[Contribution from the Research Laboratories of the Givaudan Corp.]

NITRO MUSKS. IV.[1] MISCELLANEOUS EXPERIMENTS

M. S. CARPENTER and W. M. EASTER

Received July 17, 1953

In the course of our studies on the nitro musks, a miscellany of experiments has been performed and products have been prepared which cannot be fitted neatly into any single category, as was the case in the first three papers of this series. This miscellany is grouped in the present paper, together with the results of a reinvestigation of some of the former work in this field which are at variance with the original reports.

Instances are known (see Paper I of this series) in which replacement of a methyl group by ethyl enhances the strength of the musk odor. Applying this to the case of Musk Xylene (1, 3, 5-trinitro-2,4-dimethyl-6-*tert*-butylbenzene), the two homologs have been prepared in which, respectively, one or both of the methyl groups have been replaced by ethyl. The former (V), m.p. 75–76.5°, is a musk comparable in strength and quality to Musk Xylene, while the latter, (VIII), m.p. 99°, is odorless.

1,3-Dinitro-2,5-di-*tert*-butylbenzene (X) has been reported variously to melt at 167–168° by Baur (1), who claimed it had a weak musk odor, at 177° by Verley (2), and at 190–191° by Boedtker (3), who found it to be odorless. Our preparation melted at 193–193.5° and was completely odorless.

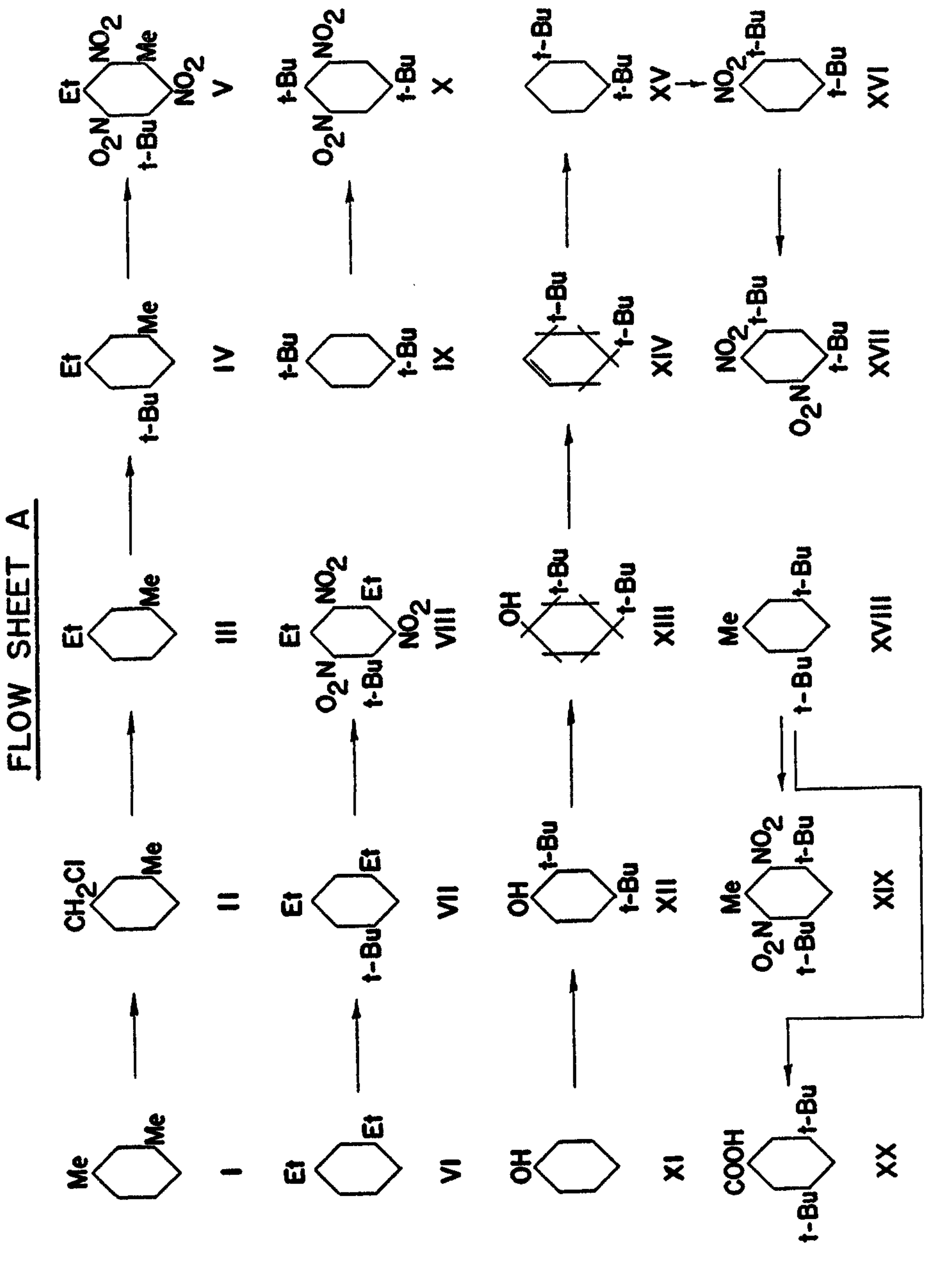
We have prepared, by a method fundamentally the same as that reported by Pines, Czajkowski, and Ipatieff (4) subsequent to the completion of our work, *m*-di-*tert*-butylbenzene (XV), and have nitrated it to a mononitro derivative, probably XVI, m.p. 52–53°, having a weak benzophenone-like odor, and a dinitro derivative, probably XVII, m.p. 164–165°, which is odorless. We have not been able to prepare a trinitro derivative.

Capeller (5) has described 3,4-di-*tert*-butyltoluene. His choice of the stated structure was based upon circumstantial evidence rather than upon direct orientational proof. The recent elegant work of Brown, *et al.* (6) indicates that the strain inherent in the *o*-di-*tert*-butyl configuration is of such magnitude that the existence of, or at any rate the ready preparation of such compounds, is highly improbable. Schlatter (7) states that di-*tert*-butyltoluene has the 1,3,5 configuration (XVIII). He offers no experimental proof, either, but in consideration of Brown's work, it is highly probable that that is the correct structure. Capeller promised to describe the nitration products in a later communication, but it has not appeared, to our knowledge. We have nitrated XVIII by both moderate and drastic methods, and in each case have obtained the same odorless dinitro compound of m.p. 173–174°, which is in all probability XIX. Oxidation of the hydrocarbon gave the acid XX of m.p. 169.5–170.5° [Schlatter (7) gives 172.6–173°]. Baur reported (1) a product of m.p. 152–153° having a weak musk odor which

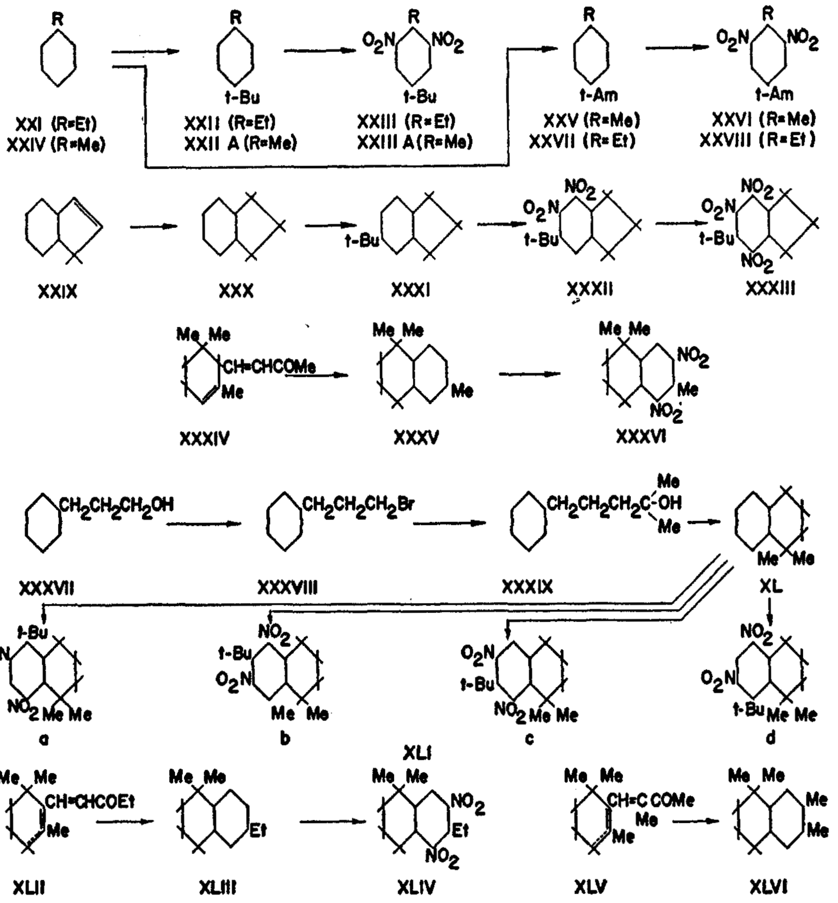
---

[1] Papers I and II, *J. Org. Chem.*, **16**, 586, 618 (1951); Paper III, preceding article, *J. Org. Chem.*, **19**, (1954) this issue.

