chloride 500-fold but decrease that of chloromethyl methyl ether more than 2500-fold.[36]

Double bond–no bond resonance may also explain the fact that α-fluoro substituents specifically increase the reactivity of methyl bromide derivatives toward methoxide ions relative to their reactivity toward iodide ions.[37] Bunnett has interpreted this observation in terms of London forces,[38] but such an interpretation seems to demand that hydrogen be at least as much more polarizable than fluorine as chlorine is.

Acknowledgment.—The author should like to acknowledge his indebtedness to the National Science Foundation for a grant in support of this investigation.

(36) J. Hine and R. J. Rosscup, *J. Am. Chem. Soc.*, **82**, 6115 (1960).

(37) J. Hine, C. H. Thomas, and S. J. Ehrenson, *ibid.*, **77**, 3886 (1955).

(38) J. F. Bunnett, *ibid.*, **79**, 5969 (1957).

[CONTRIBUTION FROM THE BOUND BROOK LABORATORIES, AMERICAN CYANAMID CO., BOUND BROOK, N. J.]

The 1,2-Dithiolium Cation. IV.[1] Conversion of the Dithiolium to the Thiothiophthene No-Bond Resonance System[2]

BY ERWIN KLINGSBERG[3]

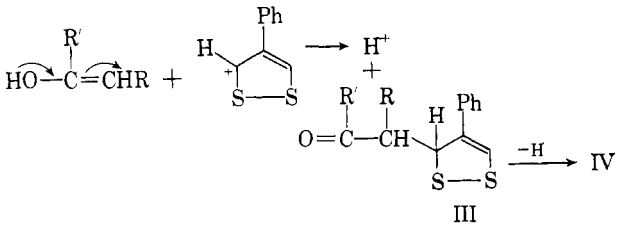
RECEIVED JUNE 8, 1963

Thiothiophthene derivatives (V) are conveniently prepared by the condensation of 4-phenyl-1,2-dithiolium hydrogen sulfate with methyl and methylene ketones to give IV, followed by treatment with P_2S_5. Chemical evidence of the "no-bond resonance" phenomenon in V is described.

4-Phenyl-1,2-dithiolium salts[4] condense smoothly with methyl and methylene ketones. The structure of the products (IV) is shown by analysis, molecular weight determination, and the lack of infrared absorption in the 1,660 cm.$^{-1}$ carbonyl region. The dimethyl analog I is known to be similar in this respect[5] and is also anomalous in its n.m.r. spectrum, showing no lines of normal shift for $COCH_3$ protons.[6] The absence of ketonic character in I and IV can be rationalized in terms of a highly polarized dithiolium enol betaine structure (*e.g.*, II); analogous polarization evidently accounts for the observation by Tarbell and Hoffman that 1,4-thiapyrone and its derivatives are lacking in infrared carbonyl absorption.[7]

I II

This condensation reaction presumably proceeds by attack of the electrophilic dithiolium cation on the enol or anionoid form of the carbonyl component; the adduct III is then dehydrogenated to the fully conjugated IV at the expense of additional dithiolium salt, which is used in excess to give yields of 40–50% based on ketone. The mild oxidizing action of dithiolium salts was earlier observed in the condensation with tertiary aromatic amines.[8] Analogous condensations followed by dehydrogenation are known in the pyridinium series.[9]

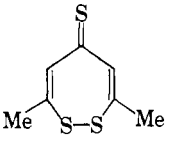


III

We speculated that, for stoichiometric or mechanistic reasons, α-haloketones might afford superior results, but an experiment with phenacyl bromide gave no product.

Compounds IV are inert to carbonyl reagents such as phenylhydrazine and alkylating agents such as dimethyl sulfate, but react smoothly with phosphorus pentasulfide. The products V, readily obtained in good yield, are derivatives of the recently discovered thiothiophthene "no-bond resonance" system, which now becomes conveniently accessible in two steps from readily obtainable dithiolium salts. Preparative details for the few known thiothiophthene derivatives are scarce in the literature. The dimethyl compound XIVa was originally obtained from diacetylacetone (XIIIa) and P_2S_5 in 40% yield,[10] but our results have been much poorer, and very recently a 15% yield has been reported.[11] We have also found the conversion of dibenzoylacetone (XIIIb) to XIVb[12] to be poor for preparative purposes.

