chelate ring involving the d-orbitals of the metal ion.

Another considerable change of the spectra resulting from metal chelate formation is found in the bands at 1283 and 1272 cm.$^{-1}$. Although the 1283 cm.$^{-1}$ band appears as a shoulder on the main band at 1272 cm.$^{-1}$, both bands are rather strong and are missing in the metal chelates. Hadzi[8] assigned the band at 1272 cm.$^{-1}$ to the in-the-plane bending mode of the C–O–H group. The fact that the corresponding band is missing in the metal chelates supports this assignment, and either one of these two bands is possibly due to the C–O–H group of the ligand.

No conclusive assignment of absorptions due to the azo linkage has been reported in the literature. Le Fèvre[11] and his co-workers have investigated some 43 aromatic diazonium and azo compounds and found common absorption bands at around 1406 and 1577 cm.$^{-1}$. The main difficulty in the assignment of a frequency to the azo linkage is that the absorption frequency of N=N stretching vibration would overlap with other absorptions such as those of the aromatic ring which are usually of strong intensity.

Of the absorption bands due to the azo linkage, a band corresponding to 1405 cm.$^{-1}$ was found in the polyazobenzenes which we have investigated,[1] and it is believed that this band can be assigned to the azo linkage with certainty. For azobenzene and *o*-hydroxyazobenzene, this absorption band is found at 1395 and 1418 cm.$^{-1}$, respectively. For the metal chelate compounds of *o*-hydroxyazobenzene, this band shifts to lower frequencies as shown in the Table II. The extent of shift is again found to be parallel to the order of decreasing stability of metal chelate compounds.

Acknowledgment.—The author wishes to express his sincere appreciation to Prof. A. E. Martell of Clark University, Worcester, Mass., who so generously carried out the measurement of infrared spectra.

KUMAMOTO-SHI, JAPAN

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[11] R. J. W. Le Fèvre, M. F. O'Dwyer and R. L. Werner, *Australian J. Chem.*, **6**, 341 (1953).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF FLORIDA STATE UNIVERSITY]

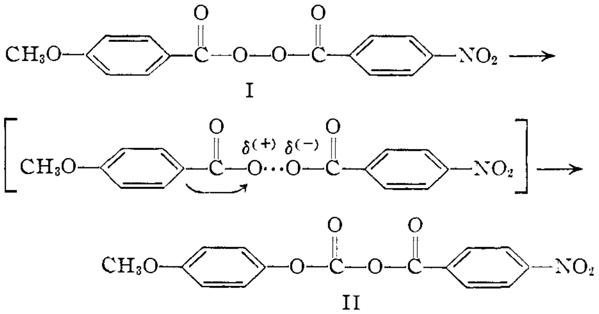
4-Methoxy-3',5'-dinitrobenzoyl Peroxide[1]

BY JOHN E. LEFFLER AND CONSTANTINE C. PETROPOULOS

RECEIVED DECEMBER 20, 1956

The decomposition of 4-methoxy-3',5'-dinitrobenzoyl peroxide is accelerated by a shift to a more polar solvent, by acids, and by 1,3,5-trinitrobenzene. Its behavior is compared with that of other diacyl peroxides.

The combined effect of the introduction of a *p*-methoxy and a *p*'-nitro substituent and the use of a polar solvent is sufficient to change the decomposition of benzoyl peroxide from a radical to a non-radical mechanism.[2] The non-radical decomposition is much more sensitive to the polarity of the solvent and can also be recognized from the products. The migration of *p*-methoxyphenyl from carbon to oxygen in the polar decomposition reduces the yield of anisic acid and its esters and in the case of thionyl chloride as a solvent produces the rearrangement or carboxy-inversion product (II).[2,3] The polar decomposition is accelerated by acids as well as by polar solvents.



Similar experiments have now been done with 4-methoxy-3,'5'-dinitrobenzoyl peroxide. This peroxide is even more sensitive to solvent changes, but the reaction is less clean cut.

