

TABLE III

REDUCTION OF PENTABROMOBENZEDIAZONIUM HYDROGEN SULFATE BY PHOSPHOROUS ACID

Time (hours)	Theoretical amount N ₂ evolved, %	Time (hours)	Theoretical amount N ₂ evolved, %
0.5	0	15.0	57.7
3.0 ^a	0	16.0 ^b	58.9
3.5	7.0	17.0 ^b	62.5
4.5	28.3	18.0	66.0
5.0	38.0		

^a At this point 0.04 g. (0.00025 mole) of potassium permanganate in 2 ml. of water was added. ^b At this point 0.02 g. (0.000125 mole) of potassium permanganate in 1 ml. of water was added.

tuted for potassium permanganate in the above experiment it was completely ineffective as a catalyst.

Five mole per cent. of copper sulfate was also without effect in a similar experiment wherein crystalline *p*-tolyl-diazonium hydrogen sulfate was treated with aqueous phosphorous acid at 0°.

Reduction of *p*-Nitrobenzenediazonium, *p*-Tolyldiazonium and *p*-Methoxybenzenediazonium Chlorides.—Here the diazonium salts were not isolated. In order to ensure that any differences observed between reductions employing hypophosphorous acid and phosphorous acid were not due to variations in the composition of the diazonium solution, the diazonium solutions were prepared at 0° from 0.4 mole of amine, 1.2 moles of hydrochloric acid, and 0.4 mole of sodium nitrite; the final volumes of these diazonium solutions were ca. 750 ml. Such a solution was divided in half, and

one portion treated with hypophosphorous acid, the other with phosphorous acid. In the hypophosphorous acid reductions 320 ml. of the ice-cold 50% solution (3 moles H₃PO₂) was added. In the phosphorous acid reductions 3 moles of the acid in 330 ml. of solution were employed; after adding the phosphorous acid at 0° the reaction mixture was brought to the desired temperature.

The reactions were allowed to proceed at either 0 or 25° for varying lengths of time (*cf.* Table II), and then the organic phase was isolated by extraction with diethyl ether. The ether extracts were washed with aqueous sodium hydroxide, then dried and distilled. The yields reported in Tables I and II refer to carefully purified products whose physical constants agree with the literature values. In the phosphorous acid reductions the aqueous phase was then allowed to react further as indicated in Table II, and the additional reaction product was isolated as before.

In the various reductions of *p*-methoxybenzenediazonium chloride by phosphorous acid an appreciable amount of crystalline residue remained after distillation of the anisole. Recrystallization from petroleum ether and then from absolute ethanol gave ca. 0.3 g. of yellow crystals of 4,4'-dimethoxyazobenzene, m.p. 164–164.8°; lit. m.p.¹⁵ 164°, 165°.

Anal. Calcd. for C₁₄H₁₄O₂N₂: N, 11.6. Found: N, 11.6.

In the reductions by hypophosphorous acid smaller amounts of a similar solid residue were obtained but were not investigated.

(18) D. Vorländer, *Ber.*, **71**, 1692 (1938); C. Weygand and R. Gabler, *ibid.*, **71**, 2399 (1938).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

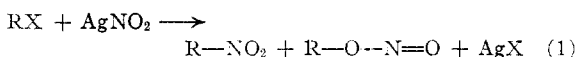
The Basis for the Report that Rearrangements Occur when Cyclopentyl Iodide and Cyclohexyl Iodide React with Silver Nitrite¹

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The report that cyclopentyl and cyclohexyl iodides on treatment with silver nitrite give rearranged tertiary nitro compounds, in addition to the expected secondary nitrocycloparaffins, has been investigated. No rearranged products were found. Instead, pure cyclopentyl and cyclohexyl nitrates were isolated.

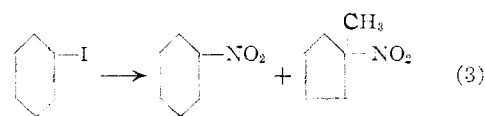
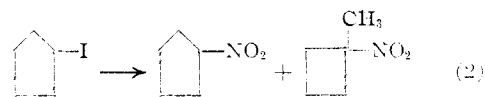
For many years it was believed that the reaction of silver nitrite with alkyl halides yields only the nitroparaffin and the alkyl nitrite.³



In 1947, however, it was found that when 2-bromooctane is treated with silver nitrite 2-nitrooctane, 2-octyl nitrite, 2-octyl nitrate, 2-octanol, 2-octanone and other, unidentified, products are formed.⁴ Analogous results were obtained with 2-iodobutane. Of special interest in connection with the present study is the fact that in neither case could the nitrate ester be removed from the nitro compound by rectification.

