[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MISSOURI]

THE ANOMALOUS ACETYLATION OF SOME DIALKYLBENZENES

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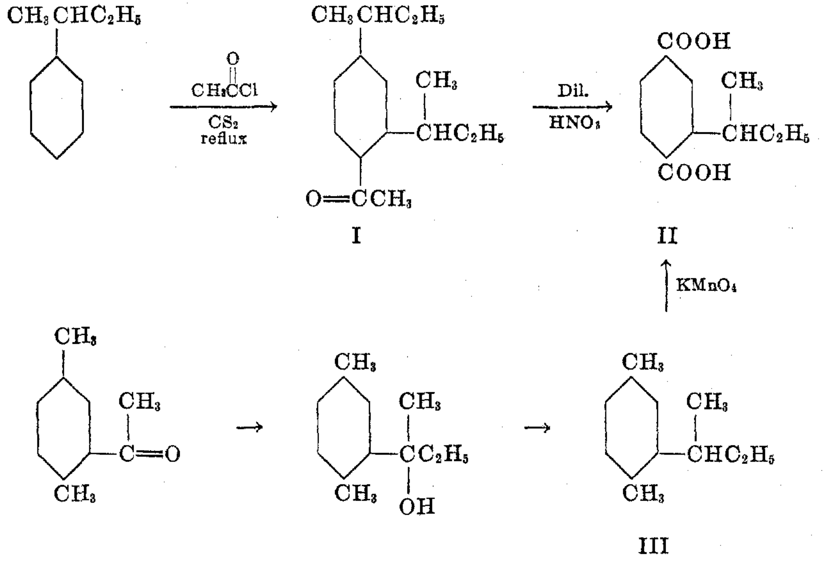
In a previous publication (1), a dibutylacetophenone (I) obtained from the acetylation of *sec*-butylbenzene at the reflux temperature of carbon disulfide was designated as 2,5-di-*sec*-butylacetophenone. The structure of this ketone has now been established as 2,4-di-*sec*-butylacetophenone by the following reactions:



The authentic *sec*-butylterephthalic acid (II) obtained from III melted at 253.5–254° and did not depress the melting point of the acid II obtained from the oxidation of I with dilute nitric acid. These reactions also establish the fact that the migrating *sec*-butyl radical did not isomerize during the realkylation.

The supposedly authentic 2,5-di-*sec*-butylacetophenone used for structure proof in the earlier experiments had been synthesized by the acetylation of *p*-di-*sec*-butylbenzene at ice-bath temperatures. Oxidation of this ketone with dilute nitric acid also yielded *sec*-butylterephthalic acid, hence it too is 2,4-di-*sec*-butylacetophenone rather than the 1,2,5 isomer.

2,4-Di-*sec*-butylacetophenone was also obtained when the acetylation of the *p*-di-*sec*-butylbenzene synthesized by the Grignard reaction was carried out at −10° to −15°. A small amount (5%) of *p*-*sec*-butylacetophenone was also isolated from the reaction product, even when the acetylation was carried out at this low temperature. The 2,4-di-*sec*-butylacetophenone from this acetylation

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[1] Abstracted from the Ph.D. dissertation of Howard B. Hucker, June 1953.

was fractionated with a Podbielniak column to obtain a very pure compound. Oxidation of this pure ketone yielded *sec*-butylterephthalic acid having the same melting point as the acid from the ketone obtained by acetylation at 0° or at reflux temperature. The semicarbazone of the pure ketone melted only one degree higher than that of the somewhat less pure ketone. The product obtained by fractionation with a Todd column is pure enough for most uses.

