b.p. 126–126.5° (623 mm.). The solid has a high vapor pressure and a camphor-like odor.

Anal. Calcd. for $C_4Br_2ClF_5$: C, 14.20; Br, 47.24; Cl, 10.47; F, 28.08. Found: C, 14.15; Br, 47.45; Cl, 10.43; F, 28.29.

1-Bromo-2,3,3,4,4-pentafluorocyclobutene (V).—A solution of 8.8 g. (0.026 mole) of the above cyclobutane in ethanol was added to a warm slurry of zinc in ethanol. A vigorous reaction ensued to yield 5 g. (85% conversion) of V, b.p. 48° (626 mm.), d^{25}_{25} 1.799, n^{25}D 1.3494, MR 26.62 (calcd., 26.74).

Anal. Calcd. for C_4BrF_5: C, 21.54; Br, 35.84; F, 42.61. Found: C, 21.68; Br, 35.48; F, 42.63.

Reaction of V with Ethylmagnesium Bromide.—To a solution of 4.9 g. (0.022 mole) of V in 10 ml. of anhydrous ether and cooled to 0°, was added rapidly 15 ml. (0.045 mole) of 3 *M* ethylmagnesium bromide. After stirring 1 hr., water was added, the ether solution was dried, and the products were separated by preparative-scale v.p.c. to yield 0.92 g. (30% recovery) of 2,3,3,4,4-pentafluorocyclobutene (VI) and 0.55 g. (23% recovery) of ethyl bromide. These compounds were identified by their infrared spectra. Also isolated was 0.06 g. (0.9% recovery) of 1-ethyl-2-bromo-3,3,4,4-tetrafluorocyclobutene (VII). The infrared spectrum of this compound was nearly identical with that for the 2-chloro analog (XIII). The low yields are attributable to poor recovery from the chromatograph. No other products were observed.

Anal. Calcd. for $C_6H_5BrF_4$: C, 30.92; H, 2.16; Br, 34.30; F, 32.62. Found: C, 30.95; H, 2.10; Br, 34.15; F, 32.81.

Reaction of 1-Ethoxy-2-chloro-3,3,4,4-tetrafluorocyclobutene (XI) with Ethylmagnesium Bromide.—A solution of 123.8 g. (0.60 mole) of XVII in 300 ml. of anhydrous tetrahydrofuran in a 1-l. three-neck flask was stirred and warmed to 50°. To this was added dropwise 400 ml. (1.2 moles) of ethylmagnesium bromide in ether. The ether was distilled during addition. After stirring for 4 hr., a heavy precipitate formed, and the reaction had to be discontinued. Water was added to dissolve the solid and the product was taken up in ether and dried over magnesium sulfate. Distillation yielded 12 g. (15.3% conversion) of 1-ethyl-2-chloro-3,3,4,4-tetrafluorocyclobutene (XIII), b.p. 98–99° (620 mm.), n^{25}D 1.3709. This was identified by comparison of the infrared spectrum with that of an authentic sample. Also recovered by distillation was a mixture of 1,2-diethyl-3,3,4,4-tetrafluorocyclobutene (XII), 1-chloro-2,3,3-trifluoro-4,4-diethylcyclobutene (XV), 1-chloro-2,3,3-trifluoro-4-ethyl-4-ethoxycyclobutene (XIV), and starting material (XI). Separation of XII was effected in 16.6% conversion using a fluorosilicone preparative-scale v.p.c. column (12.6 g., b.p. 134–136° at 620 mm.). Also separated in this manner was 40 g. of XI and a mixture of XIV and XV. This mixture was resolved by use of a tricresyl phosphate column to give 3.4 g. of XV (4.2% conversion), b.p. 133° (619 mm.), d^{25}_{25} 1.159, n^{25}D 1.4018, MR 41.91 (calcd., 42.12), and 4.2 g. of XIV (5% conversion), b.p. 136–137° (619 mm.), d^{25}_{25} 1.185, n^{25}D 1.3979, MR 43.68 (calcd. 43.76).

Anal. Calcd. for $C_8H_{10}F_3Cl$ (XV): C, 48.37; H, 5.07; Cl, 17.85; F, 28.70. Found: C, 48.33; H, 5.17; Cl, 17.86; F, 28.82.

Anal. Calcd. for $C_8H_{10}F_3ClO$ (XIV): C, 44.76; H, 4.70; Cl, 16.52; F, 26.56. Found: C, 44.82; H, 4.80; Cl, 16.71; F, 26.77.

