

REACTIONS OF FLUORO OLEFINS

COMMUNICATION 17. COMPETING CONJUGATION IN PERFLUOROALKENYLPHOSPHONIC ESTERS

I. L. Knunyants, E. Ya. Pervova, and V. V. Tyuleneva

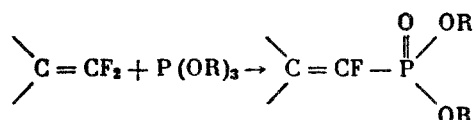
Institute of Heteroorganic Compounds, Academy of Sciences, USSR

 Translated from *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya* No. 9,

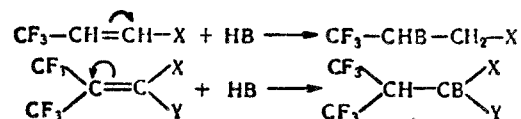
pp. 1576-1583, September, 1963

Original article submitted July 23, 1962

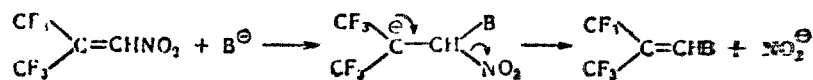
In a previous paper [1] we described a new method of preparing esters of fluorinated alkenylphosphonic acids of the formula below by the reaction of trialkyl phosphites with perfluoro olefins:



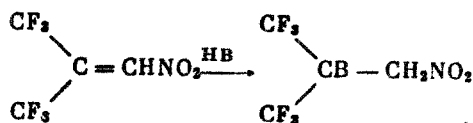
This paper is concerned with an investigation of the character of the polarization of the olefinic bond in perfluoropropenyl-, perfluoroisobutenyl-, and α -hydrohexafluoroisobutenyl-phosphonic esters. In the competition for conjugation with the olefinic bond one trifluoromethyl (or other perfluoroalkyl) group has less electron-withdrawing effect than other negative groups (carboxyl [2,3], alkoxycarbonyl [2,4], nitro [5]), and the negative part of the reagent undergoing addition goes into the α -position to the trifluoromethyl group. On the other hand, two trifluoromethyl groups have a stronger electron-withdrawing effect than other negative groups (carboxyl [6], alkoxycarbonyl [6,7], two alkoxycarbonyl [8], keto [9], nitro [8]).



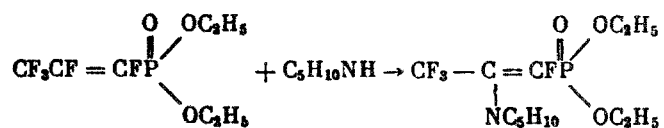
Here it must be remembered that in the cases enumerated the true addition of the nucleophilic reagent does not always occur. Thus, in the reaction of nucleophilic reagents with 2-nitro-1, 1-bistrifluoromethylethylene replacement of the nitro group occurs [8]. In this case the intermediately formed anion is stabilized not by the addition of a proton, but by the rejection of nitrite ion.



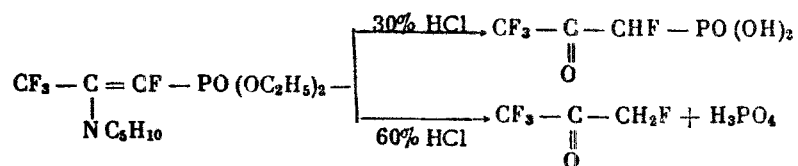
This case also provides an illustration of the more powerful electron-withdrawing effect of two trifluoromethyl groups. If this effect had been weaker than the effect of the nitro group, than the nucleophilic reagent would have added in the β -position:



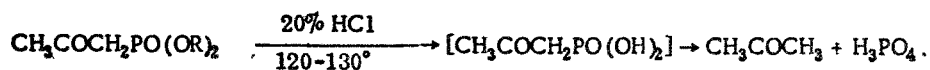
On the basis of the behavior of the diethyl esters of perfluoropropenyl-, perfluoroisobutenyl-, and α -hydrohexafluoroisobutenyl-phosphonic acids we have studied the competition for conjugation with the olefinic bond between, on the one hand, one or two trifluoromethyl groups, on the other, the esterified phosphono group. The reaction of diethyl perfluoropropenylphosphonate with piperidine at 0° leads to diethyl 2-piperidinotetrafluoropropenylphosphonate:



The structure of the ester obtained was proved by its hydrolysis by 60% sulfuric acid to tetrafluoroacetone. Under milder conditions we isolated the product of partial hydrolysis—the corresponding β -keto phosphonic acid.

