[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

Steric Hindrance in Compounds of Mesitylene and Triphenylbenzene

BY E. P. KOHLER AND L. W. BLANCHARD, JR.

In continuation of the study of mesitylenic compounds[1] we have prepared and investigated three α,β-unsaturated ketones with mesitylene residues in the β position, namely $(CH_3)_3C_6H_2CH=CHCOC_6H_5$, $(CH_3)_3C_6H_2CH=CHCOCH_3$ and $(CH_3)_3C_6H_2CH=CHCOC_6H_2(CH_3)_3$. We found that these compounds behave precisely like other α,β-unsaturated ketones which have the same groups adjacent to carbonyl and one hydrocarbon residue in the β position; the mesitylene residue has no conspicuous effect on the ease of oxidation or the addition of bromine, and it does not alter the mode of addition of Grignard reagents. As these compounds are ethylenic analogs of trimethyl benzaldehyde which forms an acetal and two oximes as readily as benzaldehyde itself, it is evident that a mesitylene residue does not by itself cause a hindrance to addition. In order to create a serious hindrance it must be associated with another hydrocarbon residue or its equivalent.

We also studied some of the addition reactions of symmetrical trimethyl phenylmagnesium bromide. From earlier work it was known that this magnesium derivative can be prepared without difficulty and that it reacts normally with acid chlorides. As this reaction does not necessarily involve addition to carbonyl we examined the behavior of the magnesium compound toward acetone and benzophenone. It combines with both ketones. The yields are not as good as those obtained with simpler reagents, but the difference may be due largely to the difficulties attending the isolation of tertiary alcohols which do not crystallize readily.

In order to secure a basis for comparing the hindrance to addition due to a mesitylene residue with that caused by another hydrocarbon residue which has substituents in the same positions but which would be expected to have a different chemical character we studied a series of derivatives of symmetrical triphenylbenzene. These derivatives generally react less readily than the derivatives of mesitylene but it is difficult to determine to what extent the difference is attributable to space relations. In some cases, doubtless, it is due to differences in solubility. Thus bromo triphenylbenzene cannot be converted into its magnesium derivative in ether in which it is sparingly soluble. In benzene and ether in which the bromo compound is readily soluble, the reaction with magnesium is much more difficult to start than the reaction with bromo mesitylene but, once it is started, it gives a better yield of magnesium derivative with the phenylated than with the methylated compound. The resulting magnesium compound is as readily carbonated as any other Grignard reagent but, unlike the corresponding derivative of mesitylene, it does not combine either with benzophenone or with acetone. It reacts with acid chlorides but not with esters and it does not couple with bromo triphenylbenzene to form hexaphenyl biphenyl. It is, therefore, distinctly less reactive than the corresponding derivative of mesitylene.

The ketones which contain a triphenylbenzene residue—aceto triphenylbenzene, triphenyl benzophenone and hexaphenyl benzophenone—are not conspicuously different from mesitylenic ketones. The hindrance to all reactions which necessarily involve addition to carbonyl is prohibitive, but all three ketones are more or less readily reduced to secondary alcohols by sodium amalgam. In benzene both triphenyl benzophenone and hexaphenyl benzophenone form dark purple ketyls with sodium. When the ketyls are decomposed with water or, as directed by Bachmann, with acetic acid they form approximately equivalent quantities of ketones and carbinols; they appear to be incapable of associating to dimolecular compounds.

