cis-bromide 0.60 g., b.p. 114–136° (0.2 mm.), n^{20}D 1.5960, and 0.47 g., b.p. 136° (0.2 mm.), n^{20}D 1.6109, and a glassy light-red residue (1.92 g.) which could not be distilled at temperatures of up to 220° at 0.2 mm. In each case the infrared spectrum closely resembled that of authentic 1,3-diphenyl-2-propyn-1-ol and the yield was 27% from *cis*-XVII and 19% from *trans*-XVII.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE REDSTONE ARSENAL DIVISION OF ROHM AND HAAS CO.]

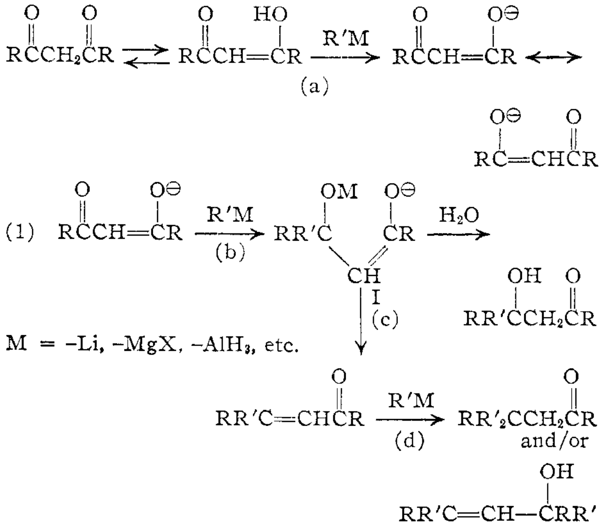
The Reaction of Enolic β-Ketoesters and β-Diketones with Phenylmagnesium Bromide

BY JEREMIAH P. FREEMAN

RECEIVED NOVEMBER 8, 1957

The reactions of a variety of β-ketoesters and analogous β-diketones with phenylmagnesium bromide have been examined with a view to maximum substitution by the Grignard reagent. The effects of the structure of the carbonyl compound on the composition of the product is discussed. In certain cases, it has been found that three to four equivalents of the reagent are consumed by the carbonyl compound.

A general equation to encompass all the reactions between enolic compounds and organometallic reagents may be expressed as



$$\mathrm{R\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}R \rightleftarrows R\overset{O}{\overset{\|}{C}}CH{=}\overset{HO}{\overset{|}{C}}R \xrightarrow[(a)]{R'M} R\overset{O}{\overset{\|}{C}}CH{=}\overset{O^{\ominus}}{\overset{|}{C}}R \longleftrightarrow R\overset{O^{\ominus}}{\overset{|}{C}}{=}CH\overset{O}{\overset{\|}{C}}R}$$

$$(1)\quad \mathrm{R\overset{O}{\overset{\|}{C}}CH{=}\overset{O^{\ominus}}{\overset{|}{C}}R \xrightarrow[(b)]{R'M} RR'\overset{OM}{\overset{|}{C}}\!-\!CH\!=\!\overset{O^{\ominus}}{\overset{|}{C}}R\ (I) \xrightarrow{H_2O} RR'\overset{OH}{\overset{|}{C}}CH_2\overset{O}{\overset{\|}{C}}R}$$

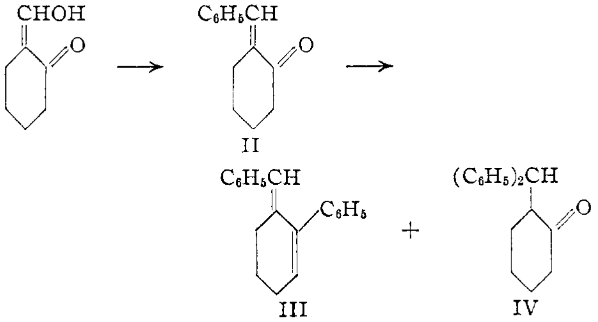
$$\mathrm{I} \xrightarrow{(c)} \mathrm{RR'C{=}CH\overset{O}{\overset{\|}{C}}R \xrightarrow[(d)]{R'M} RR'_2CCH_2\overset{O}{\overset{\|}{C}}R\ \text{and/or}\ RR'C{=}CH{-}\overset{OH}{\overset{|}{C}}RR'}$$

M = -Li, -MgX, -AlH$_3$, etc.

It has been assumed previously that the intermediate I is resistant to further attack, and yields a ketoalcohol upon hydrolysis.[1] However, the polyaddition observed with the cyclic diketones dimedon and dihydroresorcinol[2] and with 4-hydroxycoumarin[3] suggests that this intermediate can also lose an inorganic fragment as in step c to regenerate a ketonic system which undergoes further attack by the organometallic reagent. The effect of the various metal ions attached to the oxygen atom eliminated on the ease of that elimination has been considered previously[3] and the following order of effectiveness of some metal ions has been suggested: Al > Mg > Li.

