851. *The Preparation of Some Alkyl-substituted Benzoic Acids.*

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Improved general routes have been employed for the preparation of *o*- and *m*-alkylbenzoic acids applicable to primary, *sec.*-, and *tert.*-alkyl groups. The corresponding *o*- and *m*-alkylbromobenzenes are intermediates. Routes for the preparation of some 2 : 4 : 6-tri- and 2 : 3 : 4 : 6-tetra-substituted benzoic acids are also described.

DURING work which will be described in a later paper, it became necessary to prepare a number of alkyl-substituted benzoic acids. Although it is possible to obtain *p*-alkylbenzoic acids without difficulty, the methods available for *o*- and *m*-acids are mainly unsatisfactory : awkward separations of isomers are frequently involved, yields are poor, and the routes employed are often applicable only to particular alkyl groups. The Clemmensen reduction of aryl alkyl ketones, for example, can only give primary alkyl groups from ethyl upwards. The reduction of phthalides, substituted or unsubstituted, which has commonly been used for *o*-acids, is tedious and of limited application. Hence it was found necessary to devise new routes or to apply existing routes by suitable modification to the syntheses of the acids required.

The improved route A1 for *sec.*- and *tert.*- and the new route A2 for primary alkylbromobenzenes and benzoic acids have proved satisfactory when using Pr^i, Bu^t, and Et respectively. Shoesmith and Mackie (*J.*, 1928, 2339) have already used route A1 for *o*-*tert.*-butylbenzoic acid (V; $R = Bu^t$) but the bromination stage is difficult and erratic. In Derbyshire and Waters's bromination method (*J.*, 1950, 573) difficulties vanish and high yields are obtained. The deamination stage has also been improved by using hypophosphorous acid as the reducing agent, and better yields are obtained in the carboxylation of the Grignard reagent by using solid carbon dioxide. This route also gives a good yield of *o*-*iso*propylbenzoic acid (V; $R = Pr^i$) previously obtained by reduction of 3 : 3-dimethylphthalide with hydriodic acid and phosphorus in a sealed tube (Kothe, *Annalen*, 1888, **248**, 63).

* Route A1; $R = Pr^i, Bu^t$

$$\begin{tikzcd}
C_6H_5 \arrow[r] & \begin{matrix}C_6H_4R\cdot NO_2\\(1:4)\\(\text{I})\end{matrix} \arrow[r] & \begin{matrix}Br\cdot C_6H_3R\cdot NO_2\\(2:1:4)\\(\text{II})\end{matrix} \arrow[r] & \begin{matrix}Br\cdot C_6H_3R\cdot NH_2\\(2:1:4)\\(\text{III})\end{matrix} \arrow[r] & \begin{matrix}Br\cdot C_6H_4R\\(2:1)\\(\text{IV})\end{matrix} \arrow[r] & \begin{matrix}C_6H_4R\cdot CO_2H\\(1:2)\\(\text{V})\end{matrix} \arrow[d] \\
\text{* Route A2; } R = \text{Et} \quad C_6H_5R \arrow[r] & \begin{matrix}C_6H_3R(NO_2)_2\\(1:4:6)\end{matrix} \arrow[r] & \begin{matrix}Br\cdot C_6H_2R(NO_2)_2\\(2:1:4:6)\\(\text{VII})\end{matrix} \arrow[r] & \begin{matrix}Br\cdot C_6H_2R(NH_2)_2\\(2:1:4:6)\\(\text{VIII})\end{matrix} \arrow[ur] & & \begin{matrix}NO_2\cdot C_6H_3R\cdot CO_2H\\(4:1:2)\\(\text{VI})\end{matrix}
\end{tikzcd}$$

* For convenience, in these schemes R is numbered 1; this does not necessarily agree with the proper numbering of the compounds.

