BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 1515—1518(1972)

Reinvestigation of the Nitration of Ethylmesitylene and *n*-Propylmesitylene. Revision of Early Works.[1]

Hitomi SUZUKI,* Mikio SAWAKI,** and Reiji SAKIMOTO**
**Department of Chemistry, Faculty of Science, Kyoto University, Sakyo-ku, Kyoto*
****Research Institute, Nihon Soda Co. Ltd., Kohdzu, Odawara*

(Received October 22, 1971)

Ethylmesitylene reacts with fuming nitric acid in dichloromethane at −5—0°C to give mononitroethylmesitylene, 3,5-dimethyl-4-ethylbenzyl nitrate, 2-nitro-3,5-dimethyl-4-ethylbenzyl nitrate and a dinitroethyltrimethylcyclohexenone, while on nitration with mixed acid it yields mono and dinitro derivatives as the major products, together with minor quantities of 2-nitro- and 2,6-dinitro-3,5-dimethyl-4-ethylbenzyl nitrates, diphenylmethanes, and unidentified nitro-carbonyl compounds, possibly nitrobenzaldehydes. Similar results are obtained from the nitration of *n*-propylmesitylene. If the hydrocarbons are nitrated by adding into a large excess of the nitrating agent, the major product is 2,6-dinitro-3,5-dimethyl-4-alkylbenzyl nitrate soon after the reaction, or 2,6-dinitro-3,5-dimethyl-4-alkylbenzaldehyde when the mixture is left to stand at room temperature. The nitro compound melting at 123°C, obtained by Smith and Kiess[2] from the nitration of ethylmesitylene and described as trinitro-4-ethyl-*o*-xylene, is identified as 2,6-dinitro-3,5-dimethyl-4-ethylbenzyl nitrate. An uncharacterized nitration product (mp 135°C) from *n*-propylmesitylene, obtained by Töhl and Tripke,[3] is found most likely to be 2,6-dinitro-3,5-dimethyl-4-*n*-propylbenzyl nitrate (mp 139—140°C).

Action of electrophilic reagent upon polyalkylbenzenes sometimes results in the migration of alkyl groups, giving products of orientation quite different from those predicted by the ordinary substitution rules. Such anomalies are frequently met and well documented

---

[1] The Reaction of Polysubstituted Aromatics. XXIV. Part XXIII: This Bulletin, **44**, 2871 (1971).

[2] L. I. Smith and M. A. Kiess, *J. Amer. Chem. Soc.*, **61**, 989 (1939). Also *cf.* D. V. Nightingale, *Chem. Rev.*, **40**, 117 (1947).

[3] A. Töhl and H. Tripke, *Ber.*, **28**, 2459 (1895).

particularly in the sulfonation and acylation.[4] Meanwhile, the nitration of polyalkylbenzenes has generally been recognized not to involve such alkyl rearrangement, and therefore, their polynitro derivatives have been widely used for the characterization of isomeric series of polyalkylbenzenes.

Literature so far contains one exception which seems to involve both displacement and intramolecular migration of alkyl groups during the nitration. Töhl and Tripke[3] nitrated ethylmesitylene (2-ethyl-1,3,5-trimethylbenzene) with fuming nitric acid and obtained the product melting at 123°C, to which they assigned the dinitro structure on the basis of elemental analysis. Their claim was later re-examined by Smith and Kiess,[2] who showed that the hydrocarbon can afford two different nitro compounds depending on the nitrating conditions employed. When ethylmesitylene dissolved in chloroform was thoroughly stirred with sulfuric acid and slowly nitrated with fuming nitric acid at 0°C, the product was white needles melting at 110—111°C. Elemental analysis and chemical behavior were consistent with its formulation as dinitroethylmesitylene. However, treatment of the hydrocarbon with mixed acid (H_2SO_4 - HNO_3, 2: 1 v/v) at 0°C furnished the nitro compound of Töhl and Tripke, mp 123°C, which showed a large depression in melting point on admixture with the above nitro compound of mp 110—111°C. It did not afford on reduction with stannous chloride the expected diamino compound but gave an unidentified yellow substance melting at 255°C. Elemental analysis was close to that of a trinitroethylxylene, but the substance was found neither to be trinitro-4-ethyl-*m*-xylene (mp 129°C) nor trinitro-2-ethyl-*m*-xylene (mp 181°C), which could arise from ethylmesitylene through the displacement of one of methyl groups by nitro group. Hence they suggested the higher melting nitro compound as trinitro-4-ethyl-*o*-xylene (mp 121°C) on the evidences obtained from analysis and mixed melting determination. The formation of trinitro-4-ethyl-*o*-xylene from ethylmesitylene requires the intramolecular migration of at least one alkyl group during the nitration. In the lights of our present knowledge, such isomerization of polyalkylbenzenes seems to be quite unusual. Thus we have re-examined the early workers' results with the aims to solve the discrepancies in the literature as well as to ascertain if the nitration of ethylmesitylene can in fact lead to the claimed rearrangement of alkyl groups.

