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Anomalous Products Obtained by Nitration of Pentamethylbenzene, Pentaethylbenzene, and Some Mixed Penta-alkylbenzenes[1]

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Pentamethylbenzene has been nitrated with fuming nitric acid to give mainly a mixture of nitropentamethylbenzene and 2,3,4,5-tetramethylbenzyl nitrate. Other isomeric nitrates were not formed in any significant amount. 6-Nitro-2,3,4,5-tetramethylbenzyl nitrate, 2,3,4,5-tetramethylbenzyl alcohol, 2,3,4,5-tetramethylbenzaldehyde, 2,2′,3,3′,4,4′,5,5′,6-nonamethyldiphenylmethane, and 2,2′,3,3′,4,4′,5,5′-octamethyl-6-nitroxymethyldiphenylmethane were the minor products. Pentaethylbenzene gave a mixture of nitropentaethylbenzene and α-methyl-2,3,4,5-tetraethylbenzyl nitrate along with some products of oxidation. Preferential side-chain attack occurred at the primary alkyl group *ortho* to the unsubstituted ring position. Thus, 1-methyl-2,3,4,5-tetraethylbenzene was found to give benzyl nitrate and α-methylbenzyl nitrate nearly in equal amounts, while 3-methyl-1,2,4,5-tetraethylbenzene was found to give them in an approximate ratio of 1 : 3. 1,3,4-Trimethyl-2,5-diisopropylbenzene underwent extensive nitrodealkylation, and 3,4-dimethyl-2,5-diisopropylbenzyl nitrate was the only side-chain substituted product identified.

Electrophilic substitution of polysubstituted aromatic systems often gives unusual results which have deviated considerably from the established pathways for lightly substituted compounds. One of such examples is the nitration of penta-alkylbenzenes, where the action of the nitrating agent usually results in the replacement of one of the alkyl groups to form dinitrotetra-alkylbenzenes. Nitration of pentamethylbenzene to dinitroprehnitene was first observed by Gottschalk,[2] who suggested that hydrocarbon underwent disproportionation to prehnitene and hexamethylbenzene under the influence of acid, and that dinitroprehnitene was formed by nitration of prehnitene. Pentaethylbenzene was also found to behave similarly towards the nitrating agent, giving 3,6-dinitro-1,2,4,5-tetraethylbenzene.[3] Reinvestigation of the reaction, however, revealed that the products were not so simple as had been described in literature.[4,5] The present paper deals with anomalous products from nitration of pentamethylbenzene, pentaethylbenzene, and some related mixed penta-alkylbenzenes.

Results and Discussion

When pentamethylbenzene was nitrated at −5—0°C with an excess of fuming nitric acid in chloroform or methylene chloride, the product was a light brown oily solid, the major component of which was readily identified as a benzyl nitrate from very strong infrared bands at 1271 and 1624 cm^{-1} ($-ONO_2$), and a prominent PMR peak at 4.63 τ (CH_2). Weak carbonyl and hydroxylic absorptions were also observed. Careful chromatographic treatment of the crude product on alumina gave unchanged hydrocarbon, polymethyldiphenylmethanes (XV and XXI), nitropentamethylbenzene, and tetramethylbenzyl nitrates from the light petroleum eluates; 6-nitro-2,3,4,5-tetramethylbenzyl nitrate (XII) and 2,3,4,5-tetramethylbenzaldehyde (XIII) from the benzene eluates; and a substantial amount of 2,3,4,5-tetramethylbenzyl alcohol (XI) from the ether eluates. Undoubtedly the alcohol was derived from the benzyl nitrate through the hydrolysis during the elution. Thus, the original mixture was composed mainly of 2,3,4,5-tetramethylbenzyl nitrate (III), the identity of which was further confirmed by comparison with the authentic specimen, prepared from prehnitene (I) through chloromethylation and subsequent treatment of the chloride (II) with silver nitrate in acetonitrile (Fig. 1). Other isomeric tetramethylbenzyl nitrates were also formed, but only in slight amount (less than 5%) as compared to the 2,3,4,5-tetramethylbenzyl isomer. Analysis of these minor products were carried out by gas-liquid chromatography and PMR spectroscopy. Since benzyl nitrates were not thermally so stable, gas-chromatographic analysis was carried out after their conversion into acetates. 2,3,4,6-Tetramethylbenzyl nitrate (IV) greatly exceeded 2,3,5,6-tetramethylbenzyl nitrate (V) in amount.

1) The Reaction of Polysubstituted Aromatics. Part XIV. Part XIII: This Bulletin, **42**, 2618 (1969).
2) M. Gottschalk, *Ber.*, **20**, 3286 (1887).
3) L. I. Smith and C. O. Guss, *J. Amer. Chem. Soc.*, **62**, 2635 (1940).
4) R. Willstätter and H. Kubli, *Ber.*, **42**, 4151 (1909).
5) L. I. Smith and S. A. Harris, *J. Amer. Chem. Soc.*, **57**, 1289 (1935).

