Nichols, *J. Chem. Soc.*, 227 (1959).

(20) H. W. Whitlock, *J. Am. Chem. Soc.*, **84**, 3412 (1962).

(21) R. K. Hill and A. G. Edwards, *Tetrahedron*, **21**, 1501 (1965).

(22) K. V. Auwers and F. Dersch, *J. Prakt. Chem.*, **124**, 235 (1930).

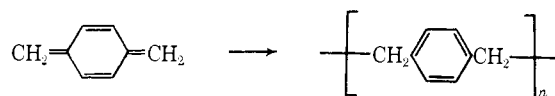
The Electrochemical Reduction of α, α' -Dibromo-*p*-xylene

Frank H. Covitz

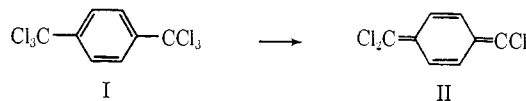
Contribution from Union Carbide Chemicals and Plastics Operations Division, Research Department, Bound Brook, New Jersey 08805. Received April 22, 1967

Abstract: Polarographic reduction of α, α' -dibromo-*p*-xylene occurs in two discrete steps. Evidence is presented that *p*-xylylene is formed during the first wave, and that this intermediate reacts rapidly to yield poly-*p*-xylylene and a small amount of [2.2]paracyclophane. The data suggest that *p*-xylylene, at very low concentration, can be reduced further polarographically. The mechanism of the electrochemical reduction of α, α' -dibromo-*p*-xylene is discussed in terms of the results of polarography, controlled-potential electrolysis, coulometry, and cyclic voltammetry.

The electrolysis of some α, α' -dihalo-*p*-xylenes was first examined in these laboratories by Gilch.¹ Several of these compounds were shown to be reduced at a mercury cathode to the corresponding *p*-xylylene polymers. It was postulated that *p*-xylylene was an intermediate in these cases, since, under appropriate conditions, this reactive species polymerizes rapidly.²



In the electrolysis of $\alpha, \alpha, \alpha, \alpha', \alpha', \alpha'$ -hexachloro-*p*-xylylene (I), $\alpha, \alpha, \alpha', \alpha'$ -tetrachloro-*p*-xylylene (II) was isolated at low temperatures.¹



(1) H. G. Gilch, *J. Polymer Sci.*, **4**, 1351 (1966).

(2) L. A. Errede and J. M. Hoyt, *J. Am. Chem. Soc.*, **82**, 436 (1960), and references cited therein.