rotary evaporator to crystallize the dinitrile; the crude product was dried over calcium chloride to give 10.2 g (96%) of dehydroadiponitrile, mp 72–74° (lit.[12] 76°). Recrystallization from ethanol or sublimation gave white needles, mp 75–76°. *Anal.* Calcd for $C_6H_8N_2$: C, 67.90; H, 5.70; N, 26.40. Found: C, 68.36; H, 5.92; N, 25.86. The dinitrile was shown to be identical with an authentic sample by comparative analytical techniques. The isomeric purity was established by vpc (2 ft × 0.25 in. 10% silanized polypropylene glycol column, 160°, 250-ml/min helium flow; t_R[13] 2.8 min from air) and by nmr: δ 5.83 (m, 2, J = 11.5 Hz, HC=CH) and 3.18 (m, 4, CH_2CN).

The dinitrile–copper(I) iodide complex was also degraded by vacuum sublimation [100° (50 mm)] or by treatment with aqueous hydrocyanic acid. In the latter case 20–40 g of complex was suspended in 100–300 ml of chloroform and 400–500 ml of 2% hydrocyanic acid. The mixture was stirred at room temperature for 1 hr and the two phases were separated. The chloroform layer contained 30% of the free dinitrile. From the aqueous layer the undecomposed complex and copper(I) cyanide were recovered. Air oxidation of the aqueous phase liberated iodine, which was assayed by thiosulfate titration and shown to be equivalent to the amount of nitrile liberated and copper(I) cyanide produced. The total material balance on the reaction was generally ~95%.

Acetonitrile was substituted for *n*-heptane as the reaction diluent. The reaction was agitated at 60° for 1 hr, and the mixture was poured into 10% sodium thiosulfate solution and extracted with methylene chloride (three 100-ml portions). The extract was dried over magnesium sulfate; the solvent was removed on a rotary evaporator to give 8.8 g (84%) of 1,4-dicyanobutene-2. From the aqueous phase was recovered 34.5 g of copper(I) salts.

Reaction of Butadiene with Copper(II) Bromide and Copper(I) Cyanide.—Into a Parr low-pressure reactor were charged 100 ml of *n*-heptane, 44.6 g (0.2 mol) of copper(II) bromide, and 0.3 mol of butadiene. The reactor was rocked at 75° for 90 min. The reaction mixture was filtered, and the filter cake was rinsed with pentane to give 29.3 g of copper(I) bromide (theory, 28.6 g). The pentane washings were combined with the filtrate, and the hydrocarbon solvents were removed on a rotary evaporator. The yield of crystalline dibromobutenes was 19.0 g (89%); the product was identified by comparative analytical techniques. Vpc analysis (1 m × 0.25 in. 20% silicone DC-200, 100°, 145 ml/min) gave the following isomer distribution: 3,4-dibromobutene-1, t_R 4.4 min (13%); *cis*-1,4-dibromobutene-2, t_R 9.0 min (5%); *trans*-1,4-dibromobutene-2, t_R 9.8 min (82%).

The bromination reaction was repeated in *n*-nonane at 75° for 45 min. The reaction was filtered, and the filtrate was added to 18 g (0.2 mol) of copper(I) cyanide. This reaction mixture was stirred at 130° for 5 hr. Filtration gave 34.7 g of a mixture of unreacted copper(I) cyanide and dehydroadiponitrile di[copper(I) bromide], which corresponded to an 80% yield of dinitrile. Degradation of the complex released the isomerically pure 1,4-dicyanide, which was identical with an authentic sample.

Registry No.—Dehydroadiponitrile, 1119-85-3.

(12) W. Reppe, *Justus Liebigs Ann. Chem.*, **596**, 133 (1955).
(13) t_R = retention time.