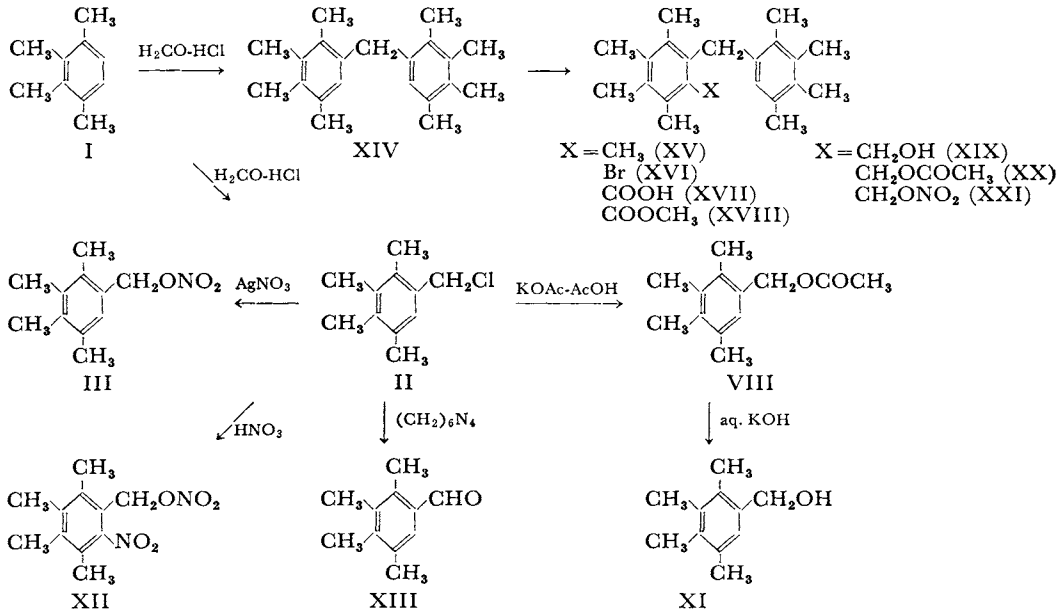


Fig. 1

PMR spectra of the light petroleum eluates showed a pair of weak, ill-resolved peaks of relative areas 1 to 2, at 3.87 and 6.05 τ. As is apparent from the structural correlations,[6] this spectral pattern strongly suggests the presence of polyalkyldiphenylmethanes. Of these the minor component was concentrated in the earlier eluates and readily identified as 2,2′,3,3′,4,4′,5,5′,6-nonamethyldiphenylmethane (XV) by spectral comparison with an authentic specimen. Another diphenylmethane with an extra peak at 4.41 τ could be isolated from a mixture of benzyl nitrates through their conversion into acetates, followed by chromatography on alumina. The later eluates gave a small amount of fine prisms, mp 170—172°C, which had the formula $C_{24}H_{32}O_2$ and showed a sharp infrared peak at 1733 cm^{-1}; PMR peaks at 8.18, 7.71—7.94, 6.09, 5.05, and 4.05 τ with relative areas 3 : 24 : 2 : 2 : 1. The peak at 8.18 τ is due to the acetoxy group, and the peaks at 7.71—7.94 τ due to eight methyl groups of two phenyl groups. The peaks at 5.05 and 6.09 τ arise from the methylene group. The remaining peak at 4.05 τ corresponds to an aromatic proton, the appearance of which at high field indicates its presence *ortho* to the methylene bridge.[6] The above spectral data agree with the structure 2,2′,3,3′,4,4′,5,5′-octamethyl-6-acetoxydiphenylmethane (XX), and therefore the original diphenylmethane is formulated as 2,2′,3,3′,4,4′,5,5′-octamethyl-6-nitroxymethyldiphenylmethane (XXI). These diphenylmethanes were probably derived from the self-condensation of III, or from the condensation of III with pentamethylbenzene. XV may also be derived from XXI through the hydride ion abstraction, as has been demonstrated by the easy conversion of pentamethylbenzyl compounds into hexamethylbenzene.[7] In fact, 2,3,4,5-tetramethylbenzyl chloride (II) heated with trifluoroacetic acid was found to give some XV besides other products.

2,3,4,5-Tetramethylbenzaldehyde (XIII) probably arose from the acid-[8] or base-catalysed[9] conversion of nitrate into aldehyde, and was isolated as a semicarbazone. The semicarbazone showed double melting which may be characteristic for the ones derived from tetramethylbenzaldehydes.[10] In contrast to nitration by mixed acid, the use of fuming nitric acid yielded dinitroprehnitene only in a small amount.

Pentaethylbenzene could be nitrated by fuming nitric acid to give a pale yellow syrup, the main component of which was again a benzyl nitrate since the product showed strong infrared bands at 1275 and 1627 cm^{-1} ($-ONO_2$) and PMR peaks at 8.26 (CH_3, d) and 2.83 τ (CH, q). Absorption due to carbonyl and hydroxylic groups was weak. Repeated chromatography of the crude product on alumina, however, gave 2,3,4,5-tetraethylstyrene (XXVII) accompanied by some unchanged hydrocarbon and nitropentaethylbenzene from the light petroleum eluates; an orange-yellow syrup with a strong carbonyl absorption from the benzene

6) H. Suzuki, This Bulletin, **42**, 2618 (1969).

7) H. Suzuki and K. Nakamura, *ibid.*, **41**, 2197 (1968).

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

9) J. W. Baker and A. J. Neale, *J. Chem. Soc.*, **1954**, 3225; J. W. Baker and T. G. Heggs, *ibid.*, **1955**, 616.

10) L. I. Smith and J. Nichols, *J. Org. Chem.*, **6**, 502 (1941).

Table 1. PMR spectral data for tetramethylbenzyl acetates, chlorides, and nitrates

Compound	Mp or bp* (°C)	PMR spectra (in CCl_4, τ)			
		ArH	CH_2	CH_3**	CH_3COO
2,3,4,5-Tetramethylbenzyl series					
Acetate	46—48	3.10	4.97	7.72 (1), 7.78 (2), 7.83 (1)	7.99
Chloride	44—46 (146—148/18 mmHg)	3.21	5.53	7.74 (1), 7.79 (1), 7.85 (1) 7.86 (1)	
Nitrate	45—46	3.07	4.68	7.76 (2), 7.83 (2)	
2,3,4,6-Tetramethylbenzyl series					
Acetate	(166—167/22 mmHg)	3.22	4.89	7.72 (1), 7.79 (2), 7.89 (1)	8.05
Chloride	34—36 (147—149/20 mmHg)	3.25	5.43	7.69 (1), 7.72 (1), 7.80 (1) 7.88 (1)	
Nitrate	42—44	3.19	4.52	7.67 (1), 7.75 (2), 7.85 (1)	
2,3,5,6-Tetramethylbenzyl series					
Acetate	92—93	3.10	4.82	7.77 (4)	8.00
Chloride	67—68 (142—144/20 mmHg)	3.21	5.43	7.76 (2), 7.82 (2)	
Nitrate	115—116	3.04	4.42	7.75 (4)	

* Bp in parentheses.
** Numerals in parentheses refer to the number of methyl groups.

