toluene, was added dropwise a mixture of sodamide (from 6.2 g. sodium) and 32.2 g. (0.255 mole) of benzyl chloride in 200 ml. of toluene. The mixture was refluxed and stirred for an additional seven hours, cooled, decomposed with water and the toluene layer separated. The aqueous layer was extracted with benzene and the combined benzene–toluene solutions were extracted several times with a 10% hydrochloric acid solution. The aqueous acid extracts were made basic with ammonia, processed in the usual manner and distilled.

To a warm, stirred suspension of sodamide (from 2.6 g. of sodium) in 200 ml. of dry xylene was added 20 g. (0.106 mole) of α-dimethylaminomethyl-β-phenylpropionitrile, followed by the cautious addition of 20 g. (0.127 mole) of 2-bromopyridine. A violet reaction occurred with the addition of each increment of 2-bromopyridine. The reaction mixture was stirred and refluxed for eight hours, cooled, decomposed with water, the organic layer separated, the solvent removed and the residue distilled. Attempts to hydrolyze and decarboxylate this nitrile with 80% sulfuric acid at 140–150° were unsuccessful.

Reduction of γ-Phenyl-γ-(2-pyridyl)-N,N-dimethylpropylamine (XII) (a) Raney Nickel in Methanol. γ-Phenyl-γ-(N-methyl-2-piperidyl)-N,N-dimethylpropylamine (XIV).—A solution of 24 g. (0.1 mole) of γ-phenyl-γ-(2-pyridyl)-N,N-dimethylpropylamine was reduced in methanol with Raney nickel catalyst and hydrogen for four hours at an initial pressure of 1,000 p.s.i. and a temperature of 170°. The catalyst was filtered, washed with methanol, the combined filtrates and washings concentrated *in vacuo* and the residue distilled to give two fractions; fraction I, wt. 8.2 g., b.p. 105–121° (1 mm.), $n^{29}\text{D}$ 1.5292; fraction II, wt. 12 g., b.p. 126–132° (1 mm.), $n^{30}\text{D}$ 1.5196. Fraction II was redistilled and boiled at 122–125° (0.5 mm.), $n^{30}\text{D}$ 1.5193. *Anal.* Calcd. for $C_{17}H_{28}N_2$: C, 78.38; H, 10.84; N, 10.84. Found: C, 78.61; H, 11.09; N, 10.88. The picrate (m.p. 200–204°) depressed the melting point of the picrate of γ-phenyl-γ-(2-pyridyl)-N,N-dimethylpropylamine (m.p. 203–204°).

Fraction I, upon redistillation, boiled at 100–105° (0.5 mm.), $n^{30}\text{D}$ 1.5299. *Anal.* Calcd. for $C_{15}H_{23}N$: C, 82.87; H, 10.67; N, 6.45; and for $C_{14}H_{21}N$: C, 82.68; H, 10.42; N, 6.89. Found: C, 82.42; H, 10.08; N, 6.79. On the basis of the analyses, it is apparent that the dimethylamino group had been lost.

(b) **Sodium and Alcohol. γ-Phenyl-γ-(2-piperidyl)-N,N-dimethylpropylamine (XV).**—To a solution of 24 g. (0.1 mole) of XII in 190 ml. of ethanol (dried over sodium) was added 27.4 g. of sodium metal (in cubes) as rapidly as possible. After the vigorous reaction had subsided, an additional 90 ml. of alcohol was added and the solution was refluxed on the steam-bath until all the sodium had dissolved. Upon vacuum concentration, the contents of the flask solidified and water was added until an oil appeared. The latter was extracted with ether, the ether layer washed with water, dried, the solvent removed and the residue distilled. After a forerun (5.2 g.), b.p. 100–125° (0.5 mm.), the main fraction, yield 14.2 g. (58%), b.p. 127–130° (0.5 mm.), $n^{28}\text{D}$ 1.5244, was obtained. Redistilled for analysis, b.p. 117–120° (0.1 mm.), $n^{28}\text{D}$ 1.5249. *Anal.* Calcd. for $C_{16}H_{26}N_2$: C, 78.00; H, 10.64. Found: C, 77.44; H, 10.26.

γ-Phenyl-γ-(N-methyl-2-piperidyl)-N,N-dimethylpropylamine (XIV).—To 6 ml. of cooled, 90% formic acid was added 8.5 g. of γ-phenyl-γ-(2-piperidyl)-N,N-dimethylpropylamine (XV). Six ml. of 37% formalin solution was then added and the reaction mixture heated on the steam-bath overnight. Twenty ml. of 10% hydrochloric acid solution was added and the solution was vacuum concentrated to a residue, made basic with sodium hydroxide solution and the oil extracted with ether. The ether layer was washed with water, dried, the solvent removed and the residue distilled; yield 7 g. (78%), b.p. 127–134° (1 mm.), $n^{27}\text{D}$ 1.5231. *Anal.* Calcd. for $C_{17}H_{28}N_2$: C, 78.42; H, 10.84. Found: C, 78.63; H, 10.60.