Thiothiophthene no-bond resonance was discovered by X-ray analysis,[13] which showed that the three sulfur atoms in the reaction product of diacetylacetone and phosphorus pentasulfide are collinear and equally spaced at 2.36 Å. distance, compared to the normal RS–SR bond distance of 2.04 Å. These results are incompatible with the cyclic disulfide structure XV



XV

originally proposed for the compound,[10] but can be explained in terms of two equivalent resonating structures (XIVa). Nuclear magnetic resonance spectroscopy has provided confirmatory evidence,[6] but relatively little is known of the chemistry of the system. The accessibility of unsymmetrically substituted thiothiophthenes (V) from dithiolium salts has now made possible a chemical demonstration of no-bond resonance. Like normal thiocarbonyl compounds, Va

(1) Paper III: E. Klingsberg, *J. Org. Chem.*, **28**, 529 (1963).

(2) Presented at the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1963.

(3) University of the City of New York, New York 31, N. Y.

(4) E. Klingsberg, *J. Am. Chem. Soc.*, **83**, 2934 (1961).

(5) G. Guillouzo, *Bull. soc. chim. France*, 1316 (1958).

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(7) D. S. Tarbell and P. Hoffman, *J. Am. Chem. Soc.*, **76**, 2451 (1954); C. G. Price and O. O. Oae, "Sulfur Bonding," Ronald Press, New York, N. Y., 1962, p. 22.

(8) E. Klingsberg and A. M. Schreiber, *J. Am. Chem. Soc.*, **84**, 2941 (1962).

(9) F. Kröhnke and K. Ellegast, *Ann.*, **600**, 176 (1956); F. Kröhnke and I. Vogt, *ibid.*, **600**, 211, 228 (1956).

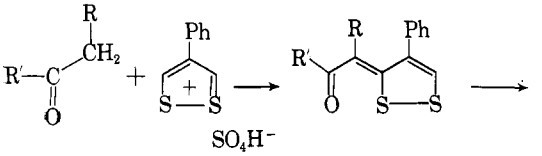
(10) F. Arndt, P. Nachtwey, and J. Pusch, *Ber.*, **58**, 1633 (1925).

(11) G. Pfister-Guillouzo and N. Lozac'h, *Bull. soc. chim. France*, 153 (1963).

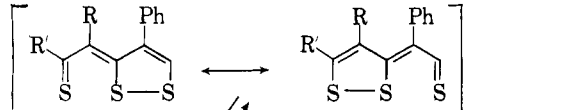
(12) G. Traverso, *Ann. chim.* (Rome), **44**, 1018 (1954).

(13) S. Bezzi, M. Mammi, and C. Garbuglio, *Nature*, **182**, 247 (1958).

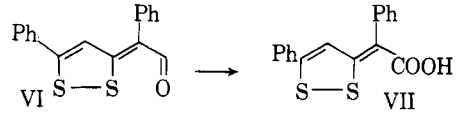
loses an atom of sulfur on treatment with mercuric acetate, giving a quantitative yield of product which, however, is not IVa, but its isomer VI; *i.e.*, the sulfur atom that is lost is not the one that had been introduced by P_2S_5. The selectivity of this reaction in the thiothiophthene series is also shown by the inertness of XIVb to mercuric acetate. The aldehydic character of VI is confirmed by oxidation to the carboxylic acid (VII); unlike IVa, it gives a 2,4-dinitrophenylhydrazone. Now VI reacts with P_2S_5 to regenerate Va. The formation of the same product Va from the isomers IVa and VI confirms the resonance interaction of the sulfur atoms; *i.e.*, sulfur-bond isomerism does not occur in this system, just as carbon-bond isomerism does not occur in benzene.[14] Similar evidence, *i.e.*, the synthesis of a single thiothiophthene from isomeric starting materials, was reported earlier this year by Pfister-Guillouzo and Lozac'h.[11]



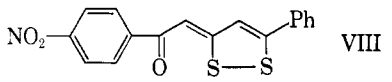
IVa, R = H, R′ = Ph
b, R = H, R′ = *m*-$NO_2C_6H_4$
c, R = H, R′ = *p*-$NO_2C_6H_4$
d, R = H, R′ = *p*-$Me_2NC_6H_4$
e, R = H, R′ = 2-thienyl
f, R = R′ = Ph
g, R = Ph, R′ = $PhCH_2$



