(51%) of neutral material consisting of diphenylcyclopropylmethane (65%), 1,1-diphenyl-1-butene (20%), and diphenylcyclopropylcarbinol (15%), the latter being an impurity in the starting material. The crude acidic product 1.24 g (49%), mp 121–135°, was recrystallized from carbon tetrachloride and afforded 0.96 g of diphenylcyclopropylacetic acid, mp 136–139°, undepressed on admixture with an authentic sample. The mother liquors (containing 277 mg of acid) were concentrated and found by nmr spectroscopy to contain diphenylcyclopropylacetic acid (75%) and γ,γ-diphenylallylacetic acid (25%). The total yield of diphenylcyclopropylacetic acid was roughly 1.17 g (46%), while the yield of γ,γ-diphenylallylacetic acid was 69 mg (3%).

Diphenylcyclopropylcarbinylpotassium (XIV) with Magnesium Bromide. The organopotassium compound was prepared in the usual manner from 2.38 g (10 mmoles) of diphenylcyclopropylcarbinyl methyl ether (X) and 1.1 ml (20 mg-atoms of potassium) of sodium–potassium alloy in a total of 55 ml of tetrahydrofuran. After 0.5 hr at 0° a solution of magnesium bromide, prepared separately under argon from 3.75 g (20 mmoles) of 1,2-dibromoethane and 0.6 g (25 mg-atoms) of magnesium in a total of 10 ml of ether, was added dropwise, whereby the red color disappeared. The mixture was carbonated as usual. The isolation procedure used for previous carbonations afforded 752 mg (36%) of neutral material consisting of diphenylcyclopropylmethane (64%), diphenylcyclopropylcarbinol (20%), 1,1-diphenyl-1-butene (14%), and a trace of starting material. A total of 1.60 g (63.5%) of γ,γ-diphenylallylacetic acid, mp 70–81°, was obtained which after one recrystallization from *n*-hexane had mp 79.5–81° (undepressed on admixture with an authentic sample). The crude acid did not contain any diphenylcyclopropylacetic acid as judged by its nmr spectrum.

Similar results were obtained using diethyl ether as solvent.

Diphenylcyclopropylcarbinylpotassium (XIV) with Mercuric Bromide. The potassium organic compound was prepared in the usual manner from 2.38 g (10 mmoles) of diphenylcyclopropylcarbinyl methyl ether (X) and 1.1 ml (20 mg-atoms of potassium) of sodium–potassium alloy in a total of 35 ml of tetrahydrofuran. After 0.5 hr at 0°, a solution of 9 g (25 mmoles) of mercuric bromide in 20 ml of tetrahydrofuran was added dropwise. Before the addition was half complete the color of the solution had turned from red to black. Stirring was continued for 0.5 hr at 0°; then water was added followed by ether. The black cloudy precipitate was removed by filtration and the aqueous layer extracted twice with ether. The combined organic layers were washed with sodium chloride solution and dried over sodium sulfate. Evaporation of the solvent yielded 2.28 g of crude material consisting mainly of diphenylcyclopropylmethane (60%), but also containing diphenylcyclopropylcarbinol (15%), 1-phenyl-3,4-dihydronaphthalene (15%), 1-phenylnaphthalene (2%), 1,1-diphenyl-1-butene (2%), and probably 1,1-diphenyl-1,3-butadiene (2%). The percentages given are approximate because of difficulties in obtaining satisfactory vpc resolution. The principal products were also identified by their nmr peaks. Reduced pressure distillation gave 1.29 g of distillate, bp 80° (0.1 mm), containing 75% of diphenylcyclopropylmethane and the other products described above in somewhat different proportions.