Four other dialkylbenzenes were acetylated at temperatures below 0°, originally with the hope of obtaining 2,5-dialkylacetophenones at the lower temperature, and finally to compare yields and types of products formed under these conditions with those obtained from acetylation at reflux temperatures.

p-Xylene formed only 2,5-dimethylacetophenone.

p-Di-*n*-butylbenzene yielded a small amount of *p*-*n*-butylacetophenone and 2,5-di-*n*-butylacetophenone. This latter ketone was oxidized with nitric acid to an acid which appears to be 4-*n*-butylisophthalic acid rather than *n*-butylterephthalic acid. 4-*n*-Butylisophthalic acid for a mixture melting point could not be synthesized by the oxidation of 1,3-dimethyl-4-*n*-butylbenzene with potassium permanganate; the product of this oxidation was methylterephthalic acid.

p-Di-*tert*-butylbenzene yielded only *p*-*tert*-butylacetophenone, as previously reported by other investigators (2) (3). The reaction of this hydrocarbon with succinic anhydride and with maleic anhydride at −15° is reported to yield mainly *p*-*tert*-butylbenzoylpropionic acid and *p*-*tert*-butylbenzoylacrylic acid respectively (4).

p-Di-(1-methylbutyl)benzene formed some *p*-(1-methylbutyl)acetophenone and a diamylacetophenone tentatively designated as 2,4-diamylacetophenone by analogy with 2,4-di-*sec*-butylacetophenone. Oxidation of this product gave an intractable mixture.

The acetylations of *p*-di-*sec*-butylbenzene, *p*-di-*tert*-butylbenzene, and *p*-di-(1-methylbutyl)benzene were carried out at the reflux temperature of carbon disulfide. The acetylation of *p*-xylene and of *p*-di-*n*-butylbenzene were also studied under these conditions for a comparison of the behavior of *n*-alkyl groups and branched alkyl groups. In each case, the monoalkylacetophenones were identified by mixture melting points of derivatives of authentic samples of the ketones and the orientation of the dialkylacetophenones was determined by oxidation to the respective alkyldicarboxylic acids.

p-Xylene yielded only 2,5-dimethylacetophenone.

p-Di-*n*-butylbenzene yielded *p*-*n*-butylacetophenone, 2,4-di-*n*-butylacetophenone, and a higher-boiling mixture distilling over a wide range which was not identified. The 2,4-di-*n*-butylacetophenone formed a semicarbazone, m.p. 76.5–77°. The semicarbazone of 2,5-di-*n*-butylacetophenone melted at 130–131° and a mixture of the two derivatives melted at 69–102°. Oxidation of the 2,4-ketone with nitric acid yielded *n*-butylterephthalic acid, m.p. and mixture m.p. with an authentic sample of the acid, 267–268°.

In our previous publication (1) the dipropylacetophenone obtained from the high temperature acetylation of *n*-propylbenzene was not identified. By analogy with the results of the acetylation of *p*-di-*n*-butylbenzene under these conditions, the ketone should be 2,4-di-*n*-propylacetophenone.

p-Di-*sec*-butylbenzene yielded *p*-sec-butylacetophenone, 2,4-di-*sec*-butylacetophenone, and a tributylacetophenone, presumably 2,4,6-tri-*sec*-butylacetophenone. The values from the carbon and hydrogen analyses of this latter product agreed with those calculated for a tributylacetophenone but the compound would not form a derivative. Newton (5) obtained 2,4,6-triisopropylacetophenone as one of the products from the acetylation of *p*-diisopropylbenzene at 40° and it is reasonable to believe that *p*-di-*sec*-butylbenzene would form a 2,4,6-tri-*sec*-butylacetophenone.