In 1915 Rosanow reported the results of experi-

ments in which cyclopentyl iodide and cyclohexyl iodide were treated with silver nitrite. In each instance he obtained an alkali-insoluble substance, isomeric with the expected nitrite ester and nitroparaffin, yet unmistakably different from these. He concluded that the alkali-insoluble substances were tertiary nitro compounds resulting from rearrangements⁵; *i.e.*



This claim that rearrangements occur is of considerable importance in evaluating the reaction of silver nitrite with organic halides as a means of ob-

(1) This is the fourth paper in the series, Paper III, N. Kornblum and G. Graham, *THIS JOURNAL*, **73**, 4041 (1951).

(2) Atomic Energy Commission Fellow 1949–1950.

(3) V. Meyer and O. Stuber, *Ber.*, **5**, 203 (1872); G. Schmidt, *J. Chem. Ed.*, **27**, 557 (1950).

(4) N. Kornblum, N. N. Lichtin, J. T. Patton and D. C. Iffland, *THIS JOURNAL*, **69**, 307 (1947); N. Kornblum, J. T. Patton and J. B. Nordmann, *ibid.*, **70**, 746 (1948).

(5) (a) N. A. Rosanow, *J. Russ. Phys. Chem. Soc.*, **47**, 591 (1915); (b) *ibid.*, **48**, 309 (1916) (*Chem. Zentr.*, **87**, I, 925 (1916)); *ibid.*, **95**, I, 2425 (1924).

taining pure nitro compounds. Clearly its synthetic value is greatly diminished if mixtures of nitro compounds are produced. Furthermore, any discussion of the mechanism of this reaction must accommodate the existence of Rosanow's rearrangements. Consequently, as part of a program concerned with the utility and the mechanism of this reaction, cyclopentyl and cyclohexyl iodides have been subjected to the action of silver nitrite.

The reaction of cyclopentyl iodide with silver nitrite gives a complex mixture from which cyclopentyl nitrite is readily separated by virtue of its volatility. Just as Rosanow reported, a sizable alkali insoluble fraction is obtained when the remainder of the reaction product is washed with aqueous alkali. However, most of this "alkali-insoluble" fraction dissolves in 85% phosphoric acid, a reagent which dissolves alcohols and ketones but not nitrate esters or nitro compounds. The material insoluble in both aqueous alkali and 85% phosphoric acid was rectified and found to consist largely of cyclopentyl nitrate. The pure nitrate thus isolated is completely identical with authentic cyclopentyl nitrate and has physical constants which are quite different from those of Rosanow's 1-methyl-1-nitrocyclobutane (see Experimental).

When cyclohexyl iodide was treated with silver nitrite it too gave an alkali-insoluble fraction; this when extracted with 85% phosphoric acid and then rectified yielded pure cyclohexyl nitrate. Just as in the cyclopentyl case, there was no evidence of the rearranged tertiary nitro compound.

Our inability to isolate Rosanow's tertiary nitro compounds, coupled with the fact that the alkali-insoluble nitrates could have been mistaken for tertiary nitro compounds, makes it unlikely that the alleged rearrangements occur to any appreciable extent.⁶

Experimental

The Cyclopentyl Series. Cyclopentyl Nitrite.—Procedure (A) of Kornblum and Oliveto⁷ was employed using 13 g. (0.15 mole) of cyclopentanol (b.p. 138°, n_D^{20} 1.4530); yield 5.5 g. (32%), b.p. 100–102° (Emich), n_D^{20} 1.4221, d_4^{20} 0.9948.

*Anal.*⁸ Calcd. for $C_5H_9NO_2$: N, 12.18; C, 52.18; H, 7.82. Found: N, 12.07; C, 51.95; H, 8.05.