FLOW SHEET A


I
II
III
IV
V
VI
VII
VIII
IX
X
XI
XII
XIII
XIV
XV
XVI
XVII
XVIII
XIX
XX

FLOW SHEET B



he described as a trinitrodibutyltoluene. It would seem that this claim should be accepted with reservations, since Baur nitrated a fraction of b.p. 240–245° which he obtained from an admittedly complex mixture of hydrocarbons, and reported only a nitrogen analysis, an error which, in another instance, led him to false conclusions (8).

Baur claimed (9) that a *tert*-butylethylbenzene obtained from ethylbenzene, isobutyl bromide, and aluminum chloride yielded upon nitration a difficultly crystallizable trinitro derivative of unspecified melting point having an intense musk odor. In a later paper (10) he stated he was never again able to obtain this compound, but instead obtained a dinitro compound of m.p. 140°, having only a faint musk odor. According to the latter paper he treated a mixture of ethylbenzene and *tert*-butyl chloride with ferric chloride at −10°. We have repeated Baur's work and find that the hydrocarbon so obtained yields upon chromic acid oxidation a mixture of acids melting at 92–155° (the m.p.'s of *m*- and *p*-*tert*-butylbenzoic acids are 127° and 164°, respectively). Nitration yielded a dinitro derivative having m.p. 94.5–95° and a weak musk odor. Butylation of ethylbenzene (XXI), with either *tert*-butyl chloride and aluminum chloride or with *tert*-butyl alcohol and sulfuric acid, led to the *p*-substituted hydrocarbon (XXII) which gave *p*-*tert*-butylbenzoic acid upon oxidation. Nitration of this product led likewise to the dinitro derivative of m.p. 94.5–95°, XXIII.

XXIIIA of m.p. 95–96.5° was prepared according to Bialobrzeski (11) who stated that the product had a weak musk odor. Our preparation was practically odorless and was definitely non-musk-like. Various attempts to halogenate the compound failed. (It was planned to treat the halogen compound with sodium methoxide in an attempt to prepare Musk Ambrette).

We have alkylated toluene (XXIV) and ethylbenzene (XXI) with *tert*-amyl alcohol in the presence of sulphuric acid to form the hydrocarbons XXV and XXVII, which yielded upon nitration XXVI, of m.p. 61–61.5°, practically odorless, and XXVIII, of m.p. 69.5–70.5°, mildly odorous, with a suggestion of musk.

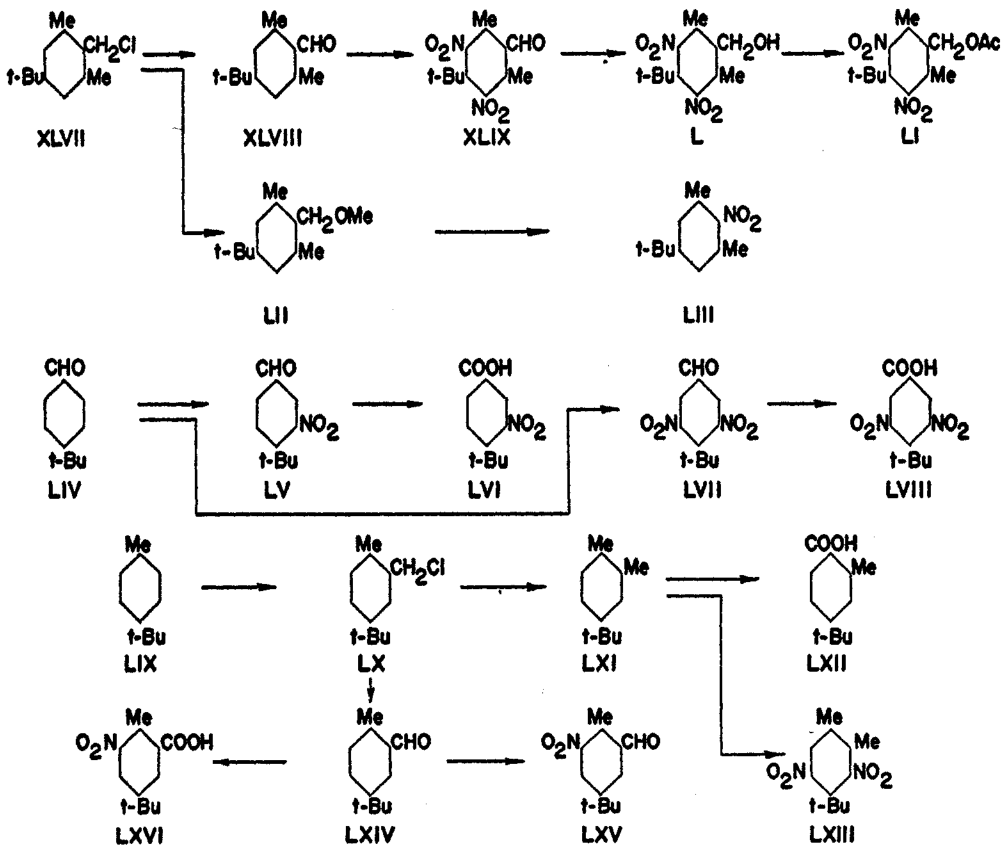
Noelting has described (12) a trinitro-*tert*-butylindan of structure XXXIII, which he claimed had "*einer sehr intensiven und feinen Moschusgeruch*". He pointed out that this product was unique in that it is the only known musk in which the nitro groups are disposed in other than the symmetrical 1,3,5 arrangement. We have repeated this work out of curiosity and have obtained a product which corresponds to his description insofar as melting point and analysis are concerned, but which, to our surprise, was totally devoid of odor.

Bogert and Fourman (13) have established the constitution of ionene to be 1,1,6-trimethyltetralin (XXXV) and have prepared a dinitro derivative of m.p. 103° which is, in all probability, XXXVI. They did not state that their dinitro compound had any odor but they alluded to the fact that Tiemann and Kruger had "observed that when irene was treated with fuming nitric acid, there resulted a product with the musky odor of the polynitrocymenes, but they failed to isolate or identify the products of the reaction, nor did they subject ionene to treatment with nitric acid". We have prepared Bogert and Fourman's dinitro ionene and find that it has indeed, a musk-like odor, although weak. It is unusual to encounter the musk odor in a nitro compound which does not contain a *tert*-butyl or *tert*-amyl group. Barbier (14) has established that a *tert*-butyltetralin readily yields a dinitro derivative which is odorless. Thus it would appear that probably the *gem*-dimethyl group in the tetralin molecule (with its attached quaternary carbon) plays an important role in the production of the musk odor in this type of compound. We have attempted to prepare 1,1-dimethyl-6-*tert*-butyltetralin by condensing citral with pinacolone to the corresponding homolog of pseudoionone, cyclizing to the homolog of ionone, and cyclo-dehydrating with iodine. We were unable to condense citral with pinacolone by any of a variety of procedures. This was somewhat surprising in view of the reported ease with which pinacolone condenses with benzaldehyde (15) or piperonal (16). As an alternate procedure we prepared 1,1-dimethyltetralin (XL) by the method of Bogert, *et al.* (17), converted it to 1,1-dimethyl-x-*tert*-butyltetralin, and nitrated the latter to a dinitro derivative XLI of m.p. 186–187.5°, which proved to be odorless. Four isomers are possible (assuming that the nitro groups are disposed in the usual *meta* relationship to each other): a, b, c, and d. Lacking any evidence as to the identity of XLI, it is not possible to decide whether its lack of odor was occasioned by the wrong structure or by excessive molecular weight.