The picrate melted at 204–205° and when mixed with the picrate of γ-phenyl-γ-(N-methyl-2-piperidyl)-N,N-dimethylpropylamine (m.p. 202–204°), obtained from the reduction of γ-phenyl-γ-(2-pyridyl)-N,N-dimethylpropylamine with Raney nickel and hydrogen in methanol, melted at 203–204°. However, a mixed melting point with the picrate of γ-phenyl-γ-(2-piperidyl)-N,N-dimethylpropylamine (m.p. 204–205°) was depressed, m.p. 192–193°.

Bloomfield, New Jersey Received June 9, 1951

[Contribution from the Department of Chemistry, University of California]

The Displacement of the Allyl Group in the Reaction between Phenylmagnesium Bromide and α-Allylisobutyromesitylene

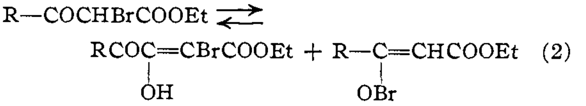
By T. A. Geissman and Robert M. Horowitz

α-Allylisobutyromesitylene is cleaved by phenylmagnesium bromide in ethyl ether solution at 125–135° to yield allylbenzene and isobutyromesitylene. In isoamyl ether at 125° but in the presence of traces of metallic magnesium the reaction takes a different course and appears to proceed with the intervention of free-radical intermediates.

The "enolization" of carbonyl compounds and the removal of halogen from α-halocarbonyl compounds by the action of Grignard reagents are well-known reactions[1] which appear to be closely related. Equation (1) represents the general reaction, which appears to involve a nucleophilic displacement on hydrogen or halogen by the group R of the Grignard reagent

$$R'COCH_2Y + RMgX \longrightarrow (R'COCH_2)MgX + RY \quad (1)$$
$$(Y = H,\ \text{halogen})$$

The details of this reaction are obscure. It has been suggested[2] that the actual species upon which the displacement occurs are in the case of an α-bromo-β-keto ester, the enol form (I) and the analogous hypobromite form (II)



$$R{-}COCHBrCOOEt \rightleftarrows \underset{\substack{|\\ OH}}{RCOC}{=}CBrCOOEt + R{-}\underset{\substack{|\\ OBr}}{C}{=}CHCOOEt \quad (2)$$

I II

Since, however, Grignard reagents can "enolize" carbonyl compounds which contain no detectable amount of enol,[3] and replace active hydrogen in compounds such as acetylenes, sulfones, indene, etc.,[4] there appears to be no reason to dismiss the more general alternative that hydrogen and halogen may be displaced from carbon directly.

It is convenient to correlate reactions of this kind with certain other reactions involving Grignard reagents, for which "cyclic mechanisms"

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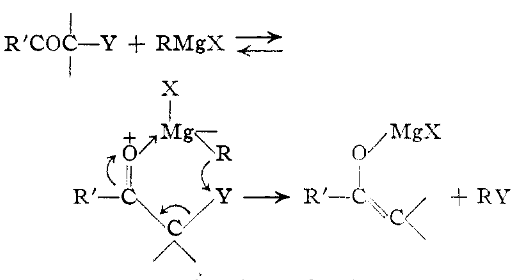
[1] See F. Runge, "Organo-Metallverbindungen," Stuttgart, 1944, Edwards Bros., Inc., Ann Arbor, Mich., 1945, p. 383.

[2] B. W. Howk and S. M. McElvain, This Journal, **55**, 3375 (1933).

[3] D. Ivanov and A. Spasov, *Bull. soc. chim.*, [4] **49**, 375 (1931); [5] **1**, 1419 (1934).

[4] H. Gilman, "Organic Chemistry," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 499.

have been proposed,[5] and to write reaction (1) in the following way (2)[6]


(3)

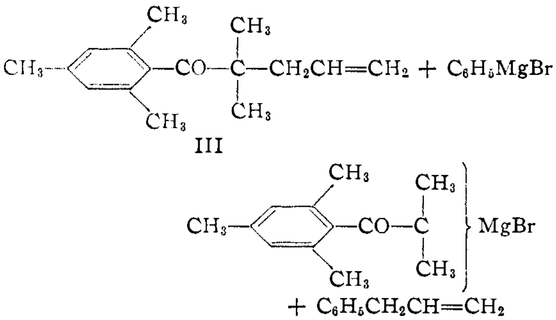
Such a formulation is preferable to one which depends upon such unsupported postulates as (a) an attack upon Y of a free carbanion (R:$^-$), or (b) a preliminary ionization of Y$^+$ followed by an electrophilic attack of this species upon RMgX. In the formulation according to equation (3) the increased electrophilic character of the carbonyl carbon atom in the complex would aid in the release of Y to the attacking group R.

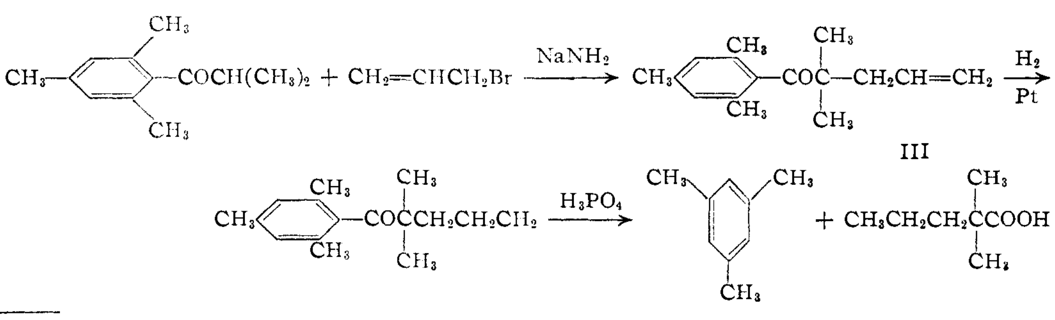
These considerations suggested that a carbon–carbon bond (the C–Y bond) might undergo cleavage provided that (a) a group Y were chosen from among those known to be highly susceptible to nucleophilic attack, (b) the competing reaction of addition to the carbonyl group were suppressed by appropriate substitution and (c) the α-carbon atoms carried no enolizable hydrogen atoms.