Va, R = H, R′ = Ph
b, R = R′ = Ph
c, R = H, R′ = *p*-$Me_2NC_6H_4$



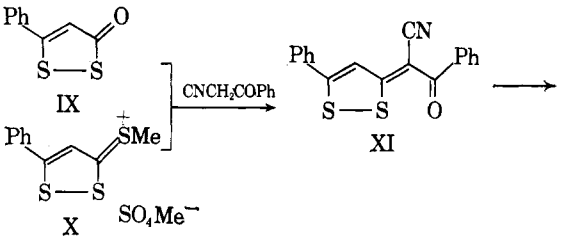
3-Phenyl-1,2-dithiolium salts react similarly (*p*-nitroacetophenone gave VIII), but in poor yield, so that

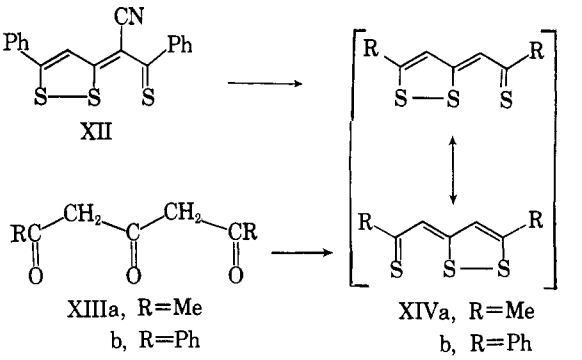


for the synthesis of XIVb, the known symmetrical isomer of Va, we found it more convenient to make use of a newly discovered reaction of 5-phenyl-1,2-dithiol-3-one (IX), its condensation with benzoylacetonitrile in phosphorus oxychloride. This is a convenient method that gives satisfactory yields of XI, which was also obtained less conveniently from benzoylacetonitrile and the "trithionium salt" (X) prepared from 5-phenyl-1,2-dithiole-3-thione and methyl sulfate. Phosphorus pentasulfide reacted normally with XI to give the thiothiophthene (XII), which was smoothly hydrolyzed and decarboxylated in acetic–hydrobromic acid to give XIVb, identical with an authentic specimen obtained from dibenzoylacetone (XIIIb).

Nomenclature.—"Thiothiophthene" is a convenient generic term, but the system proposed by Hertz, Traverso, and Walter[6] is preferable for naming individual compounds and is used for that purpose in the Experimental section of this paper. Unfortunately this terminology is not expressive of the dithiole character of these compounds. It does, however, clearly indicate the relationship between thiothiophthenes (V) and their precursors IV, and it neatly denotes the no-bond resonance phenomenon by the prefix "meribicyclo."

(14) Synthetic experiments designed to detect single–double bond isomerism in benzene derivatives were performed by A. Wohl (*Ber.*, **43**, 3474 (1910)) and J. B. Cohen and W. J. Murray, (*J. Chem. Soc.*, **107**, 847 (1915)).





Experimental

Melting points are corrected.

3,5-Epidithio-1,4-diphenyl-2,4-pentadienone-1 (IVa).—A mixture of 30.0 g. (0.109 mole) of 4-phenyl-1,2-dithiolium hydrogen sulfate[4] and 10.5 ml. (10.8 g., 0.090 mole) of acetophenone in 375 ml. of ethanol was stirred and refluxed for 3 hr., chilled, and filtered. The product (17.8 g.) was crystallized from 80 ml. of 2-methoxyethanol, yielding 11.0 g. (41%), m.p. 147–150°, suitable for reaction with P_2S_5. Crystallization from hexane or methylcyclohexane gave bright yellow product, m.p. 156–157°.

Anal. Calcd. for $C_{17}H_{12}OS_2$: C, 68.9; H, 4.1; S, 21.6; mol. wt., 296. Found: C, 69.0; H, 4.2; S, 21.6; mol. wt., 276 ±10%.

Under the same conditions, *m*-nitroacetophenone gave a similar yield of 3,5-epidithio-1-*m*-nitrophenyl-4-phenyl-2,4-pentadienone-1 (IVb), golden yellow crystals from toluene, m.p. 213–215°.