Reaction of *sym*- and *unsym*-Phthaloyl Chloride with *tert*-Butyl Hydroperoxide[1a]

NICHOLAS A. MILAS[1b] AND RAINER J. KLEIN*[2]

*Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139*

The reaction of *tert*-alkyl, *tert*-aralkyl, and acyl chlorides with *tert*-alkyl hydroperoxides to form the cor-

(1) (a) Organic Peroxides. XL. (b) Deceased, Jan 25, 1971.
(2) Postdoctorate Research Associate, 1962–1964; Gundelhardtstrasse 41, 6233 Kelkheim/Taunus, West Germany.

responding peroxides and peroxy esters is usually carried out in the presence of an organic or inorganic base[3] in order to avoid decomposition of the hydroperoxide by the hydrogen chloride liberated. In previous papers[4,5] we have shown that the addition of a base can be omitted by carrying out the solvolysis reaction under reduced pressure in a rotary evaporator at 50–70° and thereby removing the hydrogen chloride as soon as it is formed. Using this technique, substantial yields of di-*tert*-alkyl and mixed *tert*-alkyl aralkyl peroxides and peroxy esters have been prepared from the corresponding *tert*-alkyl chlorides, *tert*-aralkyl chlorides, and acid chlorides with *tert*-butyl hydroperoxide. We report here the solvolysis of phthaloyl chlorides with *tert*-butyl hydroperoxide.

The solvolysis of symmetrical phthaloyl chloride with *tert*-butyl hydroperoxide proceeds exothermically and produces a mixture of mono-*tert*-butyl peroxy hydrogen phthalate (I), di-*tert*-butyl diperoxyphthalate (II), and 3,3-di-*tert*-butyl diperoxyphthalide (III). Peroxy esters I and II have been reported in the literature;[6,7] 3,3-di-*tert*-butyl diperoxyphthalide (III), isomeric with
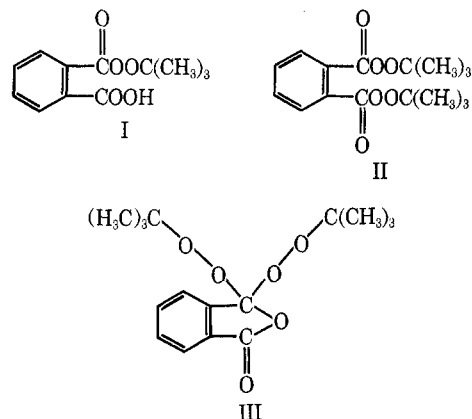
II, appears to be a new peroxide. The structure of III is based on elemental analysis, ir and nmr spectra, and hydrolysis experiments. The ir spectrum (10% in carbon tetrachloride) exhibits aromatic, *tert*-butyl peroxy, and carbonyl absorption. Compound III shows strong carbonyl absorption at 1803 cm⁻¹; compound II shows carbonyl absorption at 1772 cm⁻¹, expected for a peroxy ester. The observed carbonyl frequency for III at 1803 cm⁻¹ is attributed to the γ-lactone structure in which the CO absorption of the γ-lactone has been shifted to higher frequencies by the electron-attracting peroxy groups. Compound III fails to give a positive test for a peroxy ester with an acidified sodium iodide solution in the presence of catalytic amounts of ferrous ions.[8] Alkaline hydrolysis affords *tert*-butyl hydroperoxide and phthalic acid.

The nmr spectrum of III (25% in carbon tetrachloride, TMS) shows a single peak for the (equivalent) aliphatic protons at 1.26 ppm. The aromatic proton

(3) E. G. Hawkins, "Organic Peroxides," Van Nostrand, New York, N. Y., 1961; A. G. Davies, "Organic Peroxides," Butterworths, London, 1961.
(4) N. A. Milas, D. G. Orphanos, and R. J. Klein, *J. Org. Chem.*, **29**, 3099 (1964).
(5) N. A. Milas, R. J. Klein, and D. G. Orphanos, *Chem. Ind. (London)*, 423 (1964).
(6) A. G. Davies, R. V. Foster, and A. M. White, *J. Chem. Soc.*, 1541 (1953).
(7) N. A. Milas and D. G. Surgenor, *J. Amer. Chem. Soc.*, **68**, 6426 (1946).
(8) D. Swern and L. S. Silbert, *Anal. Chem.*, **30**, 385 (1958).

peak shows splitting, indicating the nonequivalence of these protons. The integration curve shows a ratio of aromatic/aliphatic protons of 4/18, in excellent agreement with the proposed structure III. The nmr spectrum of the symmetrical di-*tert*-butyl diperoxyphthalate (II) shows aliphatic and aromatic proton absorption at 1.36 and 7.86 ppm, respectively, but without splitting.

