of *o*-terphenyl, identified by its melting point and an infrared spectral comparison with an authentic sample.

CIS-*1,2-Diphenyl-1,2-cyclohexanediol* (VII). One gram (0.0039 mole) of osmium tetroxide was added to a solution of 0.94 g. (0.0040 mole) of 1,2-diphenylcyclohexene in 50 ml. of ether and 1.5 ml. of pyridine. After 48 hr. at room temperature, the solvent was evaporated. The gummy solid was boiled with 6 g. of sodium sulfite in 80 ml. of 50% ethanol for one hour. The mixture was filtered and the organic components were removed by extraction with methylene chloride. Removal of the solvent left 0.99 g. of a brown oil which was subjected to chromatography on alumina. A total of 0.51 g. (47%) of the *cis*-glycol (VII) was obtained, m.p. 85–86°. The analytical sample crystallized from ligroin in large prisms, m.p. 86–87°.

Anal. Calcd. for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 80.82; H, 7.39.

Treatment of 0.11 g. of glycol VII in 5 ml. of benzene with 0.19 g. of lead tetraacetate for 0.5 hr. at room temperature furnished 0.11 g. (100%) of 1,4-dibenzoylbutane (IV), m.p. 105–106°. The diketone was identified by a mixture melting point determination with a known sample.

One of the *2,3-diphenyl-1,2-cyclohexanediols* (VIII) was prepared from 2,3-diphenylcyclohexene (VI) in 51% yield by the osmium tetroxide hydroxylation method described above; the crude product melted at 129–131°. Sublimation of the diol followed by crystallization from a mixture of benzene and ligroin gave fine, colorless needles, m.p. 132–132.5°.

Anal. Calcd. for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 80.47; H, 7.76.

This same diol was obtained in 16% yield by the performic acid method.[29] A mixture of 2.00 g. of 2,3-diphenylcyclohexene, 5.2 ml. of 88% formic acid, and 1.2 ml. of 30% hydrogen peroxide was stirred for 9 hr. at room temperature. The formic acid was distilled under reduced pressure and the residue was treated with 10 ml. of 20% sodium hydroxide solution for 2 hr. on a steam bath. Extraction of the product followed by crystallization from ligroin gave 0.37 g. of glycol VIII, m.p. 131–133°.

Glycol VIII (50 mg.) was treated with 92 mg. of lead tetraacetate in 3 ml. of benzene for 20 min. at room temperature. The crude product (exhibiting conjugated ketone absorption at 1682 cm.$^{-1}$ and aldehyde bands at 2700 and 1723 cm.$^{-1}$) was oxidized in an air stream to give an acidic crystalline material. Recrystallization from ligroin yielded 34 mg. (65%) of *5-benzoyl-5-phenylpentanoic acid* (IX), m.p. 145–146°. The infrared spectrum contained typical acid absorption bands, as well as carbonyl absorption at 1705 cm.$^{-1}$ (acid) and 1682 cm.$^{-1}$ (conjugated ketone). An analytical sample crystallized from ligroin in the form of fine needles, m.p. 147–148°.

Anal. Calcd. for $C_{18}H_{18}O_3$: C, 76.57; H, 6.43; neut. equiv. 282. Found: C, 76.87; H, 6.43; neut. equiv. 285.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY UNIVERSITY OF MISSOURI]

The Reaction of Aldoketene Dimers with Grignard Reagents[1]

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When an excess of phenylmagnesium bromide reacted with *n*-butylketene dimer, two simple ketones, 6-undecanone and benzophenone, and a di-addition compound, 5-(diphenylhydroxymethyl)-6-undecanone, were isolated from the reaction products. Analogous compounds were obtained from phenylmagnesium bromide and *n*-octylketene dimer, but from *n*-hexylketenedimer, the only identified product isolated from the reaction mixture was the di-addition compound. Only two simple ketones could be isolated from the reaction product of aliphatic Grignard reagents with the ketene dimers.

Many investigations of the reactions of the aldoketene dimers have been carried out, but only one reference has been found to the reaction of these compounds with a Grignard reagent. Reid and Groszos[4] have reported that solid ethylketene dimer, which is stated to have the 2,4-diethyl-1,3-cyclobutanedione structure, behaved abnormally in a Grignard machine yielding 1.3 active hydrogens and 1.7 carbonyls. We have found no mention of the reaction of Grignard reagents with the more common liquid aldoketene dimers for which the 3-butanoic-β-lactone structure[5] is generally accepted. The results of a study of the reaction of some Grignard reagents with the latter class of compounds are reported in this paper.