The Effects of Substituents and Solvents.—Table I summarizes the combined effects of the various substituents and solvents on the first-order rate constants for the peroxide decomposition; the results are remarkably different from those obtained with symmetrical peroxides. The effects of solvent changes or of symmetrical *meta* or *para* substitution on the rate of homolysis of benzoyl peroxide are usually less than one order of magnitude. For example in acetophenone at 80° the rate constants range from 1.46×10^{-3} min.$^{-1}$ for bis-(*p*-cyanobenzoyl) peroxide to 9.32×10^{-3} min.$^{-1}$ for bis-(*p*-methoxybenzoyl) peroxide.[4] In the solvents benzene, acetophenone, dioxane and styrene the first-order constants of a given benzoyl peroxide are usually the same within a factor of two.[4–6] Benzoyl peroxide decomposes at the same rate in benzene and in nitrobenzene.[7] A drastic change in the rate of a diaroyl peroxide decomposition is therefore likely to mean a change in mechanism.

In benzene the 4-methoxy-4'-nitro substitution

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[1] This work was supported by a Frederick Gardner Cottrell grant from the Research Corporation.

[2] J. E. Leffler, THIS JOURNAL, **72**, 67 (1950).

[3] D. B. Denney, *ibid.*, **78**, 590 (1956).

[4] A. T. Blomquist and A. J. Buselli, *ibid.*, **73**, 3883 (1951).

[5] C. G. Swain, W. H. Stockmayer and J. T. Clarke, *ibid.*, **72**, 5426 (1950).

[6] W. Cooper, *J. Chem. Soc.*, 3106 (1951).

[7] K. Nozaki and P. D. Bartlett, THIS JOURNAL, **68**, 1686 (1946).

TABLE I

BENZOYL PEROXIDE DECOMPOSITION RATE CONSTANTS in sec.$^{-1}$ × 10^6

Substituents	Solvent Benzene	Nitrobenzene
None	32.8 at 79.8°^{a}	32.8 at 79.8°^{a}
	7.8 at 70°^{b}	
	0.44 at 51°^{b}	
4-CH_3O·4′-NO_2	20.8 at 70°^{c}	163 at 70°^{c}
4-CH_3O·3′,5′-$(NO_2)_2$	10.2 at 51°	961 at 51°^{d}

[a] K. Nozaki and P. D. Bartlett, THIS JOURNAL, **68**, 1686 (1946). [b] Estimated from E_{act} of reference (*a*). [c] Reference 2. [d] With 0.17 molar 1,3,5-trinitrobenzene added the rate constant is 1670 × 10^{-6} sec.$^{-1}$.

in the peroxide increases the rate by a factor of about 3 at 70°. The effect of substituents on the purely radical part of the rate can be estimated from data on symmetrically substituted benzoyl peroxides in dioxane[5] and in acetophenone,[4] except that there is undoubtedly some interaction of substituent and solvent effects even in the case of the radical reaction. Neglecting any perturbation by the difference in solvent, the 4-methoxy-4′-nitro substitution should decrease the purely radical decomposition rate somewhat. But the observed increase by a factor of three may not have any mechanistic significance since the reaction products in benzene are consistent with a purely radical decomposition. In nitrobenzene the same 4-methoxy-4′-nitro substituted peroxide decomposes about eight times as fast as in benzene. This might also be within the bounds of possible behavior for a radical reaction, but here the increase in rate is accompanied by a change in products suggesting an almost complete shift to the non-radical mechanism.[2]

The 4-methoxy-3′,5′-dinitro substitution has an even greater effect, producing a 23-fold acceleration in benzene at 51°. This is rather a large increase in rate for the radical reaction and suggests that this peroxide decomposes at least partly by a non-radical mechanism even in benzene. 4-Methoxy-3′,5′-dinitrobenzoyl peroxide decomposes in benzene without initiating the radical polymerization of styrene, although this might be due to the inhibitory effect of the dinitroaromatic compounds present. In nitrobenzene the 4-methoxy-3′,5′-dinitrobenzoyl peroxide decomposition at 51° is 94 times as fast as it is in benzene and about 2000 times as fast as the decomposition of benzoyl peroxide in benzene. Furthermore, 1,3,5-trinitrobenzene, a radical chain inhibitor, actually accelerates the reaction.