Diphenylcyclopropylcarbinylpotassium (XIV) with Cobaltous Chloride. The organopotassium compound was prepared in the usual manner from 2.38 g (10 mmoles) of diphenylcyclopropylcarbinyl methyl ether (X) and 1.1 ml (20 mg-atoms of potassium) of sodium–potassium alloy in 35 ml of tetrahydrofuran. After 0.5 hr at 0°, 63 g (0.32 g-atom) of mercury metal was added in order to remove the excess of sodium–potassium alloy, and stirring was continued for 2 hr at 0°. Finally 0.65 g (5 mmoles) of solid cobaltous chloride, dried at 100°, was added under argon through a Tygon side tube. After 2 hr at 0°, the mixture was carbonated as usual. Water and hydrochloric acid were added and the orange-colored aqueous mixture was extracted three times with ether. The combined organic layers were extracted twice with sodium hydroxide solution and dried over sodium sulfate. Evaporation of the solvent yielded 1.40 g (67%) of neutral material which according to vpc analysis and its nmr spectrum consisted of diphenylcyclopropylmethane (70%), diphenylcyclopropylcarbinol (7%), 1,1-diphenyl-1-butene (14%), and 1-phenyl-3,4-dihydronaphthalene (9%). The aqueous alkaline layer gave 707 mg (28%) of diphenylcyclopropylacetic acid (XV).

A Study of Isologous 1,2-Dithiolane, 1,2-Diselenolane, and 1-Thia-2-selenolane Derivatives[1]

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Contribution from the Department of Pharmacology, Yale University School of Medicine, New Haven, Connecticut, and the Chemical Institute, University of Uppsala, Uppsala, Sweden. Received December 15, 1965

Abstract: The dipole moments of 1,2-dithiolane-4-carboxylic acid, 1,2-diselenolane-4-carboxylic acid, 1-thia-2-selenacyclopentane-4-carboxylic acid, 2,3-dithiaspiro[4.5]decane, 2,3-diselenaspiro[4.5]decane, and 2-thia-3-selenaspiro[4.5]decane were measured. No significant polarization of the S–Se bond could be detected. The dipole moments of the carboxylic acids were in good agreement with calculated moments assuming free rotation of the carboxyl group. The moment of the methyl ester of 1,2-dithiolane-4-carboxylic acid is similar to that of the free acid. These observations indicate that there is no significant interaction between disulfide and carboxyl groups in the dithiolane system studied.

It has been observed that in noncyclic[3] or cyclic[4] carbamyl compounds substitution of oxygen by sulfur or selenium results in an increase in dipole moment considerably greater than can be attributed to an increase in molecular size. This increase in moment, which is not predictable from the respective electronegativities of oxygen, sulfur, and selenium, may presumably be attributed to the greater tendency of selenium than of sulfur to undergo octet expansion, while no octet expansion is possible for oxygen. Similarly, a relatively high tendency of selenium relative to sulfur to undergo octet expansion can be invoked to account

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[2] Public Health Service Fellow (2-F2-CA-15,695-02), 1962–1964.

[3] H. G. Mautner and W. D. Kumler, *J. Am. Chem. Soc.*, 78, 97 (1956).

[4] M. H. Krackov, C. M. Lee, and H. G. Mautner, *ibid.*, 87, 892 (1965).

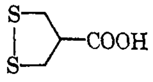
Table I. Empirical Constants, Polarizations, and Dipole Moments (D.)[c]

Compound	ϵ_1	ν_1	α	β	P	P_E	μ
Cyclopentanecarboxylic acid[a]	2.1991	0.97386	2.98	−0.026	87.22	29.26	1.70
1,2-Dithiolane-4-carboxylic acid (I)[a]	2.1998	0.97397	8.30	−0.306	235.10	36.11	3.15
1,2-Diselenolane-4-carboxylic acid (II)[a]	2.1987	0.97390	5.24	−0.545	241.80	41.50	3.16
1-Thia-2-selenolane-4-carboxylic acid (III)[a]	2.2003	0.97392	6.27	−0.458	233.57	38.74	3.11
1,2-Dithiolane-4-carboxylic acid methyl ester[a]	2.1969	0.97392	6.93	−0.228	223.69	40.87	3.02
2,3-Dithiaspiro[4.5]decane (IV)[b]	2.2584	1.14713	5.12	−0.284	213.87	50.93	2.85
2,3-Diselenaspiro[4.5]decane (V)[b]	2.2587	1.14705	3.32	−0.584	213.47	56.32	2.80
2-Thia-3-selenaspiro[4.5]decane (VI)[b]	2.2594	1.14708	4.12	−0.468	217.15	53.56	2.85

