delayed ferric chloride color as tribenzoylmethane, a total of 7 g. (0.022 mole) being obtained.

The ethereal filtrate from the tribenzoylmethane gave a strong ferric chloride test. It was washed free of acid and shaken with cupric acetate solution. The olive green copper chelate of dibenzoylmethane was collected and found to weigh 0.8 g. (equivalent to 3 mmoles of dibenzoylmethane).

Addition of Allylmagnesium Bromide to Hindered Ketones[1]

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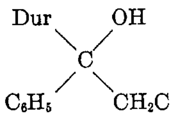
Replacement of methoxyl and other groups by Grignard reagents from *ortho* and *para* positions of hindered ketones has been interpreted to mean that such groups facilitate conjugate addition.[3] It seemed possible that reagents of the allyl type, known to condense with hindered ketones in the 1,2 manner,[4,5] might be induced by such groups to react in the conjugate way.

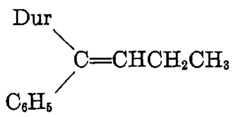
In a study of this question allylmagnesium bromide was allowed to react with duryl *o*-methoxyphenyl ketone, duryl *o*-phenoxyphenyl ketone, duryl *o*-bromophenyl ketone, and mesityl *o*-methoxyphenyl ketone. In no case was there any evidence of group displacement; only the corresponding allyl carbinols were formed. A similar product was obtained from duryl phenyl ketone.

Only the carbinol from the bromo ketone was isolated in pure form, however. The others were viscous oils that failed to crystallize and could not be distilled undecomposed. Infrared spectra showed that in all of them the ketone group was absent and the hydroxyl group was present. It was concluded that only 1,2 addition had occurred.

The unsaturated carbinol from duryl phenyl ketone formed the corresponding saturated carbinol **1** when catalytically hydrogenated. Distillation of the saturated alcohol at diminished pressure gave olefin **2**, and oxidation gave an unconjugated ketone. Pyrolysis of allyldurylphenyldicarbinol produced duryl (Dur) phenyl ketone, a hydrocarbon, and polymeric material.



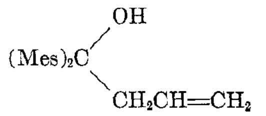
1



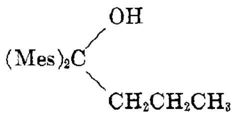
2

Condensation of the allyl reagent with dimesityl ketone gave the carbinol **3**. Neither it nor the saturated carbinol **4** could be induced to crystallize. Distillation of the latter yielded an olefin which by melting point, infrared and n.m.r. spectra, and elemental analysis was identified as 1,1-dimesityl-1-butene (**5**).[6]

1,4 addition of the allyl reagent to a hindered ketone was finally achieved by use of mesityl vinyl ketone (**6**). Mesityl 4-pentenyl ketone (**7**) was the only product isolated. Reduction converted it into known copromesitylene, the identity of which was confirmed by preparation of its dinitro derivative.[7]



3



4

$(Mes)_2C{=}CHCH_2CH_3$

5

$MesCOCH{=}CH_2$ **6** $\quad MesCOCH_2CH_2CH_2CH{=}CH_2$ **7**

Experimental Section

Reaction of Ketones with Allylmagnesium Bromide.—The reagent was prepared in 75 to 81% yield by the method of Grummitt, Budewitz, and Chudd.[9] The yield was determined each time by acidimetric titration.[10] A solution of 3.17 g. (0.01 mole) of **duryl *o*-bromophenyl ketone** in 100 ml. of ether was placed in a 200-ml., three-necked, round-bottomed flask equipped with a condenser fitted with a drying tube, a pressure-equalized dropping funnel, and a magnetic stirrer. To this solution was added rapidly a solution of allylmagnesium bromide (0.05 mole) in ether. The reaction mixture became cloudy after addition of the first drops. After being stirred 8 hr. at room temperature the gray slurry was poured into cold saturated ammonium chloride solution; the ether layer was washed twice with water, dried over magnesium sulfate, and filtered. The very viscous oil that remained after the solvent had been evaporated crystallized only after standing for many months. The infrared spectrum showed strong hydroxyl absorption at 3560 cm.$^{-1}$, no absorption in the carbonyl region, and terminal methylene absorption at 1638, 1000, and 915 cm.$^{-1}$. Recrystallization from absolute ethanol yielded white crystals, m.p. 69–70°.

Anal. Calcd. for $C_{20}H_{23}BrO$: C, 66.88; H, 6.41. Found: C, 66.99; H, 6.51.

A very similar experiment with **duryl *o*-methoxyphenyl ketone** gave an orange oil which showed infrared absorption at 3540, 1640, 1000, 918, and 1235 cm.$^{-1}$—bands assignable to allylduryl-*o*-methoxyphenylcarbinol. No absorption bands for a carbonyl group were present.