Surprisingly, *p*-di-*tert*-butylbenzene yielded both *p*-*tert*-butylacetophenone and a di-*tert*-butylacetophenone, m.p. 42–43°, which by analogy should be the 1,2,4-isomer but may be another isomer. Pines, Czajkowski, and Ipatieff (6) report a 2,4-dinitrophenylhydrazone from their 2,4-di-*tert*-butylacetophenone synthesized in four steps from 2,4-di-*tert*-butylphenol but we were unable to obtain a derivative of our ketone. In a personal communication, Dr. Pines states that the refractive index of their sample (slightly colored by long standing) is n_D^{19} 1.5050. This compares with a value of n_D^{20} 1.5088 for our sample.

p-Di-(1-methylbutyl)benzene yielded *p*-(1-methylbutyl)acetophenone, a diamylacetophenone, possibly a triamylacetophenone, and a still higher-boiling product which could be either a tetraamylacetophenone or a mixture of isomeric polyalkylacetophenones. The structure of the migrating amyl radical in the diamylacetophenone could not conveniently be determined. Yields of oxidation products were so poor that the determination of the orientation of this ketone could not be completed. By analogy it should be a 2,4-diamylacetophenone. The carbon and hydrogen values of the two high-boiling products agree with those calculated for tri-and tetra-amylacetophenones respectively. However both of them could be isomeric polyalkylacetophenones formed by cleavage of the dealkylated amyl radical and alkylation of the aromatic nucleus by the fragments.

The diamylacetophenone obtained from the acetylation of 2-phenylpentane at reflux remperature (1) appears to be a similar product. Its semicarbazone also melted at 127–128° and did not depress the melting point of the same derivative of the diamylacetophenone from the high temperature acetylation of *p*-di-(1-methylbutyl)benzene.

It was surprising to find that the *n*-butyl and *sec*-butyl radicals were not isomerized when they migrated during the acetylation of *p*-di-*n*-butylbenzene and *p*-di-*sec*-butylbenzene, especially at reflux temperatures. Previous work (7) has shown that the *n*-butyl radical was isomerized to the *sec*-butyl radical during the rearrangement of 1,3-dimethyl-4-*n*-butylbenzene of 1,3-dimethyl-5-*sec*-butylbenzene with aluminum chloride at steam-bath temperatures, and that the *sec*-butyl radical was isomerized to the *tert*-butyl radical during the rearrangement of 1,3-dimethyl-4-*sec*-butylbenzene to 1,3-dimethyl-5-*tert*-butylbenzene under the same conditions. However, the reactants and experimental conditions for the rearrangements are not entirely comparable to those for the acetylation of the *p*-di-alkylbenzenes.[2]

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[2] Since this manuscript was written, McCaulay and Lien [*J. Am. Chem. Soc.*, **75**, 2411 (1952)] have reported that in the disproportionation of mono- and di-alkylbenzenes with HF-BF_3 at room temperature, the migrating *n*-propyl, *n*-butyl and *sec*-butyl groups were

The formation of 2,5-di-*n*-butylacetophenone from *p*-di-*n*-butylbenzene at temperatures below 0° rather than the 1,2,4-isomer is understandable, since primary alkyl radicals are not readily cleaved from the benzene nucleus with aluminum chloride at temperatures up to 80° (8, 9).

The recent work of Schlatter and Clark (10) has shown that the alkylation of toluene with isopropyl alcohol and boron trifluoride by the procedure of Welsh and Hennion (11) leads to a mixture of *o*-, *m*-, and *p*-isopropyltoluenes. Since our *p*-di-*sec*-butylbenzene was prepared by this method from benzene and *n*-butyl alcohol, it could be a similar mixture of isomers. For purposes of comparison, *p*-di-*sec*-butylbenzene was synthesized by the following reactions:

$$p\text{-}sec\text{-butylacetophenone} \xrightarrow[2.\ H_2,\ CuCr_2O_4]{1.\ C_2H_5MgBr} p\text{-di-}sec\text{-butylbenzene}$$

The infrared absorption spectra of this hydrocarbon and of the *p*-di-*sec*-butylbenzene prepared by alkylation of benzene with *n*-butyl alcohol were nearly identical. It is the opinion of Dr. E. E. Pickett, spectroscopist at the University of Missouri, that the two products are the same compound and that the alkyl groups are *para*. Slight differences are easily accounted for by a very few percent of impurities in one or the other or both samples.