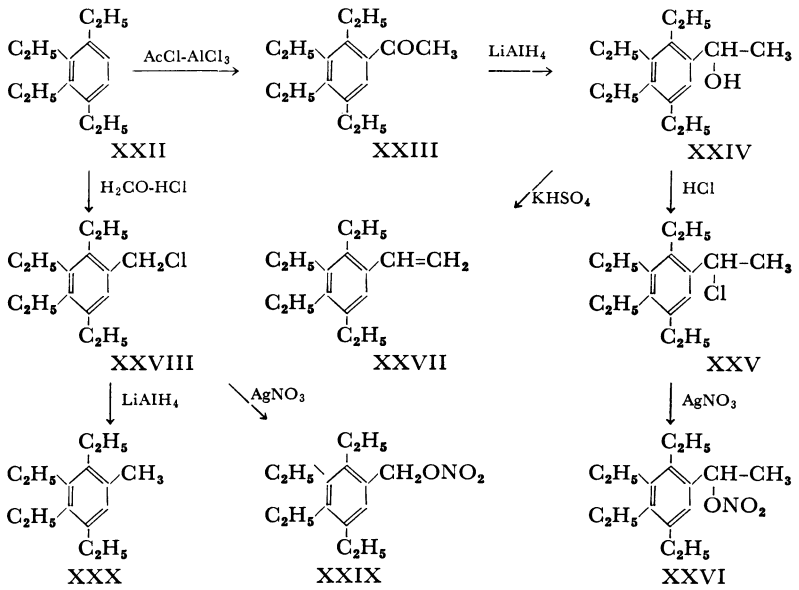
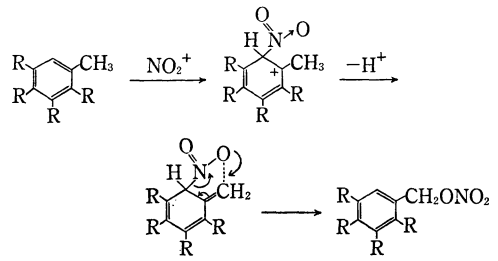


Fig. 2

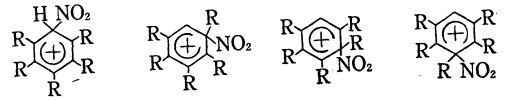
eluates; and finally a considerable amount of α-methyl-2,3,4,5-tetraethylbenzyl alcohol (XXIV) from the ether eluates. Therefore, the original nitrate was formulated as α-methyl-2,3,4,5-tetraethylbenzyl nitrate (XXVI) which underwent either hydrolysis to alcohol, or β-hydrogen elimination to the unsaturated hydrocarbon during chromatographic treatment. The structure proof of these products was made by a series of syntheses starting from 1,2,3,4-tetraethylbenzene (Fig. 2). The conversion of the α-methylbenzyl chloride (XXV) into the nitrate (XXVI) by treatment with silver nitrate in acetonitrile was not as simple as expected, and gave a mixture of several substances, although nitrate was still the main product.

With pentamethylbenzene and pentaethylbenzene, attack by nitric acid on the side-chain was almost limited to the alkyl groups adjacent to the unsubstituted position. The nuclear-to-lateral migration of the nitro group has been proposed

for such side-chain nitrooxylation of penta-alkylbenzenes.[11]



The preferred formation of the 2,3,4,5-tetra-alkylbenzyl nitrate over the 2,3,4,6-tetra-alkyl- and 2,3,5,6-tetra-alkyl isomers may be explained by the greater contribution of the intermediate benzenonium ions XXXV and XXXVII than XXXVI and XXXVIII, and the easier proton removal from the least hindered alkyl groups adjacent to the free ring position.



XXXV XXXVI XXXVII XXXVIII

High selectivity in the side-chain substitution is probably concerned with the slow step of the proton transfer from the alkyl groups of the benzenonium intermediate. Kreienbuhl and Zollinger reported that pentamethylbenzene rapidly formed an adduct with nitronium tetrafluoroborate, but showed lower reactivity towards nitration than benzene.[12] Koptyug, Krysin, and Gorfinkel also showed the nitration of 2,3,4,5,6-pentamethyldiphenyl to occur at the unsubstituted ring.[13] These results indicate that the decomposition of benzenonium ion into any side-chain products is a slower step than the nuclear hydrogen replacement, and that both processes can only compete more effectively in such a crowded system as penta-alkylbenzene.

The importance of the steric role in determining the orientation of the side-chain substitution may be understood from the nitration of some mixed penta-alkylbenzenes. The synthesis of these hydrocarbons was carried out by the routes illustrated in Figs. 2 and 3. The PMR spectra of the nitration product from 1-methyl-2,3,4,5-tetraethylbenzene (XXX) showed a methylene singlet at 4.57 τ ($-CH_2ONO_2$) and a methine quartet at 3.79 τ ($-CH(ONO_2)CH_3$), the ratio of signal intensities being 1.8 : 1, while the product from

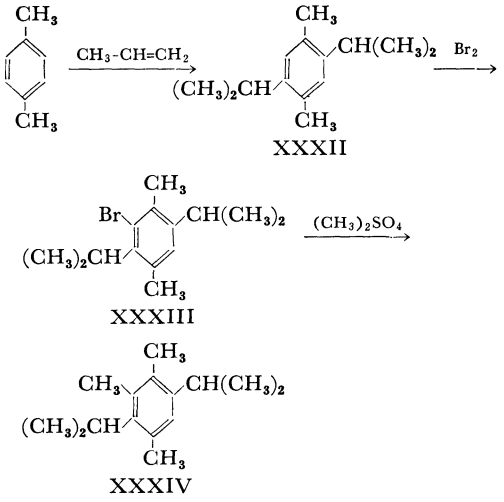


Fig. 3

3-methyl-1,2,4,5-tetraethylbenzene (XXXI) showed these signals at 4.43 and 3.78 τ with relative areas of 1 : 1.9, indicating the preferred proton release from the least hindered side-chain. Appearance of the methine signals nearly at the same position as that (3.82 τ) of XXVI indicates the attack by nitric acid on the ethyl group adjacent to the unoccupied ring position. Otherwise, the signal will appear at lower field owing to the van der Waals interactions between the $-CH(ONO_2)CH_3$ group and the two ortho alkyl groups.[14] A large downfield shift of the ring proton signal relative to the parent hydrocarbons is also consistent with the presence of $-CH(ONO_2)CH_3$ group in its vicinity. In XXX the methyl group is somewhat more reactive than the ethyl group, but the order is reversed in XXXI.

Overcrowding in pentaethylbenzene is readily understood from the marked difference in the ability of hexamethylbenzene and hexaethylbenzene to form complexes with Lewis acids.[15] Thus, the increased attack on the 3-alkyl group of XXXI as compared to XXX may be explained in terms of the increasing contribution of ion XXXVII due to the more favorable steric requirements in XXXI with respect to XXX for the access of the nitronium ion to the 2-position (Fig. 4). Attachment of the nitronium ion at the 2-position of XXXI is also facillitated not only by the favorable orientation of alkyl groups to stabilize ion XXXVII, but also by the relief of the steric strain arising from the vicinal disposition of five alkyl groups.