Acid Catalysis.—Figure 1 and Table II show the acceleration of the decomposition of 4-methoxy-3′,5′-dinitrobenzoyl peroxide by acids in benzene. The Brønsted plot of the catalysis in benzene (Fig. 1) is roughly linear with the expected exception of picric acid. Picrate ions (or ion pairs) are at a disadvantage relative to the un-ionized molecule because the latter should be more stabilized by π-complex formation with aromatic solvent molecules. Picric acid also has been observed to deviate from the Brønsted plot in the rearrangement of N-bromoacetanilide in benzene[8] and in the racemization of menthone in chlorobenzene.[9] In all three examples picric acid is less effective as a catalyst than would be predicted from its acid strength and by more than an order of magnitude. Our motive for including picric acid in the experiments is its well-known action as a radical inhibitor. However, we do not believe that the acid-

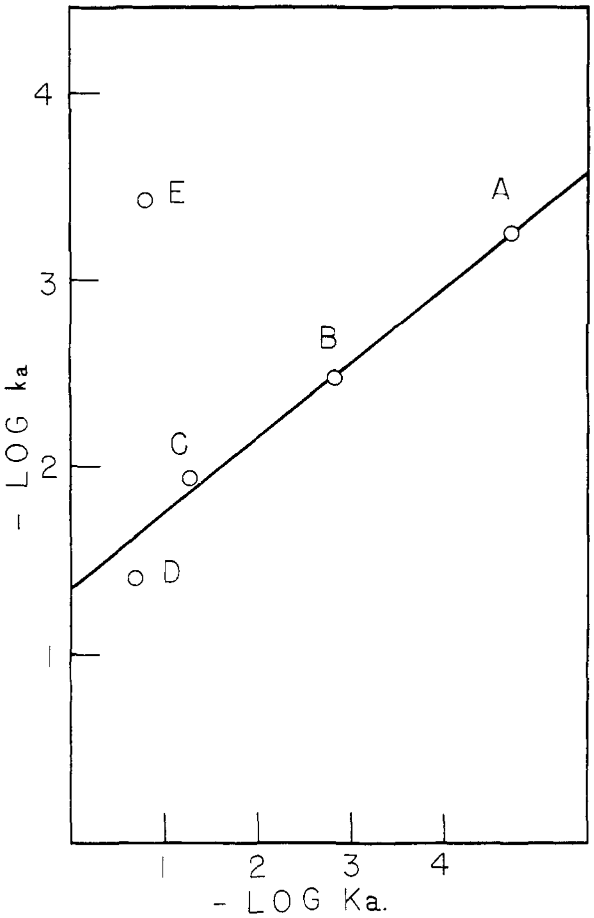

Fig. 1.—The Brønsted catalysis relationship for the acid-catalyzed decomposition of 4-methoxy-3′,5′-dinitrobenzoyl peroxide in benzene at 51°: A, acetic acid; B, chloroacetic acid; C, dichloroacetic acid; D, trichloroacetic acid; E, picric acid; k_a, the catalysis constant; K_a, the ionization constant of the catalyzing acid in water at 25°.

TABLE II

ACCELERATION OF THE DECOMPOSITION OF 4-METHOXY-3′,5′-DINITROBENZOYL PEROXIDE BY ACIDS AND COMPLEXING AGENTS

$k_{total} = k_1 + k_a$ [acid or complexing agent]

Acid or complexing agent	Catalysis constant,^{c} k_a sec.$^{-1}$ l. moles^{-1} × 10^6
Acetic acid	56.8^a
Chloroacetic acid	334^a
Dichloroacetic acid	1160^a
Trichloroacetic acid	3920^a
Picric acid	36.8^a
1,3,5-Trinitrobenzene	414^b
Acetic acid	1130^b

[a] In benzene as a solvent, 51°. [b] In nitrobenzene as a solvent, 51°. [c] The catalyst concentration was in the neighborhood of 0.17 *N*, the peroxide 0.01 *N*.

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(8) R. P. Bell, *Proc. Roy. Soc.* (*London*), **A143**, 377 (1934).

(9) R. P. Bell and E. F. Caldin, *J. Chem. Soc.*, 382 (1938).

catalyzed reaction is a radical one or that the picric acid anomaly is explicable as a compensating shortening of radical chains.