The results of this investigation and those reported by Newton (5) show that even di-*n*-alkylbenzenes should be acetylated at as low a temperature as possible to obtain maximum yields of reasonably pure dialkylacetophenones, and that 2,5-di-*sec*-alkylacetophenones will need to be synthesized by some other method than the usual Friedel-Crafts procedures.

The study of these reactions and related types of reactions is being continued.

EXPERIMENTAL[3]

Hydrocarbons. The *p*-xylene and *p*-di-*tert*-butylbenzene were obtained from Distillation Products Co. The *p*-di-*sec*-butylbenzene was prepared by the procedure of Welsh and Hennion (11). Pure *p*-di-(1-methylbutyl)benzene was best prepared *via* the Grignard reaction. The *p*-di-*n*-butylbenzene was obtained by the reduction of *p*-*n*-butyl-*n*-butyrophenone with hydrogen and a copper chromium oxide catalyst. The physical constants of the hydrocarbons agreed with those reported in the literature (12).

Low temperature acetylation. The *p*-dialkylbenzenes were acetylated with aluminum chloride and acetyl chloride in carbon disulfide solution by the procedure described in Organic Syntheses (13). Usually 0.25 mole of hydrocarbon was acetylated and the amounts of the other reactants were reduced in proportion. The reaction product was fractionated at reduced pressure through a medium bore Todd column at a reflux ratio of 10:1 unless otherwise specified. The monoalkylacetophenones were identified through their 2,4-dinitrophenylhydrazones or semicarbazones. The orientation of the dialkylacetophenones was determined by oxidation.

p-Xylene (53 g.) yielded 48 g. of *2,5-dimethylacetophenone,* b.p. 80–85° (4–5 mm.), n_D^{20} 1.5292, literature values 107° (13 mm.), n_D^{20} 1.530 (14). A hypobromite oxidation of this ketone yielded *2,5-dimethylbenzoic acid,* m.p. 134–135°, literature value 132° (15).

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not isomerized. On the basis of these data in addition to the data reported in this paper, we feel that it is advisable for us to repeat the earlier rearrangement experiments and apply the analytical techniques now available to a study of the structure of the products.

[3] The carbon and hydrogen analyses were done by Y. C. Lee, C. M. Benage, P. D. Strickler, and H. B. Hucker.

p-Di-n-butylbenzene (47 g.) yielded the following products:

(*a*). *p-n-Butylacetophenone* (2 g.) which formed a *semicarbazone*, m.p. 182–183.5°. The melting point of a mixture of this derivative and authentic *p-n-butylacetophenone* semicarbazone (m.p. 183.5–184.5°) was 182–184.5°, literature values 182–183° (16), 185° (17), and 189–190° (18).

(*b*). *2,5-Di-n-butylacetophenone* (33 g.), b.p. 140–146° (3–4 mm.), n_D^{20} 1.5073.

Anal. Calc'd for $C_{16}H_{24}O$: C, 82.70; H, 10.41.

Found: C, 82.58; H, 10.11.

The *semicarbazone* of this ketone melted at 130–131°.

Anal. Calc'd for $C_{17}H_{27}N_3O$: C, 70.54; H, 9.40.

Found: C, 70.56; H, 9.47.

Oxidation of this ketone with dilute nitric acid (3) yielded *4-n-butylisophthalic acid*, m.p. 222–222.5° dec. The melting point of a mixture of this acid and authentic 4-*n*-butylterephthalic acid (m.p. 267.5–268°) was 200–235°. 4-*n*-Butylisophthalic acid could not be conveniently synthesized for a mixture melting point.

Anal. Calc'd for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35; Neut. equiv., 111.

Found: C, 64.91; H, 6.59; Neut. equiv., 111.

p-Di-sec-butylbenzene (47 g.) yielded the following products:

(*a*). *p-sec-Butylacetophenone* (7 g.). This ketone formed a *2,4-dinitrophenylhydrazone*, m.p. and mixture m.p. with an authentic sample 146–147°, the literature value (1).