Difficulties arise when ethylbenzene—and probably any primary alkylbenzene—is used as the starting material, because of the greater amount of *o*-nitration than with the more bulky secondary and tertiary groups. The *o*- and *p*-isomers are not easily separated except when there is only a small amount of the former, which is eliminated in the crystallisation of the later stages. To avoid this difficulty the less satisfactory route A2 has been employed. A lower, but still reasonable, yield of *o*-ethylbenzoic acid (V; R = Et) is obtained. The weak stage in this route is the simultaneous elimination of the two amino-groups in the diamine (VIII). It is doubtful if this route would be practicable without the aid of hypophosphorous acid. *o*-Ethylbenzoic acid had previously been prepared in similar fashion to *o*-*iso*propylbenzoic acid (Giebe, *Ber.*, 1896, **29**, 2533).

o-*tert.*-Butylbenzoic acid readily undergoes mononitration to give what is certainly the 5-nitro-acid (VI; $R = Bu^t$). The carboxyl group apparently has little deactivating effect, as might be expected since it is prevented by the bulky *tert.*-butyl group from taking up the position, coplanar with the ring, which is necessary for the deactivation. Neither the nitro-acid nor its ethyl ester can be brominated or nitrated, an observation which indicates the reluctance of groups to enter the 6-position next to a *tert.*-butyl group when the 2-position is already occupied. This point is dealt with elsewhere (Crawford and Stewart, *Nature*, 1952, **170**, 322).

Route B has proved very satisfactory for the preparation of *m*-alkyl-substituted benzoic acids and is based on methods used for the preparation of *o*- and *p*-ethylaniline (Cline and Reid, *J. Amer. Chem. Soc.*, 1927, **49**, 3150), *m*-bromocumene (Sterling and Bogert, *J. Org. Chem.*, 1939, **4**, 20), and *m*-bromo-*tert.*-butylbenzene (Gelzer, *Ber.*, 1888, **21**, 2944). There is no need to separate the *o*- and *p*-nitro-compounds (IX), or the corresponding amines (X), or the mixture of three bromoacetanilides (XI), or even the mixed amines (XII), for on deamination the same *m*-bromohydrocarbons (XIII) result from all three. Where R is a tertiary group the amount of *o*-intermediate obtained is so small that it is

* Route B; R = Et, Pr^n, Pr^i, Bu^t

$$\begin{tikzcd}
C_6H_5R \arrow[r] & \substack{C_6H_4R\cdot NO_2 \\ (1:2+1:4) \\ (IX)} \arrow[r] & \substack{C_6H_4R\cdot NH_2 \\ (1:2+1:4) \\ (X)} \arrow[r] & \substack{Br\cdot C_6H_3R\cdot NHAc \\ (3:1:2+5:1:2+3:1:4) \\ (XI)} \arrow[d] \\
 & \substack{C_6H_4R\cdot CO_2H \\ (1:3) \\ (XIV)} & \substack{Br\cdot C_6H_4R \\ (3:1) \\ (XIII)} \arrow[l] & \substack{Br\cdot C_6H_3R\cdot NH_2 \\ (3:1:2+5:1:2+3:1:4) \\ (XII)} \arrow[l]
\end{tikzcd}$$

eliminated in the recrystallisation of the bromoacetanilides, only the pure *p*-compound being recovered. It is interesting that *m*-*iso*propylbenzoic acid was found to melt at 47°, whereas Calcott, Tinker, and Weinmeyer (*J. Amer. Chem. Soc.*, 1939, **61**, 1010) reported m. p. *ca.* 20°. *m*-Propylbenzoic acid is a new compound, *m*-ethylbenzoic acid had only been prepared by lengthy methods from *m*-diethylbenzene (Voswinkel, *Ber.*, 1888, **21**, 2830) and from *m*-nitroacetophenone (Mayer and English, *Annalen*, 1918, **417**, 87), and *m*-*tert.*-butylbenzoic acid had been prepared by various routes from *m*-*tert.*-butyltoluene, in turn obtained along with the *p*-isomer from toluene (Kelbe and Pfeiffer, *Ber.*, 1886, **19**, 1725; Shoesmith and Mackie, *J.*, 1936, 300; Serijan, Hipscher, and Gibbons, *J. Amer. Chem. Soc.*, 1949, **71**, 873), but Shoesmith and Mackie do refer to its preparation from *m*-bromo-*tert.*-butylbenzene for purposes of orientation.

Methods are available for the preparation of dialkylbenzoic acids and a number of them are referred to in the following paper. To prepare certain tri- and tetra-alkylbenzoic acids, route C has been used. 2 : 4 : 6-Trimethylbenzoic (mesitoic) acid (XVII; R = Me) is generally prepared by two of the stages in this route since mesitylene is available (*Org. Synth.*, 1941, **21**, 77). The Friedel–Crafts method used by Nightingale and Smith (*J. Amer. Chem. Soc.*, 1939, **61**, 101) to obtain 1 : 3 : 5-*tert.*-butyl-*m*-xylene (XV; R = Bu^t) from *m*-xylene renders 4-*tert.*-butyl-2 : 6-dimethylbenzoic acid readily accessible. This acid was mistakenly described as the isomeric 2-*tert.*-butyl-4 : 6-dimethylbenzoic acid by Baur-Thurgau (*Ber.*, 1898, **31**, 1348), an error corrected by Tchitchibabine (*Bull. Soc. chim.*, 1932, **51**, 1436).

