[CONTRIBUTION FROM THE EXPLOSIVES AND PROPELLANTS LABORATORY, PICATINNY ARSENAL, DOVER, N. J.]

Carbon-14 Tracer Study on the Origin of Tetranitromethane Carbon during the Nitration of Toluene

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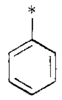
Tetranitromethane is known to form during the nitration of nitrotoluenes. Using carbon-14 as a tracer, it was found that most of the tetranitromethane originates from the aromatic ring carbons with over 50% being contributed by the ring carbon attached to the methyl group. It was also found that over 80% of all of the tetranitromethane can be traced to the dintrotoluene isomers derived from *m*-nitrotoluene. From the extent to which each of these compounds contributed to tetranitromethane formation, their relative rates of nitration are postulated. The ultimate formation of tetranitromethane is attributed to the dinitrotoluene oxidation reaction in competition with that of nitration.

Introduction

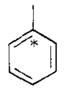
In the reaction between toluene and "mixed acid," tetranitromethane forms to the extent of less than 1% of the total weight of the trinitrotoluene produced. Since tetranitromethane is also isolated from the nitration of nitrobenzene,[1] the tetranitromethane formed in the nitration of toluene may arise from the oxidation of the aromatic ring and/or methyl group. The use of carbon-14 as a tracer offered the possibility of determining the extent to which each of the carbon atoms in the toluene skeleton of the various nitro-substituted isomers contributes to tetranitromethane carbon. Therefore, a study was undertaken to trace the origin of the tetranitromethane carbon by the nitration of specifically labeled toluenes.

Results and Discussion

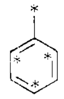
Carbon Atom Participation.—The specifically labeled toluenes used in this study were



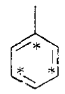
toluene-7-C^{14}



toluene-1-C^{14}



toluene-2,4,6,7-C^{14}



toluene-1,3,5-C^{14}

The contribution of the carbon atoms from the 1- and 7-positions to tetranitromethane carbon were obtained by determining the specific activity of the tetranitromethane isolated from the nitration of toluene-1-C^{14} and toluene-7-C^{14}, respectively. Similarly, by nitrating toluene-1,3,5-C^{14}, it was possible to determine the 3- and 5-contributions, since the contribution of the 1-position could be subtracted and the 3- and 5-positions were considered to be equivalent. Finally, the contributions of the 2-, 4- and 6-positions were determined from the nitration of toluene-2,4,6,7-C^{14} by subtracting the contribution of the 7-position. An approximate contribution for each of these positions (2-, 4- and 6-) was obtained by considering them to be equivalent.

Each of the labeled toluenes was converted to trinitrotoluene. The tetranitromethane was collected as potassium nitroform (eq. 1) by sparging the trinitration mixture with nitrogen and passing the gas through an alcoholic solution of potassium hydroxide.[2]

$$C(NO_2)_4 + KOH/C_2H_5OH \longrightarrow C(NO_2)_3K + C_2H_5ONO_2 \quad (1)$$

This proved to be a very convenient method of isolating and purifying the tetranitromethane. Isolating the tetranitromethane as a solid derivative removed the hazard of handling a highly volatile radioactive liquid. Because of its color, the potassium nitroform was not suitable for radioassay in a liquid scintillation counter and it was converted to 1,1,1-trinitroethane by reaction with methyl iodide (eq. 2).

$$(O_2N)_3—C^{14}—K + CH_3I \longrightarrow (O_2N)_3—C^{14}—CH_3 + KI \quad (2)$$

This compound is a white crystalline solid which yields a colorless solution when dissolved in the scintillator solution. The counting efficiency of this system has been reported by Helf and White.[3] The reproducibility of the method of isolating the 1,1,1-trinitroethane was checked by assaying this compound from four separate and complete nitrations of toluene-1-C^{14}. The specific activity obtained for these samples was 57,193 ± 341 c./m./50 mg., or well within ±1%.

The specific activity of the toluene was used as a reference standard in determining the calculated value for total participation. In order to ensure that the activity measured in the toluene was from radioactive carbon atoms in the toluene molecule and not from minute amounts of high specific activity radioactive impurities, the trinitrotoluenes from the nitration of all of the labeled toluenes were isolated, purified and assayed. The specific activity of each of the toluenes and of the trinitrotoluenes produced from them are reported in Table I.