Experimental Part

I. Mesitylene Derivatives

The unsaturated ketones were prepared without difficulty by condensing trimethyl benzaldehyde with acetophenone, acetomesitylene and acetone, and their structure was established by oxidation with permanganate in acetone. The addition of bromine was studied only in the case of trimethyl benzal acetophenone. Addition occurred readily and the presence of the mesitylene residue had no unusual influence on the properties of the dibromide; sodium methylate con-

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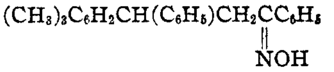
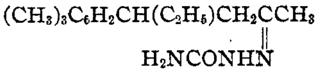
[1] Kohler and Baltzly, THIS JOURNAL, 54, 4015 (1932).

verted it into a methoxyl compound which, on ozonolysis, yielded methyl trimethyl benzoate, and which was hydrolyzed by acids to benzoyl acetomesitylene

$$(CH_3)_3C_6H_2CHBrCHBrCOC_6H_5 \longrightarrow (CH_3)_3C_6H_2C(OCH_3){=}CHCOC_6H_5 \longrightarrow (CH_3)_3C_6H_2COCH_2COC_6H_5$$

All three ketones were treated with organic magnesium compounds. The first two formed only 1,4-addition products which were hydrolyzed to saturated ketones. The last formed both 1,4- and 1,2-addition products. Owing to the ease with which permanganate oxidizes trimethyl benzoic acid to dimethyl phthalic acid it was not possible to determine the relative amounts of saturated ketone and unsaturated carbinol with any degree of accuracy but it was apparent that they do not differ much from the amounts obtained with benzalacetone.

The composition and characteristic properties of the substances employed and obtained are shown in the table.

		M. p., °C.	Calcd., %		Found, %	
			C	H	C	H
$(CH_3)_3C_6H_2CH{=}CHCOC_6H_5$	Pale yellow needles	96	86.4	7.2	86.8	7.4
$(CH_3)_3C_6H_2CHBrCHBrCOC_6H_5$	Colorless cubes	140	52.7	4.4	52.9	4.6
$(CH_3)_3C_6H_2C(OCH_3){=}CHCOC_6H_5$	Yellow needles	113	81.4	7.1	81.2	7.0
$(CH_3)_3C_6H_2CH(C_6H_5)CH_2COC_6H_5$	Tables	64	87.8	7.3	87.5	7.5
 $(CH_3)_3C_6H_2CH(C_6H_5)CH_2\underset{\underset{NOH}{\|}}{C}C_6H_5$	Diamond-shaped plates	185	84.0	7.3	84.1	7.5
$(CH_3)_3C_6H_2CH{=}CHCOC_6H_2(CH_3)_3$	Pale yellow needles	99	86.3	8.2	86.5	8.3
$(CH_3)_3C_6H_2CH(CH_3)CH_2COC_6H_2(CH_3)_3$	Liquid	194 (1 mm.)	85.7	9.1	85.4	9.1
$(CH_3)_3C_6H_2CH{=}CHCOCH_3$	Needles	67	86.8	8.2	86.6	8.2
 $(CH_3)_3C_6H_2CH(C_2H_5)CH_2\underset{\underset{H_2NCONHN}{\|}}{C}CH_3$	Needles	169	69.8	9.1	69.6	9.1
$(CH_3)_3C_6H_2C(CH_3)_2OH$	Needles	113	80.9	10.1	80.9	10.3
$(CH_3)_3C_6H_2C(C_6H_5)_2OH$	Prisms	88	87.4	7.3	87.2	7.3

II. Experiments with Triphenylbenzene

Very few derivatives of triphenylbenzene are known and fewer still have been obtained directly from the hydrocarbon. The only mono substitution product of known structure is a nitro derivative which Vorländer and his collaborators[2] obtained by nitrating the hydrocarbon in boiling glacial acetic acid. In this substance the substituent is in the para position of one of the phenyl groups.

We found that by brominating in carbon bisulfide it is possible to get an excellent yield of a mono bromo derivative. In this substance the substituent must be in the central nucleus because when it is replaced by an acetyl group the product behaves like a methyl ketone with substituents in both ortho positions.

$$\underset{\text{I}}{(C_6H_5)_3C_6H_2Br} \longleftarrow \underset{\text{II}}{(C_6H_5)_3C_6H_2MgBr} \longrightarrow \underset{\text{III}}{(C_6H_5)_3C_6H_2COCH_3}$$