(*b*). *2,4-Di-sec-butylacetophenone* (34 g.) b.p. 108–114° (2 mm.). This ketone formed a *semicarbazone*, m.p. 166.5–167°, literature value 160–161° (3).

Anal. Calc'd for $C_{17}H_{27}N_3O$: C, 70.54; H, 9.40.

Found: C, 70.70; H, 9.58.

Oxidation of this product with dilute nitric acid yielded *sec-butylisophthalic acid*, m.p. and mixture m.p. with an authentic sample 253.5–254.5°.

p-Di-tert-butylbenzene (47 g.) yielded the following products:

(*a*). A forerun (25 g.) which was a mixture of ketone and hydrocarbon.

(*b*). *p-tert-Butylacetophenone* (23 g.) which formed a *2,4-dinitrophenylhydrazone*, m.p. 211.5–212.5°.

Anal. Calc'd for $C_{18}H_{20}N_4O_4$: C, 60.65; H, 5.66.

Found: C, 60.42; H, 5.63.

The melting point of a mixture of this derivative and an authentic sample of 2,4-di-*tert*-butylacetophenone (m.p. 208–210°), kindly furnished by Dr. Herman Pines of Northwestern University, was 174–178°.

The ketone also formed a *semicarbazone*, m.p. and mixture m.p. with an authentic sample 232–233°, the literature value (19).

p-Di-(1-methylbutyl)benzene (63 g.), prepared *via* the Grignard reaction as described for *p*-di-*sec*-butylbenzene, yielded the following products:

(*a*). *p-(1-Methylbutyl)acetophenone* (6.5 g.) b.p. 100–106° (1 mm.). This ketone formed a *semicarbazone*, m.p. and mixture m.p. with an authentic sample of the derivative, 178–179°, literature value 173–174° (3).

Anal. Calc'd for $C_{14}H_{21}N_3O$: C, 67.98; H, 8.56.

Found: C, 67.71; H, 8.43.

(*b*). *2,4-Di-(1-methylbutyl)acetophenone* (23 g.) b.p. 107–114° (1 mm.). This product formed a *semicarbazone*, m.p. 116–117°, literature value 149–150° (3).

Anal. Calc'd for $C_{19}H_{31}N_3O$: C, 71.88; H, 9.84.

Found: C, 71.71; H, 10.00.

Oxidation of this ketone with dilute nitric acid gave a low yield of acid which proved to be an intractable mixture.

(*c*). Residue, 31 g.

Preparation of p-di-sec-butylbenzene via the Grignard reaction. p-sec-Butylacetophenone (112 g., 0.64 mole) was added to 0.7 mole of ethylmagnesium bromide to give 112 g. of *p-sec*-butyl-α-methyl-α-ethylbenzyl alcohol, b.p. 101–104° (1 mm.), n_D^{20} 1.5164. This product was reduced with hydrogen and a copper chromium oxide catalyst at 250° and 3400 p.s.i. to yield finally 56.4 g. of pure *p*-di-*sec*-butylbenzene after fractionation through a Todd Column, b.p. 115–117° (15–16 mm.) n_D^{20} 1.4886.

A center cut of this hydrocarbon and a center cut of a similar fraction of *p*-di-*sec*-butylbenzene prepared from benzene, *n*-butyl alcohol, and a boron trifluoride catalyst was used for the infrared absorption spectra. The spectra were determined by Dr. E. E. Pickett on a Beckman Infrared Spectrophotometer, Model IR-2, and were nearly identical.

This very pure *p*-di-*sec*-butylbenzene (50 g.) was acetylated at −10° to −15°. When the product was slowly distilled from a Clark flask, it was collected in two portions: a forerun of 8.3 g., b.p. 80–102° (1 mm.), which was mostly hydrocarbon and a main portion of 32.5 g., b.p. 102–120° (1 mm.).