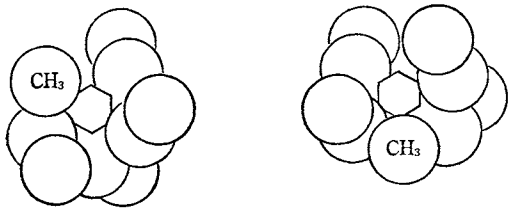
11) H. Suzuki, K. Nakamura and K. Maruyama, This Bulletin, **41**, 1487 (1968). Also *cf.* H. Suzuki and Y. Tamura, *Chem. Commun.*, **1969**, 244.

12) P. Kreienbuhl and H. Zollinger, *Tetrahedron Lett.*, **1965**, 1739.

13) V. A. Koptyug, A. P. Krysin and M. I. Gorfinkel, *Izvest. SO AN USSR, Ser. Khim.*, **1967** 61.

14) W. A. Gibbons and V. M. S. Gil, *Mol. Phys.*, **9**, 163 (1965).

15) L. J. Andrews and R. M. Keefer, *J. Amer. Chem. Soc.*, **74**, 4500 (1952); M. Tamres, D. R. Virzi and S. Searles, *ibid.*, **75**, 4358 (1953). Also *cf.* L. J. Andrews and R. M. Keefer, *ibid.*, **77**, 2545 (1955).



XXX XXXI

Fig. 4

The side-chain nitrooxylation seems to be limited to the methyl and ethyl groups; the isopropyl group remains unchanged or is replaced by a nitro group during the reaction. 2,5-Diisopropyl-1,3,4-trimethylbenzene underwent extensive nitrodealkylation, and the alumina chromatography of the product gave mainly a mixture of nitro compounds. 3,4-Dimethyl-2,5-diisopropylbenzyl alcohol was obtained from the ether eluates as the sole side-chain substituted product identified. The methyl signal due to $-C(ONO_2)(CH_3)_2$ is expected to appear at about 8.0—8.2 τ, between the two clusters of aliphatic and aromatic methyl peaks. Since the PMR spectrum of the reaction product showed only weak absorption in this region, we may conclude that side-chain substitution has not occurred to any significant extent in the isopropyl group. Because of the enhanced stability of the cation, as well as the decreased ease of hyperconjugative proton release from the isopropyl group, nitrodealkylation in this system comes to compete well with the side-chain substitution.

Experimental

Infrared spectra were determined in Nujol on a DS-402G spectrophotometer and only prominent peaks are recorded; PMR spectra were obtained in deuteriochloroform with a Varian A-60A spectrometer against internal tetramethylsilane.

Pentamethylbenzene (mp 50—52°C),[16] pentaethylbenzene (bp 155—156°C/24 mmHg),[17] 1,2,3,4-tetraethylbenzene (bp 134—136°C/23 mmHg),[18] and 1,2,4,5-tetraethylbenzene (bp 129—132°C/23 mmHg)[19] were prepared as described in literature.

2,3,4,5-Tetramethylbenzyl Nitrate (III). A warm solution of silver nitrate (10.2 g) in acetonitrile (30 m*l*) was added all at once to a magnetically stirred solution of 2,3,4,5-tetramethylbenzyl chloride (9.2 g)[20] in acetonitrile (20 m*l*). The mixture was stirred for several hours, and the silver chloride was filtered. After removal of the solvent in a vacuum, the residue was crystallized from light petroleum to yield 9.2 g (88%), mp 45—46°C. IR: 712, 751, 760, 811, 858, 882, 888, 962, 1269 ($-ONO_2$), 1289, 1620, and 1635 cm^{-1} ($-ONO_2$).

Found: C, 63.1; H, 7.4; N, 6.7%. Calcd for $C_{11}H_{15}NO_3$: C, 63.1; H, 7.2; N. 6.7%.

2,3,4,6-Tetramethylbenzyl Nitrate (IV, mp 42—44°C) and **2,3,5,6-Tetramethylbenzyl Nitrate** (V, mp 115—116°C) were prepared in a similar way from 2,3,4,6-tetramethylbenzyl chloride (VI)[21] and 2,3,5,6-tetramethylbenzyl chloride (VII)[22], respectively. The former was less stable than the other two isomers, and underwent slow decomposition on storage under diffused light.

IV: IR; 715, 755, 823, 860, 904, 1115, 1134, 1270 ($-ONO_2$), and 1631 cm^{-1} ($-ONO_2$). Found: C, 63.4; H, 7.3%. Calcd for $C_{11}H_{15}NO_3$: C, 63.1; H, H, 7.2%.

V: IR; 710, 759, 874, 895, 964, 1017, 1273 ($-ONO_2$), 1299, and 1614 cm^{-1} ($-ONO_2$). Found: C, 62.9; H, 7.2%. Calcd for $C_{11}H_{15}NO_3$: C, 62.9; H, 7.2%.

2,3,4,5-Tetramethylbenzyl Acetate (VIII). A mixture of II (3 g), sodium acetate (4.4 g), and acetic acid (7.5 g) was heated under gentle reflux for 6—7 hr. The reaction mixture was diluted with water, extracted with ether, washed with dilute sodium bicarbonate, and dried ($MgSO_4$). The ether was evaporated and the residue was crystallized from light petroleum to give colorless plates, mp 46—48°C. IR; 872, 920, 961, 1026, 1241 ($-O-COCH_3$), and 1732 cm^{-1} ($-COCH_3$).

Found: C, 75.8; H, 9.0%. Calcd for $C_{13}H_{18}O_2$: C, 75.7; H, 8.8%.

The above procedure applied to VI and VII gave **2,3,4,6-tetramethylbenzyl acetate (IX**, bp 166—167°C/22 mmHg) and **2,3,5,6-tetramethylbenzyl acetate (X**, mp 92—93°C), respectively.

IX: IR; 864, 955, 1021, 1233 ($-O-COCH_3$), and 1739 cm^{-1} ($-COCH_3$). Found: C, 75.8; H, 9.2%. Calcd for $C_{13}H_{18}O_2$: C, 75.7; H, 8.8%.