When the unsymmetrical phthaloyl dichloride[9] was allowed to undergo solvolysis with *tert*-butyl hydroperoxide, a mixture of di-*tert*-butyl diperoxyphthalate (II) and 3,3-di-*tert*-butyl diperoxyphthalide (III) was formed which was separated into its pure components by column chromatography. When the reaction was carried out under basic conditions, the symmetrical diperoxy ester II was formed exclusively. Similarly, when the symmetrical phthaloyl chloride was allowed to react with *tert*-butyl hydroperoxide in the presence of a base, the formation of III was completely suppressed and only the perester II was obtained. Under acidic conditions both symmetrical and unsymmetrical chlorides form essentially the same product mixture II and III.

Experimental Section

Solvolysis of Symmetrical Phthaloyl Chloride with *tert*-Butyl Hydroperoxide.—Freshly distilled phthaloyl chloride (8.2 g, 0.04 mol) was mixed with *tert*-butyl hydroperoxide[10] (9.0 g, 0.10 mol, 99% pure) and the mixture allowed to stand for 15–20 min and then subjected to a vacuum (60 mm) on a rotary evaporator. The reaction proceeded with strong evolution of heat and gas and as soon as it subsided, the mixture was heated at 50–60° for 3 hr. *tert*-Butyl hydroperoxide (6.0 g, 0.067 mol) was then added and the reaction allowed to continue overnight at room temperature on a rotary vacuum evaporator. The excess hydroperoxide was then removed by subjecting the reaction mixture to a vacuum of 2 mm. The residue, a colorless, viscous liquid, was dissolved in ether and shaken several times with 5% sodium bicarbonate solution. The bicarbonate layer was acidified with 10% sulfuric acid and extracted with ether, and the ethereal solution washed with water and dried over magnesium sulfate. Evaporation of the solvent under reduced pressure yielded a white solid, which was recrystallized from a 70:30 mixture of petroleum ether (bp 30–60°) and ethyl ether, mp 104–105°, yield 4.7 g (49%), and identified as mono-*tert*-butyl peroxyhydrogen phthalate.[6] Its ir spectrum (10% in chloroform) showed the following bands: 3500, 3000, 2989, 1762, 1705, 1598, 1583, 1492, 1448, 1411, 1367, 1238, 1186, 1139, 1102, 1055, 1025, 911, 833 cm⁻¹.

The ether layer was washed with water and dried over magnesium sulfate and the solvent removed under reduced pressure. A colorless, viscous liquid was obtained which failed to crystallize. Its ir spectrum (10% in carbon tetrachloride) showed two carbonyl bands at 1803 and 1772 cm⁻¹ suggestive of a mixture of two different peresters. Since we expected one of these to be the *sym*-di-*tert*-butyl diperoxyphthalate, we synthesized it by the standard procedure.[7] Instead of the reported mp 57–57.5°, the peroxy ester obtained melted sharply at 48°. An active oxygen determination[8] gave 10.08% (calcd, 10.31%). The ir spectrum of this perester (10% in carbon tetrachloride) showed the following bands: 2978, 2922, 1772, 1595, 1577, 1473, 1442, 1390, 1367, 1245, 1183, 1125, 1085, 1022, 835 cm⁻¹.

The colorless viscous liquid from the original experiment was passed through a silica gel column, employing a mixture of petroleum ether and ether (75:25) as eluent. The first eluate (combination of several fractions) yielded a viscous liquid which crystallized on standing. Recrystallization from a (75:25) mixture of petroleum ether and ethyl ether gave colorless crystals, mp 86–87°, yield 1.7 g (13.7%). This was identified as 3,3-di-*tert*-butyl diperoxyphthalide.

(9) E. Ott, "Organic Syntheses," Collect. Vol. II, Wiley, New York, N. Y., 1943, p 528.

(10) Kindly supplied by the Lucidol Division of Wallace and Tiernan, Inc., Buffalo, N. Y.

Anal. Calcd for $C_{16}H_{22}O_6$ (III): C, 61.92; H, 7.15; mol wt, 310.34. Found: C, 61.81; H, 7.05; mol wt, 309.0 (cryoscopic in benzene).

The infrared spectrum (10% in carbon tetrachloride) showed the following bands: 2988, 2928, 1803, 1609, 1470, 1392, 1370, 1347, 1286, 1258, 1198, 1139, 1103, 1067, 1047, 1028, 972, 942, 867, 694 cm⁻¹.