We next turned to methylionone to determine whether an ionene augmented by a methyl group would yield a dinitro derivative of enhanced musk odor, and found that this was, indeed, the case. There are four isomeric methyl ionones: the α- and β-forms of the normal side chain type (XLII) and the α- and β-forms of the branched or iso side chain type (XLV). The former would lead to XLIII, and the latter to XLVI, which would be incapable of yielding a *m*-dinitro derivative. Nitration of XLIII led to XLIV, of m.p. 112–113°, which had a musk odor almost comparable in intensity to those of the commercial musks. This provides another instance of the odor-enhancing effect of the ethyl group over that of the methyl group.

The Aldehyde Musk of Baur-Thurgau and Bischler (18), to which they assigned the structure 2,4-dimethyl-6-*tert*-butyl-3,5-dinitrobenzaldehyde, was later shown by Fuson and co-workers (19) to have the symmetrical structure XLIX. We have prepared this musk by a method not previously described and

FLOW SHEET C



have reduced it to the corresponding alcohol (L) which is odorless, as is the acetate (LI) of the latter.

XLVII (20, 21) was converted to the corresponding methyl ether LII and the latter was submitted to gentle nitration. The —CH_2OCH_3 group was eliminated and LIII (22) was produced.

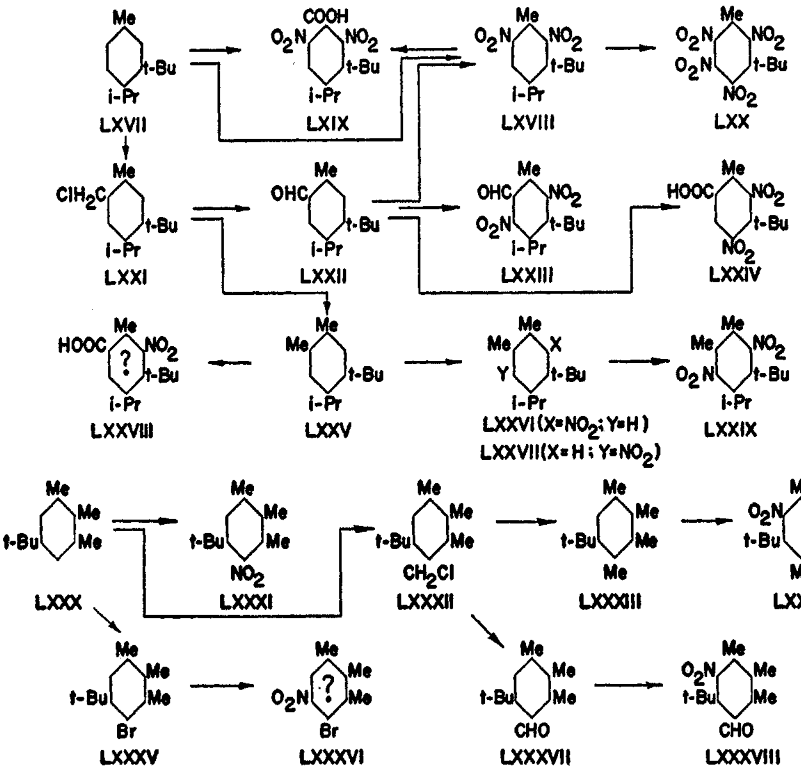
p-tert-Butylbenzaldehyde (LIV) proved to be somewhat resistant to nitration. It was unaffected by a nitric acid-acetic acid-acetic anhydride solution at 15°. Even a considerable excess of mixed acid at room temperature produced only mononitration products: LV, a greenish-yellow practically odorless oil of b.p. 138°/4 mm. and LVI, of m.p. 163–164° [Kelbe and Pfeiffer (23) reported m.p. 161°]. More drastic nitration at higher temperature produced a corresponding mixture of dinitration products: LVII, pale yellow, odorless rods of m.p. 151–152°, and LVIII of m.p. 270–272.5°.

p-tert-Butyltoluene (LIX) has been converted to the chloromethyl derivative LX, and the latter has been reduced to 4-*tert*-butyl-*o*-xylene (LXI), which upon oxidation gave LXII of m.p. 140–141° (24) and thus established the orientation of the series. Nitration of LXI gave a pale yellow, practically odorless oil, LXIII. Noelting (25) reported that nitration of *tert*-butyl-*o*-xylene gave a product having no musk odor. Nitration of the aldehyde LXIV gave LXV, of m.p. 74–75°, having a faint cumin seed-like odor similar to that of the unnitrated aldehyde. A small amount of an acid, probably the corresponding LXVI, was formed concurrently.

Numerous instances are known in which groups such as *tert*-butyl, carboxyl, acetyl, and aldehyde are eliminated and are replaced by nitro, especially if the group is in the *meta* position to an already present nitro group [Paper I of this series describes several such instances; see also Barbier (26)]. It was surprising to find that the isopropyl group in Barbier's *tert*-butyl-*p*-cymene (LXVII) (27), is quite resistant to replacement by nitro under drastic conditions. The only products which could be isolated from a nitration of LXVII with mixed acid and oleum at 120° were Moskene (LXVIII) (the normal nitration product), and the acid LXIX. Nitration of LXVIII itself under the same conditions gave the same acid and a small amount of a product which had a nitrogen content corresponding to LXX.

Chloromethylation of LXVII gave LXXI which, by the Sommelet reaction, yielded the aldehyde LXXII of m.p. 60–62°. The latter, which had an amber-like odor, exhibited a pronounced phototropism: colorless when freshly prepared, it rapidly turned bright yellow when exposed to direct or diffused sunlight, and back to colorless in the dark. Nitration in acetic acid-acetic anhydride solution gave an odorless oil, possibly LXXIII, which could not be induced to crystallize. Nitration with nitric acid or with mixed acid gave a crude product from which, after repeated crystallization, a small amount of Moskene (LXVIII) was isolated. More vigorous nitration with mixed acid and oleum gave a mixture of products having no musk odor from which there was isolated an acid which analyzed roughly for LXXIV.

FLOW SHEET D



Reduction of LXXI gave LXXV, of m.p. 48.5–49°. Nitration of the latter in acetic acid-acetic anhydride solution gave the mononitro derivative, LXXVI or LXXVII, as odorless crystals of m.p. 89.5–91°, and a product which analyzed for LXVIII, although it is doubtful if it is actually this compound, since upon treatment with alkali it liberated ammonia and produced tar upon reacidification. This behavior would indicate the possibility of a nitroso compound. Nitration of LXXV with mixed acid gave the dinitro compound LXXIX as odorless crystals of m.p. 144.5–145.5°.

Nitration of LXXX in acetic acid-acetic anhydride gave the mononitro derivative LXXXI, an odorless oil. (The dinitro derivative is the commercial Musk Tibetene). An attempt to brominate it was unsuccessful. The chloromethyl derivative LXXXII yielded upon reduction *tert*-butylprehnitene (LXXXIII) of m.p. 35°, the nitro derivative of which (LXXXIV) is an odorless oil. The bromoderivative LXXXV, of m.p. 48–49.5°, having a mild odor similar to that of LXXX, gave upon nitration a dark, odorless oil which could not be induced to congeal. It is possibly LXXXVI. Treatment of the chloromethyl derivative LXXXII with hexamethylenetetramine gave an impure aldehyde LXXXVII, nitration of which gave an odorless oil, LXXXVIII.

