[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY AT HARVARD UNIVERSITY]

Vinyl Derivatives of the Metals. II. The Cleavage of Vinyltin Compounds by the Halogens and by Protonic Acids[1]

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The halogens, hydrogen bromide, hydrogen chloride, organic acids and mercaptans cleave the vinyl group in vinyl derivatives of tin. No addition reactions were observed with these reagents. This behavior is attributed to the relatively low tin–carbon bond energy. Product studies of cleavage reactions of compounds of the type $R_2Sn(CH{=}CH_2)_2$ have shown that the vinyl group is cleaved more readily than normal alkyl groups but less readily than the phenyl group. Phenyldivinyltin halides have been found to undergo thermal redistribution, yielding trivinyltin halide and triphenyltin halide.

As part of a broad study of the reactions of the vinyl derivatives of tin,[1] we have investigated the behavior of these compounds toward the halogens and toward protonic acids. Such a study was of particular interest in view of the addition reactions that vinylsilicon compounds undergo when treated with these reagents.[2]

We have found that in all cases where completely alkylated vinyltin compounds are treated with the halogens or with protonic acids, such as the hydrogen halides, organic acids and mercaptans, *cleavage of one or more of the vinyl groups* occurs in preference to addition to the vinyl double bond, giving the corresponding organotin halide (or ester or sulfide) and the vinyl halide or ethylene, respectively

$$R_3SnCH{=}CH_2 + X_2 \longrightarrow R_3SnX + CH_2{=}CHX \quad (1)$$
$$(X = Cl, Br, I)$$
$$R_3SnCH{=}CH_2 + HX \longrightarrow R_3SnX + CH_2{=}CH_2 \quad (2)$$
$$(X = Cl, Br, O_2CR', SR')$$

An already extensive Kharasch-type[3] cleavage series for organotin compounds is known.[4] It was of theoretical interest to determine the position of the vinyl group in this series. We have carried out careful product studies of the cleavage reactions of compounds of the type $R_2Sn(CH{=}CH_2)_2$, where R is methyl, *n*-butyl and phenyl, with one equivalent of iodine in refluxing ether solution, with hydrogen bromide at −78° and with hydrogen chloride in chloroform solution at 50–60°. Use of the symmetrical $R_2Sn(CH{=}CH_2)_2$ compounds eliminated any possible probability factors which might obtain in the cleavage reactions of $R_3SnCH{=}CH_2$ and $RSn(CH{=}CH_2)_3$ compounds.

These studies, the results of which are summarized in Table I, show that the position of the vinyl group in the cleavage series is

$$C_6H_5 > CH_2{=}CH > CH_3 > C_2H_5 > n\text{-}C_3H_7 > n\text{-}C_4H_9$$

since vinyl group cleavage is the only observed reaction with dimethyl- and di-*n*-butyldivinyltin, while the phenyl group is cleaved in the case of diphenyldivinyltin.

TABLE I

PRODUCT STUDIES OF THE CLEAVAGE OF $R_2Sn(CH{=}CH_2)_2$ COMPOUNDS

R	Cleavage agent	Cleavage product	Yield, %
CH_3	I_2	$(CH_3)_2(CH_2{=}CH)SnI$	74
CH_3	HCl	$(CH_3)_2(CH_2{=}CH)SnCl$	70
CH_3	HBr	$(CH_3)_2(CH_2{=}CH)SnBr$	77
n-C_4H_9	I_2	n-$(C_4H_9)_2(CH_2{=}CH)SnI$	82
n-C_4H_9	HCl	n-$(C_4H_9)_2(CH_2{=}CH)SnCl$	79
n-C_4H_9	HBr	n-$(C_4H_9)_2(CH_2{=}CH)SnBr$	76
C_6H_5	I_2	C_6H_5I	88
C_6H_5	HBr	C_6H_6	100
$CH_2{=}CH$	I_2	$(CH_2{=}CH)_3SnI$	71

Extreme difficulties were encountered in the study of the cleavage reactions of diphenyldivinyltin by iodine, hydrogen bromide and hydrogen chloride. A careful study of the reaction of diphenyldivinyltin with iodine on a larger scale showed that thermal redistribution of the phenyldivinyltin iodide formed in the reaction had occurred during distillation of the reaction mixture

$$(C_6H_5)_2Sn(CH{=}CH_2)_2 + I_2 \longrightarrow C_6H_5(CH_2{=}CH)_2SnI + C_6H_5I \quad (3)$$
$$3C_6H_5(CH_2{=}CH)_2SnI \longrightarrow 2(CH_2{=}CH)_3SnI + (C_6H_5)_3SnI \quad (4)$$

The results of this product study are shown in Table II.