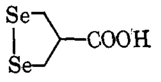
[a] Measurements were carried out in dioxane. [b] Measurements were carried out in benzene. [c] The symbols used are defined as follows: ϵ, dielectric constant; ν, specific volume, α, slope of the ϵ_{12}–ω_2 plot, β, slope of the ν_{12}–ω_2 plot, P, molar polarization at infinite dilution, P_E, molar electronic polarization at infinite dilution, μ, dipole moment. Subscripts 1, 2, and 12 refer to solvent, solute, and solution, respectively.

for the observation[5,6] that selenol esters undergo aminolysis more rapidly than isologous thiol esters.

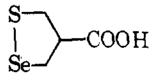
These studies raised interest in compounds in which sulfur and selenium are vicinal, since it seemed conceivable that charge separation of the sulfur–selenium bond might take place to an extent detectable by dipole-moment measurements. Such compounds became available recently during work at the University of Uppsala aimed at the study and interpretation of the absorption spectra of disulfides, diselenides, and thioselenenates related to lipoic acid, which resulted in the synthesis of 1,2-dithiolane-4-carboxylic acid[7] (I), 1,2-diselenolane-4-carboxylic acid[8] (II), and 1-thia-2-selenacyclopentane-4-carboxylic acid[9] (III).



I



II



III

The dipole moments of these compounds seemed of interest not only as a means of studying the possible polarization of sulfur–selenium bonds but also as a means of providing information about possible interactions of carboxyl groups with disulfide, diselenide, and thioselenenate bonds.

Experimental Section

Materials. 1,2-Dithiolane-4-carboxylic acid,[7] 1,2-diselenolane-4-carboxylic acid,[8] and 1-thia-2-selenacyclopentane-4-carboxylic acid[9] were synthesized according to literature methods and recrystallized until maximum ultraviolet extinction coefficients were achieved. A commercial sample of cyclopentanecarboxylic acid was purified by distillation, bp 213–215°, $n^{20.7}\text{D}$ 1.4538. The spirodecanes (IV, V, and VI), were prepared at the University of Uppsala.

1,2-Dithiolane-4-carboxylic Acid Methyl Ester. An ethereal solution of diazomethane was added dropwise, with stirring, to a solution of 2.5 g (0.0166 mole) of 1,2-dithiolane-4-carboxylic acid in approximately 25 ml of ether. Addition was continued until a deepening yellow color and the cessation of nitrogen evolution indicated that the reaction had proceeded to completion. The major portion of the ether was removed by flash evaporation, and the remaining viscous, heavy, yellow oil was distilled *in vacuo*. The weight of clear, yellow distillate was 0.9 g (33%).

Upon solution of the product in ethanol, a small amount of a white, sticky, polymeric material remained undissolved. Redistillation of the product removed this impurity, bp 69–71° (0.1 mm). Slow polymerization of the product on standing necessitated redistillation immediately prior to use for dipole moment measurements.

Anal. Calcd for $C_5H_8O_2S_2$: C, 36.56; H, 4.91; S, 39.05. Found: C, 36.47; H, 5.03; S, 38.83.

Solvents used for dipole moment measurements were purified as follows. Analytical grade benzene was permitted to reflux over sodium wire for 24 hr, and fractionated prior to use through a 4-ft vacuum-jacketed column packed with glass helices. Dioxane was refluxed over molten sodium for 24 hr and purified by fractional distillation. This procedure was carried out twice. Just prior to use the purified dioxane was refractionated from a flask containing lithium aluminum hydride.

