

carrying out the hydrolysis; the best procedure when it was used consisted in passing hydrogen chloride into a suspension of the isonitroso compound in formalin.

The diketone separated from alcohol in the form of orange plates that melted at 115–116°. The absorption spectrum has been reported.⁵

Anal. Calcd. for C₁₆H₁₈O₂: C, 81.3; H, 5.1. Found: C, 81.4; H, 5.1.

With *o*-phenylenediamine in alcohol, the diketone gave 11-methyl-11-phenylindeno[1,2-*b*]quinoxaline (Ring Index 2517), colorless crystals that melted at 129–130°.

Anal. Calcd. for C₂₂H₁₆N₂: C, 85.7; H, 5.2. Found: C, 85.5; H, 5.2

Suspended in dilute sodium hydroxide and treated with an excess of hydrogen peroxide, the diketone gave α -

(6) Koelsch and Hochmann, *J. Org. Chem.*, **3**, 503 (1938).

methyl- α -phenylhomophthalic acid, which melted at 170–172° after crystallization from ether-ligroin.

Anal. Calcd. for C₉H₁₀O₄: C, 71.1; H, 5.2. Found: C, 71.1; H, 5.4.

Summary

In the presence of three equivalents of aluminum chloride, crotonic acid and benzene interact to form 3-methylhydrindone; and cinnamic acid and benzene form 3-phenylhydrindone.

The reaction of benzene with β -chlorocrotonic acid affords a convenient preparation of β,β -diphenylbutyric acid. This acid has been converted into 3-methyl-3-phenylhydrindone and thence into 3-methyl-3-phenylindandione.

MINNEAPOLIS, MINNESOTA RECEIVED NOVEMBER 3, 1942

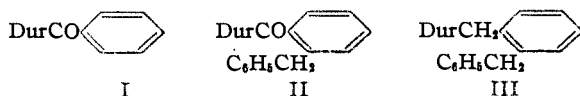
[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

para-Alkylation of Benzoyldurene by the Grignard Reagent

BY REYNOLD C. FUSON AND B. C. MCKUSICK¹

The action of phenylmagnesium bromide on certain mesityl ketones has been shown to effect the introduction of a phenyl group into an *ortho* position, presumably by 1,4 addition of the reagent² to the conjugated system formed by the carbonyl group and a double bond of the benzene ring. In an attempt to realize this type of condensation with other hindered ketones it was found that benzylmagnesium chloride could be added to benzoyldurene (I) in a similar manner.

Investigation showed, however, that the product was not the *o*-benzyl derivative (II) which would arise from 1,4 addition of the Grignard reagent. When the new ketone was reduced with sodium and alcohol it yielded not 2'-benzyl-2,3,5,6-tetramethyldiphenylmethane (III) but an isomer of it. This was established by comparison

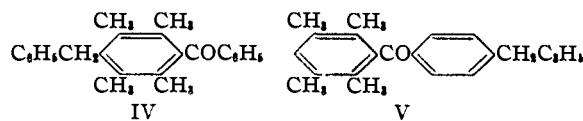


of the ketone and its reduction product with authentic specimens of II and III, respectively.

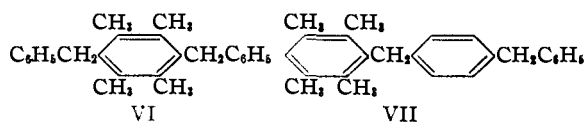
The elimination of the *o*-benzyl ketone (II) as a possibility made it appear probable that the benzyl group had entered one of the *para* positions, yielding 4-benzyl-2,3,5,6-tetramethylbenzophenone (IV) or 4'-benzyl-2,3,5,6-tetramethylbenzophenone (V).

(1) Röhlm and Haas Research Assistant.

(2) Fuson, Armstrong and Speck, *J. Org. Chem.*, **7**, 297 (1942).



The first of these possibilities was excluded when it was found that an authentic specimen of dibenzoyldurene (VI) was different from the hydrocarbon obtained by reduction of the original benzylated ketone.



There remained structure V, which proved to be the correct one. This structure was established by synthesis of the ketone from durene and *p*-benzylbenzoyl chloride by the Friedel-Crafts method. It was confirmed by the discovery that the ketone could be cleaved, by heating with sirupy phosphoric acid, to yield durene and *p*-benzylbenzoic acid. It follows that the reduction product is 4'-benzyl-2,3,5,6-tetramethyldiphenylmethane (VII).