Since so few compounds had been examined with a view to obtaining maximum interaction with a Grignard reagent, a more complete examination of the reaction of enolic β-dicarbonyl compounds with phenylmagnesium bromide has been undertaken. The results of this investigation are summarized in Table I.

The finding that 2-hydroxymethylenecyclohexanone undergoes polyaddition with phenylmagnesium bromide is particularly illuminating, since reduction of this material by lithium aluminum hydride is accompanied by expulsion of one of the oxygen atoms as an oxide fragment during the reaction.[4] Under the same conditions the Grignard reagent does not cause loss of the oxygen atom.[1c] Only under the forcing conditions employed in this study was the fragment -OMgBr lost. This difference in reactivity furnishes additional evidence in support of the hypothesis that the nature of the metal ion in the inorganic fragment determines the ease of elimination of that fragment.[3]



II

III

IV

Oxide elimination also appeared to occur with ethyl benzoylacetate, ethyl acetoacetate, acetylacetone and also to a minor extent with dibenzoylmethane indicating that this is a more common reaction path than generally realized. The main products were those predictably derived from the elimination product, although in some cases products arising from dealdolization of the ketoalcohol product were also found. All reactions followed the general equation 1 (it is presumed that the esters undergo attack at that function as a first step to form a diketone enolate), with the final steps occurring as in scheme I.

β-Phenylchalcone (V) is known to undergo predominantly 1,2-addition with the phenyl Grignard reagent.[5] In the case of acetoacetic ester reaction occurred at both carbonyl groups, but predominated

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[1] (a) E. P. Kohler and J. L. E. Erickson, THIS JOURNAL, **53**, 2301 (1931); (b) A. Chaney and M. J. Astle, *J. Org. Chem.*, **16**, 57 (1951); (c) A. S. Dreiding and S. N. Nickel, THIS JOURNAL, **76**, 3965 (1954).

[2] G. F. Woods, *ibid.*, **69**, 2549 (1947); G. F. Woods and I. W. Tucker, *ibid.*, **70**, 2174 (1948).

[3] J. P. Freeman and M. F. Hawthorne, *ibid.*, **78**, 3366 (1956).

[4] A. S. Dreiding and J. A. Hartman, *ibid.*, **75**, 939 (1953).

[5] E. P. Kohler, *Am. Chem. J.*, **38**, 511 (1907).

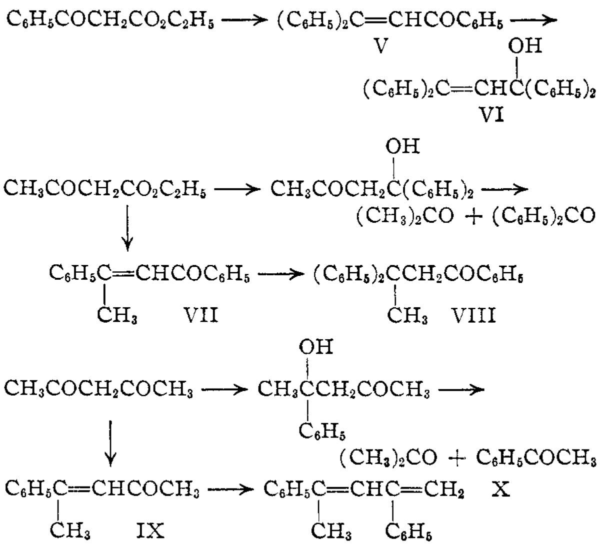
TABLE I

REACTION OF ENOLIC COMPOUNDS WITH PHENYLMAGNESIUM BROMIDE

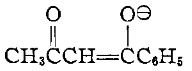
	Products		Yield,
Enol	Ordinary conditions	Forcing conditions	%
2-Hydroxymethylenecyclohexanone	2-Benzalcyclohexanone (II)[a]	2-Phenyl-3-benzylidenecyclohexene (III)	48
	1-Phenyl-2-(α-hydroxybenzyl)-cyclohexanol (compd. A)	2-Benzhydrylcyclohexanone (IV)	23
		Compound A	8
Ethyl benzoylacetate	....	Tetraphenylpropenol (VI)	56
Dibenzoylmethane	2-Hydroxy-2,2-diphenylpropiophenone[b]	β-Phenylchalcone (V)	57
		1,1,3-Triphenylindene	33
Ethyl acetoacetate	Enolate formation[c]	2,2-Diphenylbutyrophenone (VIII)	17
		Benzophenone	7
		Dypnone (VII)	4
Acetylacetone	4-Phenyl-3-penten-2-one[d] (IX)	2,4-Diphenyl-1,3-pentadiene (X)	25
		Acetophenone	8
Ethyl 2-cyclohexanone-1-carboxylate	....	1-Phenyl-2-benzoylcyclohexene (XIV)	33
		1,5-Dibenzoylpentane	21
Ethyl 2-cyclopentanone-1-carboxylate	Enolate formation[e]	1-Phenyl-2-benzoylcyclopentene	24
		1,4-Dibenzoylbutane	8
		1,1,6,6-Tetraphenylhexane-1,6-diol	8