Also isolated was 1.5 g. (1.8% conversion) of 1-chloro-2,4-diethyl-3,3-difluoro-4-ethoxycyclobutene (XVI), b.p. 175° (619 mm.) (with some decomposition), d^{25}_{25} 1.081, n^{25}D 1.4238, MR 53.00 (calcd. 52.90). The compound turns yellow after several weeks at room temperature.

Anal. Calcd. for $C_{10}H_{15}ClF_2O$: C, 53.45; H, 6.73; Cl, 15.78; F, 16.92. Found: C, 54.47; H, 7.09; Cl, 15.85; F, 17.18.

Acknowledgment.—The authors wish to express their appreciation to the Minnesota Mining and Manufacturing Company, St. Paul, Minnesota, and the U. S. Army, Quartermaster Research and Engineering Command, Natick, Massachusetts, under scientific project officer Dr. M. C. Henry for their partial support of this work. We also wish to thank Dr. George N. Sausen, Du Pont Company, Explosives Department, for F^{19} n.m.r. spectra and help in their interpretation.

Derivatives of 1,2,3,4-Tetramethylcyclobutene. Interconversion of Cations in Sulfuric Acid[1]

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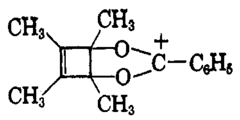
Received July 13, 1964

Semiquantitative data on the equilibria between the stable bridged cations derived from 1,2,3,4-tetramethylcyclobutene-1,2-diol benzoates are presented. The mechanism of exchange is discussed.

In a previous paper[3] it has been reported that in 97% sulfuric acid benzoate esters of 1,2,3,4-tetramethylcyclobutene-1,2-diol form the stable bridged cation I. Two properties of this cation are interesting. On the one hand an n.m.r. spectrum of I indicates that an intramolecular rearrangement occurs with sufficient rapidity so as to coalesce the two methyl bands into a single sharp peak.[4] At the same time addition of *p*-nitrobenzoic acid to sulfuric acid solutions of I lead to rapid and reversible intermolecular exchange of the benzoate fragments to provide the *p*-nitro-substituted cation analogous to I. This paper will present additional semiquantitative data on the intermolecular exchange process. The possible mechanisms and energy barriers for the intramolecular and intermolecular exchanges will be considered.



I

Results

The observation[3] of facile exchange of benzoate by *p*-nitrobenzoate in the bridged cation prompted the determination of the effect of substituents on the equilibrium constants for the exchange reaction shown in eq. 1. The equilibrium constant (eq. 2) has been defined in terms of protonated benzoic acid species since this is the predominant form of the acids in the 96–97% sulfuric acid used as the solvent.[5]

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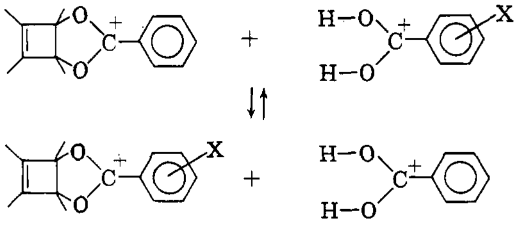
[1] Taken from the dissertation submitted by D. L. Nealy in partial fulfillment of the requirements for the Ph.D. degree, Cornell University, June, 1963.

[2] National Science Foundation Predoctoral Fellow, 1959–1963.

[3] C. F. Wilcox, Jr., and D. L. Nealy, *J. Org. Chem.*, **28**, 3446 (1963).

[4] Evidence to be presented in this paper indicates that this peak does not arise from a fortuitous overlapping of the separate methyl bands.

[5] R. Stewart and M. R. Granger, *Can. J. Chem.*, **39**, 2508 (1961); R. Stewart and K. Yates, *J. Am. Chem. Soc.*, **82**, 4059 (1960).



(1)

$$K_x = \frac{[X^+][H_2OBz^+]}{[H^+][H_2OBzX^+]} \qquad (2)$$

The equilibrium constants were evaluated by two closely related procedures. The first method, in outline form, consisted of first comparing the total integrated area of the n.m.r. signals of the methyl groups of the two cations with the total integrated area of the benzenoid absorptions arising from acid and cation species. This ratio was then combined with the relative areas of the methyl groups of the individual cations and with the stoichiometric relationship of the added reagents to the species appearing in the equilibrium to yield the equilibrium constants. The equations, which differ with the degree of substitution of the two acid species employed, and their derivation are described in the Experimental section.