Cyclopentyl Nitrate Procedure (a).—A stirred solution of 58.5 ml. of 96% sulfuric acid, 58.5 ml. of 69% nitric acid and 0.1 g. of urea was cooled to below –20° and then 11.6 g. (0.135 mole) of cyclopentanol was added over a period of 30 minutes. The solution was stirred for 15 minutes more, 100 ml. of 35–37° petroleum ether was added and the mixture was stirred for another five minutes. The two phase system was then poured into 200 g. of crushed ice layered with 100 ml. of 35–37° petroleum ether. The organic layer was separated, washed with 85% phosphoric acid, with water and then dried over anhydrous sodium sulfate. After removal of the petroleum ether on a steam-bath the residue was rectified⁹; yield 12 g. (69%); b.p. 74° at 30 mm.; b.p. 161° (Emich); n_D^{20} 1.4455; d_4^{20} 1.1261.

(6) While it is hard to avoid the conclusion that Rosanow's "tertiary nitro compounds" were actually impure nitrate esters there is one puzzling feature for which no satisfactory explanation is available. Nitrates contain one oxygen atom more than the corresponding nitro compounds and this difference should become apparent upon analysis. Yet Rosanow reports satisfactory analyses for both of his "tertiary nitro compounds."

(7) N. Kornblum and E. P. Oliveto, *THIS JOURNAL*, **69**, 465 (1947).

(8) We thank Drs. E. R. Shepard and W. L. Brown of the Eli Lilly Research Laboratory for these analyses.

(9) A modified Widmer column rated at ca. 5 plates was employed. Subsequent use of this column will be indicated by superscript 9.

Anal. Calcd. for $C_5H_9NO_2$: N, 10.69; C, 45.8; H, 6.87. Found: N, 10.63; C, 45.9, 46.0; H, 6.70, 6.78.

At 0°, it was not found possible to control the reaction. Brown fumes were evolved, the temperature rose to about 25°, and the product was completely soluble in 85% phosphoric acid.

Procedure (b).—A mixture of 22.5 g. of cyclopentyl bromide (0.15 mole) and 51.0 g. (0.3 mole) of silver nitrate was stirred overnight at room temperature and then heated on a steam-bath for five hours. During this time the flask was wrapped in a towel to minimize photochemical effects. The reaction mixture was then subjected to a vacuum of ca. 10 mm. while being heated on the steam-bath. The distillate was extracted with 85% phosphoric acid, with water, and then dried over anhydrous sodium sulfate. Removal of the solvent followed by rectification⁹ under reduced pressure gave 12 g. (38% yield) of cyclopentyl nitrate; b.p. 161° (Emich); n_D^{20} 1.4455; d_4^{20} 1.1259.

Anal. Calcd. for $C_5H_9NO_2$: N, 10.69; C, 45.8; H, 6.87. Found: N, 10.50; C, 45.8, 45.9; H, 6.72, 6.91.

Cyclopentyl Iodide, Procedure (a).—The procedure of Clark¹⁰ for 2-butyl iodide was followed using cyclopentanol except that (1) the iodide was distilled from the reaction mixture by heating on the steam-bath at 5 mm. (In some of the later preparations filtration through a bed of Celite-alumina replaced this distillation) and (2) the iodide was washed with 85% phosphoric acid before the final water washing. Rectification⁹ of the crude iodide gave 75–80% yields; b.p. 77° at 45 mm.; b.p. 160–164° (dec.) (Emich), n_D^{20} 1.5482; d_4^{20} 1.7235; M_D (calcd.) 35.9, M_D (found) 36.3. *Anal.* Calcd. for C_5H_9I : C, 30.61; H, 4.59. Found: C, 30.72, 30.40; H, 4.63, 4.69. Rosanow⁵ reports n_D^{20} 1.5447; d_4^{20} 1.7096. Other values: n_D^{20} 1.54705, d_4^{20} 1.7092¹¹; n_D^{20} 1.5457, d_4^{20} 1.7462.¹²

Procedure (b).—In a flask were placed 60 g. of fuming hydriodic acid (decolorized with a little H_3PO_3) and 20 g. (0.23 mole) of cyclopentanol. The solution was cooled in an ice-bath, saturated with gaseous hydrogen iodide, and then kept overnight below 10° whereupon separation into two layers occurred. The organic phase was washed successively with water, saturated sodium bisulfite, 85% phosphoric acid, saturated sodium bicarbonate and water; it was then dried over anhydrous sodium sulfate. Rectification⁹ gave 27 g. (59% yield) of the iodide; b.p. 160–164° (dec.) (Emich); n_D^{20} 1.5482; d_4^{20} 1.7229.