When a solution of ethylmesitylene in dichloromethane was treated with excess of fuming nitric acid ($d=1.5$) at -5—0°C, a dark red oily substance was obtained, which showed strong infrared bands due to benzyl nitrate at 1532 and 1364 (NO_2); 1648, 1272, and 844 cm^{-1} (ONO_2); a prominent PMR peak due to CH_2ONO_2 at 4.75 τ. Weak infrared bands due to carbonyl and hydroxyl groups were also observed at around 1700 and 3400—3500 cm^{-1}. Chromatography on alumina of the product mixture gave besides unchanged hydrocarbon (17%) mononitroethylmesitylene (42%) from light petroleum eluates, bis(4-ethyl-3,5-dimethylbenzyl) ether (3%) and nitro-carbonyl compounds (*ca.* 7%) from light petroleum - benzene mixture eluates, and 3,5-dimethyl-4-ethylbenzyl alcohol (7%) from ether eluates.[5] Bis-benzyl ether and benzyl alcohol were probably the secondary products from benzyl nitrate formed during the elution through activated alumina.

Chromatography on silica gel of the same product mixture proved to be unsatisfactory for the separation of nitro compounds from nitrooxymethyl compounds. However, a new alicyclic nitro-ketone, 5,6-dinitro-2,4,6-trimethyl-3-ethyl-3-cyclohexen-1-one (mp 140—141°C, crude yield 3—4%) was obtained as fine needles from the nitro-carbonyl fractions eluted with benzene-light petroleum mixture. The proof of structure for this unexpected product will be treated in the subsequent paper.[6]

When the nitration of the hydrocarbon was conducted by adding into the large excess of fuming nitric acid at -5—0°C, the major product which readily deposited from the dark reaction mixture was white needles melting at 120—122°C, the product described by Töhl and Tripke as dinitroethylmesitylene and by Smith and Kiess as trinitroethylxylene. The result of C, H analysis was quite close to that of trinitroethylxylene, as had been reported by American workers. However, its infrared spectrum contained prominent bands due to $-ONO_2$ group at 1645, 1270, and 843 cm^{-1} besides the expected absorptions of nitro group at 1530 and 1363 cm^{-1}, while PMR spectrum depicted the presence of one ethyl group (3H, 8.83 t; 2H, 7.21 q; $J=8$ Hz), two equivalent methyl groups (6H, 7.71 s) and one methylene group (2H, 4.67 s). These spectral evidences unambiguously show that the nitro compound melting at 123°C is not trinitro-4-ethyl-*o*-xylene but 2,6-dinitro-3,5-dimethyl-4-ethylbenzyl nitrate. In spite of its narrow melting range and brilliant crystalline form, the PMR spectrum revealed that the benzyl nitrate was usually accompanied by a small amount of dinitroethylmesitylene. It was quite tedious to remove this minor impurity without a considerable loss of the material. Obviously, the earlier workers have taken the less pure nitrate for trinitroethylxylene, since the presence of the dinitro derivative as impurity can contribute to the increase in the carbon content of the product. We can therefore conclude that the nitration of ethylmesitylene does not involve any rearrangement of alkyl groups under the ordinary conditions of the reaction.

Action of mixed acid (H_2SO_4 - HNO_3, 1: 1 w/w) upon ethylmesitylene in dichloromethane at -5—0°C gave an oily substance, which on alumina chromatography gave besides unchanged starting material (*ca.* 4%) mononitro and dinitro derivatives (24 and 26%, respectively) as the major products from light petro-

---

[4] For sulfonations, H. J. Shine, "Aromatic Rearrangements," Elsevier, London (1967), p. 48; H. Cerfontain, "Mechanistic Aspects in Aromatic Sulfonation and Desulfonation," Interscience, London (1968), p. 221; for acylations, P. H. Gore in "Friedel-Crafts and Related Reactions," Vol. III, Part I, ed. by G. A. Olah, Interscience, London (1964), p. 1, and S. Sethna in the same book, p. 911.