EXPERIMENTAL

FLOW SHEET A

A mixture of 742 g. of I (c.p. −48°), 742 g. of carbon tetrachloride, 283.5 g. of sulfuryl chloride, and 1.7 g. of benzoyl peroxide was refluxed 1.5 hrs. until gas evolution had ceased. The solvent was distilled off and the remainder was distilled *in vacuo*. There was obtained, in addition to 535 g. of recovered I, 245 g. of II, b.p. 65°/5 mm., colorless, having an odor like benzyl chloride. To the Grignard reagent prepared from 280 g. of II, 48 g. of magnesium turnings, and 700 ml. of ether was added, during 3 hrs., a solution of 600 g. of methyl sulfate in 500 ml. of ether. After standing 24 hrs. the thick reaction mixture was hydrolyzed in dilute hydrochloric acid, the ether was removed, and the remaining oil was refluxed 1 hr. with 10% sodium hydroxide to destroy excess methyl sulfate and finally was steam-distilled. Subsequent distillation *in vacuo* yielded 140 g. of III, b.p. 83°/63 mm.; d_{25}^{25} 0.8623; n_D^{20} 1.4961; having an odor similar to that of I. To 138 g. of III, cooled to 0°, was added 2 g. of aluminum chloride, followed, during 45 min., by 60 g. of *tert*-butyl chloride. The mixture was allowed to warm to 10°, 100 ml. of water was added, and the oil layer was removed and agitated briefly at 80° with dilute sodium hydroxide, then distilled. There was collected 43 g. of III, followed by 81 g. of IV, b.p. 71°/2 mm.; c.p. −47°; m.p. −42°; having an odor similar to that of *tert*-butyl-*m*-xylene. To a mixed acid composed of 49 g. of 93% sulfuric acid, 94 g. of 20% oleum, and 76 g. of 98% nitric acid was added with agitation 56 g. of IV during 20 min. at 60–75°; 56 g. of 20% oleum was then added and the temperature was raised to 105° during 50 min. The cooled reaction mixture was quenched on ice, and the crystals were taken up in benzene, washed with 5% sodium hydroxide solution, then with water to neutrality and the solvent was removed, leaving 98 g. of crude crystals. After six crystallizations from methanol there was obtained 33 g. of V as pale yellow, stout needles of m.p. 75–76.5°, having a musk odor similar in strength and nuance to that of Musk Xylene.

Anal. Calc'd for $C_{13}H_{17}N_3O_6$: C, 50.14; H, 5.51; N, 13.51.
Found: C, 50.20; H, 5.60; N, 13.51.

To 400 g. of *m*-*p*-diethylbenzene (Dow Chemical Co.) there was added 30 g. of 93% sulfuric acid. The temperature rose rapidly to 50° and a ball of tar separated out (presumably occasioned by the presence of divinylbenzenes). The mixture was agitated a few moments, and the hydrocarbon was decanted off, washed with dilute sodium hydroxide, and redistilled. The fraction (300 g.) boiling at 180–185° was sulfonated by a procedure similar to that of Copenhaver and Reid (28) by stirring for 16 hrs. at 20–25° with 300 g. of 93% sulfuric acid. To the three-layer system 100 ml. of water was added; the three layers persisted. The upper layer of unsulfonated hydrocarbon was removed, 150 ml. of water was added to the lower two layers and the mixture was heated in a partial vacuum to complete the removal of dissolved, unsulfonated hydrocarbon. A total of 191 g. of substantially *p*-isomer was thus recovered. The remaining acid solution was steamed to yield 72 g. of VI, having d_{25}^{25} 0.8620, n_D^{20} 1.4932. The sulfonamide prepared according to Huntress (29) had m.p. 97–99° (crude) or 99–100° (from dilute ethanol). The m.p. is reported to be 98–99° (29) or 101–101.5° (28). *tert*-Butylation of 70 g. of VI by the same procedure used for IV, yielded, in addition to 26 g. of VI, 32 g. of VII, b.p. 69–70°/3.5 mm., c.p. −28°, m.p. −25°, having an odor similar to that of IV. Nitration of 32 g. of VII by the same procedure used for V gave 53 g. of crude product which, after five crystallizations from methanol, left 9 g. of VIII as pale yellow small plates or stout needles, odorless, of m.p. 98–99°.

Anal. Calc'd for $C_{14}H_{19}N_3O_6$: C, 51.68; H, 5.88; N, 12.91.
Found: C, 51.83; H, 5.78; N, 12.59.

A solution of 47.5 g. of IX (m.p. 76°) in 50 g. of ethylene dichloride was added with vigorous agitation to a mixture of 66 g. of 98% nitric acid, 250 g. of 93% sulfuric acid, and 100 g. of ethylene dichloride during 40 min. at −5°. The mixture was quenched on ice, and the organic layer was washed with dilute sodium hydroxide, with water to neutrality, and the solvent was removed, leaving 65 g. of crude crystals. After three crystallizations from ethanol there was obtained 17 g. of X as pale yellow, stout needles, odorless, of m.p. 193–193.5°.

Anal. Calc'd for $C_{14}H_{20}N_2O_4$: C, 59.98; H, 7.19; N, 9.99.
Found: C, 60.06; H, 7.45; N, 10.19.

To a solution of 282 g. of phenol (XI) and 3 g. of aluminum chloride in 1,000 g. of ethylene dichloride was added 622 g. of *tert*-butyl chloride with agitation during 1.5 hrs. at 25°. After 2 hrs. at 25° the temperature was gradually raised to 80° during 3 hrs. and was held there for 30 min., at the end of which time hydrogen chloride evolution had practically ceased. The cooled solution was washed to neutrality and was distilled. There was collected 171 g. of *p*-*tert*-butylphenol, an intermediate fraction of 35 g., and finally 357 g. of XII of m.p. 54–55° [Pardee and Weinrich (30) give m.p. 56.5°]. XII (300 g.) was hydrogenated in the presence of 20 g. of Raney nickel at 195° and 1,000 p.s.i. Absorption was complete in 6 hrs. The semi-solid mass was taken up in benzene, the catalyst was filtered off, and the solution was distilled. There was collected, at 142–143°/23 mm., 293 g. of XIII as a semi-solid mixture of stereoisomers having a cedarwood-like odor.

A mixture of 212 g. of XIII, 212 g. of *p*-cymene, and 2 g. of 85% phosphoric acid was refluxed 1.5 hrs. under a water separator until all water had been eliminated. The cooled solution was decanted from the acid and distilled. There was obtained, after recovering the *p*-cymene, 180 g. of XIV of b.p. 113°/23 mm.; d_{25}^{25} 0.8311; n_D^{20} 1.4621. A mixture of 110 g. of XIV and 40 g. of sulfur was refluxed 4 hrs. (205–234°) until hydrogen sulfide elimination was complete. The oil was taken up in benzene, washed with dilute sodium hydroxide, steam-distilled in the presence of sodium hydroxide, and the distillate was agitated for 3 hrs. with 20 g. of Raney nickel. Distillation yielded 51 g. of XV of b.p. 81°/4.5 mm. It could not be induced to congeal [Johnson and Adams (31) report m.p. 10.6°].

Anal. Calc'd for $C_{14}H_{22}$: C, 88.35; H, 11.65.
Found: C, 88.2; H, 11.6.

XV (24 g.) was added with agitation to a solution of 25 g. of 98% nitric acid, 60 g. of acetic acid, and 51 g. of acetic anhydride during 15 min. at −3°. The temperature was allowed to rise to 15° during 30 min. and the solution was quenched on ice. The 25 g. of crude crystals obtained after washing in the usual manner yielded, after four crystallizations from ethanol, 8 g. of XVI as pale yellow needles of m.p. 52–53°, having a weak benzophenone-like odor.

Anal. Calc'd for $C_{14}H_{21}NO_2$: C, 71.41; H, 8.99; N, 5.95.
Found: C, 71.6; H, 9.1; N, 5.91.

Nitration of 24 g. of XV in ethylene dichloride solution with mixed acid, as for X (above), gave 31 g. of crude material which, after four crystallizations from alcohol, yielded 14 g. of XVII as pale yellow, odorless plates of m.p. 164–165°.

Anal. Calc'd for $C_{14}H_{20}N_2O_4$: C, 59.97; H, 7.19; N, 9.99.
Found: C, 60.3; H, 7.4; N, 9.9.

The same product was obtained upon more vigorous nitration of XV with an oleum-containing mixed acid at 105°.

XVIII, of m.p. 31.5°, was prepared according to Capeller's method (5), and 30 g. of it was added with agitation to a mixture of 56 g. of 98% nitric acid and 168 g. of 93% sulfuric acid during 15 min. at 25°. After quenching and washing as usual there was obtained 45 g. of crude crystals which, after two crystallizations from naphtha, yielded 35 g. of XIX as pale yellow, massive rods, odorless, of m.p. 173–174°.