X: IR; 876, 927, 956, 1019, 1077, 1234 ($-O-COCH_3$), and 1733 cm^{-1} ($-COCH_3$). Found: C, 75.4; H, 8.9%. Calcd for $C_{13}H_{18}O_2$: C, 75.7; H, 8.8%.

2,3,4,5-Tetramethylbenzyl Alcohol (XI). The acetate was dissolved in ethanol and hydrolysed with aqueous potassium hydroxide under gentle reflux. The mixture, when poured into water, gave alcohol, which was crystallised from ethanol to give colorless needles, mp 81—82°C. IR; 995, 1025, 1076, 3256, and 3338 cm^{-1}; PMR, 7.88 (CH_3, m), 7.6 (–OH, variable), 5.65 (CH_2), and 3.19 τ (ArH).

Found: C, 79.8; H, 9.9%. Calcd for $C_{11}H_{16}O$: C, 80.4; H, 9.8%.

6-Nitro-2,3,4,5-tetramethylbenzyl Nitrate (XII). A solution of II (3.7 g) in chloroform (10 m*l*) was carefully nitrated at 0—2°C with fuming nitric acid (d= 1.50, 6.5 g). Quenching with water and removal of the solvent gave a syrupy product, which gave nitrate from ethanol as pale yellow leaflets, mp 100—101°C. Yield was poor. IR; 708, 759, 844, 877, 975, 1277 ($-ONO_2$), 1535 ($-NO_2$), and 1636 cm^{-1} ($-ONO_2$); PMR, 7.83 (CH_3), 7.71 (2 CH_3), 7.66 (CH_3), and 4.64 τ (CH_2).

Found: C, 52.0; H, 5.8; N, 10.9%. Calcd for $C_{11}H_{14}N_2O_5$: C, 52.0; H, 5.6; N, 11.0%.

16) "Organic Syntheses," Coll. Vol. II, p. 248 (1948).
17) L. I. Smith and C. O. Guss, *J. Amer. Chem. Soc.*, **62**, 2631 (1940).
18) L. I. Smith and C. O. Guss, *ibid.*, **62**, 2625 (1940);
19) N. Rabjohn, J. W. Fronabarger and W. W. Linstromberg, *J. Org. Chem.*, **20**, 271 (1955).
20) F. Bennington, R. D. Morin and L. C. Clark, *ibid.*, **23**, 2034 (1958).
21) R. C. Fuson and C. A. Sperat, *J. Amer. Chem. Soc.*, **63**, 2643 (1941).
22) R. R. Aitken, G. M. Badger and J. W. Cook, *J. Chem. Soc.*, **1950**, 331.

2,3,4,5-Tetramethylbenzaldehyde (XIII). To a mixture of II (15 g) and ethanol (65 ml) was added with shaking hexamine (12 g) and water (15 ml). The mixture became pale yellow, and the chloride disappeared. After being stood overnight, an additional 50 ml of water was added, and the mixture was heated under reflux for 3 hr, poured into water, and the oily product was extracted with ether. Removal of the solvent, followed by distillation under reduced pressure gave aldehyde boiling at 159—160°C/23 mmHg, which soon solidified to crystalline mass, mp 39—43°C. IR; 755, 792, 836, 887, 1004, 1082, 1208, 1276, 1563, 1596, and 1692 cm^{-1}; PMR, 7.78 (2 CH_3), 7.67 (CH_3), 7.52 (CH_3), and 2.76 τ (ArH).

Found: C, 81.0; H, 9.1%. Calcd for $C_{11}H_{14}O$: C, 81.5; H, 8.6%.

The semicarbazone crystallized from ethanol as white needles. It melted at 209—210°C to a liquid which quickly solidified and remelted at 235—242°C with decomposition. Similar phenomena were reported for semicarbazones from 2,3,4,6-tetramethyl- and 2,3,5,6-tetramethylbenzaldehydes.[10]

Found: C, 65.5; H, 7.9%. Calcd for $C_{12}H_{17}N_3O$: C, 65.7; H, 7.8%.

6-Bromo-2,2',3,3',4,4',5,5'-octamethyldiphenylmethane (XVI). A solution of bromine (13 g) in chloroform (30 ml) was added dropwise to the stirred mixture of 2,2',3,3',4,4',5,5'-octamethyldiphenylmethane (XIV, 21 g)[23] and chloroform (100 ml) using a small amount of iodine as catalyst. Bromination proceeded to completion within a short time. The organic layer was washed with dilute sodium bicarbonate and dried ($CaCl_2$). The solvent was evaporated off to leave white crystals (27.2 g), mp 179—182°C. Chromatography on alumina using ligroin as eluant could raise the mp up to 187—189°C, but some dibromide could not be throughly removed from XVI because of the slight difference in solubility in ordinary solvents.

Found: C, 68.8; H, 7.4%. Calcd for $C_{21}H_{27}Br$: C, 70.2; H, 7.5%.

2,2',3,3',4,4',5,5'-Octamethyldiphenylmethane-6-carboxylic Acid (XVII). The Grignard reagent was prepared from a mixture of XVI (17 g), magnesium turnings (2.7 g), and dry tetrahydrofuran (150 ml) by the dropwise addition of ethyl bromide (10.9 g) over a period of 2 hr. The mixture was heated at 50—55°C for 3 hr, and then poured onto crushed dry ice. Dilute hydrochloric acid was added to dissolve the magnesium salt, and the tetrahydrofuran was evaporated off. The precipitated solid was dissolved in dilute sodium hydroxide and after filtration over Norit was reprecipitated with hydrochloric acid. Recrystallization from ethanol gave prisms (12 g, 78%), mp 231—232°C. IR, 880, 937, 1045, 1089, 1192, 1216, 1281, 1305, 1696 (-CO), and 3430 cm^{-1} (-OH); PMR, 8.02 (2 CH_3), 7.98 (CH_3), 7.93 (3 CH_3), 7.83 (3 CH_3) 7.75 (CH_3), 6.25 (CH_2), and 4.04 τ (ArH).

Found: C, 81.7; H, 8.9%. Calcd for $C_{22}H_{28}O_2$: C, 81.4; H, 8.9%.

Treatment of the acid XVII with ethereal solution of diazomethane gave **2,2',3,3',4,4'5,5'-octamethyl-6-carbomethoxydiphenylmethane (XVIII)**, mp 165—166°C.