The second portion was fractionated at 0.5 mm. through a Podbielniak column at a reflux ratio of 10:1 and the distillate was collected in five fractions (a) 4 g., b.p. 80–89°, n_D^{20} 1.5184; (b) 4 g., b.p. 90–96°, n_D^{20} 1.5071; (c) 14 g., b.p. 97.5°, n_D^{20} 1.5062; (d) 4.2 g., b.p. 98–100°, n_D^{20} 1.5059; (e) 3 g., b.p. 98–105°, n_D^{20} 1.5057.

Oxidation of fraction (c) with dilute nitric acid yielded *sec*-butylterephthalic acid, m.p. and mixture m.p. with an authentic sample, 255–256°.

The *semicarbazone* of (c) melted at 167.5–168.5° as compared with a value of 166.5–167.5° for the derivative of the ketone obtained by acetylation at 0°. Efforts to prepare a 2,4-dinitrophenylhydrazone of (c) resulted in an intractable oil.

The acetylation of the p-dialkylbenzenes at reflux temperature. The acetylation of *p*-di-*sec*-butylbenzene is typical. The hydrocarbon (95.2 g., 0.5 mole) was dissolved in 160 ml. of carbon disulfide in the usual apparatus and 58 g. of aluminum chloride was added with stirring at such a rate that the carbon disulfide refluxed gently. The acetyl chloride (39.4 g., 0.5 mole) was added at such a rate that the carbon disulfide refluxed slightly. After the acetyl chloride was added, the solution was refluxed gently for about three hours. The complex was decomposed with iced hydrochloric acid and the product was isolated in the usual manner. If less than 0.5 mole of hydrocarbon was used, the amounts of reactants were reduced proportionately.

Unless otherwise specified, the reaction product was fractionated at reduced pressure through a medium bore Todd column at a reflux ratio of 10:1. The distillate was collected in 9 fractions (*p*-di-*sec*-butylbenzene) to 16 fractions (*p*-di-*n*-butylbenzene) and each mono- or di-alkylketone fraction was identified by either a 2,4-dinitrophenylhydrazone or a semicarbazone and a carbon and hydrogen analysis, often of both the ketone and its derivative. Fractions which formed identical derivatives in good yield were combined. The mono- and di-alkylacetophenones so obtained were reasonably pure. Small impure intermediate fractions, hydrocarbon foreruns, and residues were discarded.

p-Xylene (51 g.) yielded 36 g. of *2,5-dimethylacetophenone*, b.p. 79–85° (4–5 mm.). Oxidation of this ketone with sodium hypobromite solution by the method of Zaki and Fahim (16) gave *2,5-dimethylbenzoic acid*, m.p. 133.5–134.5°. The 2,5-dimethylbenzoic acid prepared in the same way from 2,5-dimethylacetophenone obtained by the low temperature acetylation of *p*-xylene was 134–135°. A mixture of the two acids melted at 133.5–134.5°.

p-Di-n-butylbenzene (81 g.) yielded the following products:

(*a*). *p-n-Butylacetophenone* (9.4 g.), b.p. 122–124° (3–4 mm.). The ketone formed a *semicarbazone*, m.p. and mixture m.p. with an authentic sample of the derivative, 184–185°.

(*b*). A mixture (14 g.) which would not form solid derivatives.

(*c*). *2,4-Di-n-butylacetophenone* (8 g.), b.p. 129–130° (1 mm.).

Anal. Calc'd for $C_{16}H_{24}O$: C, 82.70; H, 10.41.
Found: C, 82.16; H, 10.30.

The ketone formed a *semicarbazone*, m.p. 76.5–77.5°.

Anal. Calc'd for $C_{17}H_{27}N_3O$: C, 70.54; H, 9.40.
Found: C, 70.69; H, 9.52.

Oxidation of this ketone with dilute nitric acid yielded *n-butylterephthalic acid*, m.p. and mixture m.p. with an authentic sample of the acid, 267–268°.