The second method of evaluating the equilibrium constants used the weights of ester and acid added to the solution in place of the ratio of benzenoid and methyl n.m.r. absorptions. This alternate method of obtaining the necessary equations required to calculate the relative concentrations of the four species appearing in the equilibrium expression is also described in the Experimental section.

Both methods required the use of the ratio of the two high-field methyl absorptions of the two bridged cations. Because these methyl peaks were badly overlapped, it was necessary to assume that the relative area of each methyl signal was proportional to its peak height. The errors brought in by this assumption are unknown, although the similarity of the cationic species suggests that the errors would not be large.[6] To minimize error from determining this ratio, the relative amounts of ester and added acid were adjusted until the ratio of peak heights (*i.e.*, cationic species) was nearly one. The individual positions of the high-field cation peaks were established independently by adding the appropriate substituted benzoic acid to a sulfuric acid solution of 3,4-dichloro-1,2,3,4-tetramethylcyclobutene. For all acids employed, a single sharp peak appeared near τ 8.1 as expected[3]; the cation methyl absorptions determined in this manner are recorded in the second column of Table I.

In the case of the *p*-methyl- and *o*-chloro-substituted cations the τ 8.1 peaks were insufficiently resolved from the methyl peak of the benzoate cation to allow any meaningful measurements. This pair of constants was determined, therefore, relative to the *p*-nitro cation (prepared by solution of the corresponding bis-*p*-nitrobenzoate ester[3] in sulfuric acid) and then corrected for the change in reference. The last column in Table I records the equilibrium constants relative to the benzoate cation I.

The errors in the equilibrium constants recorded in Table I represent the range of values obtained by both methods of calculation on two different samples. The errors recorded for the equilibrium constants involving *p*-methyl and *o*-chloro substituents include the error of the *p*-nitro constant to which they are referred. No uncertainty has been assigned to the error introduced by assuming that the areas of the individual τ 8.1 peaks are proportional to their peak heights.

TABLE I

HIGH-FIELD N.M.R. PEAKS OF $C_8H_{12}O_2C_6H_4X$ CATIONS AND THEIR RELATIVE EQUILIBRIUM CONSTANTS

X	Chemical shift, τ	K_x
H	8.13	(1.00)[a]
p-NO_2	8.08	0.55 ± 0.1
p-CH_3	8.15	0.95 ± 0.2[b]
o-NO_2	8.08	0.050 ± 0.008
o-Cl	8.12	1.1 ± 0.2[b]
o-I	8.10	0.85 ± 0.2

[a] Reference. [b] Determined relative to the *p*-nitro cation (reported error includes deviations from *p*-nitro uncertainty).

Discussion

All of the acids except *p*-nitrobenzoic acid are known to be almost completely protonated in 96–97% sulfuric acid. The dissociation constant for protonated *p*-nitrobenzoic acid has not been measured, but it can be estimated with fair reliability from the related protonation equilibria of *para*-substituted acetophenones[7] as *ca.* 1.0 × 10^8. In 96–97% sulfuric acid this corresponds to only 9% unprotonated acid or to a correction factor of 1.1 by which the $K_{p\text{-}NO_2}$ should be multiplied. Because this correction is close to the experimental error of the K-values and is not based on direct measurements, it has not been applied to the data of Table I.

It is evident that (with the striking exception of the *o*-nitro case) the equilibrium constants have a low sensitivity to the electronic nature of the substituent. Within the rather broad limits of experimental error the *p*-NO_2, *p*-CH_3, and *p*-H constants are correlated by $\log K_x = -0.2\sigma_x$. Such a low sensitivity to substituents is to be expected for these equilibria. The similarity of the n.m.r. positions of the cation methyl groups to those of the neutral esters implies that in each bridged cation the positive charge is largely localized in the aroyl moiety so that the interaction energy of the substituent with the charge will be nearly identical on both sides of eq. 1.