Anal. Calcd. for $C_{17}H_{11}NO_3S_2$: C, 59.8; H, 3.2; N, 4.1; S, 18.8. Found: C, 60.0; H, 3.3; N, 4.1; S, 19.1.

p-Nitroacetophenone gave 3,5-epidithio-1-*p*-nitrophenyl-4-phenyl-2,4-pentadienone-1 (IVc), orange crystals from toluene or acetic acid, m.p. 261–262°.

Anal. Found: C, 60.0; H, 3.3; N, 4.3; S, 19.2.

1-*p*-Dimethylaminophenyl-3,5-epidithio-4-phenyl-2,4-pentadienone-1 (IVd) was prepared by refluxing 10.0 g. (0.034 mole) of 4-phenyl-1,2-dithiolium hydrogen sulfate and 4.9 g. (0.030 mole) of *p*-dimethylaminoacetophenone for 3.5 hr. in 150 ml. of ethanol. Crystallization of the crude product from 75 ml. of 2-methoxyethanol gave 4.2 g. (41%), orange, m.p. 209–211°.

Anal. Calcd. for $C_{19}H_{17}NOS_2$: C, 67.3; H, 5.0; N, 4.1; S, 18.9. Found: C, 67.6; H, 5.3; N, 4.1; S, 19.2.

2-Acetylthiophene gave 3,5-epidithio-4-phenyl-1-(2-thienyl)-2,4-pentadienone-1 (IVe), yellow, m.p. 129–132° (hexane).

Anal. Calcd. for $C_{15}H_{10}OS_3$: C, 59.5; H, 3.3; S, 31.8. Found: C, 59.4; H, 3.4; S, 31.6.

3-Phenyl-1,2-dithiolium hydrogen sulfate[4] and *p*-nitroacetophenone in refluxing ethanol gave 3,5-epidithio-1-*p*-nitrophenyl-5-phenyl-2,4-pentadienone-1 (VIII), orange, m.p. 279–280° (AcOH).

Anal. Calcd. for $C_{17}H_{11}NO_3S_2$: C, 59.8; H, 3.2; N, 4.1; S, 18.8. Found: C, 59.6; H, 2.9; N, 4.2; S, 19.1.

3,5-Epidithio-1,2,4-triphenyl-2,4-pentadienone-1 (IVf).—A mixture of 10.0 g. (0.36 mole) of 4-phenyl-1,2-dithiolium hydrogen sulfate and 3.9 g. (0.020 mole) of desoxybenzoin in 125 ml. of ethanol was stirred and refluxed for 4 hr., chilled, and filtered, yielding 6.2 g. (83%) of crude product. Crystallization from 500 ml. of methylcyclohexane gave 3.7 g. (50%) of yellow-orange solid, m.p. 216–217°.

Anal. Calcd. for $C_{23}H_{16}OS_2$: C, 74.2; H, 4.3; S, 17.2. Found: C, 74.2; H, 4.2; S, 17.3.

Under the same conditions, dibenzyl ketone gave 4,6-epidithio-1,3,5-triphenyl-3,5-hexadienone-2 (IVg), orange, m.p. 120–120.5° (hexane).

Anal. Calcd. for $C_{24}H_{18}OS_2$: C, 74.6; H, 4.7; S, 16.6. Found: C, 74.4; H, 4.9; S, 16.8.

Meribicyclo-3,5-epidithio-1,4-diphenyl-2,4-pentadienethione-1 (Va).—A mixture of 10.0 g. (0.034 mole) of 3,5-epidithio-1,4-diphenyl-2,4-pentadienone-1 (IVa) and 8.3 g. (0.037 mole) of phosphorus pentasulfide in 175 ml. of toluene was stirred and refluxed for 1 hr., cooled, filtered, and evaporated, giving a quantitative yield (10.5 g.) of crystalline red product, m.p. 123–128°. Crystallization from hexane (100 ml./g.) gave a 72% recovery of stubby purple needles, m.p. 129–131°.

Anal. Calcd. for $C_{17}H_{12}S_3$: C, 65.4; H, 3.8; S, 30.8. Found: C, 65.0; H, 3.9; S, 30.9.

Meribicyclo-3,5-epidithio-1,2,4-triphenyl-2,4-pentadienethione-1 (Vb), prepared similarly from 3,5-epidithio-1,2,4-triphenyl-2,4-pentadienone-1 (IVf), crystallized as black needles, m.p. 178–180°, from hexane.