Found: C, 81.9; H, 9.0%. Calcd for $C_{23}H_{30}O_2$: C, 81.7; H, 8.9%.

2,2',3,3',4,4',5,5'-Octamethyl-6-hydroxymethyldiphenylmethane (XIX). The direct reduction of the carboxylic acid XVII with lithium aluminum hydride could not be accomplished. Methyl ester XVIII dissolved in dry tetrahydrofuran was reduced with lithium aluminum hydride to give alcohol XIX, which was crystallized from ligroin and melted at 195—196°C. IR, 724, 841, 869, 985, 1032, 1068, and 3300 cm^{-1}; PMR, 7.92 (2 CH_3), 7.86 (CH_3), 7.73 (3 CH_3), 7.66 (2 CH_3), 6.08 (CH_2), 5.58 (CH_2O), and 3.99 τ (ArH).

Found: C, 85.0; H, 9.9%. Calcd for $C_{23}H_{30}O$: C, 85.1; H, 9.7%.

Alcohol XIX was readily acetylated to yield **2,2',3,3',4,4',5,5'-octamethyl-6-acetoxymethyldiphenylmethane (XX)**, mp 175—176°C.

Found: C, 81.7; H, 9.1%. Calcd for $C_{24}H_{32}O_2$: C, 81.8, H, 9.1%.

2,3,4,5-Tetraethylacetophenone (XXIII). To the preformed aluminum chloride (18 g)-acetyl chloride (12 g) complex[24] in carbon tetrachloride (50 ml), a solution of 1,2,3,4-tetraethylbenzene (XXII, 25 g) in the same solvent (50 ml) was added at 0—10°C over a period of 1 hr and the reddish brown mixture was stirred for 4—5 hr, then poured into dilute hydrochloric acid. The organic layer was washed with dilute sodium carbonate followed by water, and dried ($CaCl_2$). The solvent was removed and the residue was distilled to give the ketone (21 g, 68%) as nearly colorless liquid, bp 177—178°C/37 mmHg. IR, 864, 881, 957, 1057, 1160, 1229, 1273, 1352, 1375, 1447, 1548, 1590, and 1684 cm^{-1}; PMR, 8.7—9.0 (4 CH_3, m), 7.55 (-$COCH_3$), 7.0—7.7 (4 CH_3, m), and 2.84 τ (ArH).

Prolonged treatment of the ketone with a sodium acetate-buffered solution of semicarbazide hydrochloride in aqueous methanol separated 2,3,4,5-tetraethylacetophenone semicarbazone as white needles, mp 177—181°C.

Found: C, 70.7; H, 9.7; N, 14.5%. Calcd for $C_{17}H_{27}N_3O$: C, 70.6; H, 9.4; N, 14.5%.

***α*-Methyl-2,3,4,5-tetraethylbenzyl Alcohol (XXIV).** To a suspension of lithium aluminum hydride (2.8 g) in dry ether (100 ml) was added, dropwise and with stirring, XXIII (17 g) in dry ether (80 ml). Following the completion, the mixture was refluxed for 3 hr, and then stood overnight. An excess of the reducing agent was decomposed with ethyl acetate, and dilute sulfuric acid was cautiously added with stirring to the externally cooled solution. The organic layer was separated, washed with dilute sodium carbonate followed by water, and dried ($MgSO_4$). Ether was evaporated and the residue was distilled to yield alcohol XXIV as colorless syrup (12 g, 70%), bp 182—184°C/25 mmHg, which slowly solidified to crystalline mass, mp 43—53°C (lit,[25] 51—52.5°C). IR, 863, 898, 930, 1003, 1057, 1074, 1122, 1270, and 3220—3280 cm^{-1}; PMR, 8.7—9.0 (5 CH_3, m), 7.2—7.6 (4 CH_2, m), 7.0 (OH, s, variable), 4.99 (CH, q), and 2.89 τ (ArH).

Found: C, 82.3; H, 11.4%. Calcd for $C_{16}H_{26}O$: C, 82.0; H, 11.2%.

23) H. Suzuki and K. Nakamura, *Nippon Kagaku Zasshi*, **90**, 105 (1968).

24) M. Lukin and B. B. Corson, *J. Org. Chem.*, **23**, 1007 (1958).

25) H. Hopff and F. Loechner, *Makromol. Chem.*, **84**, 261 (1965).

To a vigorously stirred solution of alcohol in methylene chloride, hydrogen chloride was passed. The reaction mixture was washed with aqueous sodium bicarbonate, dried ($MgSO_4$), and the solvent was removed *in vacuo* to give **α-methyl-2,3,4,5-tetraethylbenzyl chloride (XXV)** as colorless syrup, which on an attempt to distill in a vacuum resulted in decomposition to nondistillable polymeric substances. IR, 885, 981, 1023, 1955, 1075, 1194, 1216, 1265, 1377, and 1450 cm^{-1}; PMR, 8.6—9.0 (4 CH_3, m), 8.19 (CH_3, d, J=6.4 Hz), 7.2—7.7 (4 CH_2, m), 4.18 (CH, q, J=6.4 Hz), and 2.83 τ (ArH).

Chloride XXV in acetonitrile was treated with silver nitrate and a little calcium carbonate. The solution was filtered off from the silver salt, and the solvent was removed under reduced pressure to give a pale yellow syrup, which was identified as impure **α-methyl-2,3,4,5-tetraethylbenzyl nitrate (XXVI)** by infrared and PMR spectroscopy. Nitrate underwent decomposition on heating. IR, 869, 894, 1057, 1279 ($-ONO_2$), 1378, 1451, and 1635 cm^{-1} ($-ONO_2$); PMR, 8.6—9.0 (4 CH_3, m), 8.28 (CH_3, d, J=7 Hz), 7.2—7.6 (4 CH_2, m), 3.82 (CH, q, J=7 Hz), and 2.79 τ (ArH).

2,3,4,5-Tetraethylstyrene (XXVII). A mixture of XXIV (12 g), potassium hydrogen sulfate (0.5 g), and *t*-butylcatechol (0.5 g) was slowly distilled under reduced pressure and the fraction boiling at 99—110°C/3 mmHg was collected.[26] The oil was chromatographed on alumina using light petroleum as eluant. Redistillation of the eluate gave pure XXVII as a colorless oil, bp 103—104°C/3 mmHg. Yield, 2.0 g (18%). IR, 888 (isolated ArH), 9.05, 989, and 1624 cm^{-1} ($-CH=CH_2$); PMR, 8.7—9.0 (4 CH_3, m), 7.2—7.6 (4 CH_2,m), 4.82, 4.48 and 2.97 ($-CH=CH_2$; J_{trans}=17.8 Hz, J_{cis}=11.0 Hz, J_{gem}=1.8 Hz), and 2.87 τ (ArH).