TABLE I

CORRELATION BETWEEN SPECIFIC ACTIVITIES OF TOLUENE AND TRINITROTOLUENE

Labeled carbons	Specific activity[a]		Ratio trinitrotoluene/toluene
	Toluene	Trinitrotoluene	
1	446,934	97,293	0.217
7	151,456	34,253	.226
2, 4, 6, 7	89,342	19,283	.216
1, 3, 5	83,194	18,259	.219

[a] Each trinitrotoluene value represents an average of at least four separate runs. The deviation in the trinitrotoluene values was ±1.5%.

The constant ratio, trinitrotoluene/toluene, indicates that the activity is present in the toluene

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(1) P. V. McKie, *J. Soc. Chem. Ind.* (*London*), **44**, 430T (1925).

(2) A. Hantzsch and A. Rinckenberger, *Ber.*, **32**, 628 (1899).

(3) S. Helf and C. White, *Anal. Chem.*, **29**, 13 (1957).

molecule in each case, since impurities in any of the toluenes would have altered this ratio.

The contribution from carbon-1 to tetranitromethane carbon was determined from the values used in establishing the reproducibility of the method of isolating 1,1,1-trinitroethane. The participation of this carbon was found to be 54.2%, based upon the ratio of the observed specific activity (57,193 c./m.) of the 1,1,1-trinitroethane to the calculated value for total participation (105,522 c./m.). Therefore, over one-half of the carbon atoms in tetranitromethane were derived from carbon-1.

In determining the contribution from carbon-7, an experimental standard was prepared. A small aliquot of the methyl iodide-C^{14} used in preparing toluene-7-C^{14} was treated with unlabeled potassium nitroform to produce 1,1,1-trinitroethane-C^{14} according to eq. 3.

$$(O_2N)_3\text{—C—K} + C^{14}H_3I \longrightarrow (O_2N)_3\text{—C—}C^{14}H_3 + KI \quad (3)$$

This compound served as the standard. If all of the tetranitromethane carbon were derived from the methyl group, the 1,1,1-trinitroethane isolated from the nitration of toluene-7-C^{14} would have the same specific activity as that of the standard. For anything less than total participation, the value would be calculated from the ratio of the specific activity of the 1,1,1-trinitroethane obtained in the nitration reaction to that of the standard. The participation of carbon-7 determined by this method was 6.1%. If the calculated specific activity for total participation is used in place of the specific activity of the experimental standard in determining the percentage participation, this value is 5.5%. This agreement in the percentage participation is taken as verification of the method used to calculate the value for total participation for the three other labeled toluenes.

From the specific activity of the 1,1,1-trinitroethane isolated following the nitration of toluene-2,4,6,7-C^{14}, the participation of these carbon atoms was found to be 31%. If the contribution of the methyl carbon, 6.1%, is subtracted from the total, a value of 24.9% is obtained for the total participation of the 2-, 4- and 6-carbons. This value was divided equally among the three carbons, *i.e.*, the participation of each was considered to be 8.3%.

The final toluene species investigated in this series contained radioactive carbon atoms in the 1-, 3- and 5-positions. The total participation of these carbons was found to be 69%. Since the contribution of carbon-1 had been determined to be 54.2%, the contribution for the 3- and 5-carbon atoms was 14.8%, or 7.4% for each of the 3- and 5-positions. Figure 1 summarizes the percentages of tetranitromethane carbon arising from each position in the toluene carbon skeleton.

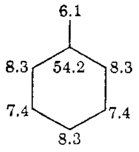

Fig. 1.—Percentage of tetranitromethane carbon arising from each position in the toluene carbon skeleton.

Determination of Specific Isomer Participation.—Although it was possible to determine the contributions from the carbon atoms in various positions in the toluene carbon skeleton, the previous experiments provide no information about specific isomer participation. For example, when the toluene-1-C^{14} is nitrated, the contribution of carbon-1 to tetranitromethane carbon was found to be 54.2%. This value represents the total contribution of carbon-1 from one or more of the six dinitrotoluene isomers present in the nitration of dinitrotoluene to trinitrotoluene. The extent to which the carbon atoms from the various isomers contribute to tetranitromethane formation was determined using an isotope dilution procedure.