The compound chosen for study was α-allylisobutyromesitylene (III), which was prepared by the allylation of isobutyromesitylene in the presence of sodamide. Since enol ethers undergo cleavage by Grignard reagents, and in the present case the formation of allylbenzene and isobutyromesitylene would be the anticipated result of the reaction between phenylmagnesium bromide and the allyl ether of the enol form of isobutyromesitylene, it was necessary to establish beyond doubt that the allylation product III was indeed the C-allyl derivative and not the enol ether. This was established in two ways: (1) treatment of the compound with sulfuric acid in acetic acid did not result in loss of the allyl group; and (2) the reduction of III yielded a product (α-n-propylisobutyromesitylene) which was cleaved by hot 85% phosphoric acid[7] to α,α-dimethylvaleric acid. Further evidence for the structure of III was secured when it was found that allylmagnesium chloride could be added to III with the formation of a carbinol.[8]

The results of the experiments in which III was allowed to react with phenylmagnesium bromide are summarized in Table I and can be summarized briefly as follows. (1) There was evidence that in all cases in which ethyl ether was used as the solvent, cleavage to allylbenzene and isobutyromesitylene occurred. Appreciable yields of allylbenzene were obtained only when the temperature of the reaction was raised above 100° by distillation of most of the solvent. The best yield was obtained in run 6 where the highest ratio of Grignard reagent to ketone and the highest temperature were used. (2) In isoamyl ether solution the reaction took a complex and entirely different course. In this case alone was the unfiltered reagent, containing residual traces of unreacted magnesium, used.

The reaction between III and phenylmagnesium bromide in ether at 125–135° appeared to proceed in the anticipated manner according to equation (4) and may be regarded as constituting new evidence for the mechanism of the reaction as postulated in general terms in equation 3. That the cleavage of III is preceded by its rearrangement into the allyl ether of the enol form of isobutyromesitylene is highly unlikely, as judged from known values of the ΔH values for reactions of the general class represented by equation (5)[9] the equilibrium of which is substantially completely on the side of the carbonyl form.


(4)



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(5) (a) R. M. Horowitz, Ph.D. Thesis, University of California, Los Angeles, 1949; (b) R. T. Arnold, *et al.*, THIS JOURNAL, **63**, 3444 (1941); **64**, 2875 (1942); **67**, 337 (1945); (c) J. R. Johnson, *ibid.*, **55**, 3029 (1933); (d) F. C. Whitmore and R. S. George, paper presented to Organic Division, American Chemical Society, Atlantic City, N. J., 102nd Meeting, September, 1941; (e) C. G. Swain and H. B. Boyles, THIS JOURNAL, **73**, 870 (1951).

(6) The halomagnesium enolate is written as an O-enolate for brevity's sake. It is probably best represented as a complex in which the MgX$^+$ moiety is ionically bound to the two electrons occupying an orbital surrounding C–C–O.

(7) A. Klages and G. Lickroth, *Ber.*, **32**, 1549 (1899).

(8) *Cf.* ref. 12.

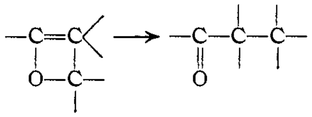
(9) (a) L. Pauling, "The Nature of the Chemical Bond," 2nd Ed., Cornell University Press, Ithaca, N. Y., 1941, pp. 53, 131. (b) G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, 1941, p. 289.

TABLE I

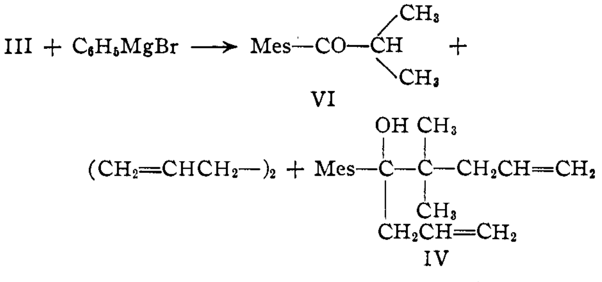
REACTION OF α-ALLYLISOBUTYROMESITYLENE (III) WITH PHENYLMAGNESIUM BROMIDE

Expt.	Moles C_6H_5MgBr / mole III	Solvent	Temp., °C.	Time, hr.	Products[b]	Yield, %
1	1.1	Ethyl ether	36–40	3	Allylbenzene	Trace
					Recovered III	57.5
2	1.5	Benzene–ethyl ether	75	6	Allylbenzene	Trace
					Recovered III	63
3	2.0	Ethyl ether	36–40	42	Allylbenzene	Trace
					Recovered III	76
4	2.0	Ethyl ether[a]	75	43	Allylbenzene	1
					Recovered III	72
5	2.0	Ethyl ether[a]	110–125	5.3	Allylbenzene	4.8
					Recovered III	70.4
6	2.5	Ethyl ether[a]	125–135	3.5	Allylbenzene	58
					Isobutyromesitylene	79
					Recovered III	4
7	2.0	*i*-Amyl ether	125	2	Diallyl	25
					Isobutyromesitylene	61.5
					Product IV[c]	7
					Product V (?)[c]	?
					Terphenyl	Trace
					Recovered III	15

[a] Temperature attained by concentration of reaction mixture by distillation. [b] All runs contained undetermined amounts of biphenyl and tarry distillation residues. [c] See text for description.