Duryl *o*-phenoxyphenyl ketone likewise gave an oil (73% yield) that showed infrared absorption bands for a terminal double bond (1638, 995, and 915 cm.$^{-1}$), a hydroxyl group (3560 cm.$^{-1}$), and a phenoxyl group (1230 cm.$^{-1}$). Similar results were obtained with **mesityl *o*-methoxyphenyl ketone.**

Dimesityl ketone yielded an oil, the infrared spectrum of which showed absorption bands for a hydroxyl group (3560 cm.$^{-1}$) and a terminal methylene group (1635, 990, and 910 cm.$^{-1}$). Hydrogenation was effected by placing a mixture of 21 g. of crude allyldimesitylcarbinol, 100 ml. of absolute ethanol, and 0.3 g. of platinum oxide in a pressure bottle set in a Parr shaker and charged with 49 lb. of hydrogen pressure. The pressure dropped substantially during the first hour and the treatment was continued for 18 hr. After removal of the catalyst and ethanol, the product was subjected to distillation; 40% of it distilled at 159–160° at 0.55 mm. and solidified. After several recrystallizations from 95% ethanol, the 1,1-dimesityl-1-butene melted at 108–109° (lit.[7] m.p. 109–110°).

Anal. Calcd. for $C_{22}H_{28}$: C, 90.35; H, 9.65. Found: C, 89.95; H, 9.76.

The n.m.r. spectrum showed the presence of a trisubstituted ethylene.

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[2] To whom correspondence should be addressed: Department of Chemistry, Parsons College, Fairfield, Iowa.

[3] See R. C. Fuson and S. B. Speck, *J. Am. Chem. Soc.*, **64**, 2446 (1942).

[4] W. G. Young and J. D. Roberts, *ibid.*, **66**, 2131 (1944).

[5] K. W. Wilson and W. G. Young, *ibid.*, **72**, 218 (1950).

[6] H. R. Snyder and R. W. Roeske, *ibid.*, **74**, 5820 (1952).

[7] R. C. Fuson, R. J. Hellmann, and W. S. Friedlander, *J. Org. Chem.*, **18**, 1263 (1953).

[8] All melting points are corrected. The infrared spectra were recorded by Mr. Paul E. McMahon and Mrs. John Verkade. The microanalysis were performed by Mr. Josef Nemeth, Miss Claire Higham, and Mrs. Frederick Ju.

[9] O. Grummitt, E. P. Budewitz, and C. C. Chudd, *Org. Syn.*, **36**, 61 (1956).

[10] H. Gilman, E. A. Zoellner, and J. B. Dickey, *J. Am. Chem. Soc.*, **51**, 1577 (1929).

Duryl phenyl ketone gave a viscous yellow oil (approximately 90% yield) which seemed to be impure allyldurylphenylcarbinol. The infrared spectrum has bands assignable to a hydroxyl group (3580 cm.$^{-1}$), as well as to a terminal methylene group (1635, 995, and 915 cm.$^{-1}$) but none in the carbonyl region. Catalytic hydrogenation evidently (infrared spectrum) gave the saturated carbinol which, however, lost water when distilled; the resulting 1-duryl-1-phenyl-1-butene boiled at 157–159° at 0.65 mm. pressure and crystallized when allowed to stand, m.p. 52.5–54°. The n.m.r. spectrum indicated the presence of a trisubstituted olefin. This olefin was made also by treating the carbinol with acetic anhydride, 20% sulfuric acid, or thionyl chloride in pyridine. In all cases the infrared spectrograms were superimposable.

The identification of the olefin was supported by the results of oxidation. The olefin (3.0 g., 0.0113 mole), dissolved in 15 ml. of chloroform, was added to 35 ml. of glacial acetic acid, and a solution of 4.2 g. of chromium trioxide, 3 ml. of water, and 22 ml. of glacial acetic acid was added dropwise. The temperature was maintained at 40–45° during the addition and then at 50° for 20 min. longer. The mixture was cooled and excess chromic acid was destroyed by the addition of 5 ml. of methanol. After the mixture was concentrated by distillation at diminished pressure, water was added and the ketone appeared as a yellow solid. It was washed with acid and then with base and recrystallized from ethanol, m.p. 123–124.5°.

Anal. Calcd. for $C_{23}H_{30}O$: C, 85.8; H, 9.31. Found: C, 85.5; H, 9.62.

The infrared spectrum has a strong carbonyl band at 1710 cm.$^{-1}$, and a propionyl group is indicated by the n.m.r. spectrum.