In the dinitration mixture there are six isomers present: 2,4-, 2,6-, 2,3-, 2,5-, 3,4- and 3,5-dinitrotoluene. The contribution from the 2,4- and 2,6-dinitrotoluene was not determined since McKie reported that no tetranitromethane formed in the nitration of these isomers even though they constitute about 96% of the weight of all of the isomers. Therefore, the number of isomers that were studied by the isotope dilution method were the four which exist in small concentrations, *viz.*, 2,3-(1.16%), 2,5-(0.56%), 3,4-(2.20%) and 3,5-dinitrotoluene (0.08%).

In an actual run, a quantity of toluene-1-C^{14} was converted to dinitrotoluene-1-C^{14}. The dinitrotoluene-1-C^{14} mixture was divided into five equal portions. One portion was converted to trinitrotoluene-C^{14} and the 1,1,1-trinitroethane isolated had a specific activity of 57,190 c./m./50 mg. This value served as a standard. An amount of unlabeled 2,3-dinitrotoluene[4] equal to the amount of that isomer normally present in the dinitrotoluene mixture was added to a second portion of the dinitrotoluene-1-C^{14}. This then was converted to trinitrotoluene and the 1,1,1-trinitrotoluene again isolated. If all of the tetranitromethane carbon came from this isomer (total participation), the 1,1,1-trinitroethane would have a count of 28,600 c./m./50 mg. (one-half of the standard). The addition of the unlabeled 2,3-dinitrotoluene caused the count of the resulting 1,1,1-trinitroethane to be 6,190 c./m. lower than the standard (*i.e.*, 51,000 c./m.). The percentage participation from carbon-1 in the 2,3-dinitrotoluene isomer then was calculated as $6{,}190/28{,}600 \times 54.2 = 11.7\%$.

This process was repeated, with each of the above-mentioned isomers being added (in an amount equal to the concentration of that isomer normally present in the dinitrotoluene mixture) to separate portions of dinitrotoluene. The percentage of carbon-1 contributed by each of these isomers as determined in the above manner is reported in Table II.

It is interesting to note that each isomer does not contribute to the same extent. Also, 82.6% of the tetranitromethane formed from carbon-1 came from dinitrotoluene isomers derived from *m*-nitrotoluene. In Table III it can be seen that the above-mentioned isomers contribute heavily even though they constitute only 4% of the dinitrotoluene mixture.

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[4] We are indebted to C. Conklin for supplying the unlabeled dinitrotoluenes.

TABLE II

CONTRIBUTION OF CARBON-1 FROM SEVERAL DINITROTOLUENE ISOMERS

Cold dinitrotoluene isomer added	Specific activity of trinitroethane c./m./50 mg.	Carbon-1 contribution, %
None	57,190	. .
2,3-	51,002	21.6
2,5-	52,401	16.8
3,4-	50,320	24.0
3,5-	51,415	20.2

TABLE III

RELATIVE PARTICIPATION OF DINITROTOLUENE ISOMERS

Dinitrotoluene isomer	Isomer in dinitrotoluene mixt., %	Participation rel. to 2,4- and 2,6-dinitrotoluene
2,3-	1.16	58.5
2,5-	0.56	93.6
3,4-	2.20	34.1
3,5-	0.08	793.0
2,4- 2,6-	96.0	1.0

The values in the last column in the table demonstrate this fact most forcefully. These values represent the factors by which the tetranitromethane concentration would increase over that of the total tetranitromethane arising from the nitration of 2,4- and 2,6-dinitrotoluene if each of these isomers constituted 96% of the dinitrotoluene mixture. For example, 793 times as much tetranitromethane would be formed if 3,5-dinitrotoluene constituted 96% of the dinitrotoluene mixture.