The nmr spectrum (25% in carbon tetrachloride using tetramethylsilane as internal standard) showed aliphatic protons at 1.26 ppm; aromatic protons at 7.71 ppm with splitting at 7.61, 7.68, 7.66, 7.79, 7.84 ppm. The nmr spectrum, under the same conditions, of the *sym*-di-*tert*-butyl diperoxyphthalate showed aliphatic and aromatic protons at 1.36 and 7.86 ppm, respectively, but without splitting.

The second eluate (combination of several fractions) also yielded a viscous liquid which crystallized on standing after several hours. Recrystallization from petroleum ether gave a product which had a mp 45–46° and identified as di-*tert*-butyl diperoxyphthalate[7] by ir spectra, mixture melting point, and a comparison of the R_f (0.542) on a paper chromatogram with an authentic sample.

Solvolysis of Unsymmetrical Phthaloyl Chloride with *tert*-Butyl Hydroperoxide.—Unsymmetrical phthaloyl chloride was prepared by heating symmetrical phthaloyl chloride with aluminum trichloride.[9] Unsymmetrical phthaloyl chloride (4.06 g, 0.02 mol) was mixed with *tert*-butyl hydroperoxide (14.40 g, 0.16 mol) and the mixture allowed to stand for 30 min and then subjected to a 60-mm vacuum on a rotary evaporator. As soon as the evolution of gas bubbles diminished, the reaction mixture was heated to 50–60° for 2 hr and then allowed to continue overnight at room temperature. The excess *tert*-butyl hydroperoxide was then removed by subjecting the mixture to a vacuum of 2 mm. The residue was separated as described above, affording 3,3-di-*tert*-butyl peroxyphthalide, yield 1.50 g (24.2%), mp 80–87° after recrystallization, and di-*tert*-butyl diperoxyphthalate, yield 0.44 g (7.10%), mp 40–46°, identified by mixture melting point, R_f, and ir.

Reaction of Unsymmetrical Phthaloyl Chloride with *tert*-butyl Hydroperoxide in the Presence of Pyridine.—Unsymmetrical phthaloyl chloride (2.03 g, 0.01 mol), dissolved in 10 ml of anhydrous ether, and *tert*-butyl hydroperoxide (3.60 g, 0.04 mol), likewise dissolved in 10 ml of anhydrous ether, were dropped simultaneously in the course of 0.5 hr to a solution of dry pyridine (1.58 g, 0.02 mol) in 20 ml of anhydrous ether at 0° with stirring. Pyridine hydrochloride precipitated during the addition. The reaction mixture was then allowed to warm to room temperature and stirring continued overnight. After separation of the pyridine hydrochloride by filtration, the ether was removed under reduced pressure leaving a colorless liquid which was subjected to a vacuum of 2 mm to remove the excess *tert*-butyl hydroperoxide. An ir spectrum taken of the final product revealed that di-*tert*-butyl diperoxyphthalate II was the only peroxidic product present. For further purification, the product was redissolved in ether, and the ether solution extracted with ice-cold 10% sodium hydroxide, the ether layer washed with water, dried over magnesium sulfate, and filtered, and the ether removed under reduced pressure, leaving a viscous liquid which crystallized on standing. The crystals were washed with petroleum ether and dried, mp 48°, and identified as di-*tert*-butyl diperoxyphthalate II, by mixture melting point and ir spectrum, yield 2.28 g (73.6%).

Effect of *tert*-Butyl Hydroperoxide on 3,3-Di-*tert*-butyl Diperoxyphthalide.—Since the unsymmetric 3,3-di-*tert*-butyl diperoxyphthalide contains a γ lactone ring, it was thought advisable to try the effect of *tert*-butyl hydroperoxide on this ring. Consequently, 0.2 g of 3,3-di-*tert*-butyl diperoxyphthalide was heated with stirring at 60–70° with excess *tert*-butyl hydroperoxide for 2.5 hr. The excess *tert*-butyl hydroperoxide was then removed at 2-mm pressure, whereby a slightly yellow viscous liquid separated which crystallized on standing. When the crystals were washed with petroleum ether and dried, they melted at 86° and were shown by melting point to be identical with the starting material.