Anal. Calcd. for C_5H_9I : C, 30.61; H, 4.59. Found: C, 30.6, 30.4; H, 4.30, 4.50.

Reaction of Silver Nitrite and Cyclopentyl Iodide.—Rosanow's conditions were followed as closely as possible. In a two-liter flask fitted with a dropping funnel, a Hershberg tantalum stirrer and a reflux condenser leading to two Dry Ice traps were placed 300 g. (1.95 moles) of silver nitrite (Mallinckrodt) and 225 g. of sea sand which had been washed with 37% hydrochloric acid, with water, and then ignited. The flask was immersed in an ice-bath and after 30 minutes a solution of 255 g. (1.3 moles) of cyclopentyl iodide in 150 ml. of diethyl ether (analytical reagent) was added with stirring over a period of two hours. The mixture was then allowed to come to room temperature and stir overnight. This was followed by six hours of refluxing after which a negative Beilstein test was obtained.

The Dry Ice traps contained ca. 5 ml. of nitrogen trioxide as indicated by the presence of a blue liquid which on warming to room temperature boiled to give a brown gas. The absence of hydrogen cyanide (which Rosanow had reported to be present) was shown by passing the brown gas into aqueous sodium hydroxide; the resulting solution gave a negative Prussian Blue test.

The silver salts were removed by filtration and repeatedly washed with "pure grade" ether. The filtrate and washings were dried over anhydrous sodium sulfate. The experiment was repeated using another 255 g. of cyclopentyl iodide and the ether solutions were combined. The solvent was removed by distillation and the residue vacuum rectified.⁹ Nineteen fractions were obtained all of which gave a nega-

(10) L. Clarke, *THIS JOURNAL*, **30**, 1149 (1908).

(11) A. I. Vogel, *J. Chem. Soc.*, 1812 (1948).

(12) M. T. Rogers and J. D. Roberts, *THIS JOURNAL*, **68**, 844 (1946).

tive Beilstein test and a positive test for nitrite esters.^{12a} All of these, with the exception of fractions 7 and 19 (6.5 g. and 4.7 g.), were further studied.

(a) **Isolation of Cyclopentyl Nitrite.**—Fractions 1-6; b.p. 48-52° (80 mm.); n_D^{20} 1.4210 to 1.4340; were combined (total 33.8 g.). To this was added the contents of the Dry Ice trap (3.7 g.; n_D^{20} 1.4122) and the mixture was then dried over anhydrous sodium sulfate. Rectification⁹ at 75 mm. gave 28.7 g. (10% yield) of cyclopentyl nitrite, b.p. 46°; b.p. 99° (Emich); n_D^{20} 1.4221, d_4^{20} 0.9941. The pure nitrite (*vide supra*) has b.p. 51° at 90 mm.; b.p. 100-102° (Emich), n_D^{20} 1.4221, d_4^{20} 0.9948.

In addition to the 28.7 g. of pure nitrite 6 g. of higher boiling material was obtained; n_D^{20} 1.4472. This was used in the isolation of cyclopentyl nitrate.

This nitrite was further characterized by using 28 g. for the diazotization of *p*-toluidine and then coupling to alkaline β -naphthol.⁴ After purifying by chromatographing on alumina the 1-*p*-tolylazo-2-naphthol had m.p. 131.5-132.5°; yield 6.7 g. (29%). A mixed m.p. with an authentic sample m.p. 131.5-132.5° gave no depression.

(b) **Isolation of Cyclopentyl Nitrate.**—Fractions 8-13; b.p. 56-70° (28 mm.); n_D^{20} 1.4490 to 1.4472; were combined (total 47.2 g.) and to this was added the 6 g. of high boiling material (n_D^{20} 1.4472) obtained in the purification of cyclopentyl nitrite. After shaking for 15 minutes with 50 ml. of aqueous 20% sodium hydroxide, 50 ml. of water was added and the shaking continued for another 15 minutes. The organic phase was then extracted with 85% phosphoric acid whereupon most of it dissolved in the phosphoric acid. (This is to be expected of cyclopentyl nitrite, cyclopentanol and cyclopentanone but not of an alicyclic nitro compound.) The insoluble material was washed with water and dried over sodium sulfate. At this point it weighed 20 g. (6% yield). It was rectified,⁹ the middle cuts (*ca.* 4.5 g.) were combined and shaken as before with aqueous sodium hydroxide, 85% phosphoric acid and water and then dried over sodium sulfate. The 4 g. remaining was then rectified through a 65 plate concentric tube column. The middle cuts, 1.5 g. (0.5% yield), consisted of pure cyclopentyl nitrate; b.p. 161° (Emich), n_D^{20} 1.4455, d_4^{20} 1.1261.