(*d*). A mixture (34 g.), b.p. 130–160° (1 mm.), which would not form derivatives. Values for the carbon and hydrogen analyses indicated that it was a mixture of polyalkylacetophenones. The fractions were combined and re-fractionated through a Podbielniak column without improvement in the carbon and hydrogen values.

p-Di-sec-butylbenzene (95 g.) yielded the following products:

(*a*). A forerun (16 g.) which was mainly hydrocarbon.

(*b*). *p-sec-Butylacetophenone*, 9 g., b.p. 104–108° (3–4 mm.), which formed a *2,4-dinitrophenylhydrazone*, m.p. and mixture m.p. with an authentic sample of the derivative, 146–147°, literature value 146–147° (1).

(*c*). *2,4-Di-sec-butylacetophenone*, 22 g., b.p. 119–126° (3–4 mm.). The *semicarbazone* of both fractions of this product melted at 129–130° rather than 166–167°, but carbon and hydrogen values agreed with those calculated for a derivative of dibutylacetophenone.

Anal. Calc'd for $C_{17}H_{27}N_3O$: C, 70.54; H, 9.40.
Found: C, 70.78; H, 9.64.

Oxidation of this ketone with dilute nitric acid gave *sec-butylterephthalic acid*, m.p. and mixture m.p. with an authentic sample, 253–254°.

(*d*). *Tri-sec-butylacetophenone*, 33 g., b.p. 135–141° (3–4 mm.), n_D^{20} 1.4927 ± 0.0003. This ketone would not form derivatives.

Anal. Calc'd for $C_{20}H_{32}O$: C, 83.27; H, 11.18.
Found: C, 83.51; H, 11.23.

p-Di-tert-butylbenzene (95 g.) yielded the following products:

(*a*). A forerun (15 g.) which was mainly hydrocarbon.

(*b*). *p-tert-Butylacetophenone*, 16 g., b.p. 142–149° (17–18 mm.), which formed a *semicarbazone*, m.p. and mixture m.p. with an authentic sample of the derivative, 232–233°, the literature value (19).

(*c*). *Di-tert-butylacetophenone*, 32 g., b.p. 149–155° (17–18 mm.) n_D^{20} 1.5088, m.p. 42.5–43.5° (aqueous alcohol). This ketone would not form derivatives.

Anal. Calc'd for $C_{16}H_{24}O$: C, 82.70; H, 1041.
Found: C, 82.72; H, 1069.

(*d*). A tarry residue, 26 g.

The p-di-(1-methylbutyl)benzene (85 g.) yielded the following products:

(*a*). *p-(1-Methylbutyl)acetophenone*, 16.5 g., b.p. 133–136° (5–6 mm.), which formed a *semicarbazone*, m.p. and mixture m.p. with an authentic sample of the derivative, 178–179°; literature value 173–174° (3).

Anal. Calc'd for $C_{14}H_{21}N_3O$: C, 67.98; H, 8.56.
Found: C, 68.13; H, 8.58.

(*b*). *A diamylacetophenone*, 8.4 g., b.p. 154–160° (5–6 mm.).

Anal. Calc'd for $C_{18}H_{28}O$: C, 83.02; H, 10.84.
Found: C, 83.04; H, 10.78.

This diamylacetophenone formed a *semicarbazone*, m.p. 127.5–128.5°, when freshly purified.

Anal. Calc'd for $C_{19}H_{31}N_3O$: C, 71.88; H, 9.84.
Found: C, 71.96; H, 9.84.

After standing ten months, the melting point of the sample had changed to 133–139°. The diamylacetophenone semicarbazone obtained from the ketone prepared by the low temperature acetylation of *p*-di-(1-methylbutyl)benzene melted at 147.5–148.5°. A mixture of these two derivatives melted at 133–139°. Hennion and McLeese (3) report m.p. 149–150° for the semicarbazone of their diamylacetophenone, but give no carbon and hydrogen analyses.

(*c*). *A triamylacetophenone*, 7 g., b.p. 158–162° (3–4 mm.). This ketone would not form a derivative.