Anal. Calc'd for $C_{15}H_{22}N_2O_4$: C, 61.21; H, 7.53; N, 9.52.
Found: C, 61.16; H, 7.52; N, 9.55.

The same product was obtained when the nitration was effected with mixed acid containing oleum at 110°.

Oxidation of 10 g. of XVIII with chromium trioxide in acetic acid, followed by treatment of the alkaline extract with potassium permanganate gave XX as colorless needles which melted, after crystallization from 70% ethanol, at 169.5–170.5° (2 g.).

Anal. Calc'd for $C_{15}H_{22}O_2$: C, 76.88; H, 9.46; Mol. wt., 234.3.
Found: C, 76.41; H, 9.48; Acid equiv., 233.3.

FLOW SHEET B

To 400 g. of XXI, cooled to −10°, was added 10 g. of ferric chloride and then, in the course of 30 min., 80 g. of *tert*-butyl chloride. The temperature was allowed to rise to 20° and was held there for 1.5 hrs. Sufficient 10% sodium hydroxide to give an alkaline reaction was added, the mixture was steam-distilled, and the oil layer was distilled *in vacuo*. There was collected, in addition to 290 g. of recovered XXI, 107 g. of *tert*-butylethylbenzene, b.p. 60°/2.5 mm.; d_{25}^{25} 0.8615; n_D^{20} 1.4928. Oxidation with chromic acid yielded a mixture of *tert*-butylbenzoic acids of m.p. 92–155°. Nitration of 40 g. of the hydrocarbon with 200 g. of 98% nitric acid at 25–80° gave, after three crystallizations from ethanol, 15 g. of pale yellow needles of m.p. 94.5–95°, having a weak musk odor.

Sulfuric acid 93% (1800 g.) was cooled to −10° and 570 g. of XXI was added, keeping the temperature at −10°. Then, with vigorous agitation, 154 g. of *tert*-butyl alcohol was added during 45 min. After quenching, washing, and distilling there was obtained 294 g. of XXII, b.p. 63°/3.5 mm.; d_{25}^{25} 0.8622; n_D^{20} 1.4910. The product prepared from XXI, *tert*-butyl chloride and aluminum chloride at 0–25° had b.p. 63°/3.5 mm.; d_{25}^{25} 0.8618; n_D^{20} 1.4910. Each of the latter two preparations yielded upon chromic acid oxidation *p*-*tert*-butylbenzoic acid of m.p. 164–165°.

XXII (77 g.) was added with agitation to a mixture of 132 g. of 98% nitric acid, 135 g. of 93% sulfuric acid, and 63 g. of 20% oleum during 30 min. at 25–50°, then 77 g. of 20% oleum was added and the mixture heated 30 min. at 95°. After working up in the usual manner and crystallizing three times from ethanol, there was obtained 64 g. of XXIII of m.p. 94.5–95°, identical with the material obtained from the hydrocarbon prepared with ferric chloride as catalyst.

Anal. Calc'd for $C_{12}H_{16}N_2O_4$: C, 57.12; H, 6.39; N, 11.10.
Found: C, 57.05; H, 6.33; N, 11.13.

XXIIA was nitrated to XXIIIA according to Bialobrzeski (11). The pale yellow needles of m.p. 95–96.5° were practically odorless and had no suggestion of a musk odor. The following attempts were made to halogenate the compound: (a) sulfuryl chloride in carbon tetrachloride solution with aluminum chloride, ferric chloride, or iodine as catalyst; (b) chlorine or bromine in carbon tetrachloride solution with the same catalysts, or with iron powder; (c) adding bromine to the molten crystals at 110°. In all cases XXIIIA was recovered unaltered.

Alkylation of 285 g. of toluene (XXIV) with 95 g. of *tert*-amyl alcohol in the presence of 900 g. of 93% sulfuric acid at −10° to −5° gave 130 g. of XXV, b.p. 69°/4.5 mm.; d_{25}^{25} 0.8684; n_D^{20} 1.4960. Nitration of 77 g. of XXV by the same method used for XXIII gave, after three crystallizations from ethanol, 63 g. of XXVI as pale yellow needles of m.p. 61–61.5°, practically odorless.

Anal. Calc'd for $C_{12}H_{16}N_2O_4$: C, 57.12; H, 6.39; N, 11.10.
Found: C, 57.0; H, 6.4; N, 11.0.

Alkylation of 570 g. of XXI with 185 g. of *tert*-amyl alcohol in the presence of 1,800 g. of 93% sulfuric acid at −10° to −5° gave 286 g. of XXVII, b.p. 77°/4 mm.; d_{25}^{25} 0.8704; n_D^{20} 1.4971. Nitration of 83 g. of XXVII by the same method used for XXIII gave, after three crystallizations from ethanol, 61 g. of XXVIII as pale yellow, stout rods of m.p. 69.5–70.5°, having a faint musk odor, weaker than that of its *tert*-butyl homolog (XXIII).

Anal. Calc'd for $C_{13}H_{18}N_2O_4$: C, 58.62; H, 6.81; N, 10.51.
Found: C, 58.6; H, 6.6; N, 10.6.

Indene (Eastman Kodak Co.) XXIX, was hydrogenated in the presence of Raney nickel at 85° and 500 p.s.i. to indan (XXX), b.p. 60°/10 mm.; d_{25}^{25} 0.9460; n_D^{20} 1.5310. To 118 g. of XXX was added 2 g. of aluminum chloride followed, during 25 min., by 46 g. of *tert*-butyl chloride, keeping the temperature at 20°. After quenching, washing, and distilling there was obtained, in addition to 44 g. of XXX, 64 g. of XXXI, b.p. 84°/2 mm.; c.p. −31°; m.p.

−29°. To a mixture of 160 g. of 98% nitric acid and 320 g. of 20% oleum was added, during 45 min., 40 g. of XXXI, keeping the temperature at −5°. After working up as usual there was obtained 59 g. of crude crystals which, after two crystallizations from ethanol, yielded 27 g. of XXXII as pale yellow, fine needles, odorless, of m.p. 122–123°.

Anal. Calc'd for $C_{13}H_{16}N_2O_4$: C, 59.07; H, 6.10; N, 10.61.

Found: C, 59.29; H, 6.10; N, 10.64.

To a mixture of 80 g. of 98% nitric acid and 160 g. of 40% oleum was added 20 g. of XXXII during 30 min. at 50°. Agitation was continued at 50–55° for 4 hrs. The 9 g. of crude crystals obtained after working up in the usual manner yielded, after two crystallizations from ethanol, 7 g. of XXXIII as pale yellow, totally odorless plates of m.p. 141.5–142.5°. [Noelting (12) gives 139–140°].

Anal. Calc'd for $C_{13}H_{15}N_3O_6$: C, 50.47; H, 4.89; N, 13.59.

Found: C, 50.64; H, 4.86; N, 13.75.

Dinitroionene (XXXVI) was prepared according to the method of Bogert and Fourman (13) by dehydrating α-ionone (XXXIV) and nitrating the resulting ionene (XXXV). The pale yellow, flat needles of m.p. 103° had a weak musk odor when examined at room temperature, but the hot vapor had a powerfully musky odor.

Attempts were made to condense pinacolone with citral under the influence of (a) aqueous or (b) alcoholic sodium hydroxide or (c) sodium methoxide in methanol. With (a) the reactants were recovered unchanged; with (b) or (c) the pinacolone was recovered but the citral resinified to a considerable extent.

XL was prepared by the method of Bogert, *et al.* (17), starting from XXXVII and following the indicated sequence. It had b.p. 78.5°/4 mm.; d_{25}^{25} 0.9440; n_D^{20} 1.5278. A mixture of 106 g. of XL and 62 g. of *tert*-butyl chloride was added with agitation to a suspension of 2 g. of aluminum chloride in 300 g. of ethylene dichloride at 10–15°. After washing and distilling there was obtained, in addition to 29 g. of XL, 84 g. of 1,1-dimethyl-x-*tert*-butyltetralin of b.p. 118°/4 mm.; d_{25}^{25} 0.9189; n_D^{20} 1.5164.

Anal. Calc'd for $C_{16}H_{24}$: C, 88.91; H, 11.19.

Found: C, 88.64; H, 11.22.

