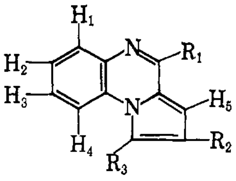
Table I[a]

N.M.R. Spectra of Pyrrolo[1,2-*a*]quinoxalines



| Compound | $R_1$ | $R_2$ | $R_3$ | τ-values $R_1$ | $R_2$ | $R_3$ | $H_1$ | $H_2$ | $H_3$ | $H_4$ | $H_5$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | $C_6H_5$ | $CH_3$ | H | ∽2.5 | 7.74 | 2.6–2.8 | 2.6–2.8 | ← 2.02 → | | | 3.29 |
| 2 | $CH_3$ | H | Cl | 7.42 | 3.30 | ... | 2.27 | ← 2.71 → | | 1.16 | 3.43 |
| 3 | $CH_3$ | $CH_3$ | Cl | 7.48 | 7.91 | ... | 2.30 | ← 2.75 → | | 1.20 | 3.48 |
| 4 | $C_6H_5$ | H | Cl | 2.60 | 3.17 | ... | ← 2.13 → | | | 1.02 | 3.38 |
| 5 | $C_6H_5$ | $CH_3$ | Cl | 2.54 | 7.73 | ... | ← 2.06 → | | | 0.97 | 3.19 |

[a] The preparation of these pyrrolo[1,2-*a*]quinoxalines is described elsewhere [E. C. Taylor and G. W. H. Cheeseman, *J. Am. Chem. Soc.*, **86**, 1830 (1964)]; a preliminary account of the synthetic work was presented at the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1963, Abstracts, p. 70Q.

measurements on models give a Cl–H distance of only 2.27 Å.

The variation of the position of the $H_1$ resonance is also worthy of attention. In compounds **2** and **3**, where $R_1$ = methyl, $H_1$ appears at lower field than $H_2$ and $H_3$, reflecting its position *ortho* to nitrogen. In compounds **4** and **5**, however, when $R_1$ = phenyl, $H_1$ is shifted to higher field, merging with the $H_2$–$H_3$ resonance. We attribute this shift to conjugation of the 1-position with the phenyl group; resonance structures can be written which place a formal negative charge at position 1.

All spectra were obtained on a Varian Associates A-60 spectrometer at normal operating temperature. Compounds were run as *ca.* 10% solutions in reagent grade carbon tetrachloride with 1% tetramethylsilane as internal standard. Chemical shifts are considered accurate to ±1 c.p.s., coupling constants to ±0.1 c.p.s.

**Acknowledgment.**—We wish to thank Dr. Pierre Laszlo for a helpful discussion. This work was supported in part by research grants to Princeton University from the National Cancer Institute, National Institutes of Health, U. S. Public Health Service (Grant No. CA-02551), and from the American Cancer Society.

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## Base-Induced Fragmentation of 2-Phenyl-1,3-dioxolane[1]

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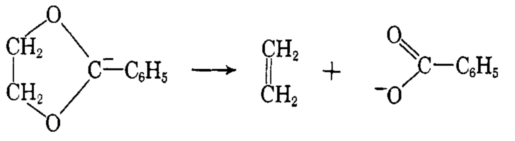
*Received February 13, 1964*

We wish to report a representative of an unexplored and potentially useful class of reactions: 1,3-eliminations of anionic fragments.[2-4]



2-Phenyl-1,3-dioxolane, treated dropwise with phenyllithium in ether at room temperature, rapidly evolved a gas which was collected (80–94% in three separate runs) and shown to be pure ethylene by mass spectrometry. Formally, the reaction proceeds by 1,3-elimination of benzoate anion from the conjugate base of 2-phenyl-1,3-dioxolane. Although benzoic acid was not recovered from the reaction mixture the observed products are consistent with the elimination of lithium benzoate and subsequent reaction with phenyllithium: from one run benzophenone and triphenylcarbinol were recovered in an over-all yield of 85% based on 2-phenyl-1,3-dioxolane.