(5)

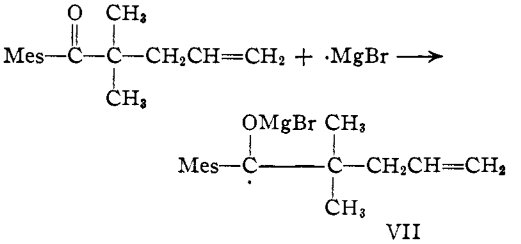
The reaction of III with phenylmagnesium bromide in isoamyl ether at 125° (Table I, expt. 7) took a course entirely different from that observed in the experiments in which ethyl ether was used as the solvent. The three chief products of the reaction were isobutyromesitylene (VI), diallyl, and α,β-diallyl-α-mesityl-β,β-dimethyl carbinol (IV); a fourth product (V) was obtained in such small amount that it could be only provisionally identified as 1-phenyl-1-mesityl-2,2-dimethylpenten-4-ol-1; and a trace of terphenyl was isolated and identified.



$$\text{III} + C_6H_5MgBr \longrightarrow \underset{\text{VI}}{\text{Mes—CO—CH}(CH_3)_2} + (CH_2{=}CHCH_2—)_2 + \underset{\text{IV}}{\text{Mes—}C(OH)(CH_2CH{=}CH_2)\text{—}C(CH_3)_2\text{—}CH_2CH{=}CH_2}$$

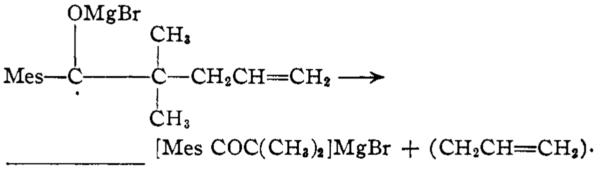
The carbinol IV was independently synthesized by the addition of allymagnesium chloride to III and the structure of IV and its identity with the synthetic sample were established by pyrolysis (to III and propylene), infrared absorption spectra, and the preparation, analysis and comparison of the crystalline iodomercurimethoxy derivatives.

The appearance of diallyl suggests the intervention of free radicals, while the formation of IV suggests the occurrence during the course of the reaction of an allylmagnesium halide-like species. The presence of traces of unreacted magnesium in experiment 7 provides an explanation for the results which accommodates both of these views. From the work of Gomberg and Bachmann[10] and Boyd and Hatt[11] it is known that the combination of magnesium and magnesium iodide in ether solution has properties which may be described in terms of a species [·Mg I] and that under certain conditions reductions brought about by magnesium-containing Grignard reagents suggest that a species [·MgX] is present as a result of the reaction of the excess magnesium with the MgX_2 component of the reagent equilibrium mixture. The application of this information to the case under present consideration offers a means of accounting for the results of Experiment 7. The reaction of the species ·MgBr with the starting material III may be represented as in Equation (6)



$$\text{Mes—}CO\text{—}C(CH_3)_2\text{—}CH_2CH{=}CH_2 + \cdot MgBr \longrightarrow \underset{\text{VII}}{\text{Mes—}\dot{C}(OMgBr)\text{—}C(CH_3)_2\text{—}CH_2CH{=}CH_2} \qquad (6)$$

The dimerization of VII into a pinacol would be expected to be inhibited by steric factors and the decomposition of VII according to equation (6) should be favored by the formation of two species with a clear gain in stabilization by resonance.



$$\text{Mes—}\dot{C}(OMgBr)\text{—}C(CH_3)_2\text{—}CH_2CH{=}CH_2 \longrightarrow [\text{Mes }COC(CH_3)_2]MgBr + (CH_2CH{=}CH_2)\cdot$$

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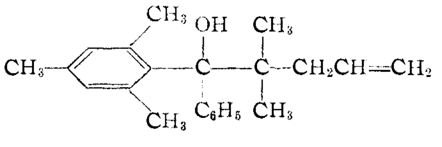
(10) M. Gomberg and W. E. Bachmann, THIS JOURNAL, **49**, 236 (1927).

(11) D. R. Boyd and H. H. Hatt, *J. Chem. Soc.*, 898 (1927).

The attack of the allyl radical upon VII leads to IV; the dimerization of the allyl radical leads to diallyl. The dissipation of allyl radicals in other ways (leading to the formation of terphenyl, product V, and the unidentified, undistillable residues) accounts for the fact that although isobutyromesitylene is formed in high yield, the accompanying products are present in relatively smaller amounts.