By means of this magnesium derivative it was possible to prepare other mono substitution products of known structure. When it was carbonated in the usual manner it gave an excellent yield of triphenyl benzoic acid and it reacted with benzoyl chloride to form triphenyl benzophenone.

$$\underset{\text{IV}}{(C_6H_5)_3C_6H_2CO_2H} \longleftarrow (C_6H_5)_3C_6H_2MgBr \longrightarrow \underset{\text{V}}{(C_6H_5)_3C_6H_2COC_6H_5}$$

By preparing the same triphenyl benzophenone from the hydrocarbon and benzoyl chloride we established that the Friedel and Crafts reaction can be employed for introducing one acyl group into the central nucleus and thus secured a second method for obtaining the mono ketones. We found it difficult, however, to prepare hexaphenyl benzophenone by either of these methods. The chloride of triphenyl benzoic acid could not be isolated by reason of the rapidity with which it was condensed to a fluorene derivative and the methyl ester of the acid resisted the action of the magnesium derivative. The hexaphenyl ketone was finally obtained by treating the hydrocarbon with phosgene and aluminum chloride. No fluorenone is formed in this reaction, but it results in two products which are formed in approximately equal quantities, namely, hexaphenyl benzophenone and hexaphenyl biphenyl.

$$(C_6H_5)_3C_6H_3 + COCl_2 \longrightarrow \underset{\text{VI}}{(C_6H_5)_3C_6H_2COC_6H_2(C_6H_5)_3} + \underset{\text{VII}}{(C_6H_5)_3C_6H_2C_6H_2(C_6H_5)_3}$$

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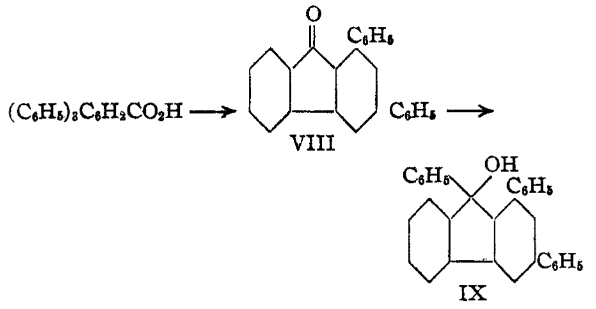
[2] Vorländer, Fischer and Wille, *Ber.*, **62**, 2836 (1929).

In order to prove the structure of hexaphenyl biphenyl we attempted to prepare it by the action of the magnesium derivative on the bromo compound but this reaction which occurs very readily with the corresponding derivatives of mesitylene here failed completely. The hydrocarbon can, however, be obtained by another reaction which proves its structure equally conclusively.

$$2(C_6H_5)_3C_6H_2MgBr + CuCl_2 \longrightarrow (C_6H_5)_3C_6H_2C_6H_2(C_6H_5)_3$$

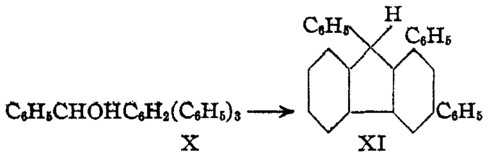
As was to be expected from their structure many of these highly phenylated compounds readily form phenylated fluorene derivatives. Thus all attempts to prepare the acid chloride of triphenyl benzoic acid ended in 1,3-diphenyl fluorenone.



VIII

IX

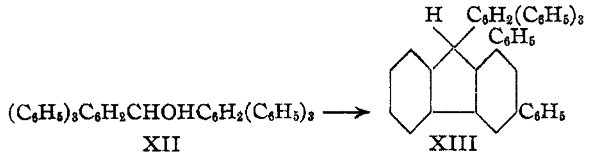
Triphenyl benzohydrol, the secondary alcohol obtained by reducing triphenyl benzophenone, readily formed 1,3,9-triphenyl fluorene when it was treated with any halogen acid.



X

XI

And, similarly, hexaphenyl benzohydrol formed 1,3-diphenyl-9-triphenyl phenyl fluorene.