### Experimental

The reaction vessel, a 250-ml. three-necked round-bottomed flask, was fitted with a gas inlet tube, addition funnel with pressure-equalizing side arm, and a condenser. The condenser was connected to a gas buret *via* two traps cooled in a Dry Ice–acetone mixture and a gas sampling tube. The Dry Ice traps prevented ether vapors from reaching the gas buret and thus facilitated the volumetric and mass spectroscopic determinations of gas evolved in the reaction. The entire system was thoroughly flushed with helium, both before and after adding 4.892 g. (32.6 mmoles) of 2-phenyl-1,3-dioxolane[5] to the reaction vessel and 100 ml. of an ethereal solution of phenyllithium (*ca.* 125 mmoles) to the addition funnel. After allowing the volume of the system to equilibrate (*ca.* 1 hr.) the solution of phenyllithium was added dropwise to the reaction vessel until gas evolution ceased. The reaction mixture was stirred (magnetically) continuously and the reaction vessel was immersed in a bath of water at room temperature. Gas evolution ceased when 17 ml. of phenyllithium solution remained unadded. The increase in volume, 769 ml. at 736 mm. and 22°, corresponded to 94% of the theoretical evolution of 1 equiv. of gas. The mass spectrum of the gas (*m/e* = 70 to 12) was indistinguishable (±2%) from a mass spectrum of pure ethylene obtained under the same conditions.

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[1] Grateful acknowledgment is made of financial support from the Petroleum Research Fund (Grant 1116-A4).

[2] An interesting and related example was reported by R. L. Letsinger and D. F. Pollart, [*J. Am. Chem. Soc.*, **78**, 6079 (1956)]. They found that treatment of 2-phenyltetrahydrofuran with propyl- or phenyllithium, followed by work-up, yielded ethylene and acetophenone in high yields. Unpublished work with Y. C. Poon has furnished another variation: ethylene glycol sulfite is reduced to ethylene in variable yield (so far not greater than 30%) by metallic sodium or potassium in refluxing xylene.

[3] 1,3-Eliminations of stable and unstable *neutral* molecules are well known and are referred to in the exhaustive documentation of 1,3-additions by R. Huisgen, *Angew. Chem. Intern. Ed. Engl.*, **2**, 565 (1963).

[4] The conversion of 1,2-diols to olefins provides an example of immediate synthetic applicability. *Cf.* E. J. Corey and R. A. E. Winter, *J. Am. Chem. Soc.*, **85**, 2677 (1963).

[5] H. Hibbert and J. A. Timm, *ibid.*, **46**, 1283 (1924).

Water and then hydrochloric acid were added to the reaction vessel; the mixture was extracted with ether. The ether solution was extracted with 2 *N* sodium hydroxide solution. Work-up of the alkaline aqueous solution yielded 129 mg. of crude phenol, identified by its characteristic odor and infrared spectrum. Work-up of the ether solution yielded 7.121 g. of a yellow oil, the infrared spectrum of which was almost reproduced by a mixture of 80% benzophenone and 20% triphenylcarbinol. (The ratio of intensities of absorption at 6.72 and 6.94 $\mu$ can be used for quantitative analysis of such mixtures.)

A portion of the crude product, 0.951 g., was chromatographed on 40 g. of acid-washed alumina (Merck). Oily fractions 4–28, eluted with hexane through 50:50 hexane–benzene, were combined (589 mg.), dissolved in ether–pentane, and cooled to −20°, yielding 557 mg. of benzophenone in three crops, m.p. 46–48°. The yield of benzophenone based on 2-phenyl-1,3-dioxolane is therefore no less than 70%. Crystalline fractions 30–35, eluted with benzene, all showed the characteristic infrared spectrum of triphenylcarbinol. They were combined, yielding 184 mg. with m.p. >150°, corresponding to a yield of triphenylcarbinol based on 2-phenyl-1,3-dioxolane of 15%. Crystallization of the combined triphenylcarbinol fractions from ether–pentane at room temperature yielded 131 mg., m.p. 159–161°, almost indistinguishable from twice crystallized authentic triphenylcarbinol, m.p. 160–162°.

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# Bisdithiocarbonate and Related Analogs of 2-Aminoethanethiol[1]

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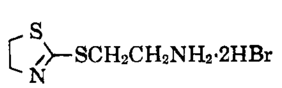
*Received January 6, 1964*

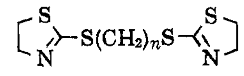
Certain modifications of the mercapto group of 2-aminoethanethiol have resulted in compounds whose radioprotective properties are not dependent *a priori* on simple release of the parent agent.[2] Continued evaluation of such changes may lead to an effective, yet relatively nontoxic antiradiation agent. In this work the excellent method provided by Crawhall and Elliott[3] for the conversion of 2-(alkylthio)-2-thiazolines to the corresponding *S*-alkyl *S'*-2-aminoethyl dithiocarbonate hydrochlorides has been extended to the preparation of several other dithiocarbonate derivatives of 2-aminoethanethiol.