The analytical results for compound V, coupled with the nature of the reaction in which it was formed, suggested that it was the result of addition of the phenylmagnesium bromide to the starting ketone

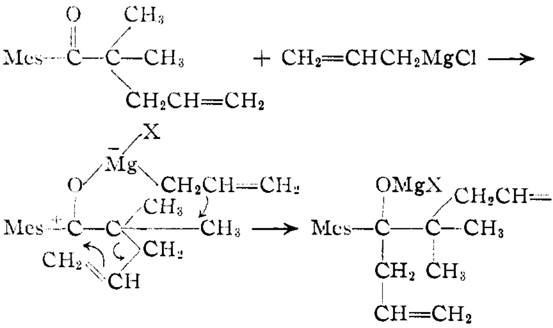


The addition of Grignard reagents, other than those of the allylic type,[12] to ketones so highly substituted as III, while not unknown,[13] is rare, but can be accounted for in the present case by the vigor of the conditions used in experiment 7. No solid derivative of V could be prepared and ultraviolet and infrared spectra determinations were inconclusive, except for the appearance in the latter of a band at 1.411 μ characteristic of the hydroxyl group.

The contrast in the results of experiment 7 with those of the experiments in which diethyl ether and filtered solutions of the Grignard reagent were used provides support for the conclusion that the formation from III of allylbenzene and isobutyromesitylene is the result of a process occurring as an ionic reaction and not a radical one. When excess magnesium metal was present,[14] even though the reaction was conducted at a somewhat lower temperature and for a shorter time than in the case of experiment 6, the consumption of the initial reactants was not only as extensive as in the latter case but led to a quite different over-all result. The relatively high yield of diallyl is of particular significance; in the cleavage of allyl phenyl ether by phenylmagnesium bromide,[15] a reaction best interpreted on an "ionic" basis, diallyl was found, but in traces only.

The cleavage of carbon–carbon bonds by the action of Grignard reagents, under what appear to be "ionic" conditions, has been observed in a number of other cases. The most noteworthy of these are the cleavage of β-dicarbonyl compounds,[16] the Stevens cleavage of α-aminoacetonitriles,[17] the formation of phenyldihydrothebaine[18] (a reaction which appears to be related to the Stevens cleavage) and the cleavage of tetraphenyldibenzoylethane into two molecules of α,α-diphenylacetophenone.[19]

It should be noted in conclusion that the addition of allylmagnesium chloride to III may proceed either by addition in the normal manner or by a mechanism which is formulated



The test of this alternative scheme will be carried out in the course of further studies.

Experimental[20]

α-Allylisobutyromesitylene (III).—Sodamide was prepared from 39 g. (1.7 moles) of sodium in 1 liter of liquid ammonia containing a trace of ferric chloride. When the conversion was complete, the ammonia was replaced with 500 ml. of dry toluene. A solution of 295 g. (1.55 moles) of isobutyromesitylene in 150 ml. of dry toluene was added with stirring over two hours, the temperature being kept between 80 and 100°. After a further hour's heating 206 g. (1.7 moles) of purified allyl bromide was added during one hour, at a temperature of 100–105°. After an additional 30 minutes the mixture was cooled, poured into water and the organic layer washed with water, dried and distilled through a heated Vigreux column (8″). The twice-distilled product (301.3 g., 82%) was a pale yellow, viscous liquid, boiling at 102.5° (1 mm.); 89.5° (0.25 mm.). It had the physical properties: n^{20}_D 1.5171; d^{20}_4 0.952; M_R found: 73.0; calcd. 72.1.

Anal. Calcd. for $C_{16}H_{22}O$: C, 83.45; H, 9.62; Br number, 115.2 g. per equiv. of bromine.[21] Found: C, 83.34; H, 9.74; Br number, 116.3 g. per equiv.

Proof of Structure of III: Formation of α,α-Dimethylvaleric Acid.—A solution of 5.0 g. of III in 15 ml. of absolute ethanol was hydrogenated in the presence of 0.1 g. of platinum oxide at room temperature and pressure until the uptake of hydrogen ceased; a total of 531 ml. of hydrogen was absorbed (calcd., 545 ml.). The solvent was removed and the residual material added to 40 g. of 85% phosphoric acid and the mixture refluxed for 10 hours. Water was added and the products removed by steam distillation. Extraction of the distillate with benzene and distillation of the extract afforded 0.4 g. of an acid boiling at 115–120° (50 mm.) (reported[22] b.p. 101–102° (11 mm.); 199–200° (760 mm.)) The acid chloride prepared from 0.1 g. of the crude acid was treated with concentrated aqueous ammonia. The amide was removed with benzene; it melted at 92–93° (reported 95–96°[22]; 94.5°[23]). The anilide, prepared by treating the acid chloride in benzene solution with aniline, melted at 72–73° after recrystallization from petroleum ether (reported 73.5°[22]).

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[12] K. W. Wilson, J. D. Roberts and W. G. Young, THIS JOURNAL, **72**, 218 (1950).

[13] A. A. Morton and L. V. Peakes, *ibid.*, **55**, 2110 (1933).

[14] Even though the commercial magnesium turnings employed were prepared from high-purity stock it must be regarded as possible that traces of heavy metal impurities might have induced a radical reaction of another kind. See M. S. Kharasch and P. O. Tawney, *ibid.*, **63**, 2308 (1941).