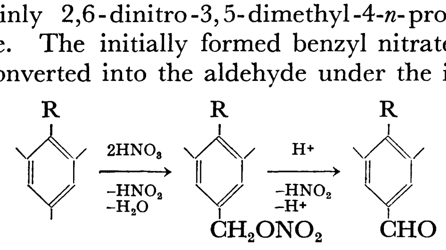
[5] Yields are expressed in weight percentage calculated on the basis of the amount of product mixture, which was subjected to chromatographic separation.

[6] H. Suzuki, M. Sawaki, and R. Sakimoto, This Bulletin, in press.

leum eluates, diphenylmethane and nitro-carbonyl compounds (less than 4%) from light petroleum-benzene eluates, and a mixture of nitrobenzyl alcohols (8%) from ether eluates. Diphenylmethane was probably formed by the sulfuric acid-catalyzed condensation of 2-nitro-3,5-dimethyl-4-ethylbenzyl nitrate with mononitroethylmesitylene.[7] The main component of the nitro-carbonyl fractions was presumably nitrobenzaldehydes, which could arise from nitrobenzyl nitrates under the influence of sulfuric acid.[8]

In connection with the present work, the nitration of *n*-propylmesitylene was re-examined with the expectation that the uncharacterized compound melting at 135°C, obtained by Töhl and Tripke[3] in the nitration of *n*-propylmesitylene, might be also a benzyl nitrate. A solution of the hydrocarbon in dichloromethane was treated with fuming nitric acid at -5—0°C to give a dark yellow oil, which on chromatography over alumina was separated into unchanged hydrocarbon (2%), mononitro-*n*-propylmesitylene (59%), impure bis(3,5-dimethyl-4-*n*-propylbenzyl) ether (3%), nitro-carbonyl compounds (*ca.* 5%), and 3,5-dimethyl-4-*n*-propylbenzyl alcohol (4%) and its nitro derivatives (2%).

When the nitration was conducted by dissolving the hydrocarbon into a large excess of cold fuming nitric acid, appreciable amounts of crystalline product were soon precipitated from the reaction mixture, which was immediately collected on a glass filter and recrystallized from a mixture of ligroin and dichloromethane. Colorless plates thus obtained melted at 139—140°C and had the formula $C_{12}H_{16}N_3O_7$. It showed infrared bands for nitro group at 1530 and 1361 cm^{-1} and those for nitrooxy group at 1644, 1277, and 857 cm^{-1}. Its PMR spectrum contained peaks due to one *n*-propyl group (3H, 8.95 t, J=7 Hz; 2H, 8.37—8.62 m; and 2H, 7.28 t, J=7 Hz), two equivalent methyl groups (6H, 7.72 s), and one methylene group (2H, 4.69 s). These analytical and spectral data were only compatible with the formulation of the product as 2,6-dinitro-3,5-dimethyl-4-*n*-propylbenzyl nitrate. Since there is no reason to believe that *n*-propylmesitylene behaves on nitration differently from ethylmesitylene, the product of Töhl and Tripke seems most likely to be the above nitrate although the original paper contains no detail to confirm its structure. If the hydrocarbon was dissolved into excess of fuming nitric acid in a ice-salt bath and the mixture was allowed to stand overnight without adding further amounts of ice, the well crystallized solid which separated on the surface of the acid medium was mainly 2,6-dinitro-3,5-dimethyl-4-*n*-propylbenzaldehyde. The initially formed benzyl nitrate was no doubt converted into the aldehyde under the influence of acid reagent.



R: Et or *n*-Pr

The syrupy product obtained by the nitration of *n*-propylmesitylene with mixed acid gave by similar chromatographic treatment unchanged hydrocarbon (3%), mononitro and dinitro derivatives (5 and 33%, respectively), diphenylmethane and nitro-carbonyl compounds (less than 2%), and a mixture of nitrobenzyl alcohols (11%). The last compounds were secondary reaction products of nitrobenzyl nitrates formed during the chromatographic treatment over activated alumina.