Dipole Moment Measurements. A WTW dipolmeter Model DM-01 (Wissenschaftlich-Technische Werkstätten GmBH, Weilheim, Germany) with a reading sensitivity of 7×10^{-6} was used for all measurements. The measuring cell employed, a DFL-2 cell with a capacity of 4 ml, was provided with a thermostated jacket to maintain the temperature of the solutions at 30.00 ± 0.03°. The instrument was calibrated periodically against cyclohexane, benzene, and carbon tetrachloride.

For each dipole moment measurement, the dielectric constants were determined for the pure solvent and for a series of six solutions of increasing concentrations; the weight fraction of solute in these varied from 0.0003 to 0.017. The density at 30.00° of the pure solvent and of each of the solutions was ascertained using a pycnometer with a capacity of *ca.* 8 ml. Within the experimental error of the measurements, the dielectric constant–concentration and density–concentration plots were linear over the range measured.

Dipole moments were calculated by the dielectric constant and density extrapolation method of Halverstadt and Kumler,[10] and were found to be reproducible within ±0.03 D. Electronic polarizations were obtained from bond refraction values reported by Vogel[11] and Smyth.[12]

Dissociation Constants. Measurements of acid dissociation constants were carried out titrimetrically in aqueous solution using a Radiometer Type TTTlc titrator with a Type SBR2c titrigraph.

Results

The dipole moments obtained are tabulated in Table I. Since carboxylic acids have strong tendencies to dimerize in nonpolar solvents such as benzene,[13] dioxane, in which dimerization takes place to a much smaller extent, was chosen as a solvent for measurements with these compounds.

It is readily apparent from the data in Table I that dipole moments of the three acids containing sulfur and selenium are not significantly different. Thus, these compounds provide no evidence to suggest the existence of any sizeable polarization of the sulfur–selenium bond.

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[5] H. G. Mautner and W. H. H. Günther, *J. Am. Chem. Soc.*, **83**, 3342 (1961).

[6] H. G. Mautner, S. H. Chu, and W. H. Günther, *ibid.*, **85**, 3458 (1963).

[7] L. Schotte and H. Ström, *Acta Chem. Scand.*, **10**, 687 (1956).

[8] G. Bergson, *Arkiv Kemi*, **19**, 195 (1962).

[9] G. Bergson and A. Biezais, *ibid.*, **18**, 143 (1961).

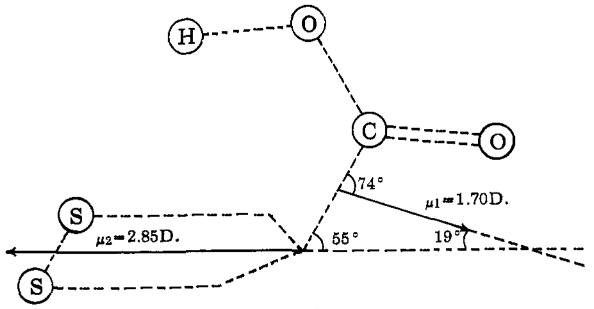
[10] I. F. Halverstadt and W. D. Kumler, *J. Am. Chem. Soc.*, **64**, 2988 (1942).

[11] A. I. Vogel, *J. Chem. Soc.*, 514 (1952).

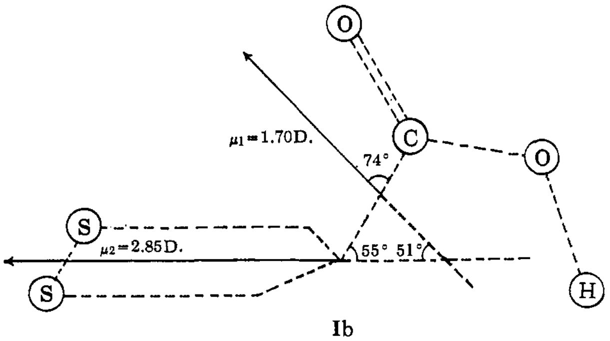
[12] C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co. Inc., New York, N. Y., 1955, p 409.

[13] C. P. Smyth, ref 12, p 303.