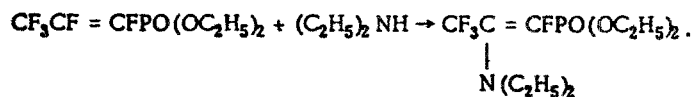


Similar breakdown of the simplest β -keto phosphonic ester was described by B. A. Arbuzov and co-workers [10], but in this case the free β -keto phosphonic acid was not isolated:

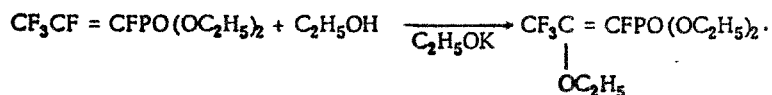


Here we again see the analogy between the phosphono and carboxy groups that we noted by A. E. Arbuzov [11]: β -keto phosphonic acids behave like β -keto carboxylic acids.

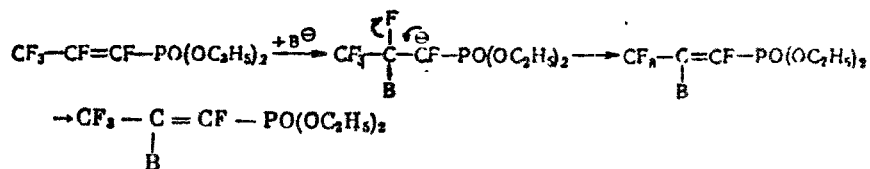
Diethylamine also reacts with perfluoropropenylphosphonic ester with formation of diethyl 2-diethylaminotetrafluoropropenylphosphonate:



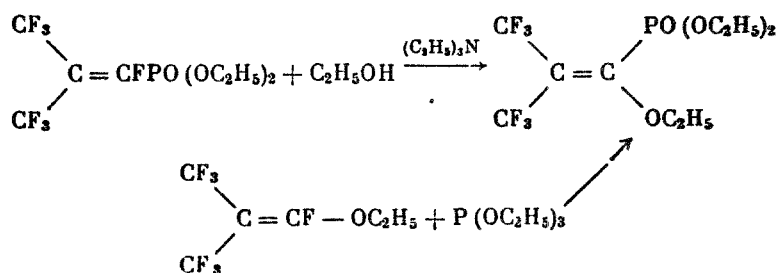
Perfluoropropenylphosphonic ester does not react with ethanol in presence of triethylamine. In presence of potassium ethoxide reaction leads to diethyl 2-ethoxytetrafluoropropenylphosphonate:



Hence, the esterified phosphono group has a more powerful electron-withdrawing effect than one trifluoromethyl group: the nucleophilic reagent attacks the carbon atom adjacent to the trifluoromethyl group. The anion is stabilized by the rejection of a fluoride ion, and the reaction results in the formation of the product of the replacement of vinyl fluorine, i.e. a β -substituted perfluoropropenylphosphonic ester:

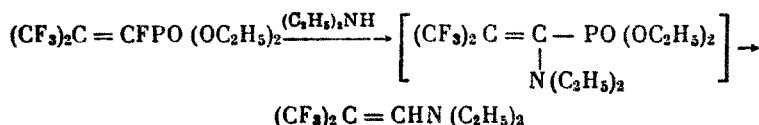


Diethyl perfluoroisobutenylphosphonate behaves quite differently. Its reaction with ethanol in presence of triethylamine gives diethyl α -ethoxyhexafluoroisobutenylphosphonate. This compound was obtained also from 1-ethoxy-1,3,3,3-tetrafluoro-2-(trifluoromethyl)propene and triethyl phosphite; the infrared spectra of the two samples were found to be identical.