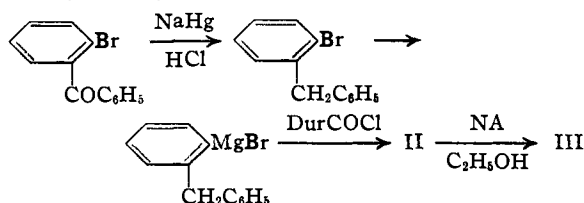
The addition of *t*-butylmagnesium chloride was found to take place in a similar manner, yielding 4'-*t*-butyl-2,3,5,6-tetramethylbenzophenone (VIII). This compound was synthesized from



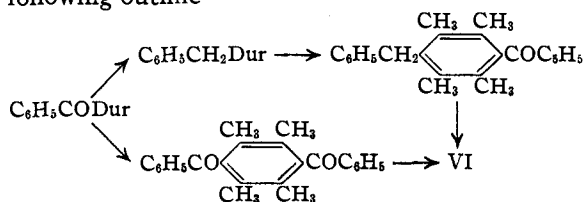
di-(*p*-*t*-butylphenyl)-cadmium and 2,3,5,6-tetramethylbenzoyl chloride. It yielded the corresponding hydrocarbon (IX) when reduced with sodium and alcohol. Heating with sirupy phosphoric acid cleaved it to *p*-*t*-butylbenzoic acid and durene.

The synthesis of benzoildurene (I) was accomplished by the condensation of benzoyl chloride with durene according to a modification of the procedure of Friedel, Crafts and Ador.³ A second method involved the reaction of 2,3,5,6-tetramethylbenzoyl chloride with diphenylcadmium.

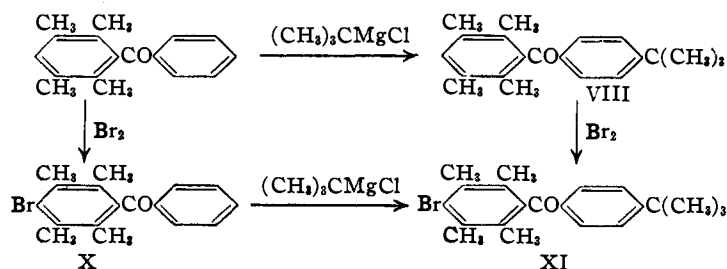
Several of the reference substances were not known previously and had to be prepared by unequivocal methods. For example, 2'-benzyl-2,3,5,6-tetramethylbenzophenone (II) and 2'-benzyl-2,3,5,6-tetramethyldiphenylmethane (III) were made from 2-bromobenzophenone and 2,3,5,6-tetramethylbenzoyl chloride by the following scheme



Dibenzoyldurene (VI) was made from benzoildurene by two methods as shown in the following outline



p-*t*-Butylbenzoildurene (VIII) yielded a dinitro derivative and a monobromide (XI). The latter was also prepared by the action of *t*-butylmagnesium chloride on 4-bromo-2,3,5,6-tetramethylbenzophenone (X). The relationship of these derivatives is shown in the following chart



4-Bromo-2,3,5,6-tetramethylbenzophenone was

(3) Friedel, Crafts and Ador, *Ann. chim. phys.*, [6] 1, 511 (1884).

prepared by bromination of benzoildurene and also by the condensation of bromodurene with benzoyl chloride.

Although the mechanism of the *para* alkylation of benzoildurene and its bromo derivative is obscure, the first step can be formulated as a 1,6 addition of the Grignard reagent to the ketones. Such a reaction would be remarkable inasmuch as 1,6 addition is very rarely observed with the Grignard reagent.

Experimental

Benzoildurene (I).³—Fifty-five grams of anhydrous aluminum chloride was added in small portions over a period of one and one-half hours to a mixture of 50 g. of durene, 48 cc. of benzoyl chloride and 350 cc. of carbon disulfide. The mixture was stirred during the addition and for three hours longer. After decomposition of the mixture with dilute hydrochloric acid, the organic layer was separated and the carbon disulfide was removed by distillation. Forty-five grams of sodium carbonate and 150 cc. of water were added to the residue, which was then steam-distilled to remove unchanged durene. The contents of the flask were cooled and filtered. The solid benzoildurene was dried and crystallized from *n*-butyl ether; yield 68 g. (77%); m. p. 119–120°.