Conclusions

During nitration, a small amount of oxidation takes place simultaneously. The slower the nitration, the greater the possibility of molecules undergoing the oxidation reaction. This supports the assumption that the tetranitromethane forms in the trinitration step since the nitration reaction would be slowest in this step. For example, the rate of nitration of 2,4-dinitrotoluene is reported to be $1/10^7$ as rapid as that of *p*-nitrotoluene.[5] The result that over one-half of the tetranitromethane carbon is derived from carbon-1 can be explained by considering the oxidation reaction more closely. The first step in this reaction probably is the conversion of the dinitrotoluene to dinitrobenzoic acid. The isolation of 3,5-dinitrobenzoic acid following unsuccessful attempts to convert 3,5-dinitrotoluene to the trinitro derivative has been reported.[6] In the dinitrobenzoic acid molecule, carbon-1 is an α-carbon atom. Chattaway[7] has proposed a mechanism for the formation of tetranitromethane from the reaction between acetic anhydride and nitric acid which involves the activation of the α-carbon by the carbonyl group. Replacement of the α-hydrogen atoms by nitro groups takes place. Hydrolysis then occurs and the trinitroacetic acid formed decomposes into carbon dioxide and nitroform, which is then nitrated to tetranitromethane. If the oxidation of dinitrotoluene proceeds in a similar manner, carbon-1 would be expected to favor the formation of tetranitromethane more than any other carbon atom since it is the only one which is attached to a methyl group.

The fact that over 80% of the tetranitromethane comes from the dinitrotoluenes derived from *m*-nitrotoluene is taken as an indication that the rate of nitration of these isomers is slower than the rate of nitration of the 2,4- and 2,6-dinitrotoluene isomers. In Table III, the values reported in the last column might be looked upon as a measure of the speed of nitration of the various isomers. That is, the larger the value of the participation in tetranitromethane formation, the slower the rate of nitration of the isomer to trinitrotoluene. Therefore, the nitration of 2,3-, 2,5- and 3,4-dinitrotoluene should be slower than that of 3,4- and 2,6-dinitrotoluene. The nitration of 3,5-dinitrotoluene should be even slower.

These data can be explained from considerations of the profound effect that the groups attached to the aromatic ring have on both orientation and ease of introduction of the entering group. In the trinitration step, the orientation of the third nitro group is determined by one of the following effects: (a) Reinforcement of the directive influence of the methyl and two nitro groups. For example, in the nitration of 2,4-dinitrotoluene, the methyl group favors substitution at the 6-position. The nitro groups also favor substitution at this position. The same situation exists in the nitration of 2,6-dinitrotoluene. When total reinforcement occurs, the rate of nitration is rapid. (b) Entering nitro group is directed to the same position by the methyl group and one nitro group. This type of directive influence is observed in the nitration of 2,3-, 2,5- and 3,4-dinitrotoluene. Since there is only partial reinforcement, the nitration proceeds at a slower rate and therefore more oxidation of the ring takes place. (c) No reinforcement of directive influence. This is observed in the nitration of 3,5-dinitrotoluene. The nitration of this compound should proceed at a much slower rate, and attempts to nitrate it have been unsuccessful. Thus it will be subject to much oxidation and will contribute heavily to tetranitromethane formation.

Experimental

Preparation of Toluene-7-C^{14}.—Sodium (55.3 g., 2.4 g.-atoms), 126.6 g. (0.81 mole) of bromobenzene, 143.6 g. (1.01 moles) of methyl iodide-C^{14} (0.74 μC./mM.) and 50 drops of ethyl acetate were added to 400 ml. of ethyl ether (dried over sodium) in a 1-l. round-bottom flask equipped with a mechanical stirrer and a reflux condenser. A Dry Ice condenser fitted with a drying tube was placed above the reflux condenser. The mixture was refluxed for 8 hours. The heat then was removed and the mixture allowed to stand overnight. The refluxing was resumed the next day and continued for 4 hours. During the reaction, a heavy blue-gray precipitate formed. The mixture was filtered and the filtrate distilled. The fraction which distilled over at 108° (uncor.) was collected; 28.6 g. (38.4%).

Toluene-1-C^{14} was prepared by the New England Nuclear Corp. according to the method of Fields, *et al.*[8]

Preparation of Toluene-1,3,5-C^{14} and Toluene-2,4,6,7-C^{14}.—The starting materials for preparing toluene-1,3,5-C^{14} and toluene-2,4,6,7-C^{14} were 1 mC. of pyruvamide-2-C^{14} and 1 mC. of pyruvamide-3-C^{14}, respectively. These compounds were converted to the carbon-14 labeled toluenes by the New England Nuclear Corp. In the first step in this

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[5] F. H. Westheimer and M. S. Kharasch, *J. Am. Chem. Soc.*, **68**, 1871 (1946).

[6] W. Will, *Ber.*, **47**, 704 (1914).