Found: C, 89.0; H, 11.2%. Calcd for $C_{16}H_{22}$: C, 88.8; H, 11.2%.

2,3,4,5-Tetraethylbenzyl Chloride (XXVIII). A mixture of XXII (17 g), 37%-formalin (30 g), and concentrated hydrochloric acid (300 m*l*) was stirred at 70—80°C, while a stream of hydrogen chloride was introduced with intermittent check of the organic part by gas chromatogaphy. Upon cooling, the chloride precipitated from the reaction mixture as white plates, which were removed, washed, and recrystallized from light petroleum to yield white prisms (14 g, 65%), mp 51—52°C. IR, 713, 887, 1161, 1251, and 1273 cm^{-1}; PMR, 8.6—9.0 (4 CH_3, m), 7.0—7.5 (4 CH_2, m), 4.95 (CH_2), and 3.05 (ArH).

Found: C, 75.6; H, 9.7%. Calcd for $C_{15}H_{23}Cl$: C, 75.4; H, 9.7%.

Treatment of chloride XXVIII with silver nitrate gave **2,3,4,5-tetraethylbenzyl nitrate (XXIX)** as colorless syrup. IR, 756, 855, 916, 938, 963, 1058, 1273 ($-ONO_2$), and 1635 cm^{-1} ($-ONO_2$); PMR, 8.7—9.0 (4 CH_3, m), 7.1—7.6 (4 CH_3, m), 4.12 (CH_2), and 3.01 τ (ArH).

Found: C, 67.9; H, 9.0%. Calcd for $C_{15}H_{23}NO_3$: C, 67.9; H, 8.7%.

Lithium aluminum hydride reduction of XXVIII in tetrahydrofuran gave **1-methyl-2,3,4,5-tetraethylbenzene (XXX)**, bp 145—146°C/21 mmHg. PMR; 8.7—9.0 (4 CH_3, m), 7.76 (CH_3, s), 7.2—7.7 (4 CH_2, m), and 3.29 τ (ArH).

Found: C, 88.1; H, 12.1%. Calcd for $C_{15}H_{24}$: C, 88.2; H, 11.8%.

3-Methyl-1,2,4,5-tetraethylbenzene (XXXI) was similarly prepared from 1,2,4,5-tetraethylbenzene, and boiled at 153—155°C/28 mmHg. PMR, 8.7—9.0 (4 CH_3, m), 7.77 (CH_3, s), 7.2—7.6 (CH_2, m), and 3.26 τ (ArH).

3-Bromo-2,5-dimethyl-1,4-diisopropylbenzene (XXXIII). A solution of 1,4-dimethyl-2,5-diisopropylbenzene (XXXII, 47.5 g)[27] in carbon tetrachloride (150 m*l*) was treated in presence of iodine catalyst with bromine (40 g) in carbon tetrachloride (40 m*l*). The reaction mixture was poured into water, the carbon tetrachloride layer was removed and washed with dilute sodium bisulfite followed by water. After drying ($CaCl_2$), the solvent was removed and the residue was distilled under vacuum to give XXXIII (31 g, 46%), bp 130—131°C/4 mmHg, which soon solidified to prisms, 36—38°C. PMR, 8.89 (2 CH_3, d, J=6.5 Hz) 8.74, (2 CH_3, d, J=6.6 Hz), 7.77 (2 CH_3), 7.07 (CH, sep J=, 6.5 Hz), and 3.60 τ (ArH).

Found: C, 62.7; H, 8.0%. Calcd for $C_{14}H_{21}Br$: C, 62.5; H, 7.9%.

1,3,4-Trimethyl-2,5-diisopropylbenzene (XXXIV). The Grignard reagent was prepared from a mixture of XXXIII (29 g), magnesium turnings (3.3 g), and dry tetrahydrofuran (80 m*l*) using ethyl bromide as the auxiliary halide. The reagent was then treated with vigorous stirring and efficient cooling with a solution of dimethyl sulfate (30 g) in tetrahydrofuran (25 m*l*), and stood overnight. The mixture was poured into dilute hydrochloric acid, and the organic layer was washed, the solvent was removed, and the residue was refluxed with ethanolic sodium ethoxide for 1 hr. Dilution with water, followed by the ordinary working-up yielded hydrocarbon (9.4 g, 42%), bp 127—129°C/11—12 mmHg. PMR, 8.91 (2 CH_3, d, J=8.2 Hz), 8.78 (2 CH_3, d, J=8.3 Hz), 8.01 (CH_3), 7.92 (CH_3), 7.86 (CH_3), 6.6—7.3 (CH, m), and 3.72 τ (ArH).

Found: C, 88.4; H, 12.0%. Calcd for $C_{15}H_{24}$: C, 88.1; H, 11.8%.

Nitration of Pentamethylbenzene. A solution of pentamethylbenzene (14.8 g) in chloroform (50 m*l*) was vigorously stirred and fuming nitric acid (d=1.50, 31.5 g) was added during a period of over 30 min. The mixture was poured into water, and the organic layer was washed with dilute sodium bicarbonate and water. Removal of the solvent in a vacuum gave a partly crystalline, syrupy substance (19.3 g), which showed strong infrared absorption at 1271 ($-ONO_2$), 1370 ($-NO_2$), 1460, 1525 ($-NO_2$), and 1624 cm^{-1} ($-ONO_2$); PMR peaks at 7.7—7.9, 6.05, 4.63, 4.67, 4.4—4.5, 3.87, 3.26, 3.22, 3.06, an 2.93 τ, indicating the presence of a considerable amount of benzyl nitrates. Weak absorption due to carbonyl and hydroxylic groups was also observed. Thin-layer chromatography of the syrup showed practically no formation of dinitroprehnitene. Chromatography on alumina using light petroleum as eluant gave unchanged pentamethylbenzene (0.8 g), and nitropentamethylbenzene (6.0 g). The latter was obtained as nearly colorless needles from ethanol, mp 158—159°C, and had strong infrared ab-

26) M. S. Newman, J. R. LeBlanc, H. A. Karnes and G. Axerad, *J. Amer. Chem. Soc.*, **86**, 868 (1964).