XII

XIII

Bromo Triphenylbenzene, I.—A mixture obtained by adding 24 cc. of bromine to a solution of 66 g. of triphenyl benzene in 500 cc. of carbon disulfide was left to itself for twelve hours, then poured into a liter of methyl alcohol. The resulting solution was allowed to evaporate spontaneously; it deposited first a solid bromo compound and then an oil from which more of the same solid was obtained by treatment with acetic acid. The solid was purified by recrystallization from methyl alcohol. The yield of pure bromo compound was 91%.

Anal. Calcd. for $C_{24}H_{27}Br$: C, 74.8; H, 4.4. Found: C, 74.7; H, 4.6.

Bromo triphenylbenzene crystallizes from methyl alcohol in plates and it melts at 129–130°.[3] It is not attacked by sodium under conditions under which bromobenzene is rapidly converted into biphenyl and bromomesitylene into hexamethyl biphenyl.

Triphenyl Phenylmagnesium Bromide and Triphenyl Benzoic Acid, IV.—It was impossible to prepare the magnesium derivative in ether—possibly because the bromo compound is too sparingly soluble even at the boiling point of the ether. After vainly trying the various forms of activated magnesium, we finally obtained excellent yields of the Grignard reagent by operating in xylene or benzene. The procedure is illustrated by the following preparation of triphenyl benzoic acid. To a solution of 20 g. of the bromo compound in 22 g. of boiling xylene were added 5 g. of magnesium, 4 cc. of a dilute ethereal ethylmagnesium bromide which had been freshly prepared and 10 drops of ethyl bromide. The mixture was boiled and stirred vigorously until the reaction started. More bromo compound was then added at fifteen-minute intervals, in 10-g. lots along with benzene and ether until 70 g. of bromo compound, 150 cc. of benzene and 50 cc. of ether had been added. After continued boiling for two and one-half hours most of the magnesium had dissolved. The solution was then cooled, saturated with carbon dioxide in the course of four and one-half hours and subjected to the usual manipulations. The result was 53.5 g. of triphenyl benzoic acid—a yield of 84.1%—and 6 g. of triphenyl benzene. No hexaphenyl biphenyl could be found. A titration of a solution of the magnesium derivative which had been obtained in the same manner, indicated a yield of 94%, which is in satisfactory agreement with the amounts of the acid and hydrocarbon that were isolated.

Triphenyl benzoic acid is moderately soluble in ether and in benzene, readily soluble in chloroform. It crystallizes from ether in prisms and melts with slight decomposition at 253–255°.

Anal. Calcd. for $C_{25}H_{18}O_2$: C, 85.7; H, 5.1. Found: C, 85.5; H, 5.3.

The Methyl Ester.—Attempts to esterify the acid by means of methyl iodide were unsuccessful owing to the difficulty of securing a pure silver salt. The ester can be prepared by shaking alkaline solutions of the acid with dimethyl sulfate but the yield is poor. It is, however, made readily by treating an ethereal solution of the acid with diazomethane. It crystallizes from ether or methyl alcohol in plates, and it melts at 91°.

Anal. Calcd. for $C_{26}H_{20}O_2$: C, 85.7; H, 5.5. Found: C, 85.5; H, 5.7.

Hexaphenyl Biphenyl, VII.—A suspension of 5 g. of anhydrous cupric chloride in ether was added to a solution of the magnesium compound which had been prepared from 11.6 g. of bromo triphenylbenzene. The mixture was boiled for two hours, then decomposed in the usual manner. The result was a mixture of triphenylbenzene and hexaphenyl biphenyl. The mixture was easily separated by crystallization from benzene–acetic acid. The hexaphenyl derivative crystallized in hexagonal prisms and

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[3] Engler and Berthold, *Ber.*, **7**, 1125 (1874), reported a bromo derivative of triphenylbenzene melting at 108° but gave no analytical results.

melted at 348°. It is moderately soluble in benzene and in chloroform, sparingly soluble in ether and in glacial acetic acid. The yield was 50%.