Benzoildurene was also prepared by the reaction of 2,3,5,6-tetramethylbenzoyl chloride⁴ with diphenylcadmium, by use of the method of Gilman and Nelson.⁵ From 1.70 g. of the acid chloride and 2 g. of bromobenzene there was obtained 1.55 g. (75%) of the ketone.

4'-Benzyl-2,3,5,6-tetramethylbenzophenone (V).—A Grignard reagent was prepared from 6.0 g. of magnesium and 31 g. of benzyl chloride in 200 cc. of dry ether. Ten grams of solid benzoildurene was added to the well-stirred solution, causing it to turn deep red. It was stirred at room temperature for an hour, refluxed for twenty minutes and decomposed with dilute hydrochloric acid. The light yellow ether layer was washed with water and the ether was removed by distillation. Alcohol was added to the residue. The alcohol solution was cooled and the precipitate was recrystallized from alcohol. The crude ketone weighed 2.8 g. and melted at 122–128°. Further recrystallization gave platelets melting at 128.5–129.5°.

The product of one run was in the form of long needles, m. p. 119–120°. This proved to be a less stable crystal form of 4'-benzyl-2,3,5,6-tetramethylbenzophenone. A mixture of the two forms melted at 128–129°. Both forms yielded 4'-benzyl-2,3,5,6-tetramethyldiphenylmethane (VII) on reduction with sodium and alcohol. Finally, the low-melting form could be converted to the high-melting form by fusion or by seeding its supersaturated alcohol solution with the high-melting form.

Anal. Calcd. for $C_{24}H_{34}O$: C, 87.75; H, 7.37; mol. wt., 328. Found (low-melting form): C, 88.05; H, 7.64; mol. wt.

(4) Fuson and Kelton, *THIS JOURNAL*, 63, 1500 (1941).

(5) Gilman and Nelson, *Rec. trav. chim.*, 55, 518 (1936).

(ebullioscopic in chloroform), 352. Found (high-melting form): C, 87.89; H, 7.35.

A Zerewitinoff determination showed the absence of active hydrogen.

4'-Benzyl-2,3,5,6-tetramethyldiphenylmethane (VII).—The general method of Klages and Allendorff⁶ for reducing diaryl ketones to diarylmethanes was used. Two grams of 4'-benzyl-2,3,5,6-tetramethylbenzophenone (V) was dissolved in 25 cc. of absolute ethanol, and small pieces (3 g.) of sodium were dropped into the boiling solution as rapidly as possible without causing the reaction to become too vigorous. When all the sodium had reacted, the hot solution was poured on a mixture of 25 cc. of hydrochloric acid and 40 g. of ice. The oil which came to the surface yielded 0.85 g. of solid when allowed to stand in an ice box overnight. Three crystallizations from methanol, to which a little chloroform was added, gave needles melting at 69–70°.

Anal. Calcd. for C₂₄H₂₆: C, 91.66; H, 8.34. Found: C, 91.72; H, 8.06.

2'-Benzyl-2,3,5,6-tetramethylbenzophenone (II).—A modified Clemmensen reduction⁷ was employed to convert 2-bromobenzophenone to 2-bromodiphenylmethane⁸; b. p. 148–150° (2 mm.); yield 33%. A Grignard reagent, made from 13.6 g. of the aryl bromide, 2.0 g. of magnesium and 75 cc. of dry ether, was filtered and added slowly to a well-stirred solution of 8.4 g. of 2,3,5,6-tetramethylbenzoyl chloride in 200 cc. of dry ether. The mixture was heated under reflux for one hour and worked up in the usual manner. Removal of solvent and addition of alcohol caused 6.9 g. (49%) of orange crystals, m. p. 113–116°, to separate. Treatment with Norite and four recrystallizations from alcohol gave white needles, m. p. 118.5–119.5°. A mixture of this product and the low-melting (m. p. 119–120°) form of 4'-benzyl-2,3,5,6-tetramethylbenzophenone (V) melted at 95–100°.

Anal. Calcd. for C₂₄H₂₄O: C, 87.75; H, 7.37. Found: C, 87.77; H, 7.59.