[15] A. Lüttringhaus, G. Wagner-V. Sääf, E. Sucker and G. Borth, *Ber.*, **71**, 1673 (1938).

[16] (a) E. P. Kohler, *et al.*, THIS JOURNAL, **53**, 205 (1931); **53**, 2301 (1931); (b) T. A. Geissman and V. Tulagin, *ibid.*, **63**, 3352 (1941); **66**, 719 (1944).

[17] (a) P. Bruylants, *Bull. Acad. roy. Belg.*, **10**, 166 (1924); **11**, 261 (1925); (b) T. S. Stevens, J. M. Cowan and J. MacKinnon, *J. Chem. Soc.*, 2568 (1931); (c) T. Thomson and T. S. Stevens, *ibid.*, 2607 (1932).

[18] R. Robinson, *Nature*, **160**, 815 (1947).

[19] A. Löwenbein and L. Schuster, *Ann.*, **481**, 106 (1931).

[20] Melting points were determined on a Fisher m.p. block.

[21] Bromine numbers were determined as follows: Ten ml. of 0.25 *N* bromine in carbon tetrachloride was added to the weighed sample in a glass-stoppered flask, with ice cooling. After 5 min. (in the dark) a solution of 1 g. of potassium iodide in 20 ml. of water was added and, after shaking, the excess iodine titrated with 0.1 *N* sodium thiosulfate.

[22] A. Haller and E. Bauer, *Compt. rend.*, **148**, 127 (1909).

[23] D. V. N. Hardy, *J. Chem. Soc.*, 464 (1938).

Acid Treatment of III.—A solution of 69 g. of III, 30 ml. of water and 3 ml. of concentrated sulfuric acid in 400 ml. of glacial acetic acid was refluxed for two hours. After dilution with water the mixture was extracted with benzene and after removal of the benzene the residue was distilled. Two main fractions were obtained: 41 g. of the original III (n^{20}_{D} 1.5172 after redistillation), and 19.5 g. of a higher-boiling (125–130° (0.5 mm.)) material containing a saponifiable grouping. This was not investigated in detail, but probably arose as the result of addition, perhaps with ring closure involving the carbonyl group, of the elements of acetic acid. No fraction corresponding to isobutyromesitylene was obtained.

Reactions of α-Allylisobutyromesitylene with Phenylmagnesium Bromide (see Table 1). **Experiment 3. In Refluxing Diethyl Ether for 42 Hours.**—A solution of phenylmagnesium bromide prepared from 124 g. of bromobenzene was filtered through a plug of glass wool, and to the refluxing solution was added 90.5 g. of α-allylisobutyromesitylene. A slightly exothermic reaction was observed. After refluxing for 42 hours the attached Dry Ice-cooled cold trap contained only ether; after hydrolysis of the reaction mixture with iced ammonium chloride solution the ether layer was separated, washed, dried and partially distilled at atmospheric pressure. The fractions which contained the ether and most of the benzene showed no unsaturation when tested with bromine.

The residual material was steam distilled and the steam-volatile portion separated and distilled. A fraction (150 mg.) which boiled from 154–170° showed unsaturation when tested with permanganate, but yielded no solid derivative when treated with silver benzoate and iodine (allylbenzene yields a crystalline derivative with this reagent[24]). A fraction boiling at 245–257° did not yield the known isobutyrodinitromesitylene, nor was methane evolved when it was treated with methylmagnesium bromide.

The non-steam-volatile material was distilled, yielding 68.8 g. (76% recovery) of α-allylisobutyromesitylene, 6.7 g. of a mixture containing biphenyl and 6.0 g. of a non-distillable residue.

Experiment 6. In Diethyl Ether at 125–135°.—To the filtered Grignard reagent prepared from 39.3 g. of bromobenzene in ether was added 23.0 g. of α-allylisobutyromesitylene. Ether was distilled out of the mixture until after 1.75 hours the temperature had risen to 135°. The temperature was maintained at 125–135° for 1.75 hours longer, during which time the reaction mixture became more viscous and a finely divided solid separated. The mixture was allowed to cool and stand overnight, after which it was diluted with ether and decomposed with ice and ammonium chloride (an attached cold trap contained no unsaturated material). The organic layer was separated, dried and distilled until all of the ether and part of the benzene had been removed. The distillate showed no unsaturation toward bromine.

The residue was steam-distilled (200 ml. of distillate) and the organic material in the distillate taken up in ether, separated, dried and distilled, giving fractions 1–3.

Fraction	B.p., °C.	Wt., g.	n^{20}_{D}
1	145–155	1.0	1.5077
2	155–158.5	5.7	1.5104
3	158.5–159		1.5109

Allylbenzene is reported to boil at 157° and to have n^{20}_{D} values of 1.7118, 1.5126, 1.5143.[25]

Fractions 2 and 3 were combined and converted into the iodomercurimethoxy derivative (see below), m.p. 58.6°. The iodomercurimethoxy derivative prepared from authentic allylbenzene melted at 58.6° and a mixture of the two showed no depression.

The non-steam-volatile material was distilled under reduced pressure; several fractions were obtained

Fraction	B.p., °C.	B.p., Mm.	Wt., g.	n^{20}_{D}
4	43	11	0.5	1.5078
5	68–75	0.5	0.9	1.5282
6	75–77.5	.5	11.3	1.5150
7	78–82.5	.5	3.6	1.5117
8	95–105	.5	1.0	1.5211
Residue			4.0	....