[7] F. D. Chattaway, *J. Chem. Soc.*, **97**, 2099 (1910).

[8] M. Fields, M. A. Leaffer, S. Rothchild and J. Rohan, *J. Am. Chem. Soc.*, **74**, 5498 (1952).

conversion, pyruvamide-C^{14} was converted to pyruvic acid-C^{14} by the method of Thomas, *et al.*[9] The remaining steps in the conversion were carried out using the procedure of Calvin, *et al.*[10] The specific activities of toluene-1,3,5-C^{14} and toluene-2,4,6,7-C^{14} were 45.9 μc./mM. and 38.4 μ C./mM.

Unlabeled Pyruvamide.—It was necesary to prepare unlabeled pyruvamide in order to dilute the radioactive pyruvamide before further reaction. This was accomplished in three steps. Acetyl bromide was prepared by the reaction between phosphorus tribromide and acetic anhydride.[11] The acetyl bromide was converted to acetyl cyanide (pyruvonitrile) by reaction with cuprous cyanide.[12] The pyruvonitrile was carefully hydrolyzed to produce pyruvamide.

Preparation of Mononitrotoluene.—Toluene (130 g., 1.4 moles) was added dropwise to 475 g. of mixed acid (63.92% H_2SO_4 and 20.50% HNO_3) while the acid was stirred with a magnetic stirrer. The temperature was maintained at 25° during the first half of the addition and then raised to 34° during the second half. After the addition was completed, the temperature was raised to 55° over a 30-minute period. The reaction mixture then was separated by means of a separatory funnel. The top layer was mononitrotoluene (170 ml.).

Preparation of Dinitrotoluene.—The mononitrotoluene was added to 430 g. of mixed acid (63.77% H_2SO_4 and 23.44 % HNO_3). The acid was stirred with a magnetic stirrer, the temperature being maintained at 55°. Following the addition, the temperature was raised slowly to 75° and maintained at this level for 40 minutes. The mixture then was poured into a separatory funnel which was heated by means of an infrared lamp. The top layer was dinitrotoluene. The acid layer was isolated and added to ice-water to precipitate the dinitrotoluene which was dissolved in the acid. This dinitrotoluene was isolated by filtration and dried. All of the dinitrotoluene was combined (190 ml.).

Preparation of Trinitrotoluene, Isolation of Potassium Nitroform and Conversion to 1,1,1-Trinitroethane.—Oleum (100 g., 33–35% SO_3) was added to 65 g. of mixed acid (38.95% H_2SO_4 and 80.28% HNO_3) stirred at 70°. The dinitrotoluene was melted and kept in a liquid state in a dropping funnel by means of an infrared lamp and added dropwise to the acid mixture while the temperature was kept at 75°. After the addition, the temperature of the mixture was raised to 110° over a 30-minute period and kept at 110° for 45 minutes. The reaction mixture then was cooled to 75°, and 500 λ of unlabeled tetranitromethane was added. The reaction mixture was then sparged with nitrogen (600 ml./minute). A flow meter was inserted in the line to help maintain a constant flow of nitrogen. After passing through the reaction flask, the nitrogen was bubbled into 150 ml. of an ice-cold alcoholic potassium hydroxide solution (1 g./10 ml. of absolute alcohol). The yellow precipitate which appeared, potassium nitroform, was formed by the reaction of tetranitromethane from the reaction mixture with the potassium hydroxide. After the 30 minutes at 75°, the temperature was raised to 95° over the next 30 minutes while the sparging continued at the same rate. The trinitration mixture was poured into 2 liters of ice-water to precipitate the trinitrotoluene. The crude trinitrotoluene then was isolated by filtration. The crude potassium nitroform was isolated on a medium sintered glass filter and washed with anhydrous ethyl ether. The precipitate was then dissolved in acetone and transferred to a stoppered flask. The acetone was then evaporated. The precipitate was redissolved in 30 ml. of fresh acetone and 2 ml. of methyl iodide was added.[13] The stoppered flask was allowed to stand for 1 week. As the reaction proceeded, crystals of potassium iodide appeared on the walls of the flask. At the end of 1 week, the acetone was removed under reduced pressure. The precipitate was then dissolved in ether and transferred to a separatory funnel. The ethereal solution was washed with three 20 ml. aliquots of a sodium bisulfite solution (30 g./100 ml. of H_2O). The ethereal solution was dried over anhydrous $MgSO_4$, and then the ether was removed under reduced pressure. The crude 1,1,1-trinitroethane was purified by sublimation, m.p. 55.0–55.5° (uncor.).