TABLE II

PRODUCT STUDY OF THE CLEAVAGE OF $(C_6H_5)_2Sn(CH{=}CH_2)_2$ AND OF THE REDISTRIBUTION OF $(C_6H_5)(CH_2{=}CH)_2SnI$

Isolated products	Yield, g. Calcd.[a]	Yield, g. Found
C_6H_5I	31.2	27.5
$(CH_2{=}CH)_3SnI$	32.6	28.2
$(C_6H_5)_3SnI$	24.4	24.2

[a] Calculated on the basis of reactions (3) and (4).

Similar results were obtained in the cleavage of diphenyldivinyltin by hydrogen bromide and hydrogen chloride.

No reports of such redistributions have appeared in the literature thus far. However, Luitjen and

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[1] Part I, D. Seyferth and F. G. A. Stone, THIS JOURNAL, **79**, 515 (1957).

[2] (a) C. A. Burkhard, *ibid.*, **72**, 1078 (1950); (b) E. Larsson, *Trans. Chalmers Univ. Technology*, **115**, 21, 25 (1951); (c) R. Nagel and H. W. Post, *J. Org. Chem.*, **17**, 1379 (1952); (d) G. H. Wagner, D. L. Bailey, A. N. Pines, M. L. Dunhan and D. B. McIntire, *Ind. Eng. Chem.*, **45**, 367 (1953); (e) L. H. Sommer, D. L. Bailey, G. M. Goldberg, C. E. Buck, T. S. Bye, F. J. Evans and F. C. Whitmore, THIS JOURNAL, **76**, 1613 (1954); (f) M. Kanazashi, *Bull. Chem. Soc. Japan*, **28**, 44 (1955).

[3] M. S. Kharasch and R. Marker, THIS JOURNAL, **48**, 3130 (1926).

[4] For a comprehensive survey of the cleavage reactions of organotin compounds see: J. G. A. Luitjen and G. J. M. van der Kerk, *Investigations in the Field of Organotin Chemistry*, Tin Research Institute, Greenford, England, 1955, pp. 75–81.

TABLE III

VINYL DERIVATIVES OF TIN PREPARED BY CLEAVAGE REACTIONS

Compound	B.p. °C.	B.p. Mm.	M.p., °C.	d^{25}_{4}	$n^{25}D$	Carbon, %[a] Calcd.	Carbon, %[a] Found	Hydrogen, %[a] Calcd.	Hydrogen, %[a] Found
$(CH_3)_2(CH_2{=}CH)SnI$	57.5–59	5.2–5.3		2.033	1.5762	15.87	16.08	3.00	3.01
$(n\text{-}C_4H_9)_2(CH_2{=}CH)SnI$	108.5–109.8	1.75		1.556	1.5384	31.04	31.30	5.47	5.34
$(CH_2{=}CH)_3SnI$	60	1.8–1.9		1.898	1.5828	22.05	22.35	2.78	2.96
$(CH_3)_2(CH_2{=}CH)SnBr$	59–61	9.5		1.838	1.5350	18.79	18.54	3.55	3.57
$(n\text{-}C_4H_9)_2(CH_2{=}CH)SnBr$	96	0.65–0.45		1.416	1.5102	35.34	35.51	6.23	6.37
$(CH_3)_2(CH_2{=}CH)SnCl$	73–75	27.0		1.575	1.5105	22.74	22.95	4.29	4.36
$(n\text{-}C_4H_9)_2(CH_2{=}CH)SnCl$	82–83	0.6		1.273	1.4973	40.75	40.60	7.17	7.19
$(CH_2{=}CH)_3SnF$			>300°			32.93	33.02	4.15	4.37
$(C_6H_5)_2(CH_2{=}CH)SnF$			>300°[c]			52.72	52.76	3.37	3.43
$C_6H_5(CH_2{=}CH)_2SnF$			>300°[d]			44.66	44.52	4.12	4.05
$(CH_3)_2(CH_2{=}CH)SnO_2CCHBrCH_3$			79–81			26.65	26.37	4.00	4.19
$(C_2H_5)_3SnSCH_2CO_2C_2H_5$[b]	107–109	1.0			1.5101	38.69	38.55	6.82	6.74