If a model of 1,2-dithiolane-4-carboxylic acid is constructed, it can be seen that the carboxyl group can be brought into close proximity to the disulfide linkage in such a way that interaction with the disulfide bond might occur either *via* hydrogen bonding of the carboxylic hydrogen atom to this bond (Ia) or as a result of overlap of the carbonyl π-electron cloud with the disulfide linkage (Ib). It seemed possible that either type of interaction with the sulfur–selenium bond in III might be obscuring the polarization of this bond.



Ia

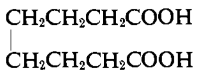


Ib

Definite proof for hydrogen bonding to a disulfide group does not appear to have been cited in the literature, although Cecil[14,15] has suggested such an interaction as a possible explanation for the differing oxidizabilities of glutathione and cysteine. The acid dissociation constants of the carboxylic acids presented in Table II do not, however, support the occurrence of such a phenomenon in the compounds studied here. If one compares the acid dissociation constants for the first proton of suberic acid (VII), 3,3′-dithiobis(propionic acid) (VIII), and 3,3′-diselenobis(propionic acid) (IX), the $\mathrm{p}K_{\mathrm{a1}}$ values are seen to be 4.52,[16] 4.05,[17] and 4.00,[18] respectively. Thus, the inductive effect of a disulfide or diselenide group in a position two carbons removed from a carboxyl group strengthens the acidity of this function by approximately 0.5 $\mathrm{p}K_{\mathrm{a}}$ unit. The acid-strengthening effects of the disulfide or deselenide group in the cyclic compounds under discussion might be expected to be roughly doubled since in these compounds we are now dealing with a 3,3-disulfide or -diselenide grouping both ends of which exert an inductive effect upon the same carboxyl group. The observed decrease in the $\mathrm{p}K_{\mathrm{a}}$ of the heterocyclic acids compared to cyclopentanecarboxylic acid (Table II), therefore, appears to be correlatable to the inductive effect discussed above and does not seem to reflect intramolecular hydrogen bonding of the carboxyl group to the S–S, Se–Se, and S–Se bonds. In any case, no acid weakening induced by a disulfide–carboxyl hydrogen bond interaction or acid strengthening by a disulfide–carbonyl interaction was observed.

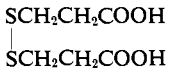
Table II. Acid Dissociation Constants at 25°

Compound	$\mathrm{p}K_{\mathrm{a}}$
Cyclopentanecarboxylic acid	4.93
1,2-Dithiolane-4-carboxylic acid (I)	3.82
1,2-Diselenolane-4-carboxylic acid (II)	3.87
1-Thia-2-selenolane-4-carboxylic acid (III)	3.87



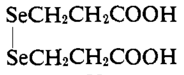
$\begin{array}{l} CH_2CH_2CH_2COOH \\ | \\ CH_2CH_2CH_2COOH \end{array}$

VII



$\begin{array}{l} SCH_2CH_2COOH \\ | \\ SCH_2CH_2COOH \end{array}$

VIII



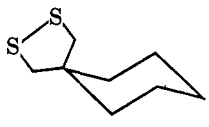
$\begin{array}{l} SeCH_2CH_2COOH \\ | \\ SeCH_2CH_2COOH \end{array}$

IX

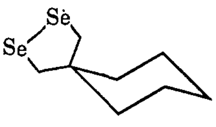
To verify this conclusion further, the synthesis and study of 1,2-dithiolane-4-carboxylic acid methyl ester was undertaken. This compound was synthesized by esterification of the corresponding acid with diazomethane and was obtained as a clear, heavy, yellow oil. The identity of the product was confirmed by (1) elemental analysis, (2) the retention of the ultraviolet absorption maximum characteristic of the strained cyclic disulfide in a five-membered ring ($\lambda_{\mathrm{max}}^{\mathrm{EtOH}}$ 327 mμ, ϵ_{max} 155.0, $\epsilon_{\mathrm{max}}/\epsilon_{\mathrm{min}}$ 4.54), and (3) the shift of the infrared carbonyl absorption from 1710 cm^{-1} for the free acid to 1750 cm^{-1} for the product ester.