Counting Instrument.—A Tricarb liquid scintillation counter equipped with two photomultiplier tubes in a coincidence circuit (Packard Instrument Co., LaGrange, Ill.) was used to radioassay all samples. The lower and upper discriminators were set at 10 volts and infinity, respectively. The high voltage was set at 1200 volts.

Counting System.—All samples were assayed using 5-dram screw-cap crystal-lite vials (Wheaton Manufacturing Co., Millville, N. J.). The counting system consisted of 50 mg. of either trinitrotoluene or 1,1,1-trinitroethane, and 20 ml. of toluene which contained 4 g. of 2,5-diphenyloxazole and 100 mg. of 1,4-bis-[2-(5-phenyloxazolyl)]-benzene per liter.

Acknowledgment.—The authors wish to express their gratitude to J. V. R. Kaufman, L. H. Eriksen and R. Frye for their encouragement and interest during this investigation, and are indebted to the Army Ordnance Corps for granting the release of this article for publication.

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(9) R. C. Thomas, Jr., C. H. Wang and B. E. Christensen, *J. Am. Chem. Soc.*, **73**, 5914 (1951).

(10) M. Calvin, C. Heidelberger, J. C. Reid, B. M. Tolbert and P. F. Yankwich, "Isotopic Carbon," John Wiley and Sons, Inc., New York, N. Y., 1949, pp. 228–231.

(11) T. M. Burton and E. F. Degering, *J. Am. Chem. Soc.*, **62**, 227 (1940).

(12) W. Tschelinzeff and W. Schmidt, *Ber.*, **62**, 2210 (1929).

(13) This reaction is similar to that reported by Hantzsch and Rinckenberger[2] who prepared the same compound by treating silver nitroform with methyl iodide in an ethereal solution.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CASE INSTITUTE OF TECHNOLOGY, CLEVELAND 6, OHIO]

Aromatic Amination with Hydroxylammonium Salts. Reactivity and Directive Effects[1]

BY PETER KOVACIC, ROBERT P. BENNETT AND J. LINDSLEY FOOTE[2]

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A variety of hydroxylamine salts was found to aminate aromatic compounds in the presence of Friedel–Crafts catalysts. Toluene and the halobenzenes gave predominant *ortho–para* orientation with a comparatively high percentage of *m-* isomer. The amount of catalyst required varied with the nature of the salt. On the basis of the selectivity factors for the amination of toluene in the presence of aluminum chloride, an activity series may be formulated: $H_2NOH{\cdot}HBr \geqslant (H_2NOH)_2{\cdot}H_2SO_4 > H_2NOH{\cdot}C_2H_5OSO_3H > H_2NOH{\cdot}CH_3CO_2H > H_2NOH{\cdot}HCl > (H_2NOH)_3{\cdot}H_3PO_4 = H_2NOH$. From competitive amination with hydroxylammonium chloride, the relative rate, $k_{\text{toluene}}/k_{\text{benzene}}$, was found to be 2.9. Factors affecting orientation in the amination reactions are discussed.

The direct amination of aromatic compounds with hydroxylammonium chloride in the presence of Friedel–Crafts catalysts was reported independently by Graebe[3] and Jaubert[4] in 1901. The use of hydroxylammonium sulfate is described[5]

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(1) Part IV of a series on "Direct Aromatic Amination"; from the Ph.D. theses of R. P. Bennett and J. L. Foote, Case Institute of Technology, 1960; presented at the 140th Meeting of the American Chemical Society, September, 1961.

(2) National Science Foundation Fellow, 1958–1960.

(3) C. Graebe, *Ber.*, **34**, 1778 (1901).

(4) G. F. Jaubert, *Compt. rend.*, **132**, 841 (1901).

(5) J. Turski, (a) German Patent 287,756 (1914); *C. A.*, **10**, 2128 (1916); (b) British Patent 626,661 (1949); *C. A.*, **44**, 2761 (1950); (c) U. S. Patent 2,585,355 (1952); *C. A.*, **47**, 875 (1953).