[a] All analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside 77, N. Y. [b] % S: calcd., 9.86; found, 10.13. [c] Turns brown and shrinks above 285°. [d] Turns tan and shrinks above 210°.

van der Kerk (ref. 4, p. 120) mention the possibility of such reactions in their discussion of the preparation of unsymmetrical organotin iodides.

Preliminary experiments have shown that organic acids cleave the vinyl group as well

$$R_3SnCH{=}CH_2 + R'CO_2H \longrightarrow R_3SnO_2CR' + CH_2{=}CH_2 \quad (5)$$

Indeed, this is an excellent method for preparing pure organotin esters in quantitative yield, and this reaction will be discussed in greater detail in a later communication. Qualitative observations of the reaction rate show that the greater the dissociation constant of the organic acid used, the faster is the cleavage of the vinyl group. Thus acetic acid reacts only very slowly with dimethyldivinyltin at room temperature, while dichloroacetic acid reacts exceedingly vigorously with the same compound.

Even weak acids such as mercaptans liberated ethylene from vinyltin compounds. When equivalent quantities of triethylvinyltin and ethyl mercaptoacetate were mixed and left to stand at room temperature for four days an 11% yield of ethyl S-(triethylstannyl)-mercaptoacetate thus resulted. Heating the reactants at 90–95° for ten hours gave a 41% yield of this cleavage product. This observed cleavage reaction again is in marked contrast to the well-known addition of mercaptans to vinylsilicon compounds.[2a,h] The structure of the cleavage product was proven by its independent synthesis by the reaction of bis-(triethyltin) oxide with ethyl mercaptoacetate

$$[(C_2H_5)_3Sn]_2O + 2HSCH_2CO_2C_2H_5 \longrightarrow 2(C_2H_5)_3SnSCH_2CO_2C_2H_5 + H_2O$$

Discussion

The results of this work are in accord with the extensive literature concerning cleavage reactions of organotin compounds.[4] However, an explanation of the ready cleavage of the vinyl group from tin, in contrast to the well-defined addition reactions exhibited by vinylsilanes, can no longer be sought in terms of a more polar metal–carbon bond in the case of organotin compounds. The most recent determinations of electronegativity[5] of the Group IVB elements have shown that the electronegativities of tin and silicon in their tetravalent organometallic compounds are about the same. The greatest differences, relevant to this discussion, between the organic compounds of silicon and tin lie in (a) the lower metal–carbon bond energy in the case of tin[6] and (b) the larger covalent radius of tin.[7] Of these, the former is probably the main contributor to the observed differences in the reactions of vinylsilicon and vinyltin compounds with the halogens and with protonic acids. Cleavage is clearly the thermodynamically favored reaction in the case of the tin compounds.

A detailed explanation of the cleavage series of organotin compounds and of the position of the vinyl group in this series must await kinetic studies which would give us an understanding of the transition state of the cleavage reaction. However, the results of this study are in harmony with that of Winstein and Traylor[8] on electrophilic substitution on saturated carbon atoms by means of acetic acid cleavage of dialkylmercury compounds. The anticipation of these authors that the rates of electrophilic substitution on carbon will fall off as attack is on: (a) an aromatic or vinyl carbon atom and (b) a saturated carbon atom, is borne out by the cleavage series for organotin compounds and by the position of the vinyl group in this series.

New compounds obtained by these reactions, their physical properties and analytical data are listed in Table III.

Experimental

1. **Starting Materials.**—The preparation of the vinyltin compounds used in this study, with the exception of diphenyldivinyltin, has been described previously.[1] **Diphenyldivinyltin** was prepared in 68% yield by treatment of 0.7 mole of crude diphenyltin dichloride with 2.0 mole of vinylmagnesium bromide[9] in tetrahydrofuran solution for 20

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(5) L. A. Allred, Ph.D. Thesis, Harvard University, 1956.