Attempted Hydrolysis of 3,3-Di-*tert*-butyl Diperoxyphthalide by Acid.—Sulfuric acid (1 ml, 50% concentrated) was added to a stirred solution of 3,3-di-*tert*-butyl diperoxyphthalide (0.20 g) in 10 ml of ether at 0°. The mixture was stirred for 2 hr without cooling. Water was then added and the sulfuric acid neutralized with magnesium carbonate, the ether layer separated, dried over magnesium sulfate, and filtered, and the ether removed under

reduced pressure. White crystals were separated, mp 84–85°, and identified by mixture melting point as the starting material.

Basic Hydrolysis of 3,3-Di-*tert*-butyl Diperoxyphthalide.— 3,3-Di-*tert*-butyl diperoxyphthalide (0.10 g, 0.3 mol) was dissolved in 6 ml of ethylene glycol monomethyl ether and to the solution was added 0.8 ml of 10% aqueous sodium hydroxide. The reaction mixture was stirred for 2 hr at 40°; then, added to it successively were 15 ml of acetic acid, 3 ml of saturated potassium iodide solution, and a piece of Dry Ice. After standing for 0.5 hr at 60°, the iodine liberated was titrated with standard sodium thiosulfate. On the basis of formula III, 86.5% of the expected 2-mol equiv of *tert*-butyl hydroperoxide was found. In a separate experiment one of the hydrolysis products, phthalic acid, was isolated by extracting the acidified reaction mixture with ether and evaporating the solvent. A white solid was obtained, mp 186–187°, and identified as phthalic acid by mixture melting point.

Registry No.—I, 15042-77-0; II, 2155-71-7; III, 15044-23-2; *sym*-phthaloyl chloride, 88-95-9; *unsym*-phthaloyl chloride, 30247-86-0; *tert*-butyl hydroperoxide, 75-91-2.

Synthesis of Methyl
14-Methyl-*cis*-8-hexadecenoate and
14-Methyl-*cis*-8-hexadecen-1-ol. Sex Attractant
of *Trogoderma inclusum* LeConte

JOSEPH I. DEGRAW* AND J. OTTO RODIN

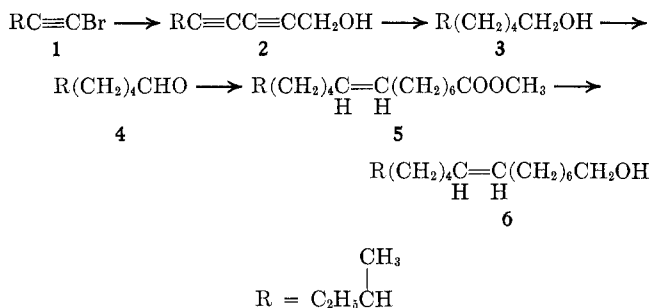*Life Sciences Research, Stanford Research Institute, Menlo Park, California 94025*

The title compounds have been previously identified[1] as components of the sex attractant of *Trogoderma inclusum* LeConte. Evidence has also been obtained that other *Trogoderma* species respond to these attractant compounds. Although the structures are relatively simple, their synthesis in acceptable yields is complicated by the unavailability of suitable starting materials for the branched portion of the chain. A convenient synthesis of the compounds is the subject of this communication.

Preparation of the key reagent, 6-methyloctanal (4), initiated with 3-methyl-1-pentyne which was brominated (NaOBr) to give the 1-bromoalkyne (1) in 80% yield. Coupling with propargyl alcohol afforded in 69% yield the diynol 2, which was easily hydrogenated to yield 6-methyloctan-1-ol (3). An alternate synthesis[2] of 3 from 4-oxo-6-methyloctanoic acid was impractical because of the difficulty in obtaining complete reduction of the keto group.

Several of the methods reported in recent years for the oxidation of primary alcohols to aldehydes were investigated for the conversion of 3 to the aldehyde 4. None were found to be acceptable; however, we were able to obtain 4 in good yield by a modification of the

(1) J. O. Rodin, R. M. Silverstein, W. E. Burkholder, and J. E. Gorman, *Science*, **165**, 904 (1969).