[a] Ref. 1c. [b] Ref. 1a. [c] V. Grignard, *Ann. chim.*, [7] **27**, 564 (1902). [d] This work and also Th. Morel, Doctoral Thesis, Delft, 1946, p. 86. A small amount of acetophenone was also found by these latter workers. [e] J. Plesek, *Coll. Czech. Chem. Communs.*, **21**, 1312 (1956).

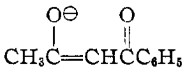
SCHEME I



at the aliphatic ketone. Structure XI would be expected to make a larger contribution to the hybrid enolate than XII because of the interaction possible between the conjugated ketone system and


$CH_3\overset{\overset{O}{\|}}{C}CH{=}\overset{\overset{O^{\ominus}}{|}}{C}C_6H_5$

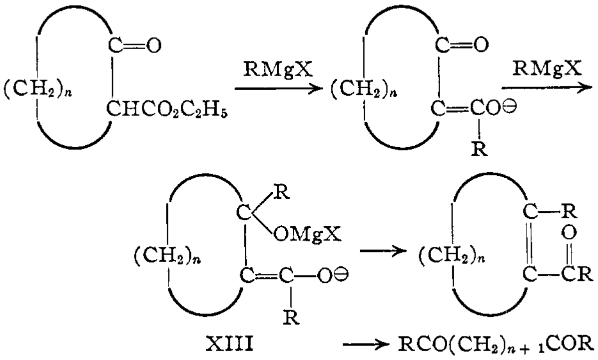
XI


$CH_3\overset{\overset{O^{\ominus}}{|}}{C}{=}CH\overset{\overset{O}{\|}}{C}C_6H_5$

XII

the benzene ring. The direction of enolization of various unsymmetrical dicarbonyl compounds seems to be governed by this enhanced stabilization.[6] The dypnone produced then underwent 1,4-addition as expected to yield[5] 2,2-diphenylbutyrophenone. Acetylacetone followed a similar course except that 1,2- rather than 1,4-addition took place. Because of the low yield of the diene whose origin could be attributed to a simple double addition of the Grignard reagent to the diketone form of acetylacetone followed by dehydration upon work-up, the magnesium chelate of acetylacetone was prepared and subjected to the reaction under identical conditions. The same product was obtained.

The high yield of polyaddition product obtained from ethyl benzoylacetate is quite interesting since β-phenylchalcone was the main product obtained from dibenzoylmethane. However, a smaller amount of a polyaddition product, in this case 1,1,3-triphenylindene, a known acid-cyclization product of tetraphenylpropenol (VI), was obtained also. Since equation 1 predicts that the diketone and ketoester should pass through the same intermediate, it is not clear why one starting material should undergo the reaction less completely than the other. Obviously the situation is more complicated than this simple picture of the reaction implies. Another example of this same type of difference may be cited. 2-*p*-Toluylcyclohexanone undergoes attack at both carbonyl groups by ethylmagnesium bromide.[7] Since the enolate of 2-benzoylcyclohexanone is proposed as an intermediate in the reaction with ethyl 2-cyclohexanone-1-carboxylate (see below), products derived from both carbonyl groups would be anticipated whereas attack occurred exclusively at the ring carbonyl group. In this case steric factors may play a role since a phenyl rather than an ethyl group is involved.



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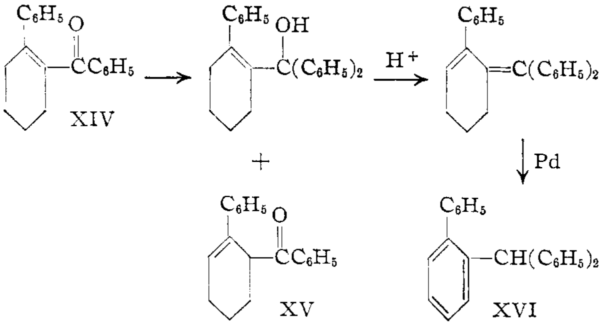
(6) P. B. Russell, *Chemistry & Industry*, 326 (1956).