The hydrocarbon (27 g.) was added, at −5°, to a mixture of 20 g. of 98% nitric acid and 130 g. of 93% sulfuric acid. The 33 g. of crude crystals obtained after quenching and washing yielded, after three crystallizations from ethanol, 4 g. of XLI as pale yellow odorless prisms of m.p. 186–187.5°.

Anal. Calc'd for $C_{16}H_{22}N_2O_4$: C, 62.71; H, 7.24; N, 9.15.

Found: C, 62.87; H, 7.18; N, 9.30.

A mixture of 1296 g. of Raldeine A (a commercial methylionone containing a preponderance of the normal side-chain isomers), 3,100 g. of water, 62 g. of ethanol, 824 g. of sodium bisulfite, and 47 g. of sodium hydroxide was refluxed and agitated for 80 hrs. After cooling, the oil layer was removed and the aqueous solution was washed several times with benzene, then made alkaline and the liberated oil was washed to neutrality and distilled. There was obtained 801 g. of the mixed α and β-isomers of methyl-*n*-ionone (XLII), b.p. 110–112°/2.5 mm.; n_D^{20} 1.4960.

XLII (683 g.) was dehydrated by heating with 3 g. of iodine, was distilled *in vacuo*, the distillate again was treated with 0.5 g. of iodine, which removed a further amount of water, and then was distilled. The oil was washed with sodium thiosulfate solution and finally was distilled over sodium. There was obtained 398 g. of XLIII as a colorless oil of b.p. 94°/1.5 mm.; d_{25}^{25} 0.9303; n_D^{20} 1.5220.

Anal. Calc'd for $C_{14}H_{20}$: C, 89.28; H, 10.72.

Found: C, 88.88; H, 10.5.

To a mixture of 40 g. of 98% nitric acid and 160 g. of 93% sulfuric acid was added 47 g. of XLIII at −5°. It was necessary to add an additional 100 g. of sulfuric acid to the thick slurry to facilitate agitation. The 60 g. of crude crystals obtained after quenching and washing yielded, after two crystallizations from ethanol, 43 g. of XLIV as pale yellow massive needles of m.p. 112–113°, having a powerful musk odor.

Anal. Calc'd for $C_{14}H_{18}N_2O_4$: C, 60.41; H, 6.52; N, 10.07.
Found: C, 60.48; H, 6.35; N, 10.18.

FLOW SHEET C

XLVII (20, 21) (421 g.) was added to a solution of 280 g. of hexamethylenetetramine in 172 g. of water and was heated with agitation. At about 100°, reaction set in and the temperature rose rapidly to the reflux point, 118°. Refluxing was continued for 3 hrs. and then the mixture was distilled with live steam, gradually increasing the pot temperature until at the end it had reached 180°. The crude aldehyde was taken up in benzene, washed with 5% sulfuric acid to remove amines, then with water to neutrality, and was distilled. There was obtained 137 g. of XLVIII, b.p. 124°/5 mm.; m.p. 60–61°.

A better yield was obtained by refluxing 421 g. of XLVII with 184 g. of sodium dichromate and 38 g. of sodium carbonate in one liter of water for 12 hrs., by which time the oil was chlorine-free. The cooled mixture was acidified with sulfuric acid, extracted with benzene, and the extract was washed with dilute sodium carbonate solution and distilled, yielding 252 g. of XLVIII. The alkaline wash yielded 51 g. of 2,6-dimethyl-4-*tert*-butylbenzoic acid of m.p. 167°.

XLVIII (47.5 g.) was added to 480 g. of 98% nitric acid at −10° to 0° during 30 min.; 24 g. of 93% sulfuric acid was added and agitation was continued 10 min. further. The 73 g. of crude crystals obtained after quenching and washing yielded, after two crystallizations from ethanol, 52 g. of XLIX as pale yellow plates of m.p. 114–115°, having a powerful musk odor. Baur (18) reported m.p. 110°.

Aluminum turnings (0.5 g.) were dissolved in 200 ml. of propanol-2, 28 g. of XLIX was added, and the solution was slowly distilled through a Widmer column, maintaining constant volume in the still by the addition of propanol-2, until the distillate was acetone-free. The remaining solvent was removed, and the residue was taken up in benzene, washed with dilute sodium hydroxide, then washed with water to neutrality and the solvent was removed. Crystallization from ethanol yielded 26 g. of L as pale yellow, odorless rods of m.p. 164–164.5°.

Anal. Calc'd for $C_{13}H_{18}N_2O_5$: C, 55.30; H, 6.43; N, 9.92.
Found: C, 55.75; H, 6.44; N, 9.94.

Acetylation of 15 g. of L with acetic anhydride and sodium acetate yielded, after crystallization from naphtha, 15 g. of LI as pale yellow, odorless plates of m.p. 140–141°.

Anal. Calc'd for $C_{15}H_{20}N_2O_6$: C, 55.54; H, 6.22; N, 8.64.
Found: C, 55.60; H, 6.27; N, 8.97.

XLVII (106 g.) was added during 30 min. to a refluxing solution of 12 g. of sodium in 400 g. of methanol. The solvent was distilled off and the chlorine-free oil was washed and distilled to yield 95 g. of LII as a colorless oil of faint ethereal odor, b.p. 111°/4.5 mm. LII (41 g.) was nitrated in a mixture of 41 g. of 98% nitric acid, 70 g. of acetic anhydride, and 250 g. of chloroform at −15° to −10°. The crude nitration product (43 g.) yielded, after two crystallizations from ethanol, 14 g. of LIII of m.p. 85° (unchanged upon admixture with an authentic specimen).

Anal. Calc'd for $C_{12}H_{17}NO_2$: C, 69.51; H, 8.21; N, 6.76.
Found: C, 69.7; H, 8.40; N, 6.97.

LIV in a solution of 98% nitric acid in acetic acid-acetic anhydride at 15° gave only the diacetate of the aldehyde, hydrolysis of which in methanol-dilute sulfuric acid yielded the original aldehyde. Nitration of 202 g. of LIV in 550 g. of 98% nitric acid and 1,100 g. of 93% sulfuric acid gave an oil which, upon distillation, yielded 172 g. of LV as a greenish-yellow, practically odorless oil of b.p. 138°/4 mm.

Anal. Calc'd for $C_{11}H_{13}NO_3$: C, 63.73; H, 6.32; N, 6.76.
Found: C, 63.8; H, 6.3; N, 6.5.

From the distillation residue there was isolated 10 g. of LVI as colorless needles of m.p. 163–164°.

Anal. Calc'd for $C_{11}H_{13}NO_4$: C, 59.18; H, 5.89; N, 6.27; Mol. wt. 223.
Found: C, 59.1; H, 6.0; N, 6.1; Mol. wt. 218.

LIV (40 g.) was added to a mixture of 110 g. of 98% nitric acid, 110 g. of 93% sulfuric acid, and 110 g. of 20% oleum at 70–80°; when all heat was dissipated, 50 g. of 20% oleum was added and the temperature was held at 80° for 30 min. The pasty crystals which separated after quenching were taken up in benzene, in which they were only partly soluble. The suspension was filtered, and the solution was washed with dilute sodium hydroxide, then to neutrality with water, and the solvent was removed. The oily crystals yielded, after two crystallizations from benzene-naphtha, 6 g. of LVII as pale yellow, odorless rods of m.p. 151–152°.

Anal. Calc'd for $C_{11}H_{12}N_2O_5$: C, 52.35; H, 4.80; N, 11.11.
Found: C, 52.25; H, 4.90; N, 11.88.

The benzene-insoluble crystals were taken up in warm dilute sodium hydroxide, and the solution was washed with benzene, acidified, and the acid recrystallized from 70% ethanol to yield 14 g. of LVIII as compact, tan prisms of m.p. 270–272.5°.

Anal. Calc'd for $C_{11}H_{12}N_2O_6$: C, 49.25; H, 4.51; N, 10.44; Mol. wt. 268.
Found: C, 49.41; H, 4.54; N, 10.90; Mol. wt. 267.