One gram of the ketone was reduced with sodium and alcohol. The product, 2'-benzyl-2,3,5,6-tetramethyldiphenylmethane (III), was in the form of white platelets and melted at 126.5–127.5° after repeated crystallization from a benzene-alcohol mixture and from glacial acetic acid.

Anal. Calcd. for C₂₄H₂₆: C, 91.66; H, 8.34. Found: C, 91.62; H, 8.44.

Benzoyldurene.—Twenty grams of benzoyldurene in 300 cc. of absolute alcohol was reduced with 30 g. of sodium. The oily product was distilled twice; b. p. 162° (4 mm.). The distillate crystallized from methanol in the form of stubby needles; m. p. 53–57°; yield 7.5 g. (40%). Further crystallization raised the melting point to 57–58°.

Anal. Calcd. for C₁₇H₂₀: C, 91.01; H, 8.99. Found: C, 91.19; H, 9.04.

Friedel, Crafts and Ador³ described benzoyldurene as melting at 60.5° while Beaurepaire⁹ reported a melting point of 145°.

An attempt to reduce benzoyldurene by the Clemmensen method failed.

4-Benzyl-2,3,5,6-tetramethylbenzophenone (IV).—A mixture of 5.0 g. of benzoyldurene, 3.1 cc. of benzoyl chloride, 3.7 g. of aluminum chloride and 75 cc. of carbon disulfide was allowed to react for one and one-half hours. The ketone formed needles melting at 165–172°; yield 5.6 g. (77%). After several recrystallizations from a mixture of absolute alcohol and benzene the product melted at 173–174°.

Anal. Calcd. for C₂₄H₂₄O: C, 87.75; H, 7.37. Found: C, 88.00; H, 7.25.

Dibenzoyldurene.³—Ten grams of benzoyldurene was dissolved in 60 cc. of benzoyl chloride, 10 g. of aluminum chloride was added and the temperature of the well-stirred mixture was slowly raised to 155° over a period of one hour. After one-half hour at this temperature, the hot solution was poured into water, 45 g. of sodium hydroxide was added and the mixture was heated on the steam-bath until there was no odor of benzoyl chloride. The diketone was separated by filtration, washed with water, digested with dilute hydrochloric acid to remove aluminum salts and finally recrystallized from benzene; yield, 5.6 g. (39%); m. p. 273–275°.

4-Benzyl-2,3,5,6-tetramethyldiphenylmethane (VI).—Both dibenzoyldurene and 4-benzyl-2,3,5,6-tetramethylbenzophenone (IV) gave white platelets when reduced with *n*-amyl alcohol and sodium. The hydrocarbon was recrystallized from an alcohol-benzene mixture; m. p. 176–177°. A mixture of the two products also melted at 176–177°.

Anal. Calcd. for C₂₄H₂₆: C, 91.66; H, 8.34. Found: C, 91.77; H, 8.35.

Cleavage of 4'-Benzyl-2,3,5,6-tetramethylbenzophenone (V) with Phosphoric Acid.¹⁰—One gram of the ketone was heated under reflux with 40 cc. of sirupy phosphoric acid for thirty-six hours. The reaction mixture was made alkaline with 20% sodium hydroxide solution and steam distilled. The distillate contained durene; m. p. 79–80°. A mixed melting point with an authentic sample of durene was 79–80°. Half of the durene was dissolved in 5 cc. of ice-cold nitric acid (d. 1.5). After fifteen minutes the solution was poured on ice and the solid was recrystallized from absolute ethanol; yield 120 mg.; m. p. 206–207°. A mixed melting point with dinitrodurene was 206–207°. The rest of the durene was converted¹¹ to 120 mg. of dibromodurene; m. p. 199–200°.

The alkaline solution was boiled with Norite and filtered. The filtrate was extracted once with chloroform to remove any chloroform-soluble impurities, was acidified with hydrochloric acid and was then extracted with three 40-cc. portions of chloroform. Evaporation of the chloroform yielded 280 mg. of crude *p*-benzylbenzoic acid. It was purified by crystallization from dilute alcohol; m. p. 157–158° (reported,¹² 159–160°); neutralization equivalent 213 (calculated 212); amide, m. p. 170–171° (reported,¹² 172–173°). The acid and amide did not depress the melting points of authentic samples.

By leaching the filter paper and Norite with chloroform, 100 mg. of starting material was recovered.

(6) Klages and Allendorff, *Ber.*, **31**, 998 (1898).