Anal. Calcd. for $C_5H_9NO_3$: N, 10.69; C, 45.8; H, 6.87. Found: N, 10.62, 10.58; C, 45.9, 46.0; H, 6.75, 6.87.

Pure cyclopentyl nitrate synthesized in two different ways (*vide supra*) has b.p. 161° (Emich), n_D^{20} 1.4455, d_4^{20} 1.1260.

Rosanow reported the following constants for his rearranged nitro product (1-nitro-1-methylcyclobutane); b.p. 80-82° at 30 mm., n_D^{20} 1.4589, d_4^{20} 1.0795.

The ultraviolet absorption spectrum of the cyclopentyl nitrate isolated from the reaction of cyclopentyl iodide with silver nitrite is identical with that of cyclopentyl nitrate prepared from cyclopentanol and nitric acid.

Nitron Test.—Cyclopentyl nitrate (0.1 g.) was added to methanolic sodium methoxide and the solution was refluxed for four hours. The methanol was then removed and the residue was dissolved in several ml. of water. The solution was heated to boiling and treated with nitron reagent⁴ (10 g. Nitron in 100 ml. of 50% acetic acid). A tan precipitate formed immediately; after standing in an ice-box overnight the solid was isolated and dried at 110°. Cyclopentyl nitrate from the reaction of silver nitrite with cyclopentyl iodide gave 0.031 g. (11% yield) of precipitate; the reference nitrate gave 0.036 g. (13% yield).

(c) **Isolation of Nitrocyclopentane.**—Fractions 14-18; b.p. 70-79° (28 mm.); n_D^{20} 1.4483 to 1.4540; were combined (total 78.7 g.). These were subjected to the usual sulfuric acid purification.⁴ Rectification⁹ of the product at 27 mm. gave 0.21 g. of forerun (n_D^{20} 1.4529) and eight fractions having b.p. 82°, n_D^{20} 1.4537-1.4538. These, however, varied in color from colorless to deep yellow. The eight fractions were combined (21 g.) and given the sodium hy-

droxide-hydroxylamine hydrochloride treatment¹³; rectification⁹ then gave colorless nitrocyclopentane b.p. 76° at 21 mm.; b.p. 180° (Emich); n_D^{20} 1.4540. The yield was 10.5 g. (3.4%); lit. values n_D^{20} 1.4518¹⁴; b.p. 181°.¹⁵

Anal. Calcd. for $C_5H_9NO_2$: N, 12.18; C, 52.17; H, 7.82. Found: N, 11.85, 11.80; C, 52.4, 52.10; H, 7.87, 7.76.

Nitrocyclopentane was converted to cyclopentanone by the Nef reaction and the ketone was derivatized as the 2,4-dinitrophenylhydrazone, m.p. 143-144°, a mixed m.p. with an authentic sample, m.p. 143-144°, was undepressed; lit. value¹⁶ m.p. 145.5-146.5°.

The Cyclohexyl Series. Cyclohexyl Nitrate.—Procedure (a) for cyclopentyl nitrate was followed; yield 12.5 g. (69%); b.p. 68° at 11 mm.; b.p. 181° (Emich); n_D^{20} 1.4562, d_4^{20} 1.1043; lit. value¹⁷ b.p. 70-72° at 12 mm.

Anal. Calcd. for $C_6H_{11}NO_3$: N, 9.65; C, 49.65; H, 7.58. Found: N, 9.63, 9.43; C, 49.20, 49.43; H, 7.70, 7.82.

No precipitate formed when an attempt was made, using the directions for cyclopentyl nitrate, to obtain a Nitron test.

Cyclohexyl Iodide.—Procedure (a) for cyclopentyl iodide was followed using 290 g. (2.9 moles) of cyclohexanol; yield 510 g. (83%); b.p. 65° at 11 mm.; n_D^{20} 1.5488; lit. values n_D^{20} 1.54765¹¹; Rosanow⁶ reports b.p. 100-101° at 45 mm.