Anal. Calcd. for $C_{48}H_{34}$: C, 94.4; H, 5.6. Found: C, 94.3; H, 5.7.

Aceto Triphenylbenzene, III.—An ethereal solution of 1.6 g. of acetyl chloride was added slowly to a solution of the magnesium compound made from 7.7 g. of bromo triphenylbenzene. The mixture was boiled for an hour, then decomposed with iced acid. The product was purified by recrystallization from methyl alcohol.

Anal. Calcd. for $C_{26}H_{20}O$: C, 89.6; H, 5.7. Found: C, 89.7; H, 5.7.

The ketone crystallizes from ether or methyl alcohol in plates and it melts at 125°. Like aceto mesitylene it liberates one mole of methane from methylmagnesium iodide and forms a magnesium derivative from which it is regenerated by acids. It can be condensed with benzaldehyde by adding a little sodium ethylate to a hot solution of equimolar quantities of the aldehyde and the ketone. The product is benzal aceto triphenylbenzene—$C_6H_5CH{=}CHCOC_6H_2(C_6H_5)_3$. It crystallizes in pale yellow needles. When it is heated in a capillary tube it melts at 192°, resolidifies and then melts again at 210°.

Anal. Calcd. for $C_{33}H_{24}O$: C, 90.8; H, 5.5. Found: C, 90.6; H, 5.6.

Triphenyl Benzophenone, V.—Triphenyl benzophenone was obtained both by boiling a solution of triphenyl phenylmagnesium bromide with benzoyl chloride and by treating triphenyl benzene with benzoyl chloride in the presence of aluminum chloride. The yield in the Grignard reaction was 60% and in the Friedel and Crafts reaction 90%. The ketone is very soluble in benzene and in chloroform, moderately soluble in ether, slightly soluble in methyl alcohol. It crystallizes from ether in transparent prisms and melts at 168–169°.

Anal. Calcd. for $C_{31}H_{22}O$: C, 90.7; H, 5.4. Found: C, 90.4; H, 5.7.

Reduction: Triphenyl Benzohydrol, X.—Owing to the sparing solubility of the ketone in alcohol it was necessary to reduce it in a mixture of benzene and alcohol. Thus 100 g. of 0.5% sodium amalgam was added to a solution of 6 g. of the ketone in 25 cc. of benzene and 100 cc. of alcohol. In a few minutes the solution developed a deep purple color which disappeared when it was shaken and reappeared when it was left to itself. In time the purple changed to yellow which was permanent. The mixture was boiled for four hours, filtered and freed from the solvents. The residue, by the usual treatment, yielded a solid which after recrystallization from ether–petroleum ether melted at 158°.

Anal. Calcd. for $C_{31}H_{24}O$: C, 90.3; H, 5.8. Found: C, 90.4; H, 6.0.

The secondary alcohol can be obtained equally well by the addition of triphenyl phenylmagnesium bromide to benzaldehyde, but the magnesium compound must be employed in considerable excess, otherwise the product is largely ketone, the aldehyde acting as an oxidizing agent. Chromic acid in acetic acid likewise rapidly oxidizes it to the ketone.

The Benzoate, $C_6H_5CH(OCOC_6H_5)C_6H_2(C_6H_5)_3$.—Attempts to benzoylate the carbinol by various modifications of the Schotten–Baumann reaction failed by reason of its sparing solubility in suitable solvents. The benzoate was, however, obtained without difficulty by first converting the carbinol into the magnesium halide derivative with ethylmagnesium bromide and then adding benzoyl chloride to the boiling ethereal solution of the magnesium derivative. It is slightly soluble in methyl alcohol, moderately soluble in ether. From ether–petroleum ether it crystallizes in needles melting at 156°. Owing to its slight solubility it is hydrolyzed very slowly by methyl alcoholic potassium hydroxide; for complete hydrolysis of 0.75 g. it was necessary to boil it for nine hours with 100 cc. of the alkaline solution.