(7) Martin, *This Journal*, **58**, 1438 (1936).

(8) Clarkson and Gomberg, *ibid.*, **52**, 2881 (1930).

(9) Beaurepaire, *Bull. soc. chim.*, [2] **50**, 678 (1888).

(10) Klages and Lickroth, *Ber.*, **32**, 1549 (1899).

(11) Smith and Moyle, *This Journal*, **55**, 1680 (1933).

(12) Wertheim, *ibid.*, **55**, 2540 (1933).

***p*-Benzylbenzoic Acid.**—The acid was prepared conveniently in 40–50% yield by a modified Clemmensen reduction⁷ of *p*-benzoylbenzoic acid,¹² using 7.5 cc. of toluene for each gram of acid. After forty hours, the hot toluene layer was separated, filtered and cooled. The product which crystallized (m. p. 156–158°) required no further purification. The yield could be increased 5% by concentrating and cooling the mother liquor. Zinc dust was much more satisfactory than granulated or mossy zinc.

Reduction with zinc and alkali resulted in a 94% yield of α -hydroxy-4-diphenylmethanecarboxylic acid.¹³ After recrystallization from water it melted at 164–165°. The neutralization equivalent was 224 (calculated, 228).

The acid chloride,¹² b. p. 208–209° (15 mm.), was prepared in 71% yield by use of thionyl chloride. With ammonia it gave *p*-benzylbenzamide; m. p. 170–171°.

Independent Synthesis of 4'-Benzyl-2,3,5,6-tetramethylbenzophenone (V).—The procedure for the preparation of benzoyldurene was used. A mixture of 10.5 g. of *p*-benzoylbenzoyl chloride, 10.5 g. of durene and 8.0 g. of aluminum chloride yielded 10.0 g. (67%) of white solid, m. p. 117–126°, after one crystallization from alcohol. In spite of repeated recrystallization of the ketone from a variety of solvents, its melting point could not be raised above 125–127°; a mixed melting point with the original sample of V was 127–129°. During the purification, the compound once crystallized in the form of needles, m. p. 116–119°. A mixed melting point with the low-melting form of V was 117–120°. This difficulty in purifying the ketone made it impossible to compare it with the sample made earlier. However, by reduction of the impure ketone (m. p. 117–126°) a hydrocarbon, melting sharply at 69–70°, was obtained which was proved by the mixed melting point method to be 4'-benzyl-2,3,5,6-tetramethyldiphenylmethane (VII).

4'-*t*-Butyl-2,3,5,6-tetramethylbenzophenone (VIII).—The procedure employed in the reaction of benzoyldurene with benzylmagnesium chloride was followed, using 6.0 g. of magnesium, 28 cc. of *t*-butyl chloride and 10.0 g. of benzoyldurene. One crystallization of the crude product from ethanol gave 4.1 g. (33%) of platelets, m. p. 126–128°. The pure ketone melted at 127–128°. A Zerewitinoff determination showed the absence of active hydrogen.

Anal. Calcd. for C₂₁H₂₈O: C, 85.66; H, 8.90; mol. wt. (ebullioscopic in chloroform), 294. Found: C, 86.04; H, 8.97; mol. wt., 274.

One gram of the ketone was added slowly to 6 cc. of ice-cold nitric acid (d. 1.5). After ten minutes, the solution was poured on ice and the dinitro derivative was recrystallized as small needles from absolute ethanol; m. p. 212–213°.

Anal. Calcd. for C₂₁H₂₄O₂N₂: C, 65.61; H, 6.29; N, 7.29. Found: C, 65.74; H, 6.62; N, 7.87.

Either a Clemmensen reduction or treatment with sodium and alcohol reduced the ketone to 4'-*t*-butyl-2,3,5,6-tetramethyldiphenylmethane (IX). It separated from alcohol as platelets; m. p. 116–117°.

Anal. Calcd. for C₂₁H₂₈: C, 89.94; H, 10.06. Found: C, 89.66; H, 9.63.

Cleavage of 4'-*t*-Butyl-2,3,5,6-tetramethylbenzophenone (VIII) with Phosphoric Acid.—The ketone was cleaved in

the same manner as was the corresponding benzyl ketone. From one gram there was obtained 155 mg. of durene (m. p. 79–80°), 120 mg. of *p*-*t*-butylbenzoic acid (m. p. 161.5–163.5° after crystallization from dilute ethanol) and 260 mg. of starting material. The durene was converted to dinitrodurene and to the trinitrobenzene addition product; m. p. 100–101° (reported m. p. 92–98°¹⁴). The durene and dinitrodurene did not depress the melting points of authentic samples.