When an excess of phenylmagnesium bromide reacted with *n*-butylketene dimer, three products were isolated and identified: 6-undecanone (16%), benzophenone (16%), and 5-(diphenylhydroxymethyl)-6-undecanone (43%).

n-Hexylketene dimer reacted with an excess of phenylmagnesium bromide, but only 7-(diphenylhydroxymethyl)-8-pentadecanone could be isolated. The remainder of the reaction product was a

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[2] Abstracted from the Ph.D. dissertation of Roy H. Turley, Jr., University of Missouri, June 1958.

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[4] E. B. Reid and S. J. Groszos, *J. Am. Chem. Soc.*, 75, 1655 (1953).

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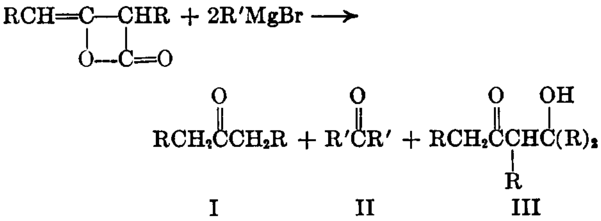
mixture of low melting solids, probably containing 8-pentadecanone and benzophenone, which could not be separated.

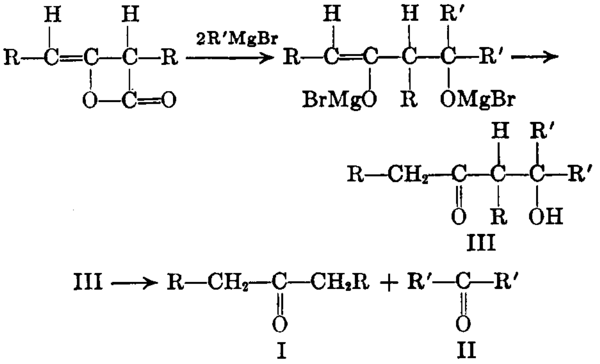
n-Octylketene dimer and phenylmagnesium bromide gave 9-(diphenylhydroxymethyl)-10-nonadecanone, benzophenone, and 10-nonadecanone.

An excess of the aliphatic Grignard reagents reacted with the aldoketene dimers to yield the two simple ketones I and II, but none of the di-addition product III could be isolated from the high boiling residues.



n-Butyllithium reacted in the same manner as *n*-butylmagnesium bromide with methylketene dimer to yield 3-pentanone and 5-nonanone.

If the β-lactone ring of the aldoketene dimer is assumed to react with the Grignard reagent in the same manner as other lactones or as an ester, the addition could proceed as follows:



The formation of the simple ketones I and II may be explained by a partial retrograde aldol reaction[6] of III, either during the reaction or during the hydrolysis of the Grignard complex, similar to that reported by Freeman[7] from his study of the reaction of enolic β-keto esters and β-diketones with phenylmagnesium bromide. Some of I may also result from the decomposition of unchanged ketene dimer.[8]

The structure of 5-(diphenylhydroxymethyl)-6-undecanone was confirmed by its infrared spectrum, which indicated the presence of an hydroxyl group and a carbonyl group, and by its cleavage with 10% sodium hydroxide solution or with acetic anhydride to yield 6-undecanone and benzophenone.

Derivatives of 5-(diphenylhydroxymethyl)-6-undecanone could not be obtained because of cleavage or because of its failure to react with carbonyl reagents. The reaction of this compound with hydroxylamine gave benzophenone oxime, and it was recovered unchanged in an attempt to form an hydantoin. With 2,4-dinitrophenylhydrazine no derivative could be isolated. Attempted dehydration of this di-addition product with iodine or acetic anhydride yielded 6-undecanone and benzophenone.

EXPERIMENTAL[9]

The ketene dimers were prepared by the method of Hanford and Sauer.[10] The ketones used for the preparation of authentic derivatives were obtained by the reaction of acid chlorides and dialkylcadmium reagents.

The reaction of phenylmagnesium bromide with n-butylketene dimer. This reaction is typical and is described in detail. To 0.9 mole of phenylmagnesium bromide in 250 ml. of ether in a 1-l. three-necked flask equipped with a condenser, mechanical stirrer and dropping funnel was added 58.8 g. (0.3 mole) of *n*-butylketene dimer in 250 ml. of anhydrous ether at such a rate that gentle refluxing was maintained. The reaction mixture was refluxed 1 to 2 hr., allowed to stand overnight, then refluxed an additional 2 hr.