(7) S. Grateau, *Compt. rend.*, **196**, 1619 (1933).

The cyclic β-ketoesters reacted in the same manner as previously reported[1] for β-dicarbonyl compounds in that no oxide elimination apparently occurred. The two reaction products presumably arise from the same reaction intermediate which is partitioned during hydrolysis. Since further reaction is dependent upon elimination of an inorganic fragment from intermediate XIII and since this elimination requires a high degree of planarity in the four atom system, $^{\ominus}$O—C=C—C, it is possible that this intermediate is prevented from undergoing the elimination because of an unfavorable steric situation.

The fact that only 1-phenyl-2-benzoylcyclohexene and none of the unconjugated isomer, which is the predominant isomer obtained from reactions involving the hydrolysis of intermediates of the type XIII, was obtained suggests that oxide elimination may have occurred but that the resultant ketone was resistant to further attack by the Grignard reagent. To test this possibility the reaction of 1-phenyl-2-benzoylcyclohexene (XIV) with phenylmagnesium bromide was examined. This proved to be a very sluggish reaction and very little pure product could be isolated. However, infrared analysis of the crude product indicated a large amount of a ketone present. The spectrum of this material resembled in many respects that of 1-phenyl-6-benzoylcyclohexene (XV) suggesting that isomerization of the double bond had occurred under base catalysis. (A similar base-catalyzed isomerization of 1-phenyl-2-cyanocyclohexene to 1-phenyl-6-cyanocyclohexene is indicated below.) The infrared analysis also indicated that an alcohol was present. Therefore the crude mixture was subjected to acid dehydration and the hydrocarbon obtained was dehydrogenated to give 2-phenyltriphenylmethane (XVI) indicating the following course for the Grignard reaction



It is possible but rather unlikely that ketone XIV was formed in the ethyl cyclohexanonecarboxylate–phenylmagnesium bromide reaction mixture before hydrolysis.

An interesting side reaction occurred with ethyl 2-cyclopentanone-1-carboxylate with the formation of 1,1,6,6-tetraphenylhexane-1,6-diol. This material probably was produced by reaction of the Grignard reagent with 1,4-dibenzoylbutane. However, how this ketone was generated in the reaction mixture is not clear unless its enolate abstracted a proton from ether present in the solvent.

Some confusion exists in the literature on the structure of 1-phenyl-2-benzoylcyclohexene. Bauer[8] reported two isomeric phenylbenzoylcyclohexenes, m.p. 110° and 91°, from the reaction of 1,5-dibenzoylpentane with sodamide to which he assigned the structures XV and XIV, respectively, on the basis of degradation evidence.[9] The 110° isomer had previously been obtained by treatment of 1,5-dibenzoylpentane with phosphorus pentoxide but no structure was assigned.[10] Recently it was reported that addition of phenylmagnesium bromide to 1-phenyl-2-cyanocyclohexene produced the 110° isomer.[11] On the basis of the starting material, this isomer was assigned the 1-phenyl-2-benzoylcyclohexene structure without further proof. Since Bauer's assignment for similar products in the cyclopentene series, based on identical degradative reactions[8,9] has since been verified,[12,13] his assignments are most probably correct. Verification of his structural assignments comes from two additional sources. The infrared spectra of the 88° ketone obtained in this investigation (identical to Bauer's 91° compound) and of 1-benzoyl-6-phenylcyclohexene[11,14] both showed their carbonyl absorption at lower frequencies (1660 and 1655 cm.$^{-1}$, respectively) than did Parham's 110° ketone (1682 cm.$^{-1}$). The latter position is characteristic of ordinary aralkyl ketones and thus the infrared data support Bauer's assignment. Secondly, in an attempt to catalytically dehydrogenate the 88° ketone, disproportionation occurred and the only compound isolated was *cis*-1-phenyl-2-benzoylcyclohexane. If this product is pictured as arising from *cis* addition of hydrogen on the catalyst surface, it is more likely that ketone XIV rather than ketone XV would produce the *cis* isomer. Apparently the 1-phenyl-2-cyanocyclohexene was first isomerized by the Grignard reagent to the 6-cyano isomer.

All the other compounds isolated have been reported unequivocally in the literature with the exception of the products from 2-hydroxymethylenecyclohexanone. Since both products from the reaction of phenylmagnesium bromide with 2-hydroxymethylenecyclohexanone also are produced by addition of phenylmagnesium bromide to 2-benzalcyclohexanone, they must be products of 1,2- and 1,4-addition to this ketone. The infrared spectrum of the ketone and the ultraviolet spectrum of its 2,4-dinitrophenylhydrazone are consistent with the formulation IV. The hydrocarbon III had an ultraviolet spectrum very similar to that of 2-benzylidenecyclohexene (XVII),[15] and was converted upon treatment with palladium to 2-benzylbiphenyl (XVIII). This latter hydrocarbon has been reported as a by-product of the benzylation of biphenyl and was assigned an "iso" struc-

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[8] E. Bauer, *Ann. chim.*, [9] **1**, 343 (1914).

