last two cases, the base and triethyl orthoformate concentrations were $0.65M$ and $0.78M$, respectively.

Radioactivity measurements. The tritium activities of the compounds were determined by the liquid scintillation method[23] employing toluene as the organic solvent. In general, counting efficiencies were about 20%. All net counting rates were converted to disintegrations per minute (d.p.m.) by measurement of the exact counting efficiencies with calibrated H^3 solutions.

Hydrogen exchange between fluoroform and deuterium oxide catalyzed by 1.11N sodium hydroxide. A stainless steel pressure vessel was charged with 90 ml. of $1.11N$ sodium hydroxide in deuterium oxide. The vessel was pressured up to 520 p.s.i.g. with 42 g. (0.60 mole) of fluoroform then shaken for 1121 hr. at 15–25°. From time to time, small gas samples were taken *via* a needle valve. After 1121 hr., <0.05% exchange could be detected by mass spectrometric analysis. Titration of the fluoroform saturated solution after venting showed that 98% of the sodium hydroxide charged was present. A qualitative test for fluoride ion (titanium(IV); hydrogen peroxide) was negative.

Hydrogen exchange between chloroform and deuterium oxide catalyzed by 1.11N sodium hydroxide. A heterogeneous mixture of chloroform (0.50 mole) and $1.11N$ sodium hydroxide (20.0 ml.) in deuterium oxide was shaken vigorously at 25° for 2 hr. The chloroform, dried over calcium chloride and distilled, had undergone complete exchange with the solvent according to mass spectrometric analysis. Titration of the aqueous layer showed that only 3.3% of the chloroform had undergone decomposition to formate salts.

Hydrogen exchange between pentafluoroethane and deuterium oxide catalyzed by sodium hydroxide. A glass ampoule was charged with 5.0 ml. of $1.65N$ sodium hydroxide in deuterium oxide, 5.0 ml. dioxane, and 2.0 g. (0.0167 mole) of pentafluoroethane.[24] The mixture was shaken at room temperature for 22 days. An infrared examination of the recovered pentafluoroethane (10 cm. gas cell) showed no diminution in the intensity of the single sharp carbon-hydrogen peak at 3.3 μ and no C-D band. A qualitative test on the aqueous layer (which was saturated with pentafluoroethane) indicated that no fluoride ion was produced. Likewise, the recovered pentafluoroethane was free of tetrafluoroethylene as indicated by its infrared spectra and negative permanganate test.

Chloroform, when similarly treated, underwent complete exchange in <2 hours as determined by mass spectrometric analysis as previously described.

Hydrogen exchange between 1-H-heptafluoropropane and deuterium oxide catalyzed by sodium hydroxide. A glass ampoule was charged with 5.0 ml. of $1.65N$ sodium hydroxide in deuterium oxide, 5.0 ml. dioxane and 6.5 g. (0.038 mole) of 1-H-heptafluoropropane.[24] The mixture was shaken at room temperature for 21 days. The recovered gas, examined by infrared spectroscopy, showed no detectable sign of exchange. Likewise, no hexafluoropropene, resulting from β-elimination, was detectable. The aqueous layer was free of fluoride ion.

Chloroform, when similarly treated, underwent complete exchange in <2 hours as determined by mass spectrometric analysis as previously described.

Attempted generation of heptafluoro-n-propyl anion from phenylheptafluoro-n-propylcarbinol and aqueous sodium hydroxide. One gram of the subject carbinol when suspended in 5 ml. of $1.3N$ sodium hydroxide formed a white solid which regenerated starting material on dilution with water. When the suspension was warmed on the steam bath for approximately one hour and the mixture diluted, only starting carbinol, free of benzaldehyde, was found in the oil layer (infrared spectrum and negative dinitrophenylhydrazine test). The aqueous layer, on acidification, gave a negative dinitrophenylhydrazine test. The white solid is presumably the sodium salt of the carbinol.

Attempted generation of dithioethylcarbene. To a suspension of 36 g. (0.32 mole) of potassium *t*-butoxide in 102 g. (1.24 moles) of dry cyclohexene was added 61.5 g. (0.314 mole) of triethyl orthothioformate. The mixture warmed up to 34° and turned red-brown. The mixture was stirred for 1 hr., warmed at 75–82° for an hour, cooled, and vacuum stripped. The 111 g. of volatiles contained approximately 93% of the starting cyclohexene contaminated with *t*-butyl alcohol. A total of 76% of the starting triethyl orthothioformate was recovered by petroleum ether extraction of the residual salts and distillation. There was no indication that dithioethylcarbene was trapped by cyclohexene.

Acknowledgment. The authors are very grateful to Dr. V. P. Guinn for the radioactivity measurements and to Dr. P. A. Wadsworth, Jr., for the mass spectrometric analyses. We are also grateful to Dr. H. E. De La Mare for criticism of this manuscript before publication.

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[23] V. P. Guinn, *Liquid Scintillation Counting,* Pergamon Press, New York, N. Y., 1958, p. 126.

[24] Procedure for preparation is published elsewhere. E. Bergman, *J. Org. Chem.,* **23,** 476 (1958).