Acetic acid also has been studied as a catalyst for the decomposition of 4-methoxy-3′,5′-dinitrobenzoyl peroxide in nitrobenzene, where it is found to be much more effective than in benzene. Apparently the degree of charge separation in the transition state for the acid-catalyzed reaction is even greater than it is for the uncatalyzed polar reaction. 1,3,5-Trinitrobenzene (0.17 molar) also accelerates the decomposition in nitrobenzene, probably by π-complex formation, a phenomenon in some ways analogous to catalysis by proton donors. Since the acceleration by trinitrobenzene was so large (more than a third of that produced by the same concentration of acetic acid), it is likely that the minor catalysis by picric acid in benzene is partly due to π-complexing rather than to the acidity of the picric acid. Trinitrobenzene inhibits the decomposition of benzoyl peroxide[7] and accelerates the decomposition of phenylacetyl peroxide.[10] The decomposition of phenylacetyl peroxide is also subject to catalysis by carboxylic acids while the decomposition of benzoyl peroxide is not.

Even though the available data are for different temperatures, it is of interest to compare the slopes of the Brønsted relationships for various peroxide decompositions. Sensitivity to acid catalysis seems to be in the order 4-methoxy-4′-nitrobenzoyl peroxide > phenylacetyl peroxide > 4-methoxy-3′,5′-dinitrobenzoyl peroxide. The first and third of these are of closely analogous structure, and it may be significant that the peroxide derived from the stronger nitro-substituted acid is the less sensitive to acid catalysis.[11]

The Products of the Decomposition of 4-Methoxy-3′,5′-dinitrobenzoyl Peroxide.—The products of the decomposition of 4-methoxy-3′,5′-dinitrobenzoyl peroxide in various solvents are reported in Table III as per cent. of the acyloxy groups surviving in the form of free acid or ester. As in the case of 4-methoxy-4′-nitrobenzoyl peroxide, there is less conservation of anisoyloxy groups in nitrobenzene than in benzene, but the yields of both anisic and dinitrobenzoic acids and esters are lower. The low recovery of the dinitrobenzoyloxy part of the peroxide may be due to the instability of the carboxy-inversion product.

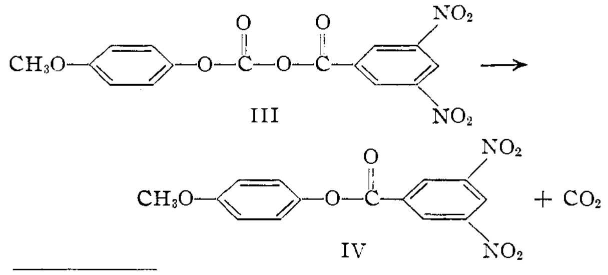
TABLE III

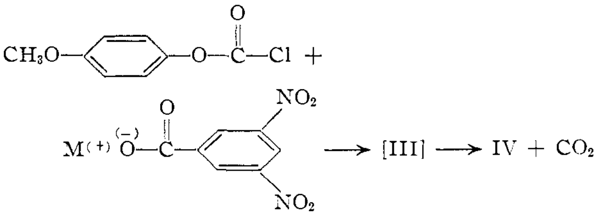
PRODUCTS OF THE DECOMPOSITION OF 4-METHOXY-3′,5′-DINITROBENZOYL PEROXIDE

Conditions	% Yield of 4-methoxybenzoyloxy groups		% Yield of 3,5-dinitrobenzoyloxy groups	
	As free acid	As esters	As free acid	As esters
In benzene at 51°	18	3	33	6
In nitrobenzene at 51°	2	0.4	10	7
In acetone at 25°	3		2	At least 19[a]
In benzene plus 0.17 *N* ClCH$_2$COOH at 51°	Trace	9	46	0
In benzene plus 0.17 *N* picric acid at 51°	Trace		17	At least 31[a]

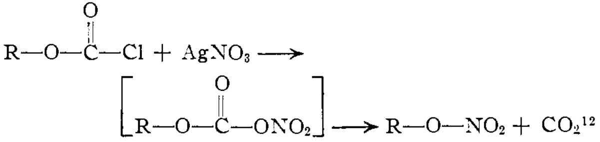
[a] Amount of 4-methoxyphenyl 3,5-dinitrobenzoate actually isolated. The other ester yields are yields of the acid after saponification of the neutral fraction.