Experimental

Ethylmesitylene [bp 104—105°C/25 mmHg. PMR: ethyl (3H 8.96 t, 2H 7.48 q, J=8 Hz), methyl (3H 7.84 s; 6H 7.80 s), and aromatic H (2H 3.36 s)] and *n*-propylmesitylene [bp 117—119°C/28 mmHg. PMR: *n*-Pr (3H 9.04 t, J=7 Hz; 2H 8.39—8.71 m; 2H 7.53 t, J=7 Hz), Me (3H 7.86 s; 6H 7.80 s), and aromatic H (2H 3.38 s)] were prepared by the Friedel-Crafts acylation of mesitylene, followed by the Clemmensen reduction of the corresponding mesitoyl ketones.[9,10]

Infrared spectra were measured on Nujol mulls with a Jasco 402G spectrophotometer and only prominent peaks are recorded. PMR spectra were determined in deuteriochloroform or carbon tetrachloride solutions with a Varian A-60A spectrometer and a JEOLCO PS-100 spectrometer against internal TMS.

The representative results obtained from the nitration with fuming nitric acid and mixed acid are shown below.

Nitrations with Fuming Nitric Acid. *a)*: Fuming nitric acid (d=1.50, 8.4 g) was added dropwise to a magnetically stirred solution of ethylmesitylene (7.4 g) in dichloromethane (30 m*l*) at -5—0°C over a period of 30 min, and after the end of addition, the mixture was stirred at room temperature for additional 1 hr. The mixture was diluted with water and the organic part was thoroughly washed with water and dilute aqueous sodium bicarbonate. After drying over anhydrous sodium sulfate, the solvent was evaporated to give a yellow oily mixture (*ca.* 10 g), part of which (7.0 g) was subjected to chromatographic resolution over alumina using light petroleum as eluant to give unchanged hydrocarbon (bp 97—98°C/22 mmHg, 1.2 g) and *2-nitro-4-ethyl-1,3,5-trimethylbenzene* (3.0 g). The latter was a pale yellow liquid boiling at 113—114°C/3 mmHg: IR: 792, 847, 869, 1022, 1038, 1059, 1183, 1369, and 1530 cm^{-1}; PMR (CCl_4): Et (3H 8.90 t, 2H 7.38 q; J=8 Hz), Me (6H 7.84 s; 3H 7.72 s), and aromatic H (1H 3.20 s). It gave on reduction with stannous chloride a liquid amine, which was treated with acetic anhydride to give *2,4,6-trimethyl-3-ethylacetanilide*, mp 161—162°C.

Found: C, 76.07; H, 9.34%. Calcd for $C_{13}H_{19}NO$: C, 76.10; H, 9.27%.

The benzene eluates gave an impure bisbenzyl ether as a pale yellow oil (0.2 g) and a mixture of nitro-carbonyl compounds as a light brown syrup (0.5 g). The major component of the former was identified as *bis(4-ethyl-3,5-dimethylbenzyl) ether* by infrared absorptions (786, 863, 1010, 1092, 1061, and 1140 cm^{-1}) and PMR peaks (CCl_4; Et (3H 8.92 t; 2H 7.42 q; J=8 Hz), Me (6H 7.74 s), $-CH_2O-$ (2H 5.71 s), and aromatic H (2H 3.17 s)), although it could not be ob-

---

7) H. Suzuki and K. Nakamura, *ibid.*, **43**, 473 (1970); H. Suzuki, *ibid.*, **42**, 2618 (1969).

8) S. D. Ross, E. R. Coburn, and M. Finkelstein, *J. Org. Chem.*, **33**, 585 (1968).

9) O. R. Noller and R. Adams, *J. Amer. Chem. Soc.*, **46**, 1889 (1924).

10) P. H. Gore and J. A. Hoskins, *J. Chem. Soc., C*, **1971**, 517.

tained in pure form. The latter mixture showed a complicated pattern of infrared spectrum with prominent carbonyl bands at 1750, 1720, and 1677 cm^{-1}. No attempt was made to resolve them.

Further elution with ether gave colorless needles (0.5 g) melting at 72—74°C, identified as *4-ethyl-3,5-dimethylbenzyl alcohol* by analysis, infrared spectrum (730, 866, 998, 1046, 1143, and 3220 cm^{-1}), and PMR spectrum (CCl_4; Et (3H 8.93 t, 2H 7.41 q; J=7 Hz), Me (6H 7.74 s), OH (1H, 8.56 broad), CH_2 (2H 5.62 s), and aromatic H (2H 3.18 s)).