(6) For instance, the Si–C mean bond energies in tetramethyl- and tetraethylsilane are 75 and 62 kcal./mole, respectively, (*cf.* S. Tannenbaum, THIS JOURNAL, **76**, 1027 (1954)), while the Sn–C mean bond energies in tetramethyl- and tetraethyltin are 44.8 and 49.5 kcal./mole, respectively (calculated from heats of combustion reported by C. R. Dillard, Final Report, U. S. Office of Naval Research Contract N9-onr-95700, August 31, 1952).

(7) T. Moeller, "Inorganic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1952, p. 135.

(8) S. Winstein and T. G. Traylor, THIS JOURNAL, **77**, 3747 (1955).

(9) H. Normant, *Compt. rend.*, **239**, 1510 (1954).

hours at reflux. Hydrolysis with a saturated aqueous solution of ammonium chloride, followed by distillation of the decanted organic layer, gave 152 g. of diphenyldivinyltin, b.p. 121.5° at 0.4 mm., $d^{25}{}_4$ 1.334, $n^{25}{}_D$ 1.5929.

Anal. Calcd. for $C_{16}H_{16}Sn$: C, 58.76; H, 4.93. Found: C, 58.88; H, 4.98.

2. Iodine Cleavage Reactions. a. Dimethyldivinyltin, Di-*n*-butyldivinyltin and Tetravinyltin.—The same procedure was used in the iodine cleavage of these three compounds. One such reaction is given as an example.

To a solution of 25 g. (0.123 mole) of dimethyldivinyltin in 500 ml. of diethyl ether was added 31.1 g. (0.123 mole) of iodine, and the mixture was refluxed for eight hours. A colorless solution resulted. The ether was distilled at atmospheric pressure, and the residue was distilled at reduced pressure to give 27.3 g. (74%) of dimethylvinyltin iodide.

b. **Diphenyldivinyltin.**—To a solution of 50 g. (0.153 mole) of diphenyldivinyltin in 400 ml. of ether was added 38.8 g. (0.153 mole) of iodine. After the mixture had been refluxed for eight hours the iodine color was discharged. The ether was removed at atmospheric pressure and then the distillation was continued at reduced pressure to give the following fractions: iodobenzene, b.p. 60.5–62° at 8.7 mm., $n^{24.5}{}_D$ 1.6160, 27.5 g.; impure trivinyltin iodide, boiling from 54° at 1.3 mm. to 60° at 0.7 mm., $n^{25}{}_D$ 1.5897, 28.2 g.; triphenyltin iodide, solid residue, 24.2 g. The latter was recrystallized from ether and identified by analysis:

Anal. Calcd. for $C_{18}H_{15}ISn$: C, 45.3; H, 3.17. Found: C, 45.00; H, 3.21.

The crude trivinyltin iodide was redistilled to give 25 g. of material, b.p. 60–62° at 1.8 mm., $n^{25}{}_D$ 1.5835.

c. **Triphenylvinyltin.**—To a solution of 20 g. (0.053 mole) of triphenylvinyltin in 350 ml. of ether was added 13.5 g. (0.053 mole) of iodine, and the mixture was refluxed for 15 hours. The ether and part of the iodobenzene were removed by distillation. The residue could not be crystallized and for this reason it was treated with an excess of neutral aqueous-alcoholic potassium fluoride solution. Recrystallization of the precipitated organotin fluoride from a tetrahydrofuran–acetone–ethanol mixture gave pure **diphenylvinyltin fluoride**, 13 g., a yield of 77%.