A dipole moment of 3.02 D. was found for the ester in dioxane. This moment for the ester, in which free rotation of the carboxyl group cannot be hindered by intramolecular hydrogen bonding, is quite similar to the moments of the corresponding free acids. This supports the conclusion that intramolecular hydrogen bonding, with its attendant hindrance of free rotation, does not occur in the free acids.

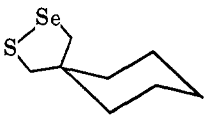
Shortly after completion of the dipole moment measurements on the carboxylic acids, we achieved the synthesis of 2-thia-3-selenaspiro[4.5]decane (VI).[19,20] The moments of this compound and its dithia and diselena isologs IV and V were subsequently measured (see Table I). Again the moments of the three isologs were found to be almost identical with each other, thus verifying that neither a hydrogen-bonding interaction nor a carbonyl interaction of the carboxyl group with the thiaselena linkage was leading to erroneous conclusions concerning the lack of polarization of the sulfur–selenium bond. Of course, it should be noted that if polarization were to occur, the new vector produced would be perpendicular to the existing moment of the nonpolarized compound so that a relatively large degree of polarization would be required in order to be detectable by the methods employed here.



IV



V



VI

The observed dipole moments of the compounds studied were found to be in good agreement with

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(14) R. Cecil, *Biochem. J.*, **47**, 572 (1950).

(15) R. Cecil, *ibid.*, **49**, 183 (1951).

(16) L. F. Fieser and M. Fieser, "Organic Chemistry," 3rd ed, D. C. Heath and Co., Boston, Mass., 1956, p 312.

(17) Loven, *Z. Phys. Chem.*, **13**, 550 (1894).

(18) A. Fredga, "Studien über Selen-di-Karbonsäuren und Diselen-di-Karbonsäuren," Uppsala Universitets Årsskrift, 1935, p 226.

(19) A. Biezais and G. Bergson, *Acta Chem. Scand.*, **18**, 815 (1964).

(20) G. Bergson and A. Biezais, *Arkiv Kemi*, **22**, 475 (1964).

values calculated from known bond moments and ring conformations.

A dipole moment of 1.87 D. has been reported[13] for tetrahydrothiophene. If one takes the CSC angle in this compound as 100°, the observed moment can be considered as the vector sum of two CS bond moments of 0.935/cos 50°, or 1.46 D.

Bond angles and bond lengths in 1,2-dithiolane-4-carboxylic acid have been determined by Foss and Tjomsland[21] based on X-ray diffraction studies. Based upon their data, the average angle between the valence bonds of each sulfur atom is 94.6° and the value of the dihedral angle between the CSS plane and the SSC plane is 26.6°. Then, by assuming the angular conformation of the 1,2-dithiolane ring in 2,3-dithiaspiro[4.5]decane to be the same as in the corresponding carboxylic acid, neglecting any small contribution of the cyclohexane ring, and taking 1.46 D. as the C–S bond moment, the calculated moment of 2,3-dithiaspiro-[4.5]decane is 2.82 D., in good agreement with the observed moment of 2.85 D.

The moments of the selenium-containing compounds cannot be treated so precisely because of lack of information about the C–Se–Se bond angles. However, monoselenides usually have moments only slightly smaller than monosulfides,[22] and it is, therefore, not unexpected to find that the dithiolanes and diselenolanes have similar moments or that the moment of the thiaselenenates, in the absence of a significant degree of polarization, is again similar to those of its isologs.