* Route C.

$$\begin{tikzcd}
C_6H_4Me_2 \arrow[r] & \substack{C_6H_3Me_2R \\ (3:5:1) \\ (XV)} \arrow[r] & \substack{C_6H_2Me_2R\cdot Br \\ (3:5:1:4) \\ (XVI)} \arrow[r] \arrow[d] & \substack{C_6H_2Me_2R\cdot CO_2H \\ (3:5:1:4) \\ (XVII)} \arrow[r] & \substack{Br\cdot C_6HMe_2R\cdot CO_2H \\ (2:3:5:1:4) \\ (XVIII)} \\
 & & \substack{C_6H_2Me_2RR' \\ (3:5:1:4) \\ (XIX)} \arrow[r] & \substack{C_6HMe_2RR'\cdot Br \\ (3:5:1:4:2) \\ (XX)} \arrow[r] & \substack{C_6HMe_2RR'\cdot CO_2H \\ (3:5:1:4:2) \\ (XXI)}
\end{tikzcd}$$

Bromination of (XVII; R = Bu^t) gives an almost quantitative yield of the mono-bromo-compound (XVIII). Little if any of the dibromo-compound appears to be formed even under the forced conditions used. This is further evidence of the resistance to substitution in the *o*-position to a *tert.*-butyl group when the other *o*-position is occupied (Crawford and Stewart, *loc. cit.*).

The replacement of bromine in (XVI; R = Me) by ethyl through the action of diethyl sulphate on the Grignard reagent gives a 55% yield of ethylmesitylene (XIX; R = Me, R′ = Et). An attempt was made to prepare *tert.*-butylmesitylene (XIX; R = Me, R′ = Bu^t) by treating mesitylmagnesium bromide with *tert.*-butyl chloride, but the main product obtained was mesitylene. Once again the *tert.*-butyl group avoids the presence of two large *o*-substituents. 3-Ethyl-2 : 4 : 6-trimethylbenzoic acid (XXI; R = Me, R′ = Et) is interesting in that it has an abnormally high melting point compared with other ethyl-substituted acids. It is hoped to report on this in a later paper.

EXPERIMENTAL

Analyses, except for copper, are by Drs. Weiler and Strauss, Oxford. M. p.s are not corrected.

2-Bromo-4-nitrocumene (II; R = Pr^i).—*p*-Nitrocumene (33 g.), prepared by Sterling and Bogert's method (*loc. cit.*), silver sulphate (34 g.), concentrated sulphuric acid (180 ml.), and water (20 ml.) were stirred with gradual addition of bromine (10·4 ml.). Stirring was continued for 2 hours, and then the mixture was poured into dilute sodium hydrogen sulphite solution (1000 ml.). The oil which separated was taken up in ether, and the remaining aqueous liquid extracted with ether. The mixed ethereal solutions were dried and distilled, finally under reduced pressure. The 2-bromo-4-nitrocumene distilled at 155—160°/15 mm. as a yellow oily liquid (78%) which did not solidify at −20°.

*3-Bromo-4-*iso*propylaniline* (III; R = Pr^i).—2-Bromo-4-nitrocumene (40 g.) was reduced with iron and ethanolic hydrogen chloride. The resulting amine was a reddish-brown oil (80%), b. p. 150°/15 mm. Its *benzoyl* derivative crystallised from aqueous ethanol in needles, m. p. 151° (Found : C, 60·0; H, 5·1. $C_{16}H_{16}ONBr$ requires C, 60·4; H, 5·1%).