Reaction of Silver Nitrite and Cyclohexyl Iodide.—The reaction was carried out using 282 g. (1.35 moles) of cyclohexyl iodide and 250 g. (1.63 moles) of silver nitrite; a negative Beilstein test was obtained after 22 hours at room temperature.

Since a preliminary experiment had indicated that no more than a trace of nitrite is produced only a cursory attempt was made to isolate the nitrite. After removal of the ether, the residue was subjected to a vacuum of 10 mm. and the bath temperature raised to 73°. There was no evidence of distillation and, since the small amount of reflux wetting the walls was colorless heating was discontinued. After cooling, the material was subjected to the sodium hydroxide-hydroxylamine hydrochloride procedure.¹³

(a) **Isolation of Cyclohexyl Nitrate.**—The alkali-insoluble material from the preceding paragraph was extracted with 85% phosphoric acid, washed with water and then dried. Upon rectification⁹ 7.5 g. (4% yield) of pure cyclohexyl nitrate was obtained; b.p. 67° at 10 mm.; b.p. 180° (Emich); n_D^{20} 1.4562; d_4^{20} 1.1032.

Anal. Calcd. for $C_6H_{11}NO_3$: N, 9.65; C, 49.65; H, 7.58. Found: N, 9.61, 9.66; C, 49.62, 49.46; H, 7.63, 7.50.

Rosanow reported n_D^{20} 1.4504, d_4^{20} 1.0395, for his rearranged product (1-nitro-1-methylcyclopentane).

(b) **Identification of Nitrocyclohexane.**—The material obtained by treating the aqueous alkaline solution of the reaction product with hydroxylamine hydrochloride (see above) was rectified⁹ at 6 mm. The n_D^{20} ranged from 1.4640-1.4658 whereas carefully purified nitrocyclohexane has n_D^{20} 1.4611.¹³ These fractions (total 3.7 ml.) were combined and from them two crystalline derivatives of nitrocyclohexane were prepared.

1-(*p*-Nitrophenylazo)-nitrocyclohexane.—Diazotized *p*-nitroaniline was coupled with an alkaline solution of the impure nitrocyclohexane. The crude product (0.89 g.) had m.p. 86-89°. After being chromatographed from benzene solution on an alumina-Celite column this gave 0.20 g. (20% yield) of the yellow azo compound m.p. 94-95°; a mixed m.p. with the azo compound prepared (in 25% yield) from du Pont nitrocyclohexane (m.p. 94-95°) was undepressed.

Anal. Calcd. for $C_{12}H_{14}N_4O_4$: N, 20.14. Found: N, 19.98, 20.07.

1-(β -Naphthylazo)-nitrocyclohexane.—Orange crystals from benzene; m.p. 62-63°. A mixed m.p. with a sample prepared from du Pont nitrocyclohexane (m.p. 62-63°) was undepressed.

Anal. Calcd. for $C_{15}H_{17}N_3O_2$: N, 14.84. Found: N, 14.96, 15.01.

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(13) N. Kornblum and G. E. Graham, *THIS JOURNAL*, **73**, 4041 (1951).

(14) S. Nametkin, *J. Russ. Phys. Chem. Soc.*, **47**, 591 (1915).

(15) H. Schlechter, Ph.D. Thesis, Purdue University, 1946.

(16) H. H. Strain, *THIS JOURNAL*, **57**, 760 (1935).

(17) F. Fichter and A. Petrovitch, *Helv. Chim. Acta*, **24**, 253 (1941).

(12a) Fractions 1-6 and the trap contents gave a negative nitro test. All the other fractions gave a positive reaction. In this test one drop of the unknown is dissolved in one ml. of methanol containing three drops of 10% aqueous sodium hydroxide and one drop of 5% ferric chloride. After shaking 30 seconds the solution is carefully acidified with 4 *N* hydrochloric acid. A maroon color indicates a primary or secondary nitroparaffin. This is a modification of the quantitative procedure of E. W. Scott and J. F. Treon [*Ind. Eng. Chem., Anal. Ed.*, **12**, 189 (1940)] for which we are indebted to Professor David Davidson of Brooklyn College.