To a mixture of 592 g. of LIX, 40 g. of paraformaldehyde, and 204 g. of 31% hydrochloric acid there was added, with vigorous agitation during 45 min., 460 g. of 93% sulfuric acid at 30–40°. The temperature was raised to 60° during 1 hr. and held there for 6 hrs., maintaining vigorous agitation throughout. After cooling, the upper layer was withdrawn, washed once with water, dried over sodium carbonate, and distilled. There was collected, in addition to 462 g. of recovered LIX, 145 g. of LX as a colorless oil of mild odor, b.p. 98°/4 mm. LX (117.5 g.) was refluxed for 24 hrs. with 46.5 g. of zinc dust and 122 g. of water until the oil was chlorine-free. The mixture was steam-distilled and the oil was vacuum-distilled to yield 83 g. of LXI, b.p. 61°/2.5 mm.; d_{25}^{25} 0.8690; n_D^{25} 1.4970. Oxidation of LXI according to Nightingale and Janes (24) gave LXII of m.p. 140–142°.

Nitration of 40.5 g. of LXI with 66 g. of 98% nitric acid and 250 g. of 93% sulfuric acid at −5° gave 60 g. of a pale yellow practically odorless oil which is probably LXIII. (The theoretical yield for the dinitro compound is 63 g.)

A mixture of 392 g. of LX, 280 g. of hexamethylenetetramine, and 172 g. of water was refluxed with agitation for 3 hrs. and then distilled with live steam, gradually concentrating the mixture until the pot temperature reached 150°. The crude aldehyde was washed with dilute sulfuric acid, then with water to neutrality, and distilled to yield 253 g. of LXIV as an oil having a cumin seed-like odor; b.p. 98°/3.5 mm.; n_D^{20} 1.5270; m.p. of *semicarbazone* 184–185°.

Nitration of 44 g. of LXIV in a mixture of 50 g. of 98% nitric acid, 120 g. of acetic acid, and 102 g. of acetic anhydride at −5° to 15° gave 75 g. of oil which, after hydrolysis with 15% sulfuric acid in methanol, left 32 g. of oil. Washing with dilute sodium hydroxide removed a small amount of tan-colored crystals which are probably LXVI. Mol. wt. by titration, 221.5; calc'd, 237. Distillation of the oil gave, in addition to 5 g. of unreacted LXIV, 6 g. of b.p. 140°/3.5 mm. which, after two crystallizations from naphtha, yielded 3 g. of LXV as pale yellow prisms of m.p. 74–75°, having a mild cumin seed-like odor similar to that of the unnitrated aldehyde (LXIV).

Anal. Calc'd for $C_{12}H_{15}NO_3$: C, 65.13; H, 6.83; N, 6.33.
Found: C, 65.28; H, 6.95; N, 6.92.

FLOW SHEET D

LXVII (27) (19 g.) was added to a mixture of 63 g. of 98% nitric acid, 50 g. of 93% sulfuric acid, and 100 g. of 20% oleum; the temperature gradually was raised to 120° and held there for 1 hr. The resinous mass obtained after cooling and quenching was taken up in benzene, washed with dilute sodium hydroxide, then with water to neutrality, and the solvent was removed. The 15 g. of tacky crystals gave, after two crystallizations from methanol, 4 g.

of LXVIII which melted, either alone or in admixture with an authentic specimen, at 132–133°. The alkaline wash yielded upon acidification 10 g. of crude acid which, after crystallization from benzene-naphtha, gave 3 g. of LXIX of m.p. 215–216°.

Anal. Calc'd for $C_{14}H_{18}N_2O_6$: C, 54.18; H, 5.84; N, 9.02; Mol. wt. 310.

Found: C, 54.3; H, 5.73; N, 8.99; Mol. wt. 313.

LXVIII (18 g.) was added to a mixture of 45 g. of 98% nitric acid, 50 g. of 93% sulfuric acid, and 100 g. of 20% oleum and the whole gradually heated to 115°. After 30 min. at that temperature 50 g. of 20% oleum was added and heating was continued 15 min. further. The resinous mass obtained after quenching was worked up as in the previous case. The 9 g. of crude crystals yielded, after two crystallizations from methanol, 0.5 g. of pale yellow odorless plates of m.p. 222° which may be LXX.

Anal. Calc'd for $C_{11}H_{12}N_4O_8$: N, 17.09. Found: N, 16.8.

The alkaline wash yielded the same acid as obtained above, LXIX, of m.p. 215–216°.

To a mixture of 1140 g. of LXVII, 60 g. of paraformaldehyde, and 360 g. of 31% hydrochloric acid there was added, with vigorous agitation during 1.5 hrs., 810 g. of 93% sulfuric acid at a temperature of 25–45°. The temperature was raised to 70° during 2 hrs. and held there for 1 hr. After cooling, the upper layer was withdrawn, washed once with water, dried over sodium carbonate, and distilled. There was collected, in addition to 769 g. of recovered LXVII, 284 g. of LXXI as an oil which readily congealed. Crystallization from naphtha gave 256 g. of m.p. 73.5–74°.

Anal. Calc'd for $C_{15}H_{23}Cl$: C, 75.44; H, 9.71; Cl, 14.85.

Found: C, 75.4; H, 9.6; Cl, 15.0.

A mixture of 260 g. of LXXI, 153 g. of hexamethylenetetramine, and 89 g. of water was refluxed and agitated for 3 hrs., then distilled with live steam while concentrating the mixture until the pot temperature reached 180°. The distillate was taken up in benzene, washed with dilute sulfuric acid, then to neutrality, and distilled. There was obtained 136 g. of crystalline material of b.p. 122°/3 mm. which, after crystallization from half its weight of ethanol, gave 103 g. of LXXII as small plates of m.p. 60–62° having an amber-like odor. The originally colorless crystals soon turned yellow upon exposure to light and reverted to colorless upon storage in the dark.

Anal. Calc'd for $C_{15}H_{22}O$: C, 82.50; H, 10.11.

Found: C, 82.7; H, 9.27.

Aldehyde (by oximation): 100%.

Nitration of a solution of 40 g. of LXXII in 40 g. of acetic acid with a solution of 40 g. of 98% nitric acid in 56 g. of acetic acid and 81 g. of acetic anhydride, at −5° to 15°, gave 74 g. of oil which was refluxed for 1.5 hrs. with 70 g. of methanol and 500 g. of 15% sulfuric acid to give 55 g. of reddish, odorless oil which is possibly LXXIII. (The theory for the dinitro aldehyde diacetate is 75 g. and for the dinitro aldehyde 56.5 g.)

Nitration of a solution of 44 g. of LXXII in 40 g. of ethylene dichloride with a mixture of 79 g. of 98% nitric acid, 200 g. of 93% sulfuric acid, and 80 g. of ethylene dichloride at −5° gave 49 g. of crude crystals having a mild musk odor. After ten crystallizations from ethanol there remained 2 g. of m.p. 129–131°. A mixture with LXVIII had m.p. 129–133°.

Anal. Calc'd for $C_{14}H_{20}N_2O_4$: C, 59.94; H, 7.20; N, 9.99.

Found: C, 60.1; H, 7.40; N, 9.90.

Nitration of 27 g. of LXXII in 240 g. of 98% nitric acid at −15° gave 36 g. of crude crystals which, after ten crystallizations from ethanol, gave 3 g. of LXVIII of m.p. 129–131°. A mixture with an authentic specimen had m.p. 129–133°.

LXXII (12 g.) was added to a mixture of 38 g. of 98% nitric acid, 25 g. of 93% sulfuric acid, and 47 g. of 20% oleum at 30–60°; then 28 g. of 20% oleum was added and the mixture was heated at 110–120° for 1 hr. After quenching, taking up in benzene, washing with dilute sodium hydroxide, and then with water, there was obtained 6 g. of odorless crystals from which no constant-melting fraction could be obtained by crystallization. From the alkaline washes there was obtained 0.5 g. of acid of m.p. 208–212° which may be LXXIV.

Anal. Calc'd for $C_{12}H_{14}N_2O_6$: C, 51.07; H, 5.00; N, 9.92.
Found: C, 52.1; H, 5.4; N, 10.0.

LXXI (175 g.) was refluxed and agitated with 66 g. of zinc dust and 130 g. of water until the oil layer was chlorine-free (6 hrs.); the mixture was steam-distilled and the oil layer was vacuum-distilled to give 134 g. of b.p. 84°/3 mm., which congealed. Crystallization from ethanol yielded 124 g. of LXXV as odorless, elongated plates of m.p. 48.5–49°.

Anal. Calc'd for $C_{15}H_{24}$: C, 88.15; H, 11.85.
Found: C, 88.50; H, 11.4.