Anal. Calc'd for $C_{18}H_{28}O$: C, 83.02; H, 10.84.
Found: C, 83.04; H, 10.78.

Preparation of the alkylterephthalic acids. The preparation of *sec*-butylterephthalic acid is typical. One mole (148 g.) of 2,5-dimethylacetophenone was added dropwise with stirring to one mole of ethylmagnesium bromide. The reaction product was isolated in the usual manner. The yield of 2,5-dimethyl-α-methyl-α-ethylbenzyl alcohol was 150 g., m.p. 43–45°, b.p. 96–97° (1 mm.).

Anal. Calc'd for $C_{12}H_{18}O$: C, 80.85; H, 10.18.
Found: C, 80.00; H, 10.00.

The carbinol was reduced with hydrogen and copper chromium oxide catalyst at 250° and 4200 p.s.i. The hydrocarbon was distilled through a Todd column and the 1,4-dimethyl-2-*sec*-butylbenzene was collected at 91.5–93° (17–18 mm.).

Anal. Calc'd for $C_{12}H_{18}$: C, 88.82; H, 11.18.
Found: C, 88.68; H, 11.04.

Oxidation of 10 g. of this hydrocarbon with potassium permanganate in aqueous pyridine (20) yielded 10 g. of crude acid, which was crystallized first from alcohol and finally from a mixture of benzene and ethyl acetate; m.p. 253.5–254° with sintering at 243°.

Anal. Calc'd for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35; Neut. equiv., 111.
Found: C, 64.62; H, 6.46; Neut. equiv., 110.

n-Butylterephthalic acid was obtained in the same way starting from 2,5-dimethyl-*n*-butyrophenone. Oxidation of the 1,4-dimethyl-2-*n*-butylbenzene obtained from it yielded *n*-butylterephthalic acid, m.p. 267.5–268°.

Anal. Calc'd for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35; Neut. equiv., 111.
Found: C, 65.04; H, 6.18; Neut. equiv., 110.

Oxidation of 1,3-dimethyl-4-*n*-butylbenzene with potassium permanganate yielded only methylterephthalic acid, m.p. 327–328°, literature values about 330° (21), 320–330° (22) rather than 4-*n*-butylisophthalic acid. The neutralization equivalent was 89.8, calc'd 90.

SUMMARY

Five dialkylbenzenes were acetylated in carbon disulfide solution at ice-bath temperatures or lower, and also at the reflux temperature of carbon disulfide.

At ice-bath temperatures *p*-xylene and *p*-di-*n*-butylbenzene yielded 2,5-dimethylacetophenone and 2,5-di-*n*-butylacetophenone. *p*-Di-*sec*-butylbenzene and *p*-di-(1-methylbutyl)benzene yielded the corresponding 2,4-di-*sec*-alkylacetophenones, rather than the 1,2,5-isomer as previously reported. A small amount of monoalkylacetophenone was formed in each acetylation. *p*-Di-*tert*-butylbenzene yielded only *p*-*tert*-butylacetophenone as previously reported.

A reflux temperature, *p*-xylene yielded 2,5-dimethylacetophenone; *p*-di-*n*-butylbenzene yielded *p*-*n*-butylacetophenone, 2,4-di-*n*-butylacetophenone, and an unidentified high-boiling mixture of ketones.

p-Di-*sec*-butylbenzene yielded *p*-*sec*-butylacetophenone, 2,4-di-*sec*-butylacetophenone, and a tributylacetophenone.

p-Di-(1-methylbutyl)benzene yielded *p*-(1-methylbutyl)acetophenone, a diamylacetophenone, and polyamylacetophenones.

p-Di-*tert*-butylbenzene yielded *p*-*tert*-butylacetophenone and a di-*tert*-butylacetophenone.

The migrating *n*-butyl and *sec*-butyl radicals were not isomerized, either at ice-bath temperature or at reflux temperature.

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