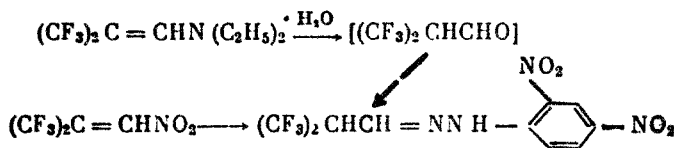


By the action of ethanol in presence of sodium ethoxide the fluorine atoms in diethyl perfluoroisobutenylphosphonate are completely mineralized, which is usual for such compounds [12]

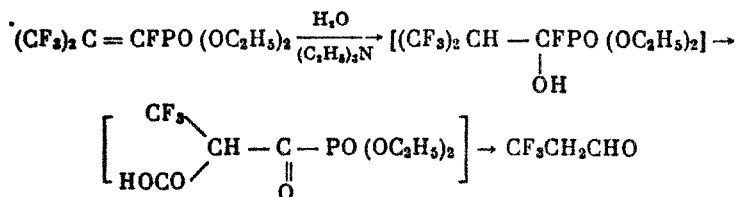
The action of diethylamine on diethyl perfluoroisobutenylphosphonate leads to *N*-(α -hydrohexafluoroisobutenyl) diethylamine:



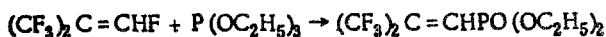
The C-P bond in the α -aminohexafluoroisobutenylphosphonic ester is evidently very weak and is broken under the action of excess of diethylamine. The structure of the enamine obtained was proved by its hydrolysis to α -hydrohexafluoroisobutyraldehyde; the 2,4-dinitrophenylhydrazone of this aldehyde was identical to the hydrazone prepared earlier [8] from 1-nitro-3,3,3-trifluoro-2-(trifluoromethyl) propene:



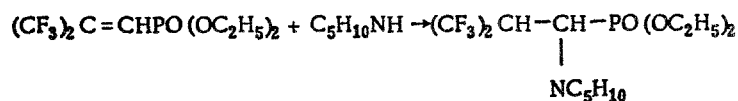
By the hydration of diethyl perfluoroisobutenylphosphonate in aqueous-dioxane solution in presence of triethylamine we obtained trifluoropropionaldehyde. It is evident that the hydroxyl adds at the α -carbon atom and the immediately formed α -hydroxy phosphonic ester is converted in an α -keto phosphonic ester with elimination of hydrogen fluoride. It is known [13] that under the action of alkaline agents α -keto phosphonic esters break down with formation of aldehydes. A similar reaction probably occurs in the present case, and also at some stage one of the trifluoromethyl groups is hydrolyzed to carboxyl and the resulting carboxylic acid is decarboxylated:



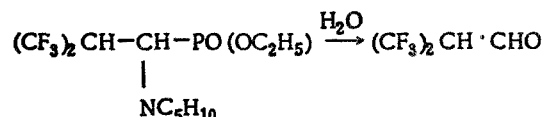
Another compound suitable for the study of the competing effect of two trifluoromethyl groups, on the one hand, and a phosphono group, on the other, in addition reaction of nucleophilic reagents is diethyl α -hydrohexafluoroisobutenylphosphonate. We synthesized this compound by the reaction of 1,3,3,3-tetrafluoro-2-(trifluoromethyl)propene with triethylphosphite:



Piperidine adds to α -hydrohexafluoroisobutenylphosphonic ester with formation of the corresponding α -substituted derivative



Boiling of diethyl α -piperidino- α , β -dihydrohexafluoroisobutylphosphonate with an alcoholic solution of 2,4-dinitrophenylhydrazine in presence of sulfuric acid leads to the 2,4-dinitrophenylhydrazone of α -hydrohexafluoroisobutyraldehyde.



It follows from the above that two trifluoromethyl groups have a more powerful electron-withdrawing effect than one phosphono group.

EXPERIMENTAL

Diethyl 2-Piperidinotetrafluoropropenylphosphonate. 15 g of diethyl perfluoropropenylphosphonate in 30 ml of dry ether was added slowly to a solution of 11 g of piperidine in 25 ml of dry ether with vigorous stirring and cooling to 0°. After one day piperidine hydrofluoride was filtered off, and by distillation of the filtrate we isolated 12.9 g (78%) of diethyl 2-piperidinotetrafluoropropenylphosphonate; b.p. 140° (8 mm); n_D^{20} 1.4310; d_4^{20} 1.298; found: MR 69.83; calculated; MR 70.32. Found: C 43.41; H 6.00; F 24.51; N 4.38%. $\text{C}_{12}\text{H}_{20}\text{F}_4\text{O}_3\text{NP}$. Calculated: C 43.24; H 6.00; F 22.82; N 4.20%.