3. Bromine Cleavage Reactions.—To a 25-g. (0.079 mole) sample of tri-*n*-butylvinyltin at −78° was added dropwise 12.6 g. (0.079 mole) of bromine. The bromine was decolorized immediately as it was added. After the addition had been completed the mixture was allowed to warm to room temperature. Distillation of the reaction mixture yielded: 1,1,2-tribromoethane, boiling from 58° at 4 mm. to 53° at 1.9 mm., $n^{25}{}_D$ 1.5855, 8 g.; a center fraction boiling from 98° at 2.5 mm. to 110° at 1.8 mm.; tri-*n*-butyltin bromide, b.p. 120° at 1.8 mm. to 122° at 1.6 mm., $d^{25}{}_4$ 1.338, $n^{25}{}_D$ 1.5022; *MR*D found, 81.64, calcd., 81.40, 15 g., a yield of 51.4%. Jones, *et al.*,[10] report $d^{20}{}_4$ 1.3365 and $n^{20}{}_D$ 1.5000 for tri-*n*-butyltin bromide. When a 100% excess of bromine was used, a 76% yield of tri-*n*-butyltin bromide resulted.

4. Chlorine Cleavage Reactions.—Into 23.5 g. (0.074 mole) of tri-*n*-butylvinyltin at −78° was bubbled 5.5 g. (0.08 mole) of dry chlorine. The reaction mixture subsequently was warmed up to room temperature and was fractionally distilled to give 20.4 g. (86.4%) of tri-*n*-butyltin chloride, b.p. 98° at 0.45 mm. to 100° at 0.35 mm., $n^{25}{}_D$ 1.4903; $n^{22}{}_D$ 1.4908 is reported by Manulkin[11] for this compound.

5. Hydrogen Bromide Cleavage Reactions. (a) Dimethyldivinyltin.—Into a cold trap at −78° was charged 25 g. (0.123 mole) of dimethyldivinyltin. The exit arm of the trap led to an Ascarite-filled tube which was connected to another trap containing a solution of 16 g. (0.1 mole) of bromine in chloroform. Hydrogen bromide gas was slowly bubbled into the organotin compound until the latter had nearly solidified. The organotin compound was then warmed up to −40°, and the addition of hydrogen bromide was continued until the bromine solution was completely decolorized. Fractional distillation of the reaction mixture gave 24.2 g. (77%) of dimethylvinyltin bromide. A small amount of dimethyltin dibromide (m.p. 74° after recrystallization from ether; m.p. in the literature,[12] 75–77°) remained in the still pot, indicating that the second vinyl group is more susceptible to cleavage than are the methyl groups after one vinyl group has been removed.

A similar procedure was followed in the hydrogen bromide cleavage of di-*n*-butyldivinyltin. In the latter case the 1,2-dibromoethane formed in the end trap was recovered in 80% yield by distillation, b.p. 129–130°.

b. **Diphenyldivinyltin.** (i).—Eight grams (0.10 mole) of liquid hydrogen bromide was allowed to vaporize slowly and was bubbled into 30 g. (0.0918 mole) of diphenyldivinyltin, initially at −78°. The organotin compound began to form a solid slush in the later stages of the reaction and therefore was warmed to −40°. Distillation at atmospheric pressure gave 8 g. (100% yield) of benzene, b.p. 79–80°.

(ii).—A similar procedure was used when 25 g. (0.0765 mole) of diphenyldivinyltin was treated with 6.2 g. (0.0765 mole) of hydrogen bromide. Fractional distillation of the high boiling organotin products gave: impure **trivinyltin bromide**, boiling from 54° at 0.4 mm. to 53° at 0.3 mm., 9 g.; a yellow oil, distilling continuously from 86° at 0.35 mm. to 132° at 0.35 mm., 10 g.; a solid residue, 4.5 g. The latter was recrystallized from ether to give triphenyltin bromide, m.p. 118–120°; m.p. reported by Krause,[13] 120.5°. The impure trivinyltin bromide was converted to pure **trivinyltin fluoride** by the potassium fluoride method.

(iii).—To 20 g. (0.061 mole) of diphenyldivinyltin was added 5 g. (0.061 mole) of hydrogen bromide in the manner described above. When the reaction mixture had warmed to room temperature it was treated with an excess of neutral aqueous-alcoholic potassium fluoride solution. A white, oily solid resulted that could be extracted with ether. Evaporation of the ethereal extracts yielded 8 g. of pure **phenyldivinyltin fluoride**. No attempt was made to recover the remaining portion of this fluoride from the precipitation solvent medium.