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

The Magnesium Enolate of 2,2-Diphenylcyclohexanone[1,2]

JAMES P. COLLMAN

Received January 12, 1961

The magnesium enolate of 2,2-diphenylcyclohexanone (I) has been prepared and its reactions have been investigated. In addition, two benzal derivatives of 2,2-diphenylcyclohexanone have been examined.

This paper records the preparation and reactions of the magnesium enolate of 2,2-diphenylcyclohexanone (I). The 2,2-diphenylcycloalkanone ring systems have been the subject of several recent reports.[3–12] The anticipated steric hindrance of the adjacent bulky phenyl groups is manifested by the

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[1] From the Ph.D. dissertation of James P. Collman, University of Illinois, 1958. Inquiries should be addressed to James P. Collman, Department of Chemistry, University of North Carolina, Chapel Hill, N. C. The author wishes to express his gratitude to Professor R. C. Fuson, who directed his graduate studies during the period in which this work was carried out, and to the National Science Foundation for a fellowship.

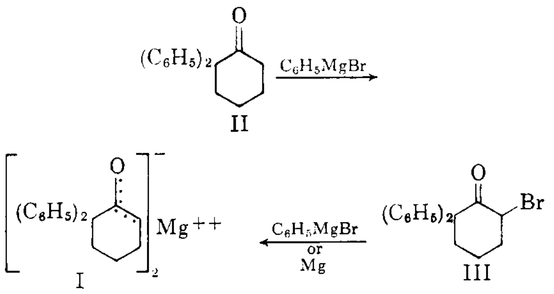
[2] Presented before the Organic Division of the American Chemical Society at the 134th Meeting at Chicago, Ill., September 7–12, 1958.

[3] N. R. Easton and S. J. Nelson, *J. Am. Chem. Soc.,* **75,** 640 (1953).

sluggish reactivity of the carbonyl group. For example, difficulty has been encountered in the preparation of carbonyl derivatives of the 2,2-diphenylcycloalkanones. Attempts to condense these ketones with organometallic reagents have met with little success. 2,2-Diphenylcyclohexanone failed to undergo the Reformatsky reaction.[5] When 7-bromo-2,2-diphenylcycloheptanone was treated with phenyllithium no 1,2-addition took place, but a lithium enolate was formed. This enolate reacted with acetyl chloride to form the enol acetate of 7-bromo-2,2-diphenylcycloheptanone.[8]

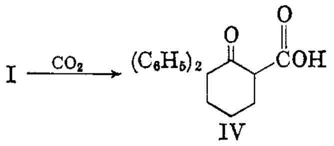
It seemed that the 2,2-diphenylcycloalkanones might form enolates that would provide a route to new derivatives of these ring systems. The readily prepared 2,2-diphenylcyclohexanone (II) was chosen as a starting point to explore this possibility.

The magnesium enolate of 2,2-diphenylcyclohexanone (I) was prepared by three conventional procedures. Treatment of 2,2-diphenylcyclohexanone (II) with the phenyl Grignard reagent produced the enolate I as a white suspension in ether. The action of magnesium on 6-bromo-2,2-diphenylcyclohexanone (III) resulted in the formation of the enolate. When the bromo ketone III was added to the phenyl Grignard reagent, a halógen exchange took place resulting in the slow formation of the enolate. The first method was found to be the most suitable.

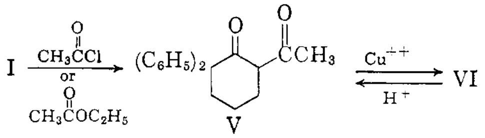


These three reactions have numerous analogies. The enolization of a hindered carbonyl group by a Grignard reagent has been illustrated many times.[13–15] The action of magnesium on an α-halo ketone was used by Malmgren,[16] in a study of the magnesium enolate derived from 3-bromocamphor. A recent report indicates that this type of reaction may be utilized in the preparation of magnesium enolates from simple aliphatic α-bromo ketones.[17] The halogen exchange between an α-bromo ketone and a Grignard reagent is the basis of the reductive debromination of α-bromo ketones.[18]

The enolate I was found to react as a "keto-Grignard" reagent, that is, to form C-condensation products. Carbonation of the enolate produced the β-keto acid IV in a 61% yield. This acid lost carbon dioxide at 135° to form 2,2-diphenylcyclohexanone (II).



Treatment of the enolate I with acetyl chloride resulted in the formation of the β-diketone V, which was purified as its copper chelate VI. The action of the enolate on ethyl acetate produced the β-diketone V in higher yield. The relatively low yields probably are best explained by the fast active-hydrogen reaction between the β-diketone and the enolate to form 2,2-diphenylcyclohexanone and the magnesium enolate of the β-diketone. The infrared spectrum of the β-diketone exhibits bands at 1720–1700 cm.$^{-1}$ and 1625–1580 cm.$^{-1}$, indicating a mixture of enol and keto forms. The spectrum of the copper chelate VI exhibits no absorption from 1600 cm.$^{-1}$ to 1800 cm.$^{-1}$ but shows strong bands at 1590 cm.$^{-1}$ and 1560 cm.$^{-1}$ These spectra are typical of a β-