27) E. C. Kooyman and A. Strang, *Rec. Trav. Chim. Pays-Bas*, **72**, 329 (1953).

sorption at 840 and 1525 cm^{-1} ($-NO_2$); PMR peaks at 7.79 and 7.89 τ. Use of a short alumina column gave tetramethylbenzyl nitrates from light petroleum fractions, but the separation was unsatisfactory. Diphenylmethanes appeared over a wide range of the eluates; XV was concentrated in the early eluates, and XXI came out with tetramethylbenzyl nitrates or nitropentamethylbenzene. A light brown syrupy substance (*ca.* 1 g) from the benzene eluates showed a strong carbonyl absorption and gave a semicarbazone, mp 209—210°C and 235—242°C, which was identified as 2,3,4,5-tetramethylbenzaldehyde semicarbazone by comparison with the authentic specimen. The presence of 6-nitro-2,3,4,5-tetramethylbenzyl nitrate was also confirmed by spectroscopy and thin-layer chromatography. Further elution with ethanol or ether yielded a soft crystalline mass, trituration of which with a little light petroleum gave white needles (*ca.* 7 g, mp 72—78°C) identified as 2,3,4,5-tetramethylbenzyl alcohol.

Nitration of Pentaethylbenzene. A solution of pentaethylbenzene (22 g) in chloroform (50 m*l*) was vigorously stirred and fuming nitric acid (d=1.50, 31.5 g) was introduced at −5—0°C over a period of 30 min. A similar working-up as above gave a light brown, syrupy substance (26 g), which showed prominent infrared peaks at 864, 896, 1059, 1280 ($-ONO_2$), 1381 ($-NO_2$), 1454, 1465, 1526 ($-NO_2$), and 1635 cm^{-1} ($-ONO_2$); PMR peaks at 8.6—9.0 (CH_3, m), 8.26 (CH_3, d, J=7 Hz), 7.2—7.6 (CH_2, m), 3.82 (CH, q, J=7 Hz), 2.35 and 2.64 τ (ArH). Thin-layer chromatography of the syrup showed two main spots, neither of which corresponded to 5,6-dinitro-1,2,3,4-tetraethylbenzene or 3,6-dinitro-1,2,4,5-tetraethylbenzene. The syrup could be separated by repeated chromatography on alumina into several substances; 2,3,4,5-tetraethylstyrene as colorless thick oil (*ca.* 7 g), readily identified by its characteristic twelve peaks due to the vinyl group and confirmed by comparison with the authentic specimen; nitropentaethylbenzene as pale yellow crystals (3.8 g, mp 86—90°C), which showed strong infrared bands at 786, 1059, and 1525 cm^{-1} ($-NO_2$); PMR peaks at 8.95—8.71 (5 CH_3, m) and 7.1—7.7 τ (5 CH_2, m). Found: C, 73.0; H, 9.8; N, 5.6%. Calcd for $C_{16}H_{25}NO_2$: C, 73.0; H, 9.5; N, 5.3%. The minor fractions from the benzene eluates showed strong carbonyl absorptions, but they were not further investigated. A syrup (9.6 g) from the ether eluates gave on cooling a white crystalline mass (5.9 g, mp 43—62°C), which was spectroscopically identical with the authentic α-methyl-2,3,4,5-tetraethylbenzyl alcohol. The original nitrate was undoubtedly converted by repeated chromatography into unsaturated hydrocarbon and alcohol.

Nitration of Mixed Penta-alkylbenzenes. A syrup obtained from nitration of 1-methyl-2,3,4,5-tetraethylbenzene showed prominent infrared peaks at 856, 1060, 1273, 1377, 1451, 1525, and 1634 cm^{-1}; PMR peaks at 8.7—9.0 (CH_3, m), 8.41 (CH_3, d, J=6.7 Hz), 7.72 (CH_3), 7.1—7.5 (CH_2, m), 4.57 (CH_2, s), 3.78 (CH, q, J=6.7 Hz), 3.14 and 2.97 τ (ArH). The methylene signal was readily attributed to 2,3,4,5-tetraethylbenzyl nitrate by comparison with the reference compound. The methine quartet probably arose from 5,α-dimethyl-2,3,4-triethylbenzyl nitrate since its PMR pattern closely resembled that of α-methyl-2,3,4,5-tetraethylbenzyl nitrate.

The nitration product from 3-methyl-1,2,4,5-tetraethylbenzene had strong infrared bands at 854, 1053, 1271, 1376, 1451, and 1632 cm^{-1}; PMR peaks at 8.7—9.0 (CH_3, m), 8.39 (CH_3, d, J=6.8 Hz), 7.77 (CH_3, s), 7.2—7.6 (CH_2, m), 4.43 (CH_2, s), 3.78 (CH, q, J=6.7 Hz), 3.12 and 2.91 τ (ArH).

A light brown syrup from the nitration of 1,3,4-trimethyl-2,5-diisopropylbenzene showed infrared peaks at 857, 1270, 1370, 1461, 1527, 1573, and 1633 cm^{-1}; PMR peaks at 8.6—8.9 (CH_3, m), 7.66 (CH_3, m), 6.2—7.1 (CH, m), 4.47 (CH_2, s), 2.93 and 2.87 τ (ArH). Chromatography on alumina using light petroleum as eluant gave a mixture of nitro compounds as the major product, and from the ether eluates a small amount of white needles was obtained, mp 140—142°C, identified as 3,4-dimethyl-2,5-diisopropylbenzyl alcohol by analysis; infrared spectra, 884, 1008, 1027, 1045, 1108, 1137, 1299, 1548, and 3290 cm^{-1}; PMR spectra, 8.82 (2 CH_3, d, J=6.8 Hz), 8.67 (2 CH_3, d, J=7.5 Hz), 7.83 (CH_3, s), 7.72 (CH_3, s), 6.4—7.2 (CH, m), 5.39 (CH_2, s), and 2.96 τ (ArH).

Found: C, 81.7; H, 11.3%. Calcd for $C_{15}H_{24}O$: C, 81.8; H, 11.0%.

When the crude syrupy product was dissolved in a small amount of carbon tetrachloride and stood in a refrigerator, some white powder (mp 131—133°C) was precipitated. It was poorly soluble in ether and had the composition, C, 45.6, H, 5.3, N, 13.2%.