Fractions 6 and 7 were nitrated with cold, fuming nitric acid, yielding derivatives with m.p. 137.5–138.5° and 136.5–137.5°, respectively. An authentic sample of isobutyrodinitromesitylene had m.p. 137–138° and did not depress the m.p. of the derivatives from fractions 6 and 7. Pure isobutyromesitylene has n^{20}_{D} 1.5084, the higher values which were observed being due to contamination by traces of biphenyl, recognized by its characteristic odor.

Iodomercurimethoxypropylbenzene.[26]—A solution of 1.59 g. of mercuric acetate in 15 ml. of methanol was added to 0.69 g. of allylbenzene. A slight excess of potassium iodide in 10 ml. of 50% methanol–water was added and the mixture cooled overnight. The colorless needles weighed 1.7 g. and melted at 56.5–57.5°. After recrystallization from methanol the pure compound had m.p. 58.6°. The substance is soluble in chloroform, insoluble in water, gave a positive Beilstein test for halogen, and deposited droplets of mercury when heated on a surface above its melting point. The analysis of the compound was carried out according to the directions of Whitmore and Sobatzki.[27]

Anal. Calcd. for $C_{10}H_{13}OIHg$: Hg, 42.09. Found: Hg, 41.84.

Experiment 7. In Isoamyl Ether at 125°.—A solution of 124 g. of bromobenzene in 105 g. of isoamyl ether (freed of peroxides and distilled from sodium) was added with stirring and heating to 19.2 g. of magnesium under purified nitrogen. When the reaction was complete, 90.5 g. of α-allylisobutyromesitylene was added over 45 minutes, the temperature being kept at 50–60°. The mixture was heated to 125° and maintained at that temperature for 2 hours. After hydrolysis with iced ammonium chloride solution the organic layer was separated and later combined with an isoamyl ether extract of the aqueous layer. The dried isoamyl ether solution was distilled through a heated Vigreux column at reduced pressure (and, when appropriate, redistilled at ordinary or reduced pressure) a total of fourteen fractions and a 52-g. residue being obtained (see below).

Isoamyl alcohol was contained in a 1-ml. fraction boiling at 123–139°. It was identified by means of its phenylurethan derivative, m.p. 54–55° (reported 55°[28]).

Diallyl was found in a 4-g. fraction boiling at 62–67°. This constitutes about 25% of the available allyl residues. A sample of the material was brominated at 0° in carbon tetrachloride solution. The white, crystalline product melted at 47–49°. A sample of pure diallyl (b.p. 60°), independently prepared from allyl bromide and magnesium in ether solution, when treated in the same way gave a solid melting at 49–52°; the mixed melting point was 47–50°. Reported melting points for the mixture of diastereomeric 1,2,5,6-tetrabromohexanes obtained in this way are 52° and 53–55°.[29]

Biphenyl was recognized in the cuts containing isobutyromesitylene by its characteristic odor, and could be induced to crystallize from these fractions by cooling and seeding with authentic material.

Isobutyromesitylene was the principal constituent of five fractions boiling from 105–107° (8 mm.) to 85–88° (0.5 mm.). Each of the fractions yielded the known dinitro derivative (m.p. and mixed m.p.) when nitrated with fuming nitric acid, and one of the fractions was further characterized by treating it successively with methylmagnesium bromide and benzaldehyde to give the known α,α-dimethyl-β-hydroxy-β-phenylpropiomesitylene, m.p. 84.5–85° (reported 85–85.5°[30]). By an estimation based upon a comparison of the refractive indices of these five fractions with those of known mixtures of biphenyl and isobutyromesitylene, it was found that there was formed 46 g. (61.5%) of isobutyromesitylene, accompanied by 9.7 g. of biphenyl.

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[24] E. B. Hershberg, *Helv. Chim. Acta*, **17**, 354 (1926).

[25] G. Egloff, "Physical Constants of Hydrocarbons," Vol. III, Reinhold Publ. Corp., New York, N. Y., 1946.

[26] *Cf.* G. F. Wright, THIS JOURNAL, **57**, 1998 (1935).

[27] F. C. Whitmore and R. J. Sobatzki, *ibid.*, **55**, 1131 (1933).

[28] R. L. Shriner and R. C. Fuson, "Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948.

[29] E. Huntress and S. Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1941.

[30] R. C. Fuson, C. H. Fisher, G. E. Ullyot and W. O. Fugate, *J. Org. Chem.*, **4**, 111 (1939).

α-Allylisobutyromesitylene was recovered in an amount of 14 g. (15%). It is to be noted that the fractions containing isoamyl ether, which boiled near the b.p. of allylbenzene (157°), showed no unsaturation when tested with permanganate and with bromine.

The residue of 52 g. from the first distillation was a viscous, orange oil. After preliminary examination, 44.5 g. of this was distilled at reduced pressure, giving the fractions:

Fraction	B.p.,		Wt., g.
	°C.	Mm.	
1	134–145	3	7.7
2	145–167	3–0.75	13.2
3	170–180	0.75	4.5
4	180–225	0.75	4.0
5	225–235	1.0	2.1
Residue	.....	..	10.0

Fraction 3 contained 0.1 g. of a white solid which when recrystallized from ligroin and from isopropyl alcohol formed white, waxy leaflets, m.p. 204°. A mixture of this with an authentic sample of *p*-terphenyl (m.p. 212°) melted at 208–212°.