o-*Bromocumene* (IV; R = Pr^i).—3-Bromo-4-*iso*propylaniline (21·5 g.) was dissolved in concentrated hydrochloric acid (40 ml.), diluted with water (80 ml.), and poured on ice (100 g.). An aqueous solution of sodium nitrite (7 g. in 15 ml.) was added, and the filtered diazonium solution treated with 50% hypophosphorous acid (150 ml.) and kept in ice for 24 hours. The oil which separated was extracted with ether, the extract dried ($MgSO_4$), the ether distilled off, and the residue distilled under reduced pressure, leaving a colourless oil (60%), b. p. 90°/15 mm. Fileti (*Gazzetta*, 1886, **16**, 131) had prepared this substance by the action of phosphorus pentabromide on *m-iso*propylphenol.

o-iso*Propylbenzoic Acid* (V; R = Pr^i).—*o*-Bromocumene (12 g.) was converted into the Grignard reagent in the usual way and poured on an excess of powdered solid carbon dioxide. The syrupy product was treated with hydrochloric acid, the ethereal layer separated and extracted with dilute sodium hydroxide solution, and the extract acidified. The crude acid so obtained crystallised from light petroleum; the product (66%) had m. p. 54°.

*2-Bromo-*1-tert.*-butyl-4-nitrobenzene* (II; R = Bu^t).—Crude *p-tert.*-butylnitrobenzene (142 g.) containing some *o*-isomer was brominated by Derbyshire and Waters's method as described above. The product crystallised from ethanol in needles (80%), m. p. 94°.

o-*Bromo-*tert.*-butylbenzene* (IV; R = Bu^t).—The foregoing nitro-compound (134 g.) was reduced with iron and ethanolic hydrogen chloride. The amine separated as the hydrochloride (85%), a portion of which (57 g.) was diazotised and the product reduced with hypophosphorous acid. The resulting oil (75%) had b. p. 96—98°/12 mm. Another portion of the hydrochloride was diazotised and treated with alkaline formaldehyde according to Brewster and Poje's method (*J. Amer. Chem. Soc.*, 1939, **61**, 2418) but the yield of *o*-bromo-*tert.*-butylbenzene was only 7%.

o-tert.*-Butylbenzoic acid* (V; R = Bu^t).—*o*-Bromo-*tert.*-butylbenzene (20 g.) was converted into the Grignard reagent and treated with solid carbon dioxide. The acid was recrystallised from light petroleum, and then had m. p. 68·5° (yield 60%). Serijan, Hipscher, and Gibbons (*loc. cit.*) give m. p. 80·8° (corr.).

2-tert.*-Butyl-5-nitrobenzoic Acid* (VI; R = Bu^t).—*o-tert.*-Butylbenzoic acid (10 g.) was heated with nitric acid (*d* 1·42; 25 ml.) on the water-bath for 2½ hours. The *nitro-acid*, obtained by pouring the mixture on ice, crystallised from benzene in needles (79%), m. p. 170° (Found : C, 59·8; H, 6·0; N, 6·3. $C_{11}H_{13}O_4N$ requires C, 59·2; H, 5·9; N, 6·3%). Attempts to brominate and nitrate this acid by heating it with bromine and nitric acid, respectively, failed. Only the starting material was recovered from the reaction mixture.

Ethyl 2-tert.-*Butyl*-5-*nitrobenzoate*.—The silver salt obtained from the free acid (5 g.) on treatment with ethyl iodide gave the ethyl ester as a yellow oil (84%), b. p. 190°/15 mm. Attempts to brominate and nitrate this ester similarly to the acid failed.

Copper 2-tert.-*Butyl*-5-*nitrobenzoate*.—Addition of excess of copper sulphate solution to a neutralised solution of the acid threw down a precipitate which was filtered off, washed, and dried. Extraction with hot benzene–ethanol gave a dark green *copper* salt (Found: Cu, 13·2. $C_{22}H_{24}O_8N_2Cu$ requires Cu, 13·1%). The insoluble residual light greenish-blue material appeared to be a basic *salt* (Found: Cu, 23·0. $C_{11}H_{13}O_5NCu$ requires Cu, 21·8%).

1-*Bromo*-2-*ethyl*-3 : 5-*dinitrobenzene* (VII; R = Et).—2 : 4-Dinitroethylbenzene (60 g.), prepared from ethylbenzene according to Brady, Day, and Allam (*J.*, 1928, 980), was brominated by Derbyshire and Waters's method except that all the bromine was added at once out of direct sunlight. 1-*Bromo*-2-*ethyl*-3 : 5-*dinitrobenzene* was isolated as a golden-yellow oil, b. p. 180°/12 mm., which solidified in the cold to yellow crystals (80%), m. p. 25° (Found: C, 36·7; H, 2·7; N, 11·2. $C_8H_7O_4N_2Br$ requires C, 34·9; H, 2·6; N, 10·2%).