The carboxy inversion product III could not be purified but is undoubtedly present in the reaction mixtures from the polar solvents as is shown by the evolution of carbon dioxide and the formation of IV on recrystallization and by the formation of ethyl 3,5-dinitrobenzoate on treatment of the crude product with ethanol. The elimination of carbon dioxide also takes place in the attempted synthesis of III from anisyl chloroformate and salts of the dinitrobenzoic acid. An analogous reaction of chloroformate esters with silver nitrate gives similar results.[12]





M = Ag or Na



$$\text{R—O—}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{—Cl} + \text{AgNO}_3 \longrightarrow \left[\text{R—O—}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{—ONO}_2\right] \longrightarrow \text{R—O—NO}_2 + \text{CO}_2{}^{12}$$

Aside from the crude carboxy-inversion product and the ester IV, no other neutral products could be isolated from the decomposition mixture.

Experimental

Preparation of 4-Methoxy-3′,5′-dinitrobenzoyl Peroxide.—To a freshly prepared solution of one gram of sodium in 40 ml. of absolute ethanol cooled to −20° is added dropwise, with stirring, a solution of 10 g. of anisoyl peroxide in 100 cc. of cold chloroform. After ten minutes of continued stirring and cooling in the Dry Ice–acetone bath, that bath is replaced with an ice-bath and the stirring continued for 20 minutes. The sodium peranisate is then extracted with two 60-ml. portions of cold water and the extract washed with 30 ml. of cold chloroform.

The aqueous peranisate solution is nearly neutralized with solid carbon dioxide pellets, and a concentrated solution of 7.6 g. of 3,5-dinitrobenzoyl chloride in dry acetone is added dropwise with stirring at 0°. Stirring is continued for 1 hr. The resulting precipitate is removed by filtration, washed with 10 ml. of 5% NaHCO$_3$ solution, dissolved in chloroform and filtered. After methanol is added to the chloroform solution, it is cooled in ice. The peroxide is obtained as white flaky crystals, wt. 4 g. after two recrystallizations, m.p. 97° with decomposition.

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[10] P. D. Bartlett and J. E. Leffler, THIS JOURNAL, **72**, 3030 (1950).

[11] See, for example, the acid catalysis mechanism and footnote 7 of reference 2.

[12] R. Boschan, Abstracts of Papers Presented at the American Chemical Society Meeting, Atlantic City, N. J., September, 1956, page 10-O.

Anal. Peroxide assay, 96–97%. Calcd. for $C_{15}H_{10}O_9N_2$: C, 49.73; H, 2.78; N, 7.73. Found: C, 50.34; H, 2.94; N, 7.91.

Kinetics.—Solutions of the peroxide were degassed, sealed in ampules and placed in a constant temperature bath. The decomposition was stopped by cooling the ampules in Dry Ice–acetone, and aliquots were analyzed by the method of Nozaki[13] using a "dead-stop" end-point.[14] It was found necessary to use carbonated water in order to get good results (±0.2%) with thiosulfate from 0.001 to 0.005 *N*.

Product Analysis.—With the exception of anisyl 3,5-dinitrobenzoate and the crude carboxy inversion product, no neutral products were formed in sufficient quantity for isolation, although various chromatographic adsorbents were tried. The acid mixtures were removed by extraction with sodium bicarbonate and analyzed for anisic and 3,5-dinitrobenzoic acid by means of infrared bands at 1612 and 1350 cm.$^{-1}$. Control analyses indicate that the results are accurate to within 9% for the 3,5-dinitrobenzoic acid and 8% for the anisic acid. The mixture of acids is not readily separated by chromatography. Esters were estimated by saponification of the neutral fraction followed by infrared analysis of the resulting mixture of acids. Anisyl 3,5-dinitrobenzoate was identified by its melting point, mixed melting point and infrared spectrum.