(2) J. Cason and F. S. Prout, *J. Amer. Chem. Soc.*, **66**, 46 (1944).

chromic acid–pyridine reagent. The yellow, solid complex was prepared in pyridine[3] and the excess pyridine was removed with hexane. The isolated solid was immediately dissolved in CH_2Cl_2 followed by addition of the alcohol. Yields of 60–70% of distilled aldehyde 4 were realized when a ratio of 6:1 of reagent to

$$RC\equiv CBr \longrightarrow RC\equiv CC\equiv CCH_2OH \longrightarrow R(CH_2)_4CH_2OH \longrightarrow$$
$$\quad\quad 1 \quad\quad\quad\quad\quad\quad 2 \quad\quad\quad\quad\quad\quad\quad 3$$

$$R(CH_2)_4CHO \longrightarrow R(CH_2)_4\underset{H}{C}=\underset{H}{C}(CH_2)_6COOCH_3 \longrightarrow$$
$$\quad\quad 4 \quad\quad\quad\quad\quad\quad\quad\quad\quad 5$$

$$R(CH_2)_4\underset{H}{C}=\underset{H}{C}(CH_2)_6CH_2OH$$
$$6$$

$$R = C_2H_5\overset{CH_3}{\underset{|}{C}H}$$

alcohol was employed. We have found the procedure to be quite reliable for the preparation of other, more complex aldehydes. A recently reported[4] variation of the related Collins reagent[5] appears to be equally effective and has an advantage in convenience.

The remainder of the carbon chain was inserted *via* the Wittig condensation of 6-methyloctanal (4) with the triphenylphosphinylide of methyl 8-bromooctanoate. When conducted in DMF solution[6] the olefinic ester product 5 was contaminated by only 5–10% undesired *trans* isomer. Reduction of the ester with LiAlH$_4$ in ether afforded the alcohol 6.

Experimental Section

1-Bromo-3-methyl-1-pentyne (1).—To a solution of 8.9 g of sodium hydroxide in 23 ml of water and 45 g of ice was added 4.9 ml of bromine over 5 min. The hypobromite solution, at 0–5°, was then added rapidly to 7.3 g of 3-methyl-1-pentyne, followed by the addition of 12 ml of pyridine. The mixture was stirred for 16 hr and extracted with 100- and 50-ml portions of ether. The ether was washed with 100 ml of water, 90 ml of 2 N HCl, 50 ml of water, and 30 ml of saturated sodium bicarbonate. After drying over magnesium sulfate the solvent was distilled off through a Vigreux head to leave 11.5 g (80%) of pale yellow liquid. A sample was distilled for analysis, bp 35–36° (24 mm).

Anal. Calcd for C$_6$H$_9$Br: C, 44.8; H, 5.63. Found: C, 44.8; H, 5.61.

6-Methyl-2,4-octadiyn-1-ol (2).—To an ice-cold mixture of 24.3 ml of 33% ethyl amine, 0.21 g of cuprous chloride, 0.43 g of hydroxylamine hydrochloride and 4.0 g (0.071 mol) of propargyl alcohol was added, dropwise with stirring, 11.5 g (0.071 mol) of crude bromopentyne (1). The yellow mixture was stirred for 16 hr at ambient temperature, becoming a blue-green color. After treatment with 0.75 g of potassium cyanide the now orange mixture was diluted with 150 ml of water and extracted twice with 60-ml portions of pentane. The pentane was washed with water (50 ml), dried over magnesium sulfate, and evaporated to leave 7.3 g of amber liquid. The material was distilled to afford 6.6 g (69%), bp 74–75° (1.25 mm), ir (film) intense 4.45 μ (conjugated diyne).

Anal. Calcd for C$_9$H$_{12}$O: C, 79.4; H, 8.88. Found: C, 79.4; H, 9.00.

6-Methyl-1-octanol (3).—A mixture of 1.00 g of diynol 2, 100 mg of platinum oxide, and 10 ml of ethanol was stirred under 1 atm of hydrogen for 18 hr. The theoretical amount of gas was consumed. The catalyst was removed and the solvent was evaporated *in vacuo* to leave 1.00 g of a clear liquid. The infrared

(3) G. I. Poos, G. E. Arth, R. E. Beyler, and L. H. Sarett, *ibid.*, **75**, 422 (1953).

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(6) L. D. Bergelson, V. A. Vaver, Y. Yu. Kovtun, L. B. Senyavina, and M. M. Shemyakin, *Zh. Obshch. Khim.*, **32**, 1802 (1962).