3 : 5-*Diamino*-1-*bromo*-2-*ethylbenzene* (VIII; R = Et).—1-Bromo-2-ethyl-3 : 5-dinitrobenzene (35 g.) was reduced with iron and ethanolic hydrogen chloride. The *diamine* was obtained as orange-brown crystals (74%) (from aqueous ethanol), m. p. 88° (Found: C, 44·7; H, 5·2; N, 13·2. $C_8H_{11}N_2Br$ requires C, 44·7; H, 5·2; N, 13·0%).

o-*Bromoethylbenzene* (IV; R = Et).—The foregoing diamine (20 g.) was diazotised and reduced with hypophosphorous acid. A large amount of tar was formed. The *o*-bromoethylbenzene had b. p. 85—90°/15 mm. (yield, 15%).

o-*Ethylbenzoic Acid* (V; R = Et).—*o*-Bromoethylbenzene (2·4 g.) was converted into the Grignard reagent and carboxylated with solid carbon dioxide. The acid (64%), crystallised from hot water, had m. p. 65°.

m-*Bromoethylbenzene* (XIII; R = Et).—Nitration of ethylbenzene (60 g.) according to Cline and Reid's method (*loc. cit.*) gave a mixture of *o*- and *p*-nitroethylbenzene (91%), which was reduced to give mixed *o*- and *p*-ethylaniline (75%). Acetylation followed by bromination afforded a mixture of three bromoacetanilides (81%). Hydrolysis of this gave the mixed bromoethylanilines (93%). m-*Bromoethylbenzene* was formed on deamination of the mixed amines by diazotisation and treatment with hypophosphorous acid; the bromo-compound (62%) had b. p. 96°/15 mm. (Found: C, 53·0; H, 5·0; Br, 42·2. C_8H_9Br requires C, 51·9; H, 4·9; Br, 43·2%); it did not possess the penetrating peppermint odour of the *o*- and *p*-isomers.

m-*Ethylbenzoic Acid* (XIV; R = Et).—*m*-Bromoethylbenzene (20 g.) was converted, by carboxylation of the Grignard reagent, into the acid (71%), long needles, m. p. 45°.

m-*Bromopropylbenzene* (XIII; R = Pr^n).—*n*-Propylbenzene (30 g.) was nitrated according to Brady and Cunningham's method (*J.*, 1934, 123) to give mixed *o*- and *p*-nitropropylbenzene (71%), which were reduced to the mixed amines (74%). These in turn were acetylated and brominated, giving the mixed bromopropylacetanilides (86%). Hydrolysis then gave the mixed bromopropylaniline hydrochlorides (91%), which were deaminated to *m*-bromopropylbenzene (65%), b. p. 100°/15 mm.

m-*Propylbenzoic Acid* (XIV; R = Pr^n).—*m*-Bromopropylbenzene (7 g.) was converted by carboxylation of the Grignard reagent into m-*propylbenzoic acid* (56%), m. p. 43° (from aqueous ethanol) (Found: C, 73·0; H, 7·3. $C_{10}H_{12}O_2$ requires C, 73·1; H, 7·4%).

p-*Aminocumene* (X; R = Pr^i).—*p*-Nitrocumene (65 g.), prepared by nitration of cumene, was reduced with tin and hydrochloric acid, giving the amine (75%) as a colourless oil, b. p. 115°/15 mm., probably containing some *o*-isomer. Sterling and Bogert (*loc. cit.*) refer to it as a golden-brown oil.

m-iso*Propylbenzoic Acid* (XIV; R = Pr^i).—*p*-Aminocumene (41·5 g.) was acetylated and brominated to give 2-bromo-4-*iso*propylacetanilide (m. p. 131°, after recrystallisation). The bulk was hydrolysed to 4-amino-3-bromocumene (87% yield on *p*-aminocumene), a reddish-brown oil, b. p. 140—145/15 mm., which was deaminated to *m*-bromocumene (67%), a colourless liquid, b. p. 90—95°/15 mm., which was converted into the acid by carboxylation of the Grignard reagent; the acid (69%) had m. p. 47—48° (from light petroleum) (Found: C, 72·6; H, 7·1. Calc. for $C_{10}H_{12}O_2$: C, 73·1; H, 7·4%).

p-tert.-*Butylacetanilide*.—*p*-*tert.*-Butylnitrobenzene (80 g.), prepared by nitration of *tert.*-butylbenzene and containing some *o*-isomer, was reduced by Craig's method (*J. Amer. Chem. Soc.*, 1935, **57**, 195). A brown solid which separated was removed (see below). The crude amine was acetylated, and the product recrystallised twice from aqueous ethanol, then having m. p. 176° (yield, 51%). This was obviously the pure *p*-isomer.