Found: C, 80.58; H, 9.52%. Calcd for $C_{11}H_{16}O$: C, 80.49; H, 9.76%.

b): Similar treatment of the nitration product (7.0 g) from *n*-propylmesitylene gave unchanged hydrocarbon (bp 110—111°C/19 mmHg, 0.15 g) and *2-nitro-4-*n*-propyl-1,3,5-trimethylbenzene* (113—114°C/2 mmHg, 4.1 g) from light petroleum eluates. The latter was slightly yellow oil, which readily solidified to large prisms (mp 34—35°C) and had infrared bands at 798, 840, 869, 1035, 1367, and 1521 cm^{-1}; PMR peaks at 8.99 (Me t, J=8 Hz), 8.42—8.67 (CH_2, m), 7.84 (2Me, s), 7.74 (Me, s), and 3.23 τ (aromatic H, s). It gave on reduction with stannous chloride and the subsequent treatment with acetic anhydride *3-*n*-propyl-2,4,6-trimethylacetanilide*, mp 163—164°C (lit,[3] mp 161°C).

Impure *bis(4-*n*-propyl-3,5-dimethylbenzyl) ether* (0.2 g) and a mixture of nitro-carbonyl compounds (0.35 g) were obtained from benzene eluates. The former product could not be isolated in crystalline form and had infrared bands at 862, 1091, and 1140 cm^{-1}; PMR peaks (CCl_4) at 9.01 (Me, t, J=8 Hz), 8.64—8.42 (CH_2, m), 7.75 (2Me, s), 5.73 (CH_2O, s), and 3.19 τ (aromatic H, s).

Elution with ether gave *4-*n*-propyl-3,5-dimethylbenzyl alcohol* (0.3 g), which crystallized from ethanol as white needles and melted at 68—69°C. IR: 732, 867, 1002, 1039, and 3200—3300 cm^{-1}; PMR (CCl_4): *n*-Pr (3H 9.00 t, J=8 Hz; 2H 8.40—8.76 m; 2H 7.48 t, J=8 Hz), OH (1H 8.44 broad), Me (6H 7.74 s), CH_2 (2H 5.63 s), and aromatic H (2H 3.18 s).

Found: C, 81.04; H, 10.41%. Calcd for $C_{12}H_{18}O$: C, 80.90; H, 10.11%.

c): Ethylmesitylene (7.4 g) was added dropwise to the fuming nitric acid (20 m*l*) during the course of 30 min at −5—0°C and the mixture slurried with precipitated crystals was rapidly filtered through a sintered glass filter to leave a white crystalline cake, which was crystallized from a mixture of *n*-hexane and dichloromethane as white needles, mp 120—122°C. It was identified as *2,6-dinitro-3,5-dimethyl-4-ethylbenzyl nitrate* on the basis of elemental analysis and spectral properties. IR: 727, 749, 759, 843, 860, 962, 993, 1059, 1270, 1363, 1530, and 1645 cm^{-1}.

Found: C, 44.27; H, 4.55%. Calcd for $C_{11}H_{14}N_2O_4$ (dinitroethylmesitylene): C, 55.46; H, 5.88%. Calcd for $C_{10}H_{11}N_3O_6$ (trinitroethylxylene): C, 44.61; H, 4.09%. Calcd for $C_{11}H_{13}N_3O_7$ (dinitrodimethylethylbenzyl nitrate): C, 44.15; H, 4.35%.

When the reaction mixture was quenched by pouring into excess of water, the precipitated nitrate was accompanied by appreciable amounts of dinitroethylmesitylene, and complete removal of the latter by simple recrystallization was quite difficult to effect.

d): A similar treatment of *n*-propylmesitylene gave *2,6-dinitro-3,5-dimethyl-4-*n*-propylbenzyl nitrate* as large plates, mp 139—140°C. IR: 754, 857, 873, 993, 1277, 1361, 1530, and 1644 cm^{-1}.

Found: C, 46.51; H, 4.96%. Calcd for $C_{12}H_{15}N_3O_7$: C, 46.01; H, 4.83%.

If the reaction mixture was left to stand at room temperature for a day or two, a large quantity of a crystalline solid was obtained. On recrystallization from a mixture of ligroin and dichloromethane, it gave colorless fine needles which began to sinter at around 135—140°C and melted away at 152—162°C. Elemental analysis and spectral properties agreed with the structure of *2,6-dinitro-3,5-dimethyl-4-*n*-propylbenzaldehyde*. IR: 743, 787, 862, 913, 1028, 1057, 1288, 1360, 1455, 1528, 1545, and 1709 cm^{-1}; PMR ($CDCl_3$): *n*-Pr (3H 8.92 t, J=7 Hz; 2H 8.35—8.58 m; 2H 7.28 t, J=7 Hz), Me (6H 7.70 s), and CHO (1H 0.26 s).