[9] This degradation procedure has been reviewed recently: R. Adams, "Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1957, Vol. IX, p. 1.

[10] F. S. Kipping and W. H. Perkin, Jr., *J. Chem. Soc.*, **57**, 13 (1890).

[11] W. E. Parham, W. N. Moulton and A. Zuckerbraun, *J. Org. Chem.*, **21**, 72 (1956).

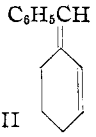
[12] H. A. Weidlich and M. Meyer-Delius, *Ber.*, **74B**, 1195 (1941).

[13] R. C. Fuson and M. W. Farlow, THIS JOURNAL, **56**, 1593 (1934).

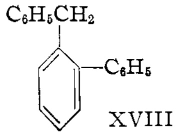
[14] We are pleased to acknowledge Dr. Parham's generous coöperation in furnishing us samples of his ketones.

[15] E. A. Braude and J. A. Coles, *J. Chem. Soc.*, 2014 (1950).

ture[16]; most probably it is the *o*-isomer and infrared examination confirms the *o*-orientation of the groups.



XVII



XVIII

Experimental[17]

Reaction of 2-Hydroxymethylenecyclohexanone with Phenylmagnesium Bromide.—A solution of 22.1 g. (0.16 mole) of 2-hydroxymethylenecyclohexanone[18] in 100 ml. of dry benzene was added to a solution of 350 ml. of 3 *M* phenylmagnesium bromide[19] in 250 ml. of dry benzene. This mixture was heated under reflux for 24 hours and decomposed with ice and hydrochloric acid. The organic extracts were then steam distilled and the residue (45 g.), after drying, was dissolved in petroleum ether and chromatographed on alumina. The first 1100 ml. contained 19 g. (48%) of a viscous oil which upon distillation yielded **2-phenyl-3-benzylidenecyclohexene**, b.p. 150° (0.4 mm.), n^{20}_{D} 1.6450; λ_{max} 278, ϵ_{max} 18,400 (ethanol).

Anal. Calcd. for $C_{19}H_{18}$: C, 92.72; H, 7.28. Found: C, 92.78; H, 7.34.

Treatment of this material with palladium-on-charcoal in boiling *p*-cymene for 4 hours yielded a white solid, m.p. 54–56° (from ethanol), which is assigned the structure of **2-benzylbiphenyl**. This material has been reported[16] to melt at 54°.

Anal. Calcd. for $C_{19}H_{16}$: C, 93.44; H, 6.56. Found: C, 93.17; H, 6.66.

Continued elution with progressively increasing amounts of benzene in the petroleum ether eluted 9.3 g. (23%) of **2-benzhydrylcyclohexanone**, m.p. 108–110° (from ethanol).

Anal. Calcd. for $C_{19}H_{20}O$: C, 86.65; H, 7.27. Found: C, 86.36; H, 7.58.

It formed a **2,4-dinitrophenylhydrazone**, m.p. 202–204° (from ethanol–ethyl acetate); λ_{max} 365, ϵ_{max} 8500 (ethanol).

Anal. Calcd. for $C_{25}H_{24}N_4O_4$: C, 67.52; H, 5.41; N, 12.61. Found: C, 67.95; H, 5.81; N, 12.54.

Finally elution with 1:1 benzene:ethyl acetate removed 4.4 g. (10%) of a yellow oil, b.p. 166–172° (1.0 mm.), which crystallized from methanol, m.p. 146–148°. Its infrared spectrum showed all the bands recorded[1c] for **1-phenyl-2-(α-hydroxybenzyl)-cyclohexanol**, m.p. 148–149°.

Reaction of 2-Benzalcyclohexanone with Phenylmagnesium Bromide.—A solution of 5.6 g. (0.03 mole) of 2-benzalcyclohexanone[20] in 50 ml. of dry ether was added slowly to 15 ml. of 3 *M* ethereal phenylmagnesium bromide. The resulting solution was boiled for 4 hours and decomposed in the usual manner. The organic product was purified by chromatography on alumina to yield 4.6 g. (52%) of **2-phenyl-3-benzylidenecyclohexene** and 2.4 g. (30%) of **2-benzhydrylcyclohexanone**. Both products were identical to those obtained from **2-hydroxymethylenecyclohexanone**. When 2.0 g. of cuprous chloride was added to the Grignard reaction, the ketone yield was increased to 42% and the hydrocarbon yield was reduced to 24%.