The equilibrium constants for exchange with *ortho*-substituted acids offer additional insight into the magnitude of the "*ortho*" effects observed in protonation equilibria of carboxylic acids in sulfuric acid. Space filling models show that there is no crowding of the *ortho* substituents against the methyl groups of the cation. Since the equilibria involving the *para*-substituted acids apparently are insensitive to electronic effects, hydrogen bonding remains as the principal mechanism for shifting the exchange equilibrium.[8] Stewart and Granger[5] have shown from their pK_{BH^+} measurements in sulfuric acid of *ortho*- and *para*-substituted benzoic acids that *o*-chloro- and *o*-iodobenzoic acids do not display significant deviations in acidity

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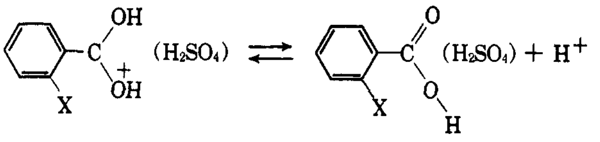
[6] The peak shapes of the high-field methyl absorption of the various cations measured separately appear to be identical within experimental error.

[7] R. Stewart and K. Yates, *J. Am. Chem. Soc.*, **80**, 6335 (1958).

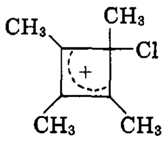
[8] Differences in solvation on the two sides of eq. 1 should be considered, but it seems reasonable to suppose that because of the identity of structural components, this is a second-order effect. The slightly smaller value of the *p*-nitro equilibrium constant may in part be due to solvation variation.

owing to hydrogen bonding. In contrast to these and other cases they have shown that protonated *o*-nitrobenzoic acid is specifically hydrogen bonded and that its dissociation constant is decreased by a factor of *ca.* 10 by this effect. Their dissociation equilibria (eq. 3) differ from the present equilibria in the important respect that the neutral *ortho*-substituted acids still have one acidic proton and are therefore potentially capable of hydrogen bonding; the bridged cations have no hydrogens available for hydrogen bonding. It is striking, therefore, that within experimental error $K_{o\text{-Cl}}$ and $K_{o\text{-I}}$ are unity and $K_{o\text{-NO}_2}$ is decreased by a similar factor of about 10. This parallelism supports the general conclusions of Stewart and Granger and suggests further that *in sulfuric acid* unprotonated (neutral) *ortho*-substituted benzoic acids do not form significantly stable intramolecular hydrogen bonds. The different behavior of neutral and protonated *o*-nitrobenzoic acid is readily understood in terms of a leveling effect of the acidic solvent.



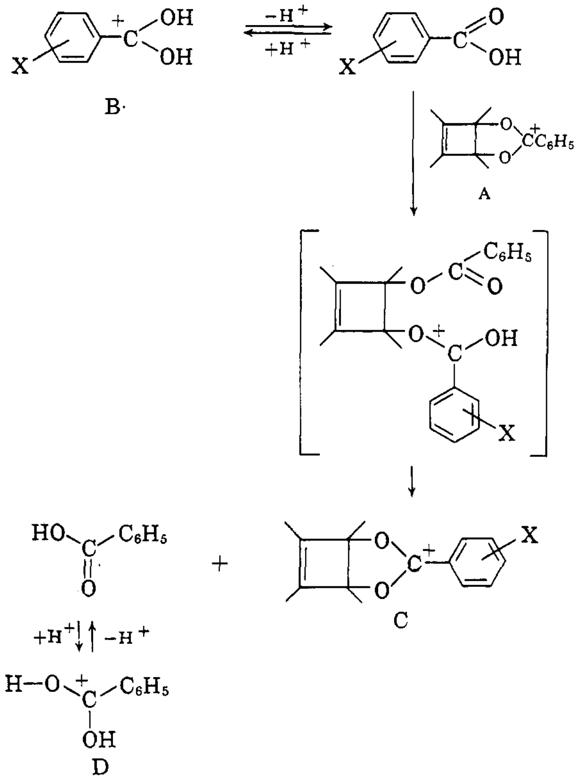
(3)