The neutralization equivalent of the acid was 183 (calculated 178). Its melting point is reported as 165°.¹⁶ The ortho and meta isomers melt at 68.5°¹⁶ and 127°,¹⁶ respectively.

Independent Synthesis of 4'-*t*-Butyl-2,3,5,6-tetramethylbenzophenone (VIII).—A Grignard reagent prepared from 9.6 g. of *p*-bromo-*t*-butylbenzene,¹⁷ 2.0 g. of magnesium and 75 cc. of dry ether was decanted into another flask. Anhydrous cadmium chloride (4.4 g.) was added to form the diaryl cadmium compound, and the mixture was heated for twenty minutes. A solution of 6.0 g. of 2,3,5,6-tetramethylbenzoyl chloride in 75 cc. of dry ether was added and the mixture was stirred and heated an hour before being decomposed with dilute hydrochloric acid. Decomposition of the mixture yielded 1.8 g. (20%) of platelets; m. p. 127–128°. A mixture with the original sample of VIII showed no depression in melting point.

4-Bromo-2,3,5,6-tetramethylbenzophenone (X).—A solution of 3.50 g. of benzoyldurene, 0.8 cc. of bromine and a crystal of iodine in 12 cc. of carbon tetrachloride was heated under gentle reflux for four hours. The mixture was diluted with ether and washed with 10% sodium bicarbonate solution, 5% sodium bisulfite solution and water. The ether was removed and alcohol added, precipitating an oil which solidified after a few hours. The ketone crystallized from alcohol in the form of long needles; m. p. 98–102°; yield 1.40 g. Repeated recrystallization from petroleum ether (b. p. 90–100°) produced a colorless product melting at 116–117°.

A better method of preparation involved adding 28 g. of aluminum chloride over a period of half an hour to a well-stirred solution of 26.5 cc. of benzoyl chloride and 44.5 g. of bromodurene¹¹ in 150 cc. of carbon disulfide. The mixture was stirred forty-five minutes longer and worked up in accordance with the procedure for benzoyldurene. The product weighed 40.5 g. (61%) and melted at 103–109° after one crystallization from alcohol. Two recrystallizations from petroleum ether (b. p. 90–100°) raised the melting point to 116–117°. A mixture with the ketone formed by direct bromination of benzoyldurene also melted at 116–117°.

Anal. Calcd. for C₁₇H₁₇OBr: C, 64.36; H, 5.40. Found: C, 64.63; H, 5.30.

4'-*t*-Butyl-2,3,5,6-tetramethyl-4-bromobenzophenone (XI).—The procedure for the bromination of benzoyldurene was followed, using 1.00 g. of *p*-*t*-butylbenzoyldurene, 0.2 cc. of bromine and 2 cc. of carbon tetrachloride. The bromo ketone crystallized from a mixture of chloroform and alcohol in the form of colorless platelets; m. p. 182–183°.

(14) Pfeiffer, *Ann.*, **412**, 298 (1916).

(15) Shoesmith and Mackie, *J. Chem. Soc.*, 300 (1936).

(16) Shoesmith and Mackie, *ibid.*, 2334 (1928).

(17) Fieser and Snow, *This Journal*, **60**, 176 (1938).

(18) Zincke, *Ann.*, **161**, 102 (1871).

This compound was also obtained when 13.0 g. of 4-bromo-2,3,5,6-tetramethylbenzophenone was treated with the Grignard reagent prepared from 30 cc. of *t*-butyl chloride, using the same procedure as in the reaction of benzoyldurene with benzylmagnesium chloride. There was obtained 6.1 g. (40%) of a product shown by the method of mixed melting points to be identical with that produced by the bromination method.

Anal. Calcd. for $C_{21}H_{25}OBr$: C, 67.56; H, 6.75; Br, 21.41. Found: C, 67.79; H, 6.86; Br, 21.25.

In addition, 1.1 g. (8%) of the original ketone was recovered by fractional crystallization.