Diethyl 2-Diethylaminotetrafluoropropenylphosphonate. This was prepared similarly to the preceding compound from 13.4 g of diethyl perfluoropropenylphosphonate and 15.6 g of diethylamine in 100 ml of dry ether. Yield 12.3 g (70%); b.p. 108-109° (6 mm); n_D^{20} 1.4120; d_4^{20} 1.184; found MR 67.61; calculated MR 66.90. Found: C 40.74; H 6.28; F 23.78%. $\text{C}_{11}\text{H}_{20}\text{F}_4\text{NO}_3$. Calculated: C 41.12; H 6.23; F 23.67%.

Aniline 1-Hydro-2-oxotetrafluoropropylphosphonate. 10 g of diethyl 2-piperidinotetrafluoropropenylphosphonate was heated with 30 ml of concentrated hydrochloric acid in a boiling water bath for 24 hours. The hydrolyzate was extracted with ether in an extractor for 20 hours. Ether was distilled off, and the residue was treated with aniline. We obtained the aniline salt; yield 7.6 g (84%); m.p. 146-147° (from acetonitrile). Found: C 35.38; 35.28; H 4.10, 4.07; F 24.76; 24.61; N 4.62; 4.61%. $\text{C}_9\text{H}_{10}\text{F}_4\text{NO}_4$. Calculated: C 35.64; H 3.26; F 25.08; N 4.63%.

Tetrafluoroacetone. 19.5 g of diethyl 2-piperidinotetrafluoropropenylphosphonate was boiled for 12 hours with 35 ml of 60% sulfuric acid. The hydrolyzate was extracted with ether for 72 hours. Ether was distilled off, and concentrated sulfuric acid was added to the residue. Distillation gave 5.2 g (74%) of tetrafluoroacetone, b.p. 50-51°; 2,4-dinitrophenylhydrazone, m.p. 146-147° (from aqueous alcohol). Found: C 34.90; H 1.98; F 24.32; N 18.02%. $\text{C}_9\text{H}_6\text{F}_4\text{H}_4\text{O}_5$. Calculated: C 34.83; H 1.61; F 24.51; N 18.06%. A mixture with the 2,4-dinitrophenylhydrazone of a known sample of tetrafluoroacetone [14] melted without depression.

Diethyl 2-Ethoxytetrafluoropropenylphosphonate. A solution of 1.2 g of potassium hydroxide in 15 ml of absolute alcohol was heated to 40°, and 11 g of diethyl perfluoropropenylphosphonate was added. After 20 hours potassium fluoride was filtered off (1 g), the filtrate was diluted with water, and the organic layer was separated and dissolved in ether. The ether layer was washed with water and dried. Ether was driven off, and two fractionations gave 3.8 g of unchanged diethyl perfluoropropenylphosphonate, b.p. 80-81° (6 mm) and n_D^{20} 1.3760, and 4 g (54%, based on the amount of the original ester that reacted) of diethyl 2-ethoxytetrafluoropropenylphosphonate; b.p. 110-111° (4 mm); n_D^{20} 1.3930; d_4^{20} 1.275; found MR 55.25; calculated MR 54.57. Found: C 36.68; 36.57; H 5.22; 4.98; F 26.56; 26.43%. $\text{C}_9\text{H}_{15}\text{F}_4\text{O}_4\text{P}$. Calculated: C 36.61; H 5.09; F 25.76%.

Diethyl α -Ethoxyhexafluoroisobutenylphosphonate. 15 g of diethyl perfluoroisobutenylphosphonate was added with stirring and cooling with cold water to a solution of 4.5 g of triethylamine in 20 ml of absolute alcohol. After 20 hours triethylamine hydrochloride was filtered off, the filtrate was poured into water, and the organic layer was

separated, washed with water, and dried. After the removal of ether fractional distillation gave 12.1 g (72%) of diethyl α -ethoxyhexafluoroisobutenylphosphonate; b.p. 111-112° (7 mm); n_D^{20} 1.3910; d_4^{20} 1.317; found MR 62.22; calculated MR 61.88. Found: C 34.78; 34.76; H 4.38; 4.42; F 32.67; 32.96%. $C_{10}H_{15}F_6O_3P$. Calculated: C 34.78; H 4.33; F 33.04%.