Fractions 1 **and** 2 were combined and redistilled. The first fractions (b.p. 117–120° (1 mm.); n^{20}_{D} 1.5162–1.5202) were chiefly unchanged α-allylisobutyromesitylene (7.5 g.). After a cut of about 6 g. boiling from 121–132° (0.75 mm.), a fraction with b.p. 132–135° (0.75 mm.), n^{20}_{D} 1.5390 (4.5 g.), was obtained and was examined in detail. Quantitative bromination and hydrogenation gave values of 77.4 and 79.5 g./equiv., respectively. These values suggested that the compound contained two double bonds, and that it might be α,β-diallyl-α-mesityl-β,β-dimethylethanol (IV).

Anal. Calcd. for $C_{19}H_{28}O$: C, 83.8; H, 10.34. Found: C, 83.1; H, 10.32.

For the purpose of direct comparison of derivatives and properties, this compound was synthesized as follows. To an ether solution of 0.09 mole of allylmagnesium chloride was added 18.7 g. of α-allylisobutyromesitylene. The solution became intensely yellow, the color gradually disappearing. After 2 hours of refluxing the mixture was hydrolyzed with ammonium chloride solution and worked up in the usual fashion. Distillation of the product yielded a series of fractions, of which two, b.p. 126–129° and 130–137° (0.75 mm.), n^{20}_{D} 1.5400 and 1.5403, weighing 8.9 and 2.3 g., contained the desired product. The yield was thus 52%.

Anal. Calcd. for $C_{19}H_{28}O$: C, 83.8; H, 10.34. Found: C, 83.6; H, 10.27. Calcd. hydrogenation number: 68 g./equiv. of hydrogen; found, 67 g.

Treatment of 0.272 g. of IV with 0.61 g. of mercuric acetate in 50 ml. of methanol, followed by the addition of 0.365 g. of potassium iodide in 3 ml. of water, resulted (on cooling) in the formation of a white solid which could be recrystallized from chloroform–methanol.

(a) From Expt. 7	m.p. 155.5–157°
(b) From the synthesis	m.p. 157.5–158.5°
(c) A mixture of the two	m.p. 156.5–157.5°

Under the microscope the compound appeared as elongated flattened prisms.

Anal. Calcd. for $C_{21}H_{34}O_3Hg_2I_2$: Hg, 40.56. Found: Hg, 40.77.

Absorption Spectra.—Absorption spectra of the samples of IV from the two sources were determined in the range 1.4 to 2.4 μ with the use of a quartz-prism recording infrared spectrograph.[31] The two samples showed bands at the various wave lengths:

From Expt. 7				From the synthesis			
1.411 μ	1.437	...	1.632	...	1.437	1.471	1.635
1.695	1.730	1.743	1.769	1.694	1.740	1.750	1.780
2.009	2.042	2.120	2.177	...	2.042	2.120	2.177
2.232	2.263	2.287	2.306	2.232	2.264	2.289	2.305
2.348	2.377			2.349	2.377		

A hydroxyl group is indicated by the band at 1.437 μ, attributable to O–H stretching. The close correspondence of the two spectra is evidence for the identity of the compounds.

Pyrolysis.—A 1.66-g. sample of IV ("synthetic") was heated at 250–290° in a flask connected with a cold trap suited for use with the mass spectrometer. A slow evolution of gas took place and in the cold trap appeared a liquid which readily absorbed bromine. The boiler contents lost 0.24 g.; calculated for loss of propylene, 0.256 g. Distillation of the residual material at atmospheric pressure gave 0.94 g. of α-allylisobutyromesitylene.

Anal. Calcd. for $C_{16}H_{22}O$: C, 83.45; H, 9.62. Found: C, 83.24; H, 9.84.

The pyrolysis of a 1.27-g. sample of IV from Expt. 7 resulted in a loss of 0.15 g.; calcd., 0.20 g.

The gases evolved from the samples of IV from the two sources were examined in the mass spectrometer and were found to be identical with an authentic sample of propylene.

These results establish the structure of IV as α,β-diallyl-α-mesityl-β,β-dimethylethanol, and indicate that the sample obtained in Expt. 7 was slightly less pure than that prepared by the addition of allylmagnesium chloride to III.

Fraction 4 was a viscous orange liquid from which a small amount of *p*-terphenyl was separated by centrifugation. The oily supernatant showed a bromine number of 145 g./equiv.

Anal. Calcd. for $C_{22}H_{28}O$ (1-phenyl-1-mesityl-2,2-dimethylpenten-4-ol): C, 85.7; H, 9.15; bromine number 154 g./equiv. Found: C, 85.10; H, 9.44.

Attempts to oxidize this material with the expectation of obtaining benzoic acid yielded inconclusive results (a small amount of crystalline solid, m.p. 105–109°, was isolated; this gave a m.p. of 105–115° when mixed with benzoic acid). Pyrolysis of the compound gave no propylene. Its infrared absorption spectrum showed a hydroxyl band (in the first overtone region) at 1.411 μ, but no definite conclusions could be drawn from the rest of the spectrum.

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