The complex was decomposed with iced dilute sulfuric acid, the ether layer was separated and washed successively with water, saturated sodium bicarbonate solution, and water. The sodium bicarbonate washings were made distinctly acid and extracted with ether. Distillation of this ether extract yielded no organic acid.

The ether extract containing the neutral compounds was dried over anhydrous magnesium sulfate. After the ether had been removed by distillation, the material remaining was steam distilled to remove any benzene formed from unused Grignard reagent. The residue from the steam distillation partially solidified upon cooling. The solid was separated by filtration and recrystallized from ethanol to yield 45.3 g. (43%) of 5-(diphenylhydroxymethyl)-6-undecanone, m.p. 84–85°.

Anal. Calcd. for $C_{24}H_{32}O_2$: C, 81.77; H, 9.15. Found: C, 81.91; H, 9.26.

The oil (48.5 g.) from the filtration of the solid distilled at 67–192° (1 mm.). This material was fractionally distilled at 1 mm. to yield finally 8.2 g. of 6-undecanone, 9 g. of benzophenone, and an intractable high boiling residue.

The 6-undecanone, b.p. 220–221°, m.p. 13–14°, lit.[11,12] m.p. 14–15°, formed a hydantoin, m.p. 134–135°, lit.[13] m.p. 137–138°. Values of carbon and hydrogen analyses of both the ketone and its hydantoin agreed with those calculated.

The 2,4-dinitrophenylhydrazone of the benzophenone melted at 236–237° and did not depress the melting point of an authentic sample of this derivative.

Another reaction of 0.15 mole of phenylmagnesium bromide and 10 g. (0.05 mole) of *n*-butylketene dimer yielded 13.5 g. (75%) of di-addition product.

Phenylmagnesium bromide and n-hexylketene dimer. *n*-Hexylketene dimer (25.2 g., 0.1 mole) was added to 0.3 mole of phenylmagnesium bromide.

The semisolid reaction product was separated by filtration and recrystallized from ethanol to yield 15 g. (36.8%) of 7-(diphenylhydroxymethyl)-8-pentadecanone, m.p. 42–43°.

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[9] The carbon-hydrogen analyses were performed by the Weiler and Strauss Laboratories, Oxford, England. All melting points and boiling points are uncorrected.

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Anal. Calcd. for $C_{28}H_{40}O_2$: C, 82.30; H, 9.87. Found: C, 82.50; H, 9.83.

After removal of the ethanol from the filtrate no pure ketones could be isolated from the high boiling, semisolid residue presumably containing benzophenone and 8-pentadecanone.

n-Octylketene dimer and phenylmagnesium bromide. n-Octylketene dimer (92.4 g., 0.3 mole) in 200 ml. of ether was added to 0.9 mole of phenylmagnesium bromide in 150 ml. of ether. After the addition was complete, the solution was refluxed an additional 4.5 hr.

The semisolid reaction product (127.2 g.) was crystallized from ethanol to yield 13.3 g. of 9-(diphenylhydroxymethyl)-10-nonadecanone, m.p. 60–61°.

Anal. Calcd. for $C_{32}H_{48}O_2$: C, 82.70; H, 10.41. Found: C, 82.42; H, 10.44.

When the alcohol filtrate was concentrated, an additional 11.1 g. of white solid, m.p. 48–59° separated. No pure compound could be isolated from this material.

The product remaining after complete removal of the solvent distilled at 110–200° (2 mm.). This distillate yielded 17 g. of nearly pure benzophenone (2,4-dinitrophenylhydrazone m.p. 236–238°) and 10 g. of 10-nonadecanone, m.p. 57–58°, lit.[11,12] m.p., 58–59°.

Anal. Calcd. for $C_{19}H_{38}O$: C, 80.78; H, 13.56. Found: C, 81.06; H, 13.77.

Action of sodium hydroxide on 5-(diphenylhydroxymethyl)-6-undecanone. This compound (1 g.) was heated on a steam bath with 15 ml. of 10% sodium hydroxide solution for 2 hr. The mixture was extracted with ether and the ether layer was washed with water. After removal of the solvent, less than 1 ml. of oily liquid remained. A 2,4-dinitrophenylhydrazone of this liquid melted at 238–239° and did not depress the melting point of an authentic sample of the same derivative of benzophenone.

n-Butylketene dimer and n-butylmagnesium bromide. *n*-Butylketene dimer (79.8 g., 0.4 mole) in 250 ml. of ether was added to 1.2 moles of *n*-butylmagnesium bromide in 150 ml. of ether during 3 hr. The solution stood overnight at room temperature and then was refluxed an additional 3 hr.