Anal. Calcd. for $C_{23}H_{16}S_3$: C, 71.2; H, 4.1; S, 24.7. Found: C, 70.9; H, 4.0; S, 24.8.

Meribicyclo-1-*p*-dimethylaminophenyl-3,5-epidithio-4-phenyl-2,4-pentadienethione-1 (Vc), obtained similarly from IVd, crystallized from methylcyclohexane as purple plates, m.p. 174.5–176°.

Anal. Calcd. for $C_{19}H_{17}NS_3$: C, 64.3; H, 4.8; N, 3.9; S, 27.0. Found: C, 64.0; H, 4.9; N, 3.9; S, 26.7.

3,5-Epidithio-2,5-diphenyl-2,4-pentadienal (VI).—A solution of 3.2 g. (0.010 mole) of Va in 200 ml. of warm acetone was poured into a solution of 4.0 g. (0.013 mole) of mercuric acetate in 100 ml. of acetic acid. The resulting mixture was stirred overnight at room temperature and filtered. Dilution of the filtrate gave 3.0 g. (100%) of orange product, m.p. 119–120°. It crystallized as orange needles from hexane with unchanged melting point.

Anal. Calcd. for $C_{17}H_{12}OS_2$: C, 68.9; H, 4.1; S, 21.6. Found C, 68.4; H, 4.0; S, 21.7.

It readily gave a 2,4-dinitrophenylhydrazone in methanol containing a little concentrated HCl; blue crystals from dimethylformamide, m.p. 250–253° dec.

Anal. Calcd. for $C_{23}H_{15}N_4O_4S_2$: C, 58.1; H, 3.2; N, 11.8; S, 13.5. Found: C, 57.8; H, 3.5; N, 12.2; S, 13.3.

Compound VI reacted rapidly with phosphorus pentasulfide in refluxing toluene to give a 93% yield of Va, identified by m.p., mixture m.p., and infrared comparison.

3,5-Epidithio-2,5-diphenyl-2,4-pentadienoic Acid (VII).—A solution of 1.50 g. of VI and 1.00 g. of 40% peracetic acid in 50 ml. of acetone was refluxed for 6 hr., cooled, diluted, and filtered. Starting material was removed by extraction with 150 ml. of boiling hexane. The residue (0.25 g.) was crystallized from dilute acetic acid and then from propanol; brick-red needles, m.p. 147–151°.

Anal. Calcd. for $C_{17}H_{12}O_2S_2$: C, 65.4; H, 3.8; S, 20.5. Found: C, 65.3; H, 3.8; S, 20.9.

2-Cyano-3,5-epidithio-1,5-diphenyl-2,4-pentadienone-1 (XI).—A solution of 19.4 g. (0.100 mole) of 5-phenyl-1,2-dithiole-3-one[4] (IX) and 10.0 g. (0.069 mole) of benzoylacetonitrile in 100 ml. of phosphorus oxychloride was warmed on the steam bath for 5 hr., left overnight at room temperature, and then poured carefully over ice. The solid was filtered, washed, dried, and freed of starting material by digestion with carbon disulfide. The crude product thus obtained (13.2 g.) was crystallized from 125 ml. of trichloroethylene, giving 10.0 g. (45%) of orange needles, m.p. 200–201°, unchanged on crystallization from methylcyclohexane.

Anal. Calcd. for $C_{18}H_{11}NOS_2$: C, 67.3; H, 3.4; N, 4.4; S, 19.9. Found: C, 66.9; H, 3.4; N, 4.3; S, 20.3.

From "Trithionium Salt."—Three grams (0.021 mole) of benzoylacetonitrile and 3.4 g. (0.010 mole) of the addition product[2] (X) of methyl sulfate with 5-phenyl-1,2-dithiole-3-thione were refluxed overnight in 30 ml. of acetic acid containing 3 drops of pyridine, cooled and filtered. The product was digested with water, filtered, dried, and crystallized from about 50 ml. of acetic acid, yielding 1.3 g. (41%) of slightly impure XI, m.p. 196–199°.