A characteristic feature of the sulfuric acid solutions of the different bridged cations is the occurrence of the methyl absorptions as a single sharp peak near τ 8.1. As the range of τ-values for methyl bands of the different cations is 0.07 p.p.m., a value much greater than the resolution of the n.m.r. instrument, these spectra provide further evidence that the two pairs of methyls absorb at different frequencies but are coalesced by a rapid exchange process. The simultaneous appearance of separate peaks for mixtures of two cations and their slow (time scale of minutes to hours) approach to equilibrium demonstrates that the equivalence of the methyls of a given cation must be an intramolecular phenomenon and independent of the acid-exchange process. A plausible mechanism for the intramolecular process is an opening of the bridge to form an unbridged cation analogous to the Katz[9] monochloro cation II. Reclosure of the bridge to the other adjacent carbon atom and repetition of the process around the ring makes the methyls equivalent. Examples of such a rapid allylic rearrangement in a neutral tetramethylcyclobutene substrate are the Lewis acid catalyzed chloride and bromide migrations observed by Katz and Gold.[10] The present cases are analogous except that because of their inherent electron deficiency they do not require an external catalyst. An upper limit to the energy barrier to this intramolecular exchange cannot be estimated reliably because of the uncertainty of the peak separation of the two pairs of equivalent methyl groups of I. If it is assumed that the peak separation is at least 0.1 p.p.m., (the methyls of the neutral dibenzoate shift by 0.14 and 0.17 p.p.m. on solution in sulfuric acid), the barrier is less than 14 kcal./mole. This is not out of line with the barrier of 9 to 12 kcal./mole that has been estimated for methyl equilibration in the related monochloro cation.[3] A lower limit on this energy barrier for the bridged cations cannot be set with the available data.



II

There are many possibilities for the mechanism of exchange of the cations with external acids. One is for a neutral acid (present in *ca.* 0.1 to 1% in these solutions) to displace one end of the bridging group to give a protonated diester that, after proton exchange, could lose the original acid group and cyclize to the new bridged cation C. The displacement could occur by either SN2 or SN2′ mechanisms. It seems unlikely that a protonated acid could be involved in the displacement since the extra electrostatic repulsion present in a diprotonated transition state would be expected to more than wipe out the advantage of higher concentration. It should be possible to determine the state of protonation of the acid involved in the exchange by determining the exchange kinetics as a function of the acidity function of the medium. Kinetics have not been run on any of the exchange reactions beyond crudely noting that several minutes or hours were required for complete equilibration. With the concentrations of cation and acid employed in these exchange measurements, these time periods correspond to a barrier to exchange of roughly 20 kcal./mole.



Finally, it is worth noting that in a sense the relative stabilities of the cations and the probable transition states for their interconversion represent an inversion of the usual stability found in solvolysis. In an ester solvolysis involving neighboring group participation the transition state could be considered analogous to

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[9] T. J. Katz, J. R. Hall, and W. C. Neikam, *J. Am. Chem. Soc.*, **84**, 3199 (1962).

[10] T. J. Katz and E. H. Gold, *ibid.*, **86**, 1600 (1964).

the stable cations, whereas the starting state would be analogous to what has been pictured here as the intermediate to exchange between the cations.

Experimental

Materials.—The preparations of 1,2,3,4-tetramethylcyclobutene-1,2-diol dibenzoate and di-*p*-nitrobenzoate have been described previously.[3] The substituted benzoic acids employed were Eastman White Label or samples of comparable purity. Concentrated sulfuric acid (Baker's analyzed, 96–97% H_2SO_4) was used.

Determination of N.m.r. Spectra of Bridged Cations.—The positions of the methyl absorption of the different bridged cations (I and derivatives) were determined by addition of 30–60 mg. of the substituted benzoic acid to a solution (chilled to 0°) of about 50 mg. of 3,4-dichloro-1,2,3,4-tetramethylcyclobutene in 0.4 ml. of concentrated sulfuric acid. After 5–10 mg. of tetramethylammonium fluoborate had been added, the n.m.r. spectrum was determined immediately. In all cases, in addition to the reference signal of the tetramethylammonium ion (τ 6.87) and the peak due to the chloro τ 8.0–8.2 cation II (τ 7.44), a new sharp singlet was observed in the region. Several successive determinations of the n.m.r. spectrum of any particular solution gave an intensification of the new peak and a corresponding decrease in intensity of the peak at τ 7.44. In all cases, these two peaks reached constant relative values in less than 30 min.

Determination of Exchange Equilibrium Constants.—In a manner similar to the above procedure there was added to solutions (at room temperature) of 40–70 mg. of the diesters in 0.4 ml. of concentrated sulfuric acid 30–70 mg. of a substituted benzoic acid and a few milligrams of tetramethylammonium fluoborate. The mixtures were shaken until they were homogeneous and then their n.m.r. spectra were determined immediately followed by additional spectral determinations at 5 to 10 min. intervals. In each case, an additional peak appeared after a few minutes and intensified as the peak due to the cation from the original diester decreased in intensity. The peaks reached constant relative intensities within 2 hr. and no further changes were noted after 24 hr. at room temperature.