A mixture of 8.3 g of triethyl phosphite and 17 g of 1-ethoxy-1,3,3,3-tetrafluoro-2-(trifluoromethyl)propene was heated in an autoclave in a boiling water bath for eight hours. A low-boiling fraction was distilled from the mixture at room temperature under a residual pressure of 20 mm. The residue was dissolved in ether, and the ethereal solution was washed with sodium bicarbonate solution and with water and then dried. Fractional distillation gave 6.0 g of the original ethoxy tetrafluoro (trifluoromethyl)propene, b.p. 113-114° and n_D^{20} 1.3240, and 5.9 g [38.0% based on the amount of the ethoxytetrafluoro-(trifluoromethyl)propene that reacted] of diethyl α -ethoxyhexafluoroisobutenylphosphonate; b.p. 94-95° (2 mm); n_D^{20} 1.3910; d_4^{20} 1.315. The infrared spectrum of the product was identical with that of the α -ethoxyhexafluoroisobutenylphosphonic ester obtained from diethyl perfluoroisobutenylphosphonate.

N-(α -Hydrohexafluoroisobutenyl)diethylamine. 14 g of diethyl perfluoroisobutenylphosphonate in 30 ml of dry ether was added to a solution of 14.6 g of diethylamine in 50 ml of dry ether at room temperature. After a few days diethylamine hydrofluoride was filtered off. Distillation of the filtrate gave 5.6 g (54.4%) of N-(α -hydrohexafluoroisobutenyl)diethylamine; b.p. 59-60° (5 mm); n_D^{20} 1.3820; d_4^{20} 1.280; found MR 42.5; calculated MR 42.46; Found: C 41.29; 41.21; H 4.91; 4.88; F 47.09; 47.02; N 6.16; 6.07%. $C_8H_{11}F_6N$. Calculated: C 41.60; H 4.80; F 49.50; N 5.98%. In addition we obtained a fraction of b.p. 60-90° (5 mm); this was not investigated further.

2,4-Dinitrophenylhydrazone of α -Hydrohexafluoroisobutyraldehyde. A small amount of N-(α -hydrohexafluoroisobutenyl)diethylamine was boiled with an excess of an alcoholic solution of 2,4-dinitrophenylhydrazine in presence of sulfuric acid. The precipitate formed was crystallized from heptane; the hydrazone had m.p. 115-116°, undepressed by admixture of a known sample [8]. Found: C 33.67; 33.49; H 1.57; 1.72; F 30.98; 30.56%. $C_{10}H_6F_6O_4N_4$. Calculated: C 33.34; H 1.68; F 31.65%. The 2,4-dinitrophenylhydrazone of α -hydrohexafluoroisobutyraldehyde was prepared also from diethyl α -piperidino- α , β -dihydrohexafluoroisobutylphosphonate (see below).

2,4-Dinitrophenylhydrazone of 3,3,3-Trifluoropropionaldehyde. 1.4 g of triethylamine was added cautiously to a solution of 14 g of diethyl perfluoroisobutenylphosphonate in 18 ml of dioxane and 2 ml of water; much heat was evolved, and the mixture came to the boil. After one day the mixture was treated with excess of an alcoholic solution of 2,4-dinitrophenylhydrazine in presence of sulfuric acid. We obtained 5.45 g (44%) of the 2,4-dinitrophenylhydrazone of 3,3,3-trifluoropropionaldehyde, m.p. 148-149° (from heptane). The literature [15] gives m.p. 150.2-150.8°. Found: C 37.31; H 2.43; F 17.96%. $C_9H_7F_3O_4N_4$. Calculated: C 36.96; H 2.38; F 19.50%.

Diethyl α -Hydrohexafluoroisobutenylphosphonate. A mixture of 25 g of triethyl phosphite and 18.0 g of 1,3,3,3-tetrafluoro-2-(trifluoromethyl)propene was kept at room temperature in an autoclave for 16 hours. A low-boiling fraction was driven from the mixture at room temperature under a residual pressure of 20 mm. The residue was dissolved in ether, and the ethereal solution was washed with sodium bicarbonate solution and with water, and was dried. Distillation gave 10 g (40%) of diethyl α -hydrohexafluoroisobutenylphosphonate; b.p. 80-82° (6 mm); n_D^{20} 1.3765; d_4^{20} 1.321; found MR 52.20; calculated MR 50.78. Found: C 31.64; 31.80; H 4.22; 4.36; F 37.10; 36.91; P 9.74%. $C_8H_{11}F_6O_3P$. Calculated: C 32.00; H 3.66; F 38.00; P 9.68%.