An olefin, evidently 4-duryl-4-phenyl-1-butene, was obtained by heating allyldurylphenylcarbinol at 225–230° for 6 hr.; the mixture was then treated with boiling 95% ethanol and the ethanol was removed from the solution by evaporation. The red oil, chromatographed on Fluorisil or activated alumina, gave early fractions that separated from ethanol as colorless crystals, m.p. 50–51°.

Anal. Calcd. for $C_{20}H_{24}$: C, 90.85; H, 9.15. Found: C, 90.77; H, 9.27.

The infrared spectrum has bands assignable to a terminal methylene group (1635, 995, and 915 cm.$^{-1}$).

A second compound, obtained during the development of the chromatogram, melted at 118–120° after recrystallization from *n*-butyl ether. A mixture melting point with a pure sample of duryl phenyl ketone showed no depression.

An ether solution of 5.57 g. (0.032 mole) of **mesityl vinyl ketone** was added dropwise over a period of 1 hr. to 100 ml. of a solution which contained 0.128 mole of the allyl reagent. The gray slurry that formed was agitated for an additional 1 hr. and poured into an iced, saturated solution of ammonium chloride. The organic portion, when extracted with ether and distilled, gave mesityl 4-pentenyl ketone, b.p. 106.5–108° (0.65 mm.), $n^{24.5}\text{D}$ 1.523. The infrared spectrum has bands that can be assigned to a conjugated carbonyl group (1690 cm.$^{-1}$), a terminal methylene group (1635, 995, and 915 cm.$^{-1}$), and a mesityl group (852 cm.$^{-1}$). Hydrogenation of the pentenyl ketone over platinum oxide gave capromesitylene as an oil that boiled at 100–103° (0.6 mm.), $n^{22}\text{D}$ 1.5048 [lit.[7] b.p. 105–107° (0.8 mm.), $n^{20}\text{D}$ 1.5042]. The dinitro derivative was prepared and found to melt at 121.5–122.5° (lit.[7] m.p. 122.5–123°).

Anal. Calcd. for $C_{15}H_{20}N_2O_5$: N, 9.08. Found: N, 8.89.

Quinodimethans, Analogs of the Intensely Colored Langenbeck Compound

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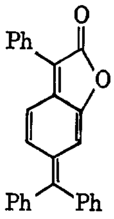
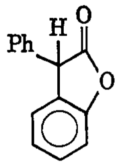
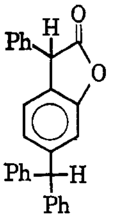
From the pyrolysis of benzilic acid, Langenbeck isolated an intensely purple-black, crystalline compound,[2] whose structure was shown by Wasserman to be the quinodimethan I.[3] Wasserman synthesized I from reaction of the enolate of 3-phenylisocoumaranone, II, with diphenylmethylene chloride and also reduced I with phosphorus and iodine to form III.[3]



I



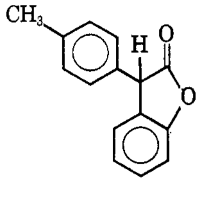
II



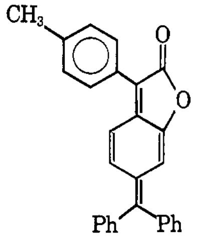
III

The reactions leading to I and III were repeated in the present study. The n.m.r. spectra of I, II, and III were recorded and are consistent with the assigned structures.

p-Tolualdehyde was converted to the cyanohydrin, *p*-methylmandelonitrile, which was not purified but was treated directly with phenol and 73% sulfuric acid for the synthesis of 3-(*p*-tolyl)isocoumaranone (IV). The enol of IV with diphenylmethylene chloride gave the analog, V. The color and spectral properties of V resembled those of I. The infrared spectrum of V had absorption peaks at 5.72 and 5.79 μ, which were also present in I.[3,4]

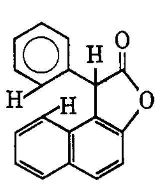


IV

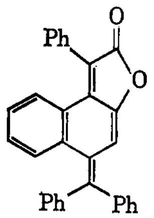


V

The reaction of the enolate of VI with diphenylmethylene chloride produced an intensely red-orange crystalline product. That this material was VII, the expected analog of the Langenbeck compound, was indicated by the analysis and by the infrared and the n.m.r. spectra.



VI



VII

It is unlikely that the diphenylmethylene chloride reacted with the enolate of VI at the phenyl ring rather than the naphthalene ring. The negative charge of the enolate is delocalized onto the naphthalene ring,

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[1] (a) To whom correspondence concerning this paper should be addressed. (b) National Science Foundation College Faculty Research Participant, summer 1963. (c) National Science Foundation Undergraduate Research Participant, summer 1963.

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[3] H. H. Wasserman, H. W. Ackerman, H. H. Wotiz, and T. C. Liu, *J. Am. Chem. Soc.*, **77**, 973 (1955).

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