Calculation of Exchange Equilibrium Constants.—Calculation of each exchange equilibrium constant required the knowledge of the relative concentration of the four species shown in eq. 1 and 2. In the case of equilibria established by adding a monosubstituted benzoic acid to the dibenzoate ester to give benzoate cation A, protonated substituted benzoic acid B, substituted cation C, and protonated benzoic acid D, four sufficient and independent relations are the following.

$$5A + 4B + 4C + 5D = \text{low-field area (in arbitrary units)}$$

$$12A + 12C = \text{high-field area (in arbitrary units)}$$

$A + 2C - D = 0$ (condition that equates benzoate fragments to twice the cyclobutyl fragments)

$RA - C = 0$ (condition that peak heights of the high-field absorptions are in the ratio of $R{:}1$ = substituted benzoate cation–benzoate cation)

When these equations are solved simultaneously, the expression for K_x in terms of the relative total low-field to total high-field areas and the ratio, R, between the pair of high field peaks is

$$K_x = \frac{4R^2 + 2R}{(6R + 6)(\text{low-field area–high-field area}) - 7R - 5}$$

In the special case where $R = 1$, this expression reduces to the much simpler expression.

$$K_x(R = 1) = \frac{1}{\text{low-field area–high field area}) - 2}$$

In the second case of equilibria established by adding benzoic acid to a nitro-substituted ester, the third condition changes to

$2A - B + C = 0$ (substituted benzoate fragments are equal to twice the cyclobutyl fragments)

and the expression for K_x becomes

$$K_x = \frac{(\text{low-field area–high-field area})(12R^2 + 12R) - 8R^2 - 13R}{5R + 10}$$

where R is the ratio of nitrobenzoate cation–benzoate cation.

In the third case of equilibria established by adding X-substituted benzoic acid to a nitro-substituted ester, conditions one and three differ from those of the first case.

$$4A + 4B + 4C + 4D = \text{low-field area}$$
$$2A - B + C = 0$$

and the expression for K_x becomes

$$K_x = \frac{[\text{nitro cation}][\text{protonated added acid}]}{[\text{cation from added acid}][\text{protonated nitrobenzoic acid}]} = \frac{(\text{low-field area–high-field area})(3R^2 + 3R) - 2R^2 - 3R}{R + 2}$$

where R is the ratio of nitrobenzoate cation–X-substituted benzoate cation.

In all three cases the first two conditions involving low-field and total high-field areas can be replaced by either the pair of weight conditions a and b or the pair b and c.

(a) $A + C$ = relative amount (in moles) of ester added
(b) $B + C$ = relative amount (in moles) of acid added
(c) $A + D$ = two times the relative amount (in moles) of ester added

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Chemistry of Aliphatic Disulfides. VIII. Alkoxide Cleavage of 1,6-Diphenyl-3,4-dithia-1,6-hexanedione (Diphenacyl Disulfide)[1,2]

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Received September 3, 1964

The previously reported conversion of 1,6-diphenyl-2,3-dithia-1,6-hexanedione (diphenacyl disulfide, I) to 1,4-diphenyl-1,4-butanedione (V) with 1 equiv. of ethoxide ion has been confirmed. In addition a 1,2,4,5-tetrathiane salt (XI) and acetophenone are obtained. Treatment of I with 2 equiv. of ethoxide provides dipotassio 1,4-diphenyl-1,4-butanedione-2,3-dimercaptide (XXVIII). With 0.25 to 0.1 equiv. of ethoxide 1,5-diphenyl-3-thiapentane-1,5-dione (XXIV) resulted.

Reactions involving nucleophilic attack on a bivalent sulfur atom have received considerable attention during the last 30 years. Within this general area, fission of disulfides with alkaline reagents has attracted con-

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[1] Supported in part by a Frederick Gardner Cottrell Grant from the Research Corporation and by Research Grant RG-7966 from the National Institute of General Medical Sciences of the National Institutes of Health, U. S. Public Health Service.

[2] Part VII of this series: R. G. Hiskey and D. N. Harpp, *J. Am. Chem. Soc.*, **86**, 2014 (1964).

[3] Union Carbide Chemical Corp. Fellow, 1959–1960.

[4] Abstracted in part from dissertations submitted to the University of North Carolina in partial fulfillment of the requirements for the Ph.D. degree, by B. D. Thomas, June, 1962, and J. A. Kepler, Aug., 1963.

[5] Shell Chemical Corp. Fellow, 1962–1963.