Summary

Benzoyldurene has been found to react with benzyl- and *t*-butylmagnesium chloride to undergo para alkylation, yielding the corresponding duryl *p*-alkylphenyl ketones. The introduction of the alkyl groups into the para position of the benzoyl group corresponds to 1,6 addition of the Grignard reagent followed by loss of a molecule of hydrogen or its equivalent.

URBANA, ILLINOIS

RECEIVED OCTOBER 14, 1942

[CONTRIBUTION FROM THE DIVISION OF CHEMISTRY, NATIONAL INSTITUTE OF HEALTH, U. S. PUBLIC HEALTH SERVICE]

The Ring Structure of Polygalitol

BY NELSON K. RICHTMYER AND C. S. HUDSON

Polygalitol is an anhydrohexitol which was discovered by Chodat¹ in an extract of *Polygala amara*, L. It has been isolated also from *P. vulgaris*, L.,² from *P. tenuifolia*,³ and from *P. Senega*, L.⁴ According to Shinoda, Sato and Sato,³ polygalitol is the epimer of styracitol, a 1,5-anhydro-D-hexitol which was isolated from *Styrax Obassia*, Sieb and Zucc., by Asahina,⁵ and later synthesized by Zervas.⁶ The 1,5-ring structure of styracitol is based upon the reasonable assumption that no shift in the size of the ring has occurred during the synthesis from acetobromoglucose. Although this synthesis by the addition of hydrogen to the 1,2 double bond in tetraacetylhydroxyglucal does not enable one to distinguish between the mannitol and sorbitol configurations for this compound, evidence has been presented by Zervas and Papadimitriou⁷ to prove that styracitol is 1,5-anhydro-D-mannitol. Consequently, if polygalitol is the epimer, it must be 1,5-anhydro-D-sorbitol.

However, W. Freudenberg and Sheehan⁸ have claimed that tetramethylstyracitol is identical with their synthetic tetramethyl-1,5-anhydro-sorbitol. Tetramethylpolygalitol, on the other hand, appeared to be quite different from their synthetic tetramethyl-1,5-anhydromannitol and especially from their tetramethyl-1,5-anhydro-

sorbitol. They have concluded, therefore, that polygalitol is neither 1,5-anhydro-D-sorbitol nor 1,5-anhydro-D-mannitol, and also that styracitol is 1,5-anhydro-D-sorbitol.

In view of these conflicting opinions and the lack of satisfactory experimental evidence concerning the structure and configuration, especially of polygalitol, we have decided to examine these substances by the application of some new methods of study.

The present communication deals with the oxidation of styracitol and polygalitol by periodic acid⁹ and by sodium metaperiodate.¹⁰ These reagents can be used to determine directly and conclusively the ring structures of such compounds. With each of the two anhydrohexitols (I) the reaction with sodium metaperiodate consumed two equivalents of oxidant, and liberated one equivalent of formic acid; the rotations of the resulting solutions had the same value, indicating the formation of the same dialdehyde (II). The reactions with periodic acid likewise consumed two equivalents of oxidant. In each case, the presumed dialdehyde (II), upon further oxidation with bromine water and strontium carbonate, yielded a crystalline, hydrated strontium salt; the salts were identical, as could be shown by analyses for carbon, hydrogen, strontium and water of crystallization and by their rotations in water and in excess hydrochloric acid. The strontium salt (III), named in accordance with the established terminology,⁹ is strontium D-hy-

(1) Chodat, *Arch. sci. phys. nat.*, [3] 18, 228 (1887); [3] 19, 290 (1888).

(2) Picard, *Bull. soc. chim. biol.*, 9, 692 (1927).

(3) Shinoda, Sato and Sato, *Ber.*, 65, 1219 (1932).

(4) (a) W. Freudenberg and Rogers, *THIS JOURNAL*, 59, 1602 (1937); (b) Carr and Krantz, *J. Am. Pharm. Assoc.*, 27, 318 (1938).

(5) Asahina, *Arch. Pharm.*, 245, 325 (1907); 247, 157 (1909).

(6) Zervas, *Ber.*, 63, 1689 (1930).

(7) Zervas and Papadimitriou, *ibid.*, 73, 174 (1940).

(8) W. Freudenberg and Sheehan, *THIS JOURNAL*, 62, 558 (1940).

(9) Jackson and Hudson, *ibid.*, 59, 994 (1937).

(10) Jackson and Hudson, *ibid.*, 61, 1520 (1939).