4 : 4′-*Di*-tert.-*butylazobenzene*.—The brown solid from the previous preparation, on recrystal-

lisation from ethanol, gave reddish-brown needles, m. p. 185° (Malherbe, *Ber.*, 1919, **52**, 323, gives m. p. 183°) (Found: C, 81·2; H, 8·9; N, 9·7. Calc. for $C_{20}H_{26}N_2$: C, 81·6; H, 8·9; N, 9·5%).

m-tert.-*Butylbenzoic Acid* (XIV; R = Bu^t).—*p-tert.*-Butylacetanilide (10 g.) was brominated to the 3-bromo-compound (XI; R = Bu^t) which, recrystallised from benzene, had m. p. 138·5° (85%). This was hydrolysed to the amine (90%), b. p. 140°/15 mm. This in turn was deaminated to *m*-bromo-*tert.*-butylbenzene (70%), b. p. 100°/40 mm. Carbonation of the Grignard reagent then gave *m-tert.*-butylbenzoic acid which, recrystallised from light petroleum, had m. p. 127° (60%).

2-*Bromo*-5-tert.-*butyl*-m-*xylene* (XVI; R = Bu^t).—1-*tert.*-Butyl-*m*-xylene (70 g.), prepared by Nightingale and Smith's method (*loc. cit.*), was cooled in ice and treated with iodine (0·5 g.) followed by bromine (23·5 ml.) added during 2 hours. Next morning, the mixture was washed with warm sodium hydroxide solution and then warm water. The oily layer was separated, dried, and distilled. Redistillation gave the substituted *m*-xylene (81%), b. p. 140°/15 mm., m. p. 45°. Tchitchibabine (*loc. cit.*) prepared this substance by an indirect method from the following acid.

4-tert.-*Butyl*-2 : 6-*dimethylbenzoic Acid* (XVII; R = Bu^t).—2-Bromo-5-*tert.*-butyl-1 : 3-dimethylbenzene (20 g.) was converted into the acid by carboxylation of the Grignard reagent; recrystallised from petroleum (b. p. 100—120°), it (68%) had m. p. 168°.

3-*Bromo*-4-tert.-*butyl*-2 : 6-*dimethylbenzoic Acid* (XVIII; R = Bu^t).—The foregoing acid (1 g.) was treated with a crystal of iodine followed by bromine (0·5 ml.) added during a short period at room temperature. Hydrogen bromide was evolved and there resulted a practically quantitative yield of the *bromo-acid*, needles [from petroleum (b. p. 100—120°)], m. p. 169° (Found: C, 53·9; H, 6·2. $C_{13}H_{17}O_2Br$ requires C, 54·7; H, 6·0%). The acid remained unchanged even when boiled with bromine.

Ethylmesitylene (XIX; R = Me, R′ = Et).—Prepared by treating the Grignard reagent formed from bromomesitylene (30 g.) with ethyl sulphate (100 ml.), this had b. p. 214° (60%).

2-*Bromo*-6-*ethylmesitylene* (XX; R = Me, R′ = Et).—Ethylmesitylene (5·8 g.) in glacial acetic acid (10 ml.) was treated with iodine (one crystal) and bromine (2·2 ml.) in glacial acetic acid (6·2 ml.). The mixture was poured into a cooled dilute solution of sodium hydrogen sulphite and extracted with ether, and the extract dried and distilled. The product (74%) had b. p. 135—140°/15 mm.

3-*Ethyl*-2 : 4 : 6-*trimethylbenzoic Acid* (XXI; R = Me, R′ = Et).—Bromoethylmesitylene (5 g.) was converted into the acid by carboxylation of the Grignard reagent. The *acid* (64%) was obtained as micro-crystals, m. p. 143° (Found: C, 74·0; H, 8·3. $C_{12}H_{16}O_2$ requires C, 75·0; H, 8·4%).

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