The complex was decomposed in the usual manner, and the dried reaction product (90 g.) was first partially separated by slow distillation from a Clark flask. The temperature range was 50° (35 mm.)–140° (1.2 mm.), n_D^{20} 1.4057–1.4521. Fractions of nearly the same refractive indices were combined and fractionated thru a Podbielniak column to yield 14.8 g. of 5-nonanone n_D^{20} 1.4196, b.p. 93–95° (35 mm.) and 19.4 g. of 6-undecanone, n_D^{20} 1.4285, b.p. 92–93° (3.5 mm)., m.p. 14–15°, lit.[11] m.p. 14–15°.

The semicarbazone of the 5-nonanone melted at 88–89°, lit.[14] m.p. 89°, and did not depress the melting point of the same derivative of the authentic ketone.

The hydantoin of the 6-undecanone melted at 133–134°, lit.[13] m.p. 137–138°, and did not depress the melting point of the same derivative of the authentic ketone.

Efforts to obtain a pure compound by fractionation through a Podbielniak column of material distilling at 100°–130° (1.5 mm.), n_D^{20} 1.4478–1.4521, were unsuccessful.

The reaction was repeated three times with a similar distribution of products.

n-Butylketene dimer with ethylmagnesium bromide. n-Butylketene dimer (57.2 g., 0.29 mole) and 0.87 mole of ethylmagnesium bromide yielded 40.7 g. of distillate b.p. 97° (atm.)–135° (1 mm.), n_D^{20} 1.3845–1.4620. Fractionation of this material yielded 5.4 g. (21.6%) of 3-pentanone, which was identified by its 2,4-dinitrophenylhydrazone, m.p. and mixture melting point with an authentic sample 156–157°, and 15.4 g. (30.8%) of 6-undecanone, identified by its hydantoin, m.p. 133–134°.

n-Butylketene dimer and n-octylmagnesium bromide. *n*-Butylketene dimer (58.8 g.) was added to 0.9 mole of *n*-octylmagnesium bromide. The complex from this reaction was hydrolyzed with saturated ammonium chloride solution rather than with dilute sulfuric acid.

Distillation of the reaction product gave 33.1 g. of *n*-octane from the hydrolysis of unused Grignard reagent, 19.3 g. (37.6%) of 6-undecanone identified by its hydantoin and 16.3 (6.4%) of 9-heptadecanone, m.p. 51.5–52.5°, lit.,[11,12] m.p. 52–53°.

n-Hexylketene dimer and ethylmagnesium bromide. n-Hexylketene dimer (94.0 g., 0.37 mole) was added to 1.12 moles of ethylmagnesium bromide. The reaction product was distilled at atmospheric pressure to yield 6.4 g. of 3-pentanone, semicarbazone, m.p. and mixed m.p. with an authentic sample, 138–139°.

The residue in the distilling flask partially solidified on cooling and was recrystallized from ethanol to yield 43.2 g., (51%) of 8-pentadecanone, m.p. 43–44°, lit.,[12] m.p. 43°. Its semicarbazone melted at 46–46.7°, lit.,[15] m.p. 43°.

Anal. Calcd. for $C_{15}H_{30}O$: C, 79.57; H, 13.36. Found: C, 79.70; H, 13.21.

n-Butyllithium and methylketene dimer. A solution of 21 g. (0.187 mole) of methylketene dimer in 20 ml. of dry ether was added to 0.5 mole of *n*-butyllithium in 300 ml. of ether. The refluxing was continued for 3 hr., then after standing overnight, the solution was refluxed an additional 2 hr.

The product (25 g.) distilled at 40° (atm.)–110° (1 mm.), n_D^{20} 1.3550–n_D^{20} 1.4683.

Fractionation of this material yielded 11.1 g. of 3-pentanone (69%) and 7.9 g. (29.7%) of 5-nonanone. The higher boiling fractions were intractable.

The 2,4-dinitrophenylhydrazone of the 3-pentanone melted at 154–155°, literature[14] value 156°.

The semicarbazone of the 5-nonanone melted at 88–89° lit.[14] m.p. 90°.

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