Nitration of 38 g. of LXXV in a solution of 33 g. of 98% nitric acid, 79 g. of acetic acid, and 67 g. of acetic anhydride at −5° to 15° gave, after quenching and washing with dilute sodium hydroxide and water, 46 g. of a dark red odorless oil which partially congealed after standing a few days. Filtration yielded 16 g. of crystals which, after three crystallizations from ethanol, left 2 g. of bright yellow odorless plates of m.p. 122–126°. The crystals were insoluble in cold 5% sodium hydroxide, but dissolved upon warming with evolution of ammonia. Reacidification of the alkaline solution produced tar.

Anal. Calc'd for $C_{15}H_{21}NO_4$ (LXXVIII): C, 64.50; H, 7.57; N, 5.01.
Found: C, 64.55; H, 7.63; N, 5.17.

A second nitration was made in the same manner as above and the crude nitration product, in benzene solution, was refluxed for 30 min. with 5% sodium hydroxide solution. The odor of ammonia was apparent. Acidification of the alkaline solution produced a black tar. The benzene solution yielded 34 g. of crystals which, after three crystallizations from ethanol, gave 5 g. of LXXVI (or LXXVII) as pale yellow, odorless flat plates of m.p. 89.5–91°.

Anal. Calc'd for $C_{15}H_{23}NO_2$: C, 72.23; H, 9.30; N, 5.62.
Found: C, 72.55; H, 8.94; N, 6.00.

Nitration of 34 g. of LXXV in 67 g. of 98% nitric acid and 200 g. of 93% sulfuric acid at 25–30° gave 43 g. of crude crystals which, after two crystallizations from ethanol, yielded 26 g. of LXXIX as pale yellow odorless flat needles of m.p. 144.5–145.5°.

Anal. Calc'd for $C_{15}H_{22}N_2O_4$: C, 61.53; H, 7.57; N, 9.56.
Found: C, 61.54; H, 7.50; N, 9.59.

Nitration of 88 g. of LXXX (20, 21) in a solution of 100 g. of 98% nitric acid, 240 g. of acetic acid, and 204 g. of acetic anhydride at −5° to 15° gave, after quenching and washing, 111 g. (110.5 g. = theory) of LXXXI as an odorless red oil which could not be induced to congeal. Attempts to brominate it were unsuccessful.

A mixture of 528 g. of LXXX, 45 g. of paraformaldehyde, and 300 g. of 31% hydrochloric acid was warmed to 80° and 625 g. of 93% sulfuric acid was added with vigorous agitation during 4 hrs. at 80–85°. Agitation was continued for 2 hrs. further at 90–92°. After cooling, the oil layer was washed once with water, dried over sodium carbonate, and distilled to yield 450 g. of recovered LXXX and 86 g. of LXXXII as a colorless, practically odorless oil of b.p. 127°/2 mm.; d_{25}^{25} 1.0488; n_D^{20} 1.5490.

Reduction of 100 g. of LXXXII by refluxing for 24 hrs. with 46 g. of zinc dust and 120 g. of water gave 33 g. of LXXXIII as colorless needles of m.p. 34.5–35°; b.p. 111°/3 mm.

Anal. Calc'd for $C_{14}H_{22}$: C, 88.34; H, 11.66.
Found: C, 88.2; H, 11.5.

Nitration of 30 g. of LXXXIII in a solution of 34 g. of 98% nitric acid, 80 g. of acetic acid, and 68 g. of acetic anhydride at −5° to 15° gave 35 g. of an odorless red oil which refused to congeal. (Theory for LXXXIV = 37 g.)

A mixture of 175 g. of LXXXII, 109 g. of hexamethylenetetramine, and 66 g. of water was agitated and refluxed for 3 hrs., then steamed while concentrating the batch to a final pot temperature of 165°. The distillate, after washing with dilute sulfuric acid and distilling, yielded 62 g. of oily crystals of b.p. 137°/3.5 mm. which, after several crystallizations from ethanol and several from naphtha, left 37 g. of impure LXXXVII as odorless crystals of m.p. 59–102°. Nitration in nitric acid-acetic acid-acetic anhydride, followed by hydrolysis of the aldehyde diacetate with dilute sulfuric acid in methanol, gave an odorless oil (LXXXVIII).

Bromination of 88 g. of LXXX in acetic acid at 45° gave 121 g. of crude product which, after two crystallizations from ethanol, yielded 93 g. of LXXXV as odorless plates of m.p. 48–49.5°.

Anal. Calc'd for $C_{13}H_{19}Br$: C, 61.17; H, 7.50; Br, 31.3.

Found: C, 61.65; H, 7.49; Br, 31.4.

Nitration of 90 g. of LXXXV with a solution of 71 g. of 98% nitric acid, 176 g. of acetic acid, and 143 g. of acetic anhydride at −5° to 15° gave, after quenching and washing, 80 g. of a dark red odorless oil which refused to congeal (86 g. = theory for LXXXVI).

All analyses were performed by Mr. D. Johnston and the staff of the Analytical Laboratory.

DELAWANNA, NEW JERSEY

BIBLIOGRAPHY

(1) BAUR, *Ber.*, **27**, 1608 (1894).
(2) VERLEY, *Bull. soc. chim.*, [3] **19**, 67 (1898).
(3) BOEDTKER, *Bull. soc. chim.*, [3] **35**, 825 (1906).
(4) PINES, CZAJKOWSKI, AND IPATIEFF, *J. Am. Chem. Soc.*, **71**, 3798 (1949).
(5) CAPELLER, *Helv. Chim. Acta*, **11**, 166 (1928).
(6) BROWN, *et al.*, *J. Am. Chem. Soc.*, **75**, 1 (1953).
(7) SCHLATTER, U. S. Patent 2,635,114 (April 14, 1953).
(8) DUBININ, *J. Gen. Chem.* (*U.S.S.R.*), **18**, 2145 (1948); *Chem. Abstr.*, **43**, 3804 (1949).
(9) BAUR, *Ber.*, **24**, 2842 (1891).
(10) BAUR, *Ber.*, **27**, 1611 (1894).
(11) BIALOBRZESKI, *Ber.*, **30**, 1773 (1897).
(12) NOELTING, German Patent 80,158 (1888) [*Frdl.*, **4**, 1295 (1894–1897)]; *Chimie & industrie*, **6**, 719 (1921).
(13) BOGERT AND FOURMAN, *J. Am. Chem. Soc.*, **55**, 4670 (1933).
(14) BARBIER, Givaudan & Co., unpublished work.
(15) VORLANDER AND KALKOW, *Ber.*, **30**, 2268 (1897).
(16) BOON AND WILSON, *J. Chem. Soc.*, **97**, 1751 (1910).
(17) BOGERT, DAVIDSON, AND APFELBAUM, *J. Am. Chem. Soc.*, **56**, 959 (1934).
(18) BAUR-THURGAU AND BISCHLER, *Ber.*, **32**, 3647 (1899).
(19) FUSON, MILLS, KLOSE, AND CARPENTER, *J. Org. Chem.*, **12**, 587 (1947).
(20) FUSON, DENTON, AND KNEISLEY, *J. Am. Chem. Soc.*, **63**, 2652 (1941).
(21) CARPENTER, U. S. Reissue Patent 22,944 (Dec. 2, 1947).
(22) BAUR, *Ber.*, **24**, 2832 (1891); **33**, 2562 (1900).
(23) KELBE AND PFEIFFER, *Ber.*, **19**, 1723 (1886).
(24) NIGHTINGALE AND JANES, *J. Am. Chem. Soc.*, **66**, 154 (1944).
(25) NOELTING, *Chimie & industrie*, **6**, 719 (1921).
(26) BARBIER, *Helv. Chim. Acta*, **11**, 157 (1928).
(27) BARBIER, *Helv. Chim. Acta*, **19**, 1345 (1936).
(28) COPENHAVER AND REID, *J. Am. Chem. Soc.*, **49**, 3157 (1927).
(29) HUNTRESS, *J. Am. Chem. Soc.*, **63**, 3446 (1941).
(30) PARDEE AND WEINRICH, *J. Ind. Eng. Chem.*, **36**, 595 (1944).
(31) JOHNSON AND ADAMS, U. S. Patent 2,429,691 (Oct. 28, 1947).