Ethyl Benzoylacetate and Phenylmagnesium Bromide.—The same general procedure was followed using 19.2 g. (0.1 mole) of ethyl benzoylacetate except that the mixture was refluxed for 18 hours. Upon concentration of the organic extracts a gummy material was obtained which solidified when triturated with petroleum ether. Upon recrystallization from ethanol, white crystals, m.p. 135–139°, were obtained; yield 20.2 g. (56%). Recrystallization from ligroin raised the melting point to 140–142°; **1,1,3,3-tetraphenylpropen-1-ol**[21] melts at 138°. Upon treatment with acetic anhydride and recrystallization from ethanol, a white solid, m.p. 164–166°, was obtained; **tetraphenylallene**[21] melts at 164°.

Dibenzoylmethane and Phenylmagnesium Bromide.—The same procedure was employed as with ethyl benzoylacetate using 22.4 g. (0.1 mole) of dibenzoylmethane. Distillation of the oily reaction product yielded only 12.8 g. (45%) of **β-phenylchalcone**, m.p. 85–87° (lit.[22] m.p. 88°) and an intractable residue. When the oily residue (36 g.) was first treated with acetic anhydride to effect dehydration of any alcoholic materials and then chromatographed, 11 g. (33%) of 1,1,3-triphenylindene, m.p. 132–134° (lit.[21] m.p. 134°) was obtained in addition to 16.1 g. (57%) of **β-phenylchalcone**. The identity of the indene was established by comparison with an authentic sample.[21]

Ethyl Acetoacetate and Phenylmagnesium Bromide.—The general procedure was employed with 13 g. (0.1 mole) of ethyl acetoacetate. Again the reflux period was 18 hours; distillation produced two fractions: (1) **benzophenone** (1.3 g., 7%), identified as its 2,4-dinitrophenylhydrazone and (2) **dypnone**, also identified as the **2,4-dinitrophenylhydrazone**, m.p. 167–169° dec.

Anal. Calcd. for $C_{22}H_{18}N_4O_4$: C, 65.66; H, 4.51; N, 13.92. Found: C, 65.69; H, 4.53; N, 14.24.

The distillation residue was chromatographed on alumina and 3.2 g. (17%) of a solid was eluted with ligroin. This material, **2,2-diphenylbutyrophenone**, along with its oxime was identical with authentic samples. A yellow **2,4-dinitrophenylhydrazone**, m.p. 185°, also was prepared.

Anal. Calcd. for $C_{28}H_{24}N_4O_4$: C, 69.99; H, 5.03. Found: C, 70.40; H, 5.37.

Acetylacetone and Phenylmagnesium Bromide.—The general procedure outlined for ethyl benzoylacetate was followed using 10 g. (0.1 mole) of acetylacetone. The oily reaction product showed hydroxyl absorption in its infrared spectrum and was dehydrated by boiling with 30 ml. of acetic anhydride containing a drop of sulfuric acid. The product of this reaction was distilled to yield 1 g. (8%) of **acetophenone** and 5.5 g. (25%) of **2,4-diphenyl-1,3-pentadiene**, b.p. 110–112° (0.03 mm.), n^{20}_{D} 1.6109, whose infrared spectrum was identical to that of an authentic sample.[23]

Preparation of 4-Phenyl-3-penten-2-one.—To a solution of the Grignard reagent prepared from 79 g. (0.5 mole) of bromobenzene, 12 g. (0.5 g. atom) of magnesium turnings and 300 ml. of dry ether was added 10 g. (0.1 mole) of acetylacetone in 50 ml. of ether. The mixture was boiled under reflux for 3 hours and decomposed with iced hydrochloric acid. The organic extracts were steam distilled and the residue was dissolved in ether and dried as was the distillate. Both the distillate and residue contained a hydroxy ketone, presumably 4-phenyl-4-hydroxy-2-pentanone. Treatment of this oil with acetic anhydride and a drop of sulfuric acid produced 4-phenyl-3-penten-2-one as a yellow oil; yield 5.2 g. (32%). It formed an **oxime**, m.p. 192° (lit.[24] m.p. 191°) and a dark red **2,4-dinitrophenylhydrazone**, m.p. 183° dec.

Anal. Calcd. for $C_{17}H_{16}N_4O_4$: C, 59.99; H, 4.74; N, 16.46. Found: C, 59.77; H, 4.79; N, 16.25.