6. Hydrogen Chloride Cleavage Reactions. a. Di-*n*-butyldivinyltin.—A solution of 28.7 g. (0.1 mole) of di-*n*-butyldivinyltin in chloroform was prepared in a trap. The exit arm of the trap led to a tube filled with Ascarite which was connected to a trap containing 12.8 g. (0.08 mole) of bromine in chloroform solution. The di-*n*-butyldivinyltin solution was maintained at 50–60° with a hot water-bath and hydrogen chloride gas was bubbled through the solution until the bromine in the end trap was decolorized. The chloroform was removed by rapid distillation and the residue was fractionally distilled, giving 23.4 g. (79.3%) of di-*n*-butylvinyltin chloride, b.p. 82–83° at 0.6 mm.

A similar procedure was used in the hydrogen chloride cleavage of dimethyldivinyltin.

b. **Diphenyldivinyltin.**—Into a solution of 21.5 g. (0.0657 mole) of diphenyldivinyltin in chloroform, maintained at 60–70°, was bubbled about 2.4 g. (0.066 mole) of hydrogen chloride gas. After removal of the chloroform by rapid distillation the residue was distilled at reduced pressure. The following fractions were collected: 44° at 0.5 mm. to 64° at 0.35 mm., 4 g.; 65–68° at 0.35 mm., 5 g.; 83–105° at 0.35 mm., 3 g.; a solid residue, 4 g. The latter was recrystallized from ether to give fairly pure triphenyltin chloride, m.p. 100–102°; m.p. reported[14] 105–106°.

7. Cleavage by Organic Acids. a. Acetic Acid.—To 10 g. (0.0428 mole) of triethylvinyltin was added 2.57 g. (0.0428 mole) of glacial acetic acid. The reactants were heated on the steam-bath for 1.5 hours and then cooled to give a quantitative yield of triethyltin acetate, m.p. 132–134°; Luijten and van der Kerk (ref. 10, p. 99) report a m.p. of 134–135°.

b. **α-Bromopropionic Acid.**—The same procedure was followed in the reaction of 5 g. (0.0243 mole) of dimethyldivinyltin with 3.06 g. (0.02 mole) of α-bromopropionic acid. A quantitative yield of dimethylvinyltin α-bromopropionate resulted after the crystals were washed with chilled petroleum ether and dried.

8. Cleavage by Mercaptans.—To 23.3 g. (0.1 mole) of triethylvinyltin was added 36.0 g. (0.3 mole) of ethyl mercaptoacetate. The mixture was heated on the steam-bath

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(10) W. J. Jones, D. P. Evans, T. Gullwell and D. C. Griffiths, *J. Chem. Soc.*, 39 (1935).

(11) Z. M. Manulkin, *J. Gen. Chem.* (*U.S.S.R.*), **18**, 299 (1948).

(12) A. C. Smith, Jr., and E. G. Rochow, THIS JOURNAL, **75**, 4105 (1953).

(13) E. Krause, *Ber.*, **51**, 912 (1918).

(14) K. A. Kocheshkov, *ibid.*, **67**, 1348 (1934).

for ten hours. Fractional distillation gave 27.5 g. of a mixture of unreacted starting materials, boiling from 44° to 52° at 8.9, mm, and 14.5 g. of ethyl S-(triethylstannyl)-mercaptoacetate, boiling from 99° at 0.44 mm. to 110° at 0.65 mm. This fraction was redistilled (107–109° at 1.0 mm.) to give the pure compound. Reference to the analytical data in Table III shows that this is not the addition product, $Et_3SnCH_2CH_2SCH_2CO_2Et$. (Calcd. for the addition product: C, 40.82; H, 7.42; S, 9.08.)

9. **Ethyl S-(Triethylstannyl)-mercaptoacetate: Proof of Structure.**—The method of Sasin[15] was used. To 6.2 g. (0.0144 mole) of bis-(triethyltin) oxide was added 5.2 g. (0.432 mole) of ethyl mercaptoacetate. After the initially vigorous reaction had subsided the mixture was refluxed for one hour and then was distilled to give a small fraction boiling at 115–117° at 1.5 mm., n^{25}_{D} 1.5099, whose infrared absorption spectrum was identical with that of the cleavage product described above.

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[15] G. Sasin, *J. Org. Chem.*, **18**, 1142 (1953).