2-(2-Aminoethylthio)-2-thiazoline dihydrobromide (I) was hydrolyzed in refluxing 6 *N* hydrobromic acid to give *S,S'*-bis(2-aminoethyl) dithiocarbonate dihydrobromide (II). The dihydrochloride corresponding to II had previously been isolated as one of the products of prolonged hydrolysis of 2-thiazolidinethione in refluxing concentrated hydrochloric acid.[4] Hydrolysis of the 2,2'-(alkylenedithio)bis-2-thiazolines (IIIa–e) in 6 *N* hydrochloric (or hydrobromic) acid gave the corresponding *S,S'''*-bis(2-aminoethyl) *S',S''*-alkylene bisdithiocarbonate dihydrohalides (IVa–e). The intermediate bisthiazolines were obtained in good yields from 2-thiazolidinethione and the appropriate dibromoalkane in *N,N*-dimethylformamide with potassium carbonate as acid acceptor, the crude products so obtained being used without further purification. The two lower members of the series, 2,2'-(methylenedithio)bis-2-thiazoline (IIIa) and 2,2'-(ethylenedithio)bis-2-thiazoline (IIIb), were isolated as characterizable solids. Hydrolysis of IIIb was carried out in 6 *N* hydrobromic acid instead of the usual 6 *N* hydrochloric acid, and therefore *S,S'''*-bis(2-aminoethyl) *S',S''*-ethylene bisdithiocarbonate was isolated as the dihydrobromide IVb.

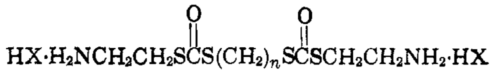

I

$$\mathrm{HBr{\cdot}H_2NCH_2CH_2S\overset{\overset{\displaystyle O}{\|}}{C}SCH_2CH_2NH_2{\cdot}HBr}$$

II



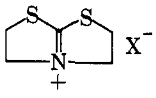
IIIa, *n* = 1
b, *n* = 2
c, *n* = 3
d, *n* = 4
e, *n* = 5

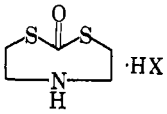


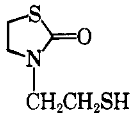
$$\mathrm{HX{\cdot}H_2NCH_2CH_2S\overset{\overset{\displaystyle O}{\|}}{C}S(CH_2)_nS\overset{\overset{\displaystyle O}{\|}}{C}SCH_2CH_2NH_2{\cdot}HX}$$

IVa, *n* = 1; X = Cl
b, *n* = 2; X = Br
c, *n* = 3; X = Cl
d, *n* = 4; X = Cl
e, *n* = 5; X = Cl

The preparation of 2,3,5,6-tetrahydrothiazolo[2,3-*b*]thiazolium chloride (Va) from 2,2'-dichlorodiethylamine and carbon disulfide has been recently described,[5,6] and the structural similarity of Va to the thiazolines described above suggests that it might be converted in hydrochloric acid to the cyclic dithiocarbonate hydrochloride VI. Refluxing a solution of Va in 6 *N* hydrochloric acid in the usual way resulted in a rather high recovery of unchanged starting material, but prolonged refluxing of a solution of Va in concentrated hydrochloric acid gave in medium yield a distillable nitroprusside-positive oil, whose infrared absorption spectrum is incompatible with the spectra of the dithiocarbonates described above. The identity of the oil as 3-(2-mercaptoethyl)-2-thiazolidinone (VII) was strongly indicated by a spectral comparison with 2-thiazolidinone itself and confirmed by elemental analyses and iodometric assay. Seto and Ikegami[6] iso-


Va, X = Cl
b, X = Br


VI


VII

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[1] This investigation was supported by the U. S. Army Medical Research and Development Command under Contract No. DA-49-193-MD-2028.

[2] For example: (a) R. Shapira, D. G. Doherty, and W. T. Burnett, Jr., *Radiation Res.*, **7**, 22 (1957); (b) B. Holmberg and B. Sörbo, *Nature*, **183**, 832 (1959); (c) B. Hansen and B. Sörbo, *Acta Radiol.* **56**, 141 (1961); (d) W. O. Foye, J. R. Marshall, and J. Mickles, *J. Pharm. Sci.*, **52**, 406 (1963); (e) L. Field, A. Ferretti, R. R. Crenshaw, and T. C. Owen, *J. Med. Chem.*, **7**, 39 (1964).

[3] J. C. Crawhall and D. F. Elliott, *J. Chem. Soc.*, 3094 (1952).

[4] R. J. Gaul and W. J. Fremuth, *J. Org. Chem.*, **25**, 869 (1960).

[5] W. Schulze, G. Letsch, and H. Willitzer, *J. prakt. Chem.*, [4]**19**, 101 (1963).

[6] S. Seto and Y. Ikegami, *Bull. Chem. Soc. Japan*, **36**, 730 (1963).