Reaction of Ethyl 2-Cyclohexanone-1-carboxylate with Phenylmagnesium Bromide.—A solution of 17 g. (0.1 mole) of ethyl 2-cyclohexanone-1-carboxylate[25] in 100 ml. of dry benzene was added slowly to a solution of 175 ml. (0.5 mole) of 3 *M* ethereal phenylmagnesium bromide in 200 ml. of dry benzene. The resulting mixture was heated under reflux for six hours and then decomposed with iced hydrochloric acid. The oil obtained after steam distillation was dried and chromatographed on alumina using 1:1 petroleum ether–benzene as eluent. The first material eluted was a yellow oil that distilled at 125° (1 mm.) and crystallized upon chilling. Recrystallization from petroleum ether furnished white prisms of **1-phenyl-2-benzoylcyclohexene**, m.p. 87–88°, yield 8.5 g. (33%). The infrared spectrum of this material measured as a Nujol mull showed strong carbonyl absorption at 1652 cm.$^{-1}$ (CCl_4 solution, 1660 cm.$^{-1}$).

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[16] M. Goldschmidt, *Monatsh.*, **2**, 432 (1881); J. B. Lal and S. Dult, *J. Indian Chem. Soc.*, **12**, 384 (1935).

[17] We are indebted to Dr. Keith S. McCallum for infrared interpretations.

[18] Pl. A. Plattner, P. Treadwell and C. Scholz, *Helv. Chim. Acta*, **28**, 771 (1945).

[19] Arapahoe Special Products, Inc., Boulder, Colorado.

[20] H. O. House and R. L. Wasson, THIS JOURNAL, **78**, 4394 (1956).

[21] D. Vorlander, J. Osterburg and O. Meye, *Ber.*, **56**, 1136 (1923).

[22] G. R. Clemo, R. Raper and A. C. Robson, *J. Chem. Soc.*, 431 (1939).

[23] J. P. Freeman, *J. Org. Chem.*, **22**, 1608 (1957).

[24] J. D. A. Johnson and G. A. R. Kon, *J. Chem. Soc.*, 2748 (1926).

[25] A. H. Blatt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 531.

Anal. Calcd. for $C_{19}H_{18}O$: C, 86.99; H, 6.91. Found: C, 87.06; H, 7.83.

The second material eluted was a gummy solid which yielded 3.6 g. of microscopic white crystals of **1,5-dibenzoylpentane,** m.p. 65–67° (lit.[8] m.p. 64°), upon crystallization from petroleum ether.

Anal. Calcd. for $C_{19}H_{20}O_2$: C, 81.43; H, 7.14. Found: C, 81.53; H, 7.27.

It formed a **bis-2,4-dinitrophenylhydrazone,** m.p. 235° dec.

Anal. Calcd. for $C_{31}H_{28}N_8O_8$: C, 58.12; H, 4.41. Found: C, 58.13; H, 4.67.

An additional 2.3 g. of this diketone was obtained by chromatography of the distillation residue; total yield 5.9 g. (21%). Additional oily material whose infrared spectrum indicated the presence of hydroxyl groups was obtained by exhaustive elution of the column, but identification was not possible.

Disproportionation of 1-Phenyl-2-benzoylcyclohexene.—Two grams of the 88° ketone was dissolved in 30 ml. of *p*-cymene containing 0.2 g. of palladium-on-charcoal and the resulting mixture was heated overnight at reflux under dry nitrogen. Upon filtration and concentration, a gummy yellow solid was obtained which produced white needles, m.p. 116–117°, upon recrystallization from methanol.

Anal. Calcd. for $C_{19}H_{20}O$: C, 86.32; H, 7.63. Found: C, 86.67; H, 8.07.

***cis*-1-Phenyl-2-benzoylcyclohexane** is reported[26] to melt at 116.5–117°. An authentic sample was prepared by addition of phenylmagnesium bromide to benzoylcyclohexene[26] and proved to be identical to the disproportionation product.

Dehydrohalogenation of 1-Phenyl-2-bromo-2-benzoylcyclohexane.—In an attempt to obtain 1-phenyl-2-benzoylcyclohexene by an independent route, a sample of 1-phenyl-2-bromo-2-benzoylcyclohexane[26] was prepared and refluxed with 2,6-lutidine. Upon evaporation of the solvent a dark red solid was obtained which yielded white crystals, m.p. 100–102°, upon recrystallization from ether. Its infrared spectrum was identical to that of **1-benzoyl-6-phenylcyclohexene** previously obtained by addition of phenylmagnesium bromide to 6-phenyl-1-cyanocyclohexene,[11] m.p. 95–96°. The reason for the difference in melting points is not known.

