[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF FORDHAM UNIVERSITY]

THE SULFONATION OF FURAN AND FURAN HOMOLOGS. PREPARATION OF FURANSULFONAMIDES[1]

JOHN F. SCULLY AND ELLIS V. BROWN

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Since furan and its homologs are easily resinified by acids, sulfonated furans have not been obtained by the usual methods except with the furoic acids (1). Anhydropyridiniumsulfonic acid has been used by Terent'ev and Kazitsyna (2) to effect the sulfonation of furan and several of its homologs. The products obtained by them were isolated as barium salts and characterized as *alpha* or *beta* isomers according to their reactions with hot mineral acids or bromine water. On the basis of these reactions, the authors have reported that furan, even on treatment with excess sulfonating agent, yields 90% of furan-2-sulfonic acid (2), 2-methylfuran gives a 3,5-disulfonic acid in 20–77% yield, and 2,5-dimethylfuran forms a 3-sulfonic acid in 62% yield (3).

Reproduction of this sulfonation method with furan, 2-methylfuran, and 2,5-dimethylfuran and investigations of the sulfonation products, as the barium salts, have shown that the products were not homogeneous as reported by Terent'ev and Kazitsyna but were essentially binary, consisting of both the mono- and di-sulfonic acids of the respective furans. This was shown by the partial solubility of the dry barium salts in 95% ethyl alcohol. The barium salts of the monosulfonic acids of furan and 2-methylfuran were soluble while those of the disulfonic acids were insoluble. In the case of sulfonated 2,5-dimethylfuran, the barium monosulfonate was insoluble while the disulfonate was soluble. On the basis of the alcohol separation of the barium salts of the mono- and disulfonic acids, the respective yields are recorded in Table I under Sulfonation Method A. It is noteworthy that the barium salt of furan-2,5-disulfonic acid, not of furan-2-sulfonic acid (2) is the principal product obtained from furan in this method.

Terent'ev and co-workers (4) have also reported the conversion of 2-methylfuran to the 5-sulfonic acid by allowing an equimolar mixture of the sulfonating agent and 2-methylfuran to react in 1,2-dichloroethane at room temperature for one month. It was thought that the time required for sulfonation could be reduced by heating the sulfonation mixture under efficient reflux. Refluxing the furans in this solvent for four hours yielded the amounts recorded in Table I under Sulfonation Method B. Furan again produced mostly the disulfonic acid while the yields of the monosulfonic acids of 2-methylfuran and 2,5-dimethylfuran showed marked increase. The low yield of furan-2-sulfonic acid is apparently due to the high volatility of furan which decreases its concentration relative to the sulfonating agent.

Since it was desired to determine the effect of temperature on the sulfonation method and also to prepare the monosulfonic acids of furan and 2-methylfuran

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exclusive of their disulfonic acids, the furan compound with a three to one molar ratio of the sulfonating agent was allowed to react in 1,2-dichloroethane for 72 hours. The products were obtained as in Method B and the yields are recorded in Table I under Sulfonation Method C. A comparison of Methods A, B, and C in Table I shows that the yield of disulfonic acid tends to increase with higher reaction temperature. The use of an equimolar ratio of the sulfonating agent was expected to result in the predominant formation of the desired monosulfonic acids of furan and 2-methylfuran.

As might be expected the yield of 2,5-dimethylfuran-3-sulfonic acid falls sharply in Methods C and D from that obtained by Method B, indicating the need of greater activation of the *beta* position of the furan ring over that required for the *alpha* position.

A comparison of the different sulfonation methods is found in Table I and, since the yields in the sulfonations were not reproducible, a range is given showing the maximum and minimum yields in at least five runs for each compound.

Because Terent'ev and Kazitsyna had not conclusively demonstrated the structures of the furansulfonic acids, we converted then to the corresponding furansulfonamides since it was possible to prepare some of these sulfonamides by alternate syntheses. The yield of sulfonamide varied with the sulfonation method by which the barium salt was obtained, particularly in the case of furan-2,5-disulfonic acid and 2,5-dimethylfuran-3-sulfonic acid. The barium salts of these acids obtained by Method A gave lower yields of the respective sulfonamides than those obtained by Methods B, C, and D, all of which gave approximately the same yield. In the preparation of the furansulfonyl chlorides, it was noted that large quantities of polymer were formed. Since it was not known whether the polymer arose from this reaction or was already present in the barium salts as obtained from the sulfonation mixtures, it was necessary to prepare pure barium salts of all the sulfonic acids through the *p*-toluidine salts which were prepared from the crude barium salts by adding an equivalent of dilute sulfuric acid, filtration of the barium sulfate, and neutralization with *p*-toluidine. The *p*-toluidine salts of 2-methyl-3,5-furandisulfonic acid and 2,5-dimethylfuran-3,4-disulfonic acid were difficult to obtain. The barium salts of these acids prepared by Method A gave no crystalline salts but only viscous black oils. The *p*-toluidine salts were prepared from the barium salts obtained by Method B.

TABLE I

SULFONATION METHODS

FURAN CPD.	BARIUM SALTS OF SULFONIC ACIDS	SULFONATION METHOD (% yield)			
		A	B	C	D
Furan	Furan-2-	12–18	4	20–46	0–20
	Furan-2,5-di	34–75	77–85	15–55	0–20
2-Methylfuran	2-Methylfuran-5-	0–20	48–56	36–44	28–64
	2-Methylfuran-3,5-di-	50–58	30–33	36–42	0
2,5-Dimethylfuran	2,5-Dimethylfuran-3-	60–80	86–95	58–66	0–32
	2,5-Dimethylfuran-3,4-di	10–24	0	0	0

The *p*-toludine salts, when heated with a slight excess of barium hydroxide in aqueous solution, were easily converted to the barium furansulfonates. In general, the purified barium salts were converted to the sulfonamides in yields superior to those previously obtained. The furansulfonyl chloride preparations were again accompanied by the production of large quantities of resinous material. In the case of 2-methylfuran-3,5-disulfonic acid and also 2,5-dimethylfuran-3,4-disulfonic acid, the entire reaction mixture solidified into a black mass which was insoluble in ether. For this reason, these sulfonamides could not be obtained. There was little, if any, polymer production in the preparation of the acid chloride of 2,5-dimethylfuran-3-sulfonic acid and the yield of sulfonamide was correspondingly higher than those obtained from the other sulfonic acids.

The structure of furan-2- and 2-methylfuran-5-sulfonamides were shown by alternate syntheses and 2-methylfuran-3-sulfonamide was shown to be isomeric with 2-methylfuran-5-sulfonamide by elemental analysis. Cinneide (5) has published a preliminary report on the preparation of furan-2- and 3-sulfonamides but the promised complete paper does not seem to have appeared. Using the same general approach, we have prepared furan-2-sulfonamide. In a similar manner 2-methyl-3-sulfonamido-5-furoic acid (6) has been prepared and has been decarboxylated to 2-methylfuran-3-sulfonamide. 2-Methyl-3-furoic acid has been sulfonated, converted to the diamide, then to the sulfonamidofuroic acid, followed by decarboxylation to 2-methylfuran-5-sulfonamide. Since 2,5-dimethyl-3-furoic acid would not sulfonate, it was not possible to prepare 2,5-dimethylfuran-3-sulfonamide by this method. Several alternate syntheses for this compound were unsuccessful. It was not possible to synthesize furan-2,5-disulfonamide by this method but the structure of this compound was shown by the conversion of the disulfonic acid to 2,5-dinitrofuran. Lithium furan-2-sulfinate was prepared from 2-furyllithium by a method that proved almost identical with that of Truce and Wellisch (7) and was oxidized to furan-2-sulfonic acid as shown by its conversion to furan-2-sulfonamide.

The replacement reactions of the furansulfonic acids were investigated as possible preparative methods for other substituted furans. It was shown by Hill and White (8) that the sulfonic acid group of 5-sulfo-2-furoic acid is replaceable by the nitro group. The mono- and di-sulfonic acids of furan, 2-methylfuran, and 2,5-dimethylfuran, as the barium salts, were reacted with fuming nitric acid but only in the case of the furan-2,5-disulfonic acid was the corresponding nitro compound obtained. It was shown to be 2,5-dinitrofuran by its identity with that prepared from 5-sulfo-2-furoic acid by Hill and White (8). Barium sulfate was precipitated from all of the reaction mixtures on dilution with water, indicating cleavage of the sulfonic acid group. It is not clear, however, whether replacement of the sulfonic group did occur, followed by decomposition of the product in the oxidizing medium, or whether the cleavage was due to rupture of the nucleus. The furansulfonamides were substituted for the sulfonic acids in this reaction, which was strongly exothermic, but the nitrofurans were not obtained. It was shown that the sulfoamido group can be replaced by the nitro group since 5-

sulfonamido-2-furoic acid was converted to 5-nitro-2-furoic acid by nitric acid. To avoid the drastic action of the fuming nitric acid, an acetic anhydride-nitric acid mixture was used with the furansulfonamides but without success.

The replacement of the sulfonic by the carboxylic group, reported by Meyer (9) and applied by Gilman and co-workers (10) gave negative results with all the furansulfonic acids. The attempted conversion of the potassium furansulfonates to the corresponding nitriles with sodium cyanide was also unsuccessful. It seems that the replacement reactions are not easily applicable to the furansulfonic acids except when the carboxyl group is also present. An exception to this is the formation of 2,5-dinitrofuran from furan-2,5-disulfonic acid.

EXPERIMENTAL

Anhydropyridiniumsulfonic acid. To 250 ml. of dichloroethane was added 95 g. of sulfur trioxide (Sulfan B, General Chem. Co.) with efficient stirring. The reaction flask was immersed in an ice-salt bath and a solution of 100 g. of dry pyridine in 100 ml. of dichloroethane was added dropwise. The white crystalline product separated from the solution during the addition. It was filtered, the last traces of pyridine and solvent being removed *in vacuo* to give 180 g. (95%) of the acid. The reagent was stored in a vacuum desiccator over sulfuric acid or in sealed glass ampules.

Sulfonation methods. The furans[2] used in these sulfonations were dried over metallic sodium and then were distilled several times from sodium.

Method A. The furan compound was added in a three to one molar ratio to the sulfonating agent in a Carius tube. The tube was sealed and heated for eight hours between 95 and 100°. The brown viscous oil that resulted was dissolved in hot water and treated with barium carbonate until there was no further evolution of carbon dioxide. The solution was heated to boiling and the barium sulfate was filtered. The precipitate was washed with hot water, the filtrate was evaporated to dryness on a steam-bath at reduced pressure, and the barium salt was extracted with 300 ml. of 95% ethyl alcohol under reflux for two hours. The insoluble barium salt was filtered and the filtrates evaporated to obtain the alcohol soluble barium salt which was crystallized from alcohol by dilution with toluene. The alcohol-insoluble barium salt was crystallized from hot concentrated aqueous solution by dilution with alcohol.

In typical runs, 11.4 g. of furan gave 4 g. (12%) of furan-2-sulfonic acid and 46 g. (75%) of furan-2,5-disulfonic acid as barium salts. 2-Methylfuran (13.8 g.) gave 8.5 g. (20%) of 2-methylfuran-5-sulfonic acid and 39 g. (58%) of 2-methylfuran-3,5-disulfonic acid as barium salts. 2,5-Dimethylfuran (10.8 g.) yielded 4 g. (10%) of 2,5-dimethylfuran-3,4-disulfonic acid and 23 g. (80%) of 2,5-dimethylfuran-3-sulfonic acid both as barium salts.

Method B. The furan compound (0.25 mole) was heated with 120 g. (0.75 mole) of anhydropyridiniumsulfonic acid in 250 ml. of dichloroethane for four hours, furan at 35–40°, 2-methylfuran at 50–55°, and 2,5-dimethylfuran at 60–65°. The reaction mixture was then poured into one liter of warm water and the solvent was removed by steam-distillation. After treatment with barium carbonate until there was no more evolution of carbon dioxide, the hot mixture was filtered and the precipitate was washed with 500 ml. of boiling water. The combined filtrates were evaporated to dryness and the barium salts were obtained as above described. Furan (17 g.) gave 2.2 g. (4%) of the mono- and 31 g. (60%) of the di-sulfonate. 2-Methylfuran (21 g.) yielded 30 g. (52%) of the mono- and 36.8 g. (32%) of the di-sulfonate while 2,5-dimethylfuran (24 g.) produced 53.5 g. (90%) of the monosulfonate.

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[2] The furan and 2-methylfuran used in these investigations were obtained through the courtesy of E. I. du Pont de Nemours and Company. The 2,5-dimethylfuran was furnished by the Union Carbide and Carbon Corporation, Chemicals Division.

Method C. The furan compound (0.25 mole) was added to 120 g. (0.75 mole) of the sulfonating agent suspended in 250 ml. of dichloroethane and the mixture allowed to stand for three days. The barium salts were obtained as before. Furan (38 g.) gave 49 g. (41%) of the mono- and 27 g. (15%) of the di-sulfonate. 2-Methylfuran (21 g.) yielded 23.5 g. (40%) of the mono- and 39 g. (40%) of the di-sulfonate while 2,5-dimethylfuran (24 g.) gave 40 g. (66%) of the mono- and only a trace of the di-sulfonate.

Method D. This method is identical with *Method C* with the exception that 40 g. (0.25 mole) of the sulfonating agent was used with 100 ml. of solvent. By this procedure, furan (17 g.) gave 10.7 g. (20%) of the mono- and 18 g. (20%) of the di-sulfonate while 2-methylfuran (21 g.) yielded 36.6 g. (64%) of the mono- and only traces of the di-sulfonate and 2,5-dimethylfuran (24 g.) produced 18 g. (32%) of the monosulfonate only.

A summary of the sulfonation methods with respect to the percentage yields of the barium salts of the sulfonic acids is given in Table I.

p-Toluidine salts of furansulfonic acids. The barium salts of the furansulfonic acids were dissolved in water and were hydrolyzed with sulfuric acid until there was no further precipitation of barium sulfate. The solution was filtered and the excess sulfuric acid was removed with dilute barium hydroxide solution. The hot solutions of the sulfonic acids were then neutralized with *p*-toluidine, heated to boiling, and clarified with activated charcoal. The volume of the solution was reduced until crystallization took place; the solutions of the toluidine salts of the monosulfonic acids were evaporated to dryness at reduced pressure and the salts were crystallized from the minimum of hot water. The toluidine salts of the disulfonic acids crystallized readily from hot water in almost quantitative yield.

The melting points and analytical data for the *p*-toluidine salts of the acids prepared are recorded in Table II.

Barium furansulfonates. The *p*-toluidine salts were dissolved in hot water and heated with a 10% excess of barium hydroxide under reflux for one hour. The *p*-toluidine separated as an oil which was steam-distilled and the excess barium hydroxide was precipitated with carbon dioxide. The solution was heated to boiling, filtered, and the precipitate was washed with water. The combined filtrates were evaporated to dryness to obtain the white crystalline barium salts which were dried *in vacuo* over phosphorus pentoxide. The yield was almost quantitative.

Preparation of furansulfonamides. The purified barium salts were dissolved in warm water to which was added sodium carbonate to slight alkalinity and the barium carbonate was filtered hot. Evaporation of the filtrate yielded the dry sodium salts which were treated cautiously with an equimolar quantity of phosphorus pentachloride. After the reaction had subsided, heat was applied for ten minutes, and the mixture was cooled and poured over ice and water. The furansulfonyl chloride separated as a brown oil which was extracted

TABLE II

p-TOLUIDINE SALTS

SULFONIC ACID SALT	M.P.,[a] °C.	EMPIRICAL FORMULA	ANALYSES			
			Calc'd		Found	
			C	H	C	H
Furan-2-	139–140	$C_{11}H_{13}NO_4S$	51.77	5.10	51.50	5.26
2-Methylfuran-5-	151–152	$C_{12}H_{15}NO_4S$	53.52	5.58	53.36	5.65
2,5-Dimethylfuran-3-	159–160	$C_{13}H_{17}NO_4S$	55.11	6.01	55.35	6.38
Furan-2,5-di-	224–225	$C_{18}H_{22}N_2O_7S_2$	48.88	4.98	48.68	5.23
2-Methylfuran-3,5-di-	213–214	$C_{19}H_{24}N_2O_7S_2$	49.79	5.26	50.10	5.60
2,5-Dimethylfuran-3,4-di-	209–210	$C_{20}H_{26}N_2O_7S_2$	51.07	5.41	51.03	5.80

[a] All melting points are corrected.

TABLE III

FURANSULFONAMIDES

SULFONAMIDE	M.P.,[a] °C.	YIELD,[b] %	ANALYSES					
			Calc'd			Found		
			C	H	N	C	H	N
Furan-2-	121–122[c]	20			21.77[d]			21.71[d]
2-Methylfuran-5-	117	22	37.27	4.35	8.70	37.53	4.09	8.68
2-Methylfuran-3-	115	90	37.27	4.35	8.70	37.72	4.10	8.31
2,5-Dimethylfuran-3-	94–95	65	41.14	5.11	8.00	41.02	4.95	8.03
Furan-2,5-di-	199–200	28	21.24	2.65	12.40	21.36	2.53	12.69

[a] All melting points are corrected. [b] Based on the purified barium salts. [c] Reported in Reference 5. [d] This analysis for sulfur.

with ether and the ether solution was added dropwise to cooled concentrated ammonium hydroxide. The mixture was allowed to stand overnight at room temperature and was then evaporated to dryness *in vacuo*. The solid residue was extracted with ethyl acetate and the solvent was evaporated to give the furansulfonamides. The monosulfonamides were crystallized from either water or benzene and furan-2,5-disulfonamide was recrystallized from hot water after treatment with activated charcoal. In Table III are recorded the analytical data, percentage yields, and melting points of the sulfonamides obtained.

Sulfonation of furoic acid and its homologs. To 270 g. of fuming sulfuric acid (*sp. gr.* 1.95) was added 90 g. (0.8 mole) of furoic acid at the rate of 5 g. every ten minutes. The temperature was not allowed to rise noticeably during the reaction. After standing overnight at room temperature the mixture was poured over 1 kg. of ice and water. The dark brown solution was neutralized with barium carbonate, heated to boiling, and filtered. The precipitate was boiled with 500 ml. of water, filtered, and the combined filtrates were evaporated to 500 ml. On cooling, 183 g. of the white crystalline barium salt of 5-sulfo-2-furoic acid separated. Concentration and alcohol dilution of the filtrate gave another 95 g. of the barium salt. The combined yield was 278 g. (80%) of the crude barium salt.

2-Methyl-3-furoic acid and 2-methyl-5-furoic acid were sulfonated in 54% and 90% yields respectively by the same method.

Preparation of the sulfonamidofuramides. The barium salt of 5-sulfo-2-furoic acid (193 g.) was dissolved in a liter of hot water and treated with sodium carbonate until just alkaline. The disodium salt was obtained by removing the barium carbonate and evaporating the filtrate. It was then treated with 300 g. of phosphorus pentachloride with cooling until the initial vigorous reaction had subsided. After the reaction mixture had almost entirely liquified, it was heated for one-half hour, cooled, and poured over cracked ice. The diacid chloride was extracted with ether and the ether solution was added dropwise to cooled ammonium hydroxide. Concentration and cooling of the ammoniacal solution yielded 34.7 g. (45%) of 5-sulfonamido-2-furamide which melted 212–213° (1).

The barium salt of 2-methyl-3-sulfo-5-furoic acid was converted to 44% of 2-methyl-3-sulfonamido-5-furamide, m.p. 196–197° (6). In the same way the barium salt from the sulfonation of 2-methyl-3-furoic acid was converted to 2-methyl-5-sulfonamido-3-furamide, m.p. 208–209°, in 28% yield.

Anal. Calc'd for $C_6H_8N_2O_4S$: C, 35.29; H, 3.92.
Found: C, 35.20; H, 4.01.

Preparation of the sulfonamidofuroic acids. 5-Sulfonamido-2-furamide (41.7 g.) was refluxed with 120 g. of barium hydroxide in 500 ml. of water until no more ammonia was evolved and then was treated with carbon dioxide to remove the barium. Acidification, filtration, and recrystallization from hot water yielded 24.2 g. (60%) of 5-sulfonamido-2-uroic acid, m.p. 204–205° (1).

2-Methyl-3-sulfonamido-5-furamide yielded 2-methyl-3-sulfonamido-5-furoic acid, m.p. 216–217° (6) in 64% yield. By the same procedure 2-methyl-5-sulfonamido-3-furoic acid was prepared from the diamide in 70% yield and melted at 209.5–210.5°.

Anal. Calc'd for $C_6H_7NO_5S$: C, 35.12; H, 3.41.
Found: C, 35.62; H, 3.43.

Decarboxylation of the sulfonamidofuroic acids. One gram of the acid, 10 g. of quinoline, and 1 g. of finely divided copper were heated and carbon dioxide was evolved at 180–195° in the case of 5-sulfonamido-2-furoic acid and at 220–230° in the cases of 2-methyl-3-sulfonamido-5-furoic acid and 2-methyl-5-sulfonamido-3-furoic acid. The reaction mixture was taken up in 100 ml. of ether, and washed with dilute hydrochloric acid, and then with water. After evaporation of the ether there remained the respective sulfonamides, furan-2-sulfonamide, m.p. 121–122° (5); 2-methylfuran-5-sulfonamide, m.p. 117°; and 2-methylfuran-3-sulfonamide, m.p. 115°. See Table III.

Preparation of lithium furan-2-sulfinate. Butyllithium (0.5 mole) was prepared from 8.3 g. of lithium wire and 80 g. of *n*-butyl bromide by the usual procedure (11). This was added to 40 g. of furan and the mixture refluxed for four hours. Using a Dry Ice-acetone bath, sulfur dioxide was then passed through the solution at −25 to −30°. The yellow solid that separated was removed by decantation and washed thoroughly with acetone. There was obtained 32 g. (48%) of lithium furan-2-sulfinate.

Oxidation of the sulfinate. To an aqueous solution of lithium furan-2-sulfinate (13.8 g.) (0.1 mole) was added an aqueous solution of 10.6 g. of potassium permanganate at room temperature. The temperature was not allowed to rise during the addition. The manganese dioxide was filtered and the filtrate was evaporated to dryness after careful neutralization with dilute hydrochloric acid. The residue was extracted with hot ethanol and, after the evaporation of the alcohol, there was obtained 12.8 g. of a light yellow solid which was converted to 1.0 g. of furan-2-sulfonamide, m.p. 121–122°, by the previously described procedure. The over-all yield of the sulfonamide was 7% based on the lithium furan-2-sulfinate.

Replacement reactions with fuming nitric acid. The method used was that of Hill and White (8) with some modifications. 5-Sulfo-2-furoic acid (62 g.) was slowly added to 200 g. of fuming nitric acid (*sp. gr.* 1.5) while cooling. After standing several hours at room temperature, the excess nitric acid was removed by gentle heating. On cooling, the mixture almost completely solidified. The white solid was filtered, washed, dissolved in ether, and extracted with 5% sodium carbonate solution. The ether extract yielded 1 g. of 2,5-dinitrofuran, m.p. 102–102.5° (8). Acidification of the sodium carbonate solution gave 20.2 g. (40%) of 5-nitro-2-furoic acid, m.p. 181–182° (8).

5-Sulfonamido-2-furoic acid (10.6 g.) was added portionwise to 50 g. of fuming nitric acid and treated as above. Evaporation of the ether solution yielded only a small amount of red oil. Acidification of the sodium carbonate solution gave 1.5 g. (20%) of 5-nitro-2-furoic acid, m.p. 181–182°.

The barium salt of furan-2,5-disulfonic acid (39.6 g.) was added to 120 g. of fuming nitric acid and treated in the manner previously described. There was obtained 2.1 g. of 2,5-dinitrofuran (11%), m.p. 102–102.5°.

SUMMARY

The sulfonation method of Terent'ev and Kazitsyna has been investigated and modifications of this reaction have been described. The structures of some of the furansulfonic acids have been demonstrated. The preparation of the furansulfonic acid *p*-toluidine salts and the furansulfonamides has been described. Studies on the displacement reactions of the furansulfonic acids have been reported.

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REFERENCES

(1) HILL AND PALMER, *Am. Chem. J.*, **10,** 373, 409 (1889).

(2) TERENT'EV AND KAZITSYNA, *J. Gen. Chem. U. R. S. S.*, **18,** 723 (1948) [*Chem. Abstr.*, **43,** 214 (1949)]; *Compt. rend. Acad. Sci. U. R. S. S.*, **51,** 603 (1946) [*Chem. Abstr.*, **41,** 2033 (1947)].

(3) TERENT'EV AND KAZITSYNA, *J. Gen. Chem. U. R. S. S.*, **19,** 531 (1949) [*Chem. Abstr.*, **43,** 7015 (1949)].

(4) TERENT'EV, KAZITSYNA, AND TUROVSKAYA, *Vestnik Moskov Univ.*, **3,** 159 (1948). [*Chem. Abstr.*, **44,** 5862 (1950)].

(5) CINNEIDE, *Nature*, **160,** 260 (1946).

(6) HILL AND SYLVESTER, *Am. Chem. J.*, **32,** 190 (1905).

(7) TRUCE AND WELLISCH, *J. Am. Chem. Soc.*, **74,** 5177 (1952).

(8) HILL AND WHITE, *Am. Chem. J.*, **27,** 193 (1902).

(9) MEYER, *Ber.*, **3,** 112 (1870).

(10) GILMAN, GALLOWAY, AND SMITH, *Rec. trav. chim.*, **51,** 407 (1932).

(11) GILMAN, *et al.*, *J. Am. Chem. Soc.*, **71,** 1499 (1949).