Found: C, 54.60; H, 5.52; N, 10.46%. Calcd for $C_{12}H_{14}N_2O_5$: C, 54.15; H, 5.30; N, 10.52%.

On storage under diffused light, it gradually became greenish yellow.

Nitrations with Mixed Acid. *a)*: Ethylmesitylene (7.4 g) was dissolved in dichloromethane (30 m*l*) and the solution was stirred thoroughly with concentrated sulfuric acid (11.7 g) at −5—0°C. Fuming nitric acid (11.7 g, d=1.5) was introduced during the course of 30 min and the reaction mixture was worked up as usual to yield an oil (10.5 g), part of which (5 g) was chromatographed on alumina to give unchanged hydrocarbon (0.18 g), 2-nitro-4-ethyl-1,3,5-trimethylbenzene (1.2 g), and *2,6-dinitro-4-ethyl-1,3,5-trimethylbenzene* (mp 110—111°C, 1.3 g) from light petroleum eluates. The dinitro compound showed the PMR peaks at 8.85 (Me t, J=7 Hz), 7.79 (2Me s), 7.29 (CH_2 q, J=7 Hz), and 7.90 τ (Me s), and IR bands at 762, 781, 807, 856, 866, 1045, 1202, 1369, and 1529 cm^{-1}. Benzene eluted a diphenylmethane (mp 186—188°C, *ca.* 0.1 g) and nitro-carbonyl compounds (0.2 g). The former product had peaks at 8.87 (Me t), 7.95 (Me s), 7.83 (Me s), 7.64 (3Me s), 7.36 (CH_2 q), 6.13 (CH_2 s), and 3.77 τ (aromatic H s) in the PMR spectrum, and was probably a dinitropentamethyldiethyldiphenylmethane, although no attempt was made to clarify its structure. Ether eluted a mixture of mono and dinitroethyldimethylbenzyl alcohols as a dark glassy substance (*ca.* 0.4 g). *2-Nitro-3,5-dimethyl-4-ethylbenzyl alcohol* had IR bands: 755, 795, 849, 878, 1006, 1048, 1368, 1529, and 3360—3380 cm^{-1}, and PMR peaks: Et (3H 8.92 t, 2H 7.45 q; J=7 Hz), Me (3H, 7.84 s; 3H 7.71 s), CH_2 (2H 5.69 s), and aromatic H (1H 2.96 s).

b): On a similar treatment of the nitration product (7.0 g) from *n*-propylmesitylene gave unchanged hydrocarbon (*ca.* 0.2 g), 2-nitro-4-*n*-propyl-1,3,5-trimethylbenzene (0.35 g), and *2,6-dinitro-4-*n*-propyl-1,3,5-trimethylbenzene* (mp 117—118 °C; lit.[3] mp 93—94°C, 2.3 g) from light petroleum eluates. The dinitro compound had IR bands: 741, 797, 854, 864, 886, 1023, 1055, 1363, and 1521 cm^{-1}, and PMR peaks: *n*-Pr (3H 8.95 t, 2H 8.30—8.68 m, 2H 7.34 t), and Me (3H 7.88 s; 6H 7.78 s). Benzene eluted a small amount of a diphenylmethane (0.1 g) and nitro-carbonyl compounds (0.1 g). The former showed PMR peaks at 8.98 (Me t, J=8 Hz), 8.64—8.42 (CH_2 m), 7.98 (Me s), 7.87 (Me s), 7.78 (Me s), 7.41 (CH_2 t), 6.18 (CH_2 s), and 3.88 τ (aromatic H s), and was probably a dinitropentamethyldi-*n*-propyldiphenylmethane, although it could not be obtained in quantity sufficient for positive identification. Further elution with ether gave a mixture of nitrodimethyl-*n*-propylbenzyl alcohols as a dark red glass, which had PMR peaks due to *n*-propyl group at 9.01 (3H t, J=7 Hz), 8.46—8.77 (2H m), and 7.47 (2H t, J=7 Hz); those due to two methyl groups at 7.88 and 7.75; and those due to hydroxyl, methylene, and ring protons at 6.41 (broad), 5.74, and 2.98 τ, respectively.