Anal. Calcd. for $C_{33}H_{28}O_2$: C, 88.4; H, 5.4. Found: C, 88.4; H, 5.6.

Dimolecular Reduction.—All attempts to get a dimolecular product by treating benzoyl triphenylbenzene with sodium, liquid sodium–potassium alloy, or 40% sodium amalgam were unsuccessful. Thus, in a typical experiment a solution of 2 g. of the ketone in 50 cc. of dry benzene was shaken in an atmosphere of nitrogen with 2.5 cc. of freshly prepared 40% sodium amalgam. It developed a purple color which soon became so dense as to appear black. After it had been shaken for four and one-half hours the black suspension was drawn into a solution of acetic acid in benzene, whereupon the color was discharged immediately. The resulting solution gave 0.8 g. of ketone, 0.55 g. of carbinol and a residue which was not separated because it evidently contained no dimolecular reduction product.

Hexaphenyl Benzophenone, VI.—To a solution of triphenyl phenylmagnesium bromide, which had been made in benzene and ether from 50 g. of bromo compound and cooled in ice, was added gradually 5 cc. of phosgene in 50 cc. of benzene. The solution was allowed to come to the temperature of the room, then gradually brought to the boiling point and finally boiled for an hour. The result was a mixture which was separated by fractional crystallization into 8 g. of hexaphenyl biphenyl, 6 g. of hexaphenyl benzophenone and a large quantity of triphenyl benzene. The ketone was recrystallized from a mixture of boiling chloroform and methyl alcohol. It is moderately soluble in chloroform and in benzene, sparingly soluble in other common solvents. It crystallizes in diamond shaped plates and melts at 266°.

Anal. Calcd. for $C_{49}H_{34}O$: C, 92.2; H, 5.3. Found: C, 92.0; H, 5.4.

Reduction: Hexaphenyl Benzohydrol, XII.—The ketone was reduced with 0.5 sodium amalgam in benzene and methyl alcohol. The color changes were the same as those observed in the case of triphenyl benzophenone but the purple color was much more persistent. The carbinol was recrystallized from ether–methyl alcohol. It is slightly more soluble than the ketone in the common organic solvents and melts with decomposition at 248–249°.

Anal. Calcd. for $C_{49}H_{36}O$: C, 91.9; H, 5.6. Found: C, 91.6; H, 5.7.

1,3-Diphenyl Fluorenone, VIII.—A solution of 5 g. of triphenyl benzoic acid in 9 cc. of thionyl chloride slowly evolved hydrogen chloride and developed a yellow color when it was digested on a steam-bath. After thirty minutes the excess of thionyl chloride was evaporated and the residue dissolved in ether. The fluorenone derivative crystallized in stout pale yellow needles and it melted at 183°. The yield was 4.6 g.

Anal. Calcd. for $C_{25}H_{16}O$: C, 90.4; H, 4.8; mol. wt., 332. Found: C, 90.2; H, 5.0; mol. wt., 321.

1,3,9-Triphenyl Fluorenol, IX.—The tertiary alcohol was obtained without difficulty by treating the ketone with phenylmagnesium bromide. It crystallizes from ether-petroleum ether in colorless needles and melts at 207°.

Anal. Calcd. for $C_{31}H_{22}O$: C, 90.7; H, 5.4. Found: C, 90.3; H, 5.6.

1,3,9-Triphenyl Fluorene, XI.—The hydrocarbon was first obtained in an attempt to reduce triphenyl benzohydrol with hydrogen iodide. It is formed equally rapidly by the action of other halogen acids on the secondary alcohol. It crystallizes in colorless needles and it melts at 149°.

Anal. Calcd. for $C_{31}H_{22}$: C, 94.4; H, 5.6. Found: C, 94.4; H, 5.8.

1,3-Diphenyl Triphenylphenyl Fluorene, XIII.—The hydrocarbon was obtained by the action of hydrogen iodide on hexaphenyl benzohydrol. It crystallizes in minute needles and melts at 221°.