The Carboxy-inversion Product III.—The neutral fraction of the decomposition products from the reaction in nitrobenzene gave a small amount of ethyl 3,5-dinitrobenzoate on treatment with ethanol, presumably because of the presence of III. The ester IV was isolated by crystallization of the decomposition products from the reaction in acetone and in benzene–picric acid, with the carboxy-inversion product as a likely precursor. The decomposition products from the reaction in thionyl chloride contained a substance of variable melting point (137–139 for one sample, 139–149 for another), evidently III in crude form. This crude product has an anhydride band at 1830 cm.$^{-1}$, absent in the spectrum of the ester IV. All attempts at recrystallizing the crude product gave only the ester IV. Warming the crude III in methanol evolved 70% of the theoretical amount of carbon dioxide; saponification gave 94% of the theoretical amount of *p*-methoxyphenol. Attempts at synthesizing III from anisyl chloroformate and the sodium or silver salt of 3,5-dinitrobenzoic acid also gave the ester IV.

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(13) K. Nozaki, *Ind. Eng. Chem., Anal. Ed.*, **18**, 583 (1946).

(14) E. W. Abrahamson and V. H. Linshitz, *Anal. Chem.*, **24**, 1355 (1952).

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT OF WESTVACO CHLOR-ALKALI DIVISION OF FOOD MACHINERY AND CHEMICAL CORPORATION]

Phosphorus(V) Acid Esters of Oximes

BY J. FORREST ALLEN[1]

RECEIVED JANUARY 12, 1957

Alkyl esters of trivalent phosphorus acids react with α-halonitro compounds to form alkyl halide and oxime esters of the corresponding pentavalent phosphorus acids.

The similarity in the chemical behavior of the nitro and carbonyl groups in certain reactions suggested that α-halonitroparaffins should react with esters of trivalent phosphorus acids to form products which are analogous to the vinyl esters of pentavalent phosphorus acids which have recently been reported from this Laboratory[2] and by several other groups. The reaction of triethyl phosphite with several representative halonitroparaffins has been studied and the reaction shown to proceed according to the equation

$$RR'XCNO_2 + 2(R''O)_3P \longrightarrow \underset{\mathrm{I}}{RR'C{=}NOP(O)(OR'')_2} + (R''O)_3PO + R''X$$

Ia, R = R′ = Cl; R″ = Et
Ib, R = R′ = Me; R″ = Et

Trimethyl phosphite and diethyl phenylphosphonite react in an analogous fashion, but triphenyl phosphite appears to react by a different mechanism. The ease with which the reaction takes place increases with the number of halogen atoms on the α-carbon atom and bromine compounds are more active than chlorine compounds. 1-Chloro-1-nitroethane and triethyl phosphite did not react at 50°, but 1,1-dichloro-1-nitroethane and triethyl phosphite reacted rapidly at 25°, and trichloronitromethane reacted violently with the phosphite at −40° producing smoke and flame unless carefully controlled. 2-Bromo-2-nitropropane reacted rapidly with the phosphite at 50°.

Arbuzov and co-workers[3] reported the reaction of triethyl phosphite with α-bromonitro compounds but were able to identify only triethyl phosphate and ethyl bromide. These investigators observed a two-stage reaction, the first occurring at or below ordinary temperatures and the second at about 90–100°. They found that nitromethane did not react with triethyl phosphite, indicating that the halogen atom plays an important role in the oxidation of the phosphite to the phosphate. The work reported in this paper indicates that the second reaction observed by the Russian workers was probably the Beckmann rearrangement of the primary reaction product I as reported recently by Kenner, Todd and Webb.[4] Kamai[5] treated trichloronitromethane with triethyl phosphite and tributyl phosphite and reported the corresponding dialkyl phosphorochloridates as the only identifiable products. The author has found that the reaction of two moles of triethyl phosphite with one mole of trichloronitromethane converts about 3 to 11% of the phosphite to the phosphorochloridate, about 50% to the phosphate and the remainder to Ia and other products. Ia has been obtained in yields of 32 to 63%. When

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(1) Food Machinery and Chemical Corporation, Chemical Divisions, Central Research Laboratory, Princeton, New Jersey.

(2) J. F. Allen and O. H. Johnson, THIS JOURNAL, **77**, 2871 (1955).

(3) A. E. Arbuzov, B. A. Arbuzov and B. P. Lugovkin, *Bull. acad. sci. U.R.S.S., Classe sci. chim.*, 538 (1947).

(4) G. W. Kenner, A. R. Todd and R. F. Webb, *J. Chem. Soc.*, 1231 (1956).

(5) G. Kamai, *Doklady Akad. Nauk S.S.S.R.*, **79**, 795 (1951).