Meribicyclo-2-cyano-3,5-epidithio-1,5-diphenyl-2,4-pentadienethione-1 (XII).—A mixture of 1.50 g. (4.7 mmoles) of 2-cyano-3,5-epidithio-1,5-diphenyl-2,4-pentadienone-1 (XI) and 2.0 g. (9.0 mmoles) of phosphorus pentasulfide in 25 ml. of xylene was stirred and refluxed for 1 hr. and filtered hot. The orange product crystallized at once from the xylene; m.p. 203–205°, yield 1.55 g. (99%). Crystallization from 30 ml. of 2-methoxyethanol raised the m.p. to 216–217°, with a 73% recovery.

Anal. Calcd. for $C_{18}H_{11}NS_3$: C, 64.1; H, 3.3; N, 4.2; S, 28.5. Found: C, 64.0; H, 3.3; N, 4.3; S, 28.5.

Meribicyclo-3,5-epidithio-1,5-diphenyl-2,4-pentadienethione-1 (XIVb).—Meribicyclo-2-cyano-3,5-epidithio-1,5-diphenyl-2,4-pentadienethione-1 (XII, 3.37 g., 0.0100 mole) was stirred and refluxed in 250 ml. of acetic acid; 10 ml. of 48% HBr was added through the condenser. The addition of HBr was repeated after 24 and again after 48 hr. After 72 hr. the reaction mixture was diluted with 50 ml. of water, cooled, and filtered, yielding 2.25 g. (72%) of purple red product, m.p. 153–165°. Crystallization from methylcyclohexane (65–70 ml./g.) gave an 80% recovery of pure product, m.p. 166–168° (lit.[12] m.p. 162°), unchanged on admixture with a specimen obtained from dibenzoylacetone (XIIIb) and P_2S_5 in refluxing benzene.

Anal. Calcd. for $C_{17}H_{12}S_3$: C, 65.4; H, 3.8; S, 30.8. Found: C, 65.0; H, 3.9; S, 30.8.

Acknowledgment.—The author is indebted to John J. Kobliska and his staff for microanalyses and to Mrs. Karen Reber for technical assistance.

[CONTRIBUTION FROM THE EDGAR C. BRITTON RESEARCH LABORATORY, THE DOW CHEMICAL CO., MIDLAND, MICH.]

Nucleophilic Reactivity of Phosphoramidothionates. I. Halogen Displacements on Tetrahedral Carbon by Phosphorotriamidothionates[1]

BY HENRY TOLKMITH

RECEIVED APRIL 26, 1963

The scope of novel reactions of phosphorotriamidothionates with alkyl halides in the absence of polar solvents to produce new types of onium compounds is strongly dependent upon the structure of the reactants. The parent amide $(H_2N)_3PS$ reacts with primary alkyl halides to form the onium derivatives to be expected. The hydrocarbon derivatives $(R'NH)_3PS$ undergo the same reaction and react also with isopropyl bromide, subject to the inductive effect of R'. Hydrocarbon analogs of the structure $[(R')(R'')N]_3PS$ react only with primary alkyl iodides, depending upon the steric effects of the R groups and alkyl groups involved. The steric limitations operative in the scope of formation of the onium compounds $\{[(R')(R'')N]_3PS\ alkyl\}^+I^-$ apparently arise from a relatively narrow valence angle formed at the sulfur atom. Hydrocarbon derivatives of $(H_2N)_3PO$ and $(H_2N)_3PS$ do not react with *t*-butyl chloride but do react with *t*-butyl bromide without formation of onium compounds. New n.m.r. shift data as obtained for various compounds containing the N–P–S linkage are discussed. The findings described are compared with the extent of formation and the cation structure of isothiouronium halides.

In previous investigations on organic thionophosphorus compounds, relatively little attention was given to those reactions that involved nucleophiles containing the thionophosphorus group P=S. Our own previous work had revealed that phosphorohydrazidothionates and N^1,N^2-bis-(phosphorothionyl)-hydrazides showed greater nucleophilicity than was to be expected from the known reactivity of these hydrazides.[2] In regard to the nucleophilic reactivity of phosphoramidothionates very little was reported in the past.[3–6] The phos-

(1) Presented in part at the XIXth IUPAC Congress (Section A4, Modern Aspects of Organometallic and Related Compounds), London, July, 1963, p. 183 of Abstracts.

(2) H. Tolkmith, *J. Am. Chem. Soc.*, **84**, 2097 (1962).