Turning now to the carboxylic acids, 1,2-dithiolane-4-carboxylic acid (I) can be treated as containing a planar ring with a moment of 2.85 D. The contribution of the carboxyl group in I is taken from the observed moment of cyclopentanecarboxylic acid (1.70 D.) and the angle of the C–COOH bond to the plane of the ring is assumed to be one-half the normal tetrahedral angle of 110°. The angle of the carboxyl moment to the C–COOH bond is taken as 74°.[23]

Hydrogen bonding of the carboxylic hydrogen to the disulfide bond would restrict rotation of the carboxyl group and result in a molecule with conformation Ia, having a calculated dipole moment of 1.4 D. Conversely, conformation Ib, resulting from interaction of the S–S bond with the carbonyl oxygen, would produce a moment of 4.1 D. The moments observed for the free acids as well as for the methyl ester of 1,2-dithiolane-4-carboxylic acid are in surprisingly good agreement with the moment calculated assuming unrestricted rotation of the carboxyl group, 3.1 D. This further substantiates the contention that little, if any, interaction occurs between the carboxyl group and the disulfide bond.

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[21] O. Foss and O. Tjomsland, *Acta Chem. Scand.*, **12**, 1810 (1958).

[22] For example, the moment of diphenyl sulfide is quoted as 1.5 D., that of diphenyl selenide 1.4 D.: R. J. W. Le Fèvre, "Dipole Moments," Methuen and Co., Ltd., London, 1963, pp 134,135.

[23] C. P. Smyth, ref 12, p 308.

Sulfoxide–Carbodiimide Reactions. III.[1] Mechanism of the Oxidation Reaction

A. H. Fenselau[2] and J. G. Moffatt

Contribution No. 36 from the Syntex Institute of Molecular Biology, Stanford Industrial Park, Palo Alto, California. *Received December 23, 1965*

Abstract: The mechanism of the oxidation reaction resulting from treatment of an alcohol with dimethyl sulfoxide and dicyclohexylcarbodiimide in the presence of a proton source has been elucidated through isotope experiments. Hydrolysis of dimethylsulfur dibromide with ^{18}O-water gave ^{18}O-dimethyl sulfoxide which was used for the oxidation of *p*-nitrobenzyl alcohol. The resulting *p*-nitrobenzaldehyde contained no isotope but the concomitantly formed dicyclohexylurea was labeled to the same extent as the starting sulfoxide. This confirms the initial formation of a sulfoxide–carbodiimide adduct (I) which can be attacked by the alcohol to give the alkoxysulfonium salt (II). Oxidation of 1,1-dideuteriobutanol led to 1-deuteriobutyraldehyde and monodeuteriodimethyl sulfide which were isolated by gas–liquid chromatography. Isolation of the latter compound confirms that proton abstraction from the alkoxy group of II is brought about *via* a cyclic mechanism involving a sulfur ylid. The same conclusion can be drawn from oxidation of butanol in hexadeuteriodimethyl sulfoxide which gives pentadeuteriodimethyl sulfide and butyraldehyde.

In earlier papers of this series[1,3] we have described the development of an efficient and extremely mild method for the oxidation of alcohols to the corresponding aldehydes or ketones. This method involves the reaction at room temperature of the alcohol with dimethyl sulfoxide (DMSO) and dicyclohexylcarbodiimide (DCC) in the presence of a proton source such as anhydrous phosphoric acid or pyridinium trifluoroacetate. The reaction has recently been applied with considerable success by a number of workers.[4]

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[1] Part II is K. E. Pfitzner and J. G. Moffatt, *J. Am. Chem. Soc.*, **87**, 5670 (1965).

[2] Syntex Postdoctoral Fellow, 1964–1965.

[3] (a) K. E. Pfitzner and J. G. Moffatt, *J. Am. Chem. Soc.*, **85**, 3027 (1963); (b) K. E. Pfitzner and J. G. Moffatt, *ibid.*, **87**, 5661 (1965).

[4] For examples see (a) B. R. Baker and D. H. Buss, *J. Org. Chem.*, 30, 2304, 2308 (1965); (b) G. Buchi, D. L. Coffen, K. Kocsis, P. E. Sonnet, and F. E. Zeigler, *J. Am. Chem. Soc.*, **87**, 2073 (1965); (c) J. D. Albright and L. Goldman, *J. Org. Chem.*, 30, 1107 (1965); (d) J. R. Dyer, W. E. McGonigal, and K. C. Rice, *J. Am. Chem. Soc.*, **87**, 654 (1965).