Anal. Calcd. for $C_{49}H_{34}$: C, 94.5; H, 5.5. Found: C, 94.4; H, 5.6.

Summary

A comparison of a series of derivatives of triphenylbenzene with the corresponding derivatives of mesitylene shows that while the former are uniformly less reactive than the latter there is no conspicuous difference in behavior which can be attributed to a difference in space relations.

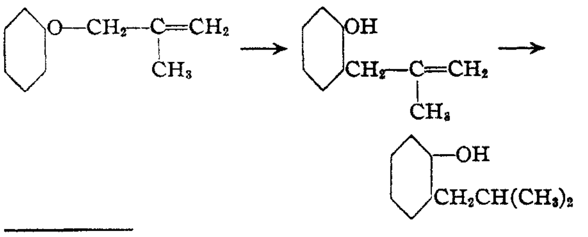
CAMBRIDGE, MASS. RECEIVED DECEMBER 4, 1934

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

The Introduction of Isobutyl Groups into Phenols, Cresols and Homologous Compounds

BY QUENTIN R. BARTZ,[1] RICHARD F. MILLER AND ROGER ADAMS

Pyman[2] demonstrated that the introduction of a higher alkyl group into phenol, cresol or one of the homologs, greatly enhanced the antiseptic action of the molecule. Numerous methods of preparation[3] for various types of alkylated phenols have been described in recent years, but none of these is suitable for the introduction of the isobutyl group. The isobutyl derivatives may be formed conveniently by rearrangement of the proper methylallyl phenol ether to the corresponding methylallyl phenol, followed by catalytic reduction.



Through the kindness of Dr. H. W. Cromwell of the Abbott Laboratories, North Chicago, Illinois, the various isobutyl and diisobutyl phenols were tested bactericidally. These phenols are only slightly soluble in water; the more complex ones give clear solutions at 37° only in dilutions of 1:10,000 or higher. The phenol with the highest bactericidal value was 2-isobutyl-4,5-dimethylphenol. By the F. D. A. method with *staphylococcus aureus* at 37°—transfer method—the product showed kills in five minutes, diln. 1:1000, 1:2000 and 1:5000, but not in 1:10,000 in fifteen minutes. It is obvious that the isobutyl derivatives are not so effective as the corresponding *n*-butyl or higher alkylated analogs.

Methylallyl chloride reacts similarly to allyl halides in the formation of phenol ethers,[4] though with certain phenols it is found preferable to substitute a Williamson synthesis for the potassium carbonate and acetone method used by Claisen and Eisleb. In general, the yields were not as great as those of the allyl ethers.

The methylallyl phenyl ethers rearrange more rapidly than the allyl phenyl ethers either by direct pyrolysis or by heating in a solvent. The

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(1) Submitted as part of a thesis for the Degree of Doctor of Philosophy in Chemistry.

(2) Coulthard, Marshall and Pyman, *J. Chem. Soc.*, 281 (1930). See also Johnson and Lane, THIS JOURNAL, **43**, 348 (1921); Dohme, Cox and Miller, *ibid.*, **48**, 1688 (1926).

(3) Rosenmund and Schnurr, *Ann.*, **460**, 56 (1928); Rosenmund, Bushwald and Deligiannis, *Arch. pharm.*, **271**, 342 (1933); Read, Reddish and Burlingame, THIS JOURNAL, **56**, 1377 (1934); Niederl and Storch, *ibid.*, **53**, 272, 1928 (1931); **54**, 1063 (1932); Sowa, Hinton and Nieuwland, *ibid.*, **54**, 2019 (1932); Smith, *ibid.*, **55**, 849, 3718 (1933); Natelson, *ibid.*, **56**, 1583 (1934).

(4) Claisen and co-workers, *Ber.*, **45**, 3157 (1912); **58**, 275 (1925); **59**, 2344 (1926); *Ann.*, **401**, 21 (1913); **418**, 69 (1919); **442**, 210 (1925); **449**, 81 (1926); *Z. angew. Chem.*, **36**, 478 (1923).