Reaction of Ethyl 2-Cyclopentanone-1-carboxylate with Phenylmagnesium Bromide.—The same procedure was used as for the cyclohexanone derivative, employing 175 ml. of 3 *M* phenylmagnesium bromide solution and 15.6 g. (0.1 mole) of ethyl 2-cyclopentanone-1-carboxylate. After steam distillation, the residue was taken up in ligroin and chilled. A white solid precipitated and was recrystallized from alcohol, m.p. 213–215°, yield 1.4 g. Its infrared spectrum showed a strong unassociated hydroxyl band at 3500 cm.$^{-1}$. An additional 2 g. was obtained during chromatography of the filtrate; yield 3.4 g. (8%).

Anal. Calcd. for $C_{30}H_{30}O_2$: C, 85.27; H, 7.16. Found: C, 84.96; H, 7.38.

1,1,6,6-Tetraphenylhexane-1,6-diol is reported[27] to melt at 212°. Upon treatment with acetic acid, a white solid, m.p. 107–108°, was obtained. 1,1,6,6-Tetraphenyl-1,5-hexadiene is reported[27] to melt at 106°. The diol was identical to an authentic sample prepared by the reaction of phenylmagnesium bromide with diethyl adipate.

The remaining ligroin solution was chromatographed on alumina. An oil, yield 6 g. (24%), whose infrared spectrum showed intense carbonyl absorption at 1660 cm.$^{-1}$ (cap. layer) was eluted first and converted to its 2,4-dinitrophenylhydrazone, m.p. 174° dec.

Anal. Calcd. for $C_{24}H_{20}N_4O_4$: C, 67.27; H, 4.71. Found: C, 67.44; H, 4.89.

The 2,4-dinitrophenylhydrazone of 1-phenyl-2-benzoylcyclopentene is reported[12] to melt at 173°. An authentic sample of this derivative was prepared and the two samples proved to be identical. Continued elution with ether yielded 2.2 g. (8%) of **1,4-dibenzoylbutane,** m.p. 104–106° (lit.[28] m.p. 106–107°).

Nine fractions from the chromatographic column that came off between 1-phenyl-2-benzoylcyclopentene and 1,4-dibenzoylbutane were combined (wt. 0.6 g.) and treated with 2,4-dinitrophenylhydrazine reagent. An orange-red dinitrophenylhydrazone, m.p. 219–220°, isomeric with that from the phenylbenzoylcyclopentene, was obtained. The identity of this compound is unknown.

Anal. Calcd. for $C_{24}H_{20}N_4O_4$: C, 67.29; H, 4.67; N, 13.08. Found: C, 66.90; H, 4.65; N, 12.66.

Reaction of 1-Phenyl-2-benzoylcyclohexene with Phenylmagnesium Bromide.—A mixture of 5.2 g. (0.02 mole) of 1-phenyl-2-benzoylcyclohexene and 15 ml. of 3 *M* phenylmagnesium bromide was heated in 70 ml. of dry ether for 4 hours. The mixture was worked up in the usual manner and the crude product (5.5 g.) was heated for 30 minutes in 25 ml. of acetic anhydride containing two drops of sulfuric acid. The product from this treatment (3.7 g.) was chromatographed to give 1.6 g. of a hydrocarbon fraction which was heated in *p*-cymene with 0.2 g. of palladium-on-charcoal to produce a white solid, m.p. 122–126°. Recrystallization from methanol produced white crystals of 2-phenyltriphenylmethane, m.p. 136–138° (lit.[29] m.p. 138°). Its infrared spectrum was identical to that of an authentic sample.

A small ketonic fraction was eluted but could not be positively identified. Its infrared spectrum was very similar to but not identical to that of 1-phenyl-6-benzoylcyclohexene. It most probably was a mixture of materials.

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[CONTRIBUTION FROM THE IPATIEFF HIGH PRESSURE AND CATALYTIC LABORATORY, DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

Isomerization of Saturated Hydrocarbons. XVI.[1] The Aluminum Bromide Catalyzed Isomerization of Ethyl-β-C^{14}-cyclohexane

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Aluminum bromide catalyzed isomerization of ethyl-β-C^{14}-cyclohexane promoted by *sec*-butyl bromide was studied. The relative concentrations of a new species of ethylcyclohexane and 1,2-, 1,3-, and 1,4-dimethylcyclohexanes were found to be in the order of, although the first two compounds exceed, their thermodynamic equilibrium concentrations. About 9–11% of the C^{14} was found in the ring of the dimethylcyclohexanes, which is equivalent to 12–15% of isotopic equilibration. The mechanism of isomerization is discussed and compared with that of hydroisomerization.

In a previous paper of this series[1] it was reported that ethyl-α- and ethyl-β-C^{14}-cyclohexane undergo a hydroisomerization reaction at 360° in the presence of a nickel–silica–alumina catalyst. The prod-

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(1) For paper XV of this series see H. Pines and A. W. Shaw, THIS JOURNAL, **79**, 1474 (1957).

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