Diethyl α -Piperidino- α , β -dihydrohexafluorobutylphosphonate. 7.8 g of diethyl α -hydrohexafluoroisobutenylphosphonate was added gradually to a solution of 3.4 g of piperidine in 20 ml of dry ether. After 24 hours the mixture was distilled and gave 7.6 g (76%) of diethyl α -piperidino- α , β -dihydrohexafluoroisobutylphosphonate; b.p. 60-62° (0.1 mm); n_D^{20} 1.4120; d_4^{20} 1.2182; found MR 77.87; calculated MR 76.12. Found: C 40.18; 39.86; H 6.14; 6.24; F 26.93; 27.08; N 3.13; 3.14; P 8.66; 8.34%. $C_{13}H_{22}F_6NO_3P$. Calculated: C 40.50; H 5.88; F 29.34; N 3.81; P 8.05%.

By boiling diethyl α -piperidino- α , β -dihydrohexafluoroisobutylphosphonate with excess of an alcoholic solution of 2,4-dinitrophenylhydrazine in presence of sulfuric acid we obtained the 2,4-dinitrophenylhydrazone of α -hydrohexafluoroisobutyraldehyde in 79% yield; m.p. 115-116° (from heptane). A mixture with a known sample [8] melted without depression.

SUMMARY

1. In competition for conjugation with an olefinic bond the phosphono group has a more powerful electron-withdrawing effect than the trifluoromethyl group. The reaction of diethyl perfluoropropenylphosphonate with various nucleophilic reagents leads to products in which a fluorine atom in the β -position relative to the phosphono group is replaced.

2. It was found that the electron-withdrawing effect of two trifluoromethyl groups is more powerful than the effect due to one phosphono group: in the reaction of diethyl perfluoroisobutenylphosphonate with nucleophilic reagents it is the α -fluorine atom that is replaced; in the case of diethyl α -hydrohexafluoroisobutenylphosphonate, addition products are formed with nucleophilic reagents, i.e. α -substituted- α , β -dihydrohexafluoroisobutylphosphonic esters.

LITERATURE CITED

1. I. L. Knunyants, E. Ya. Pervova and V. V. Tyuleneva, Dokl. AN SSSR 129, 576, (1959).
2. H. Walborsky and M. Scharz, J. Amer. Chem. Soc. 75, 3241 (1953).
3. E. McBee, O. Pierce, and D. Smith, J. Amer. Chem. Soc. 76, 3722 (1954).
4. H. Walborsky and M. Baum, J. Organ. Chem. 21, 539 (1956).
5. D. Cook, O. Pierce, and E. McBee, J. Amer. Chem. Soc. 76, 83 (1954).
6. I. L. Knunyants and Yu. A. Cheburkov, Izv. AN SSSR. Otd. khim. n. 2162 (1960).
7. I. L. Knunyants and Yu. A. Cheburkov, Izv. AN SSSR. Otd. khim. n. 1516 (1960).
8. Ch'ên Ch'ing-yün, N. P. Gambaryan and I. L. Knunyants, Dokl. AN SSSR 133, 1113 (1960).
9. V. F. Plaskhova and N. P. Gambaryan, Izv. AN SSSR. Otd. khim. n. 681 (1962).
10. A. E. Arbuzov, Zh. russk. fiz. obshch. 59, 243 (1927).
11. B. A. Arbuzov, B. P. Lugovkin and N. P. Bogonostseva, Zh. obshch. khimii 20, 1468 (1950).
12. M. W. Buxton, M. Stacey, and I. C. Tatlow, J. Chem. Soc. 366 (1954).
13. M. I. Kabachnik and P. A. Rossiiskaya, Izv. AN SSSR. Otd. khim. n. 365 (1945).
14. E. McBee, O. Pierce, H. Kilbourne, and E. Wilson, J. Amer. Chem. Soc. 75, 3152 (1953).
15. H. Shechter and F. Conrad, J. Amer. Chem. Soc. 72, 3371 (1950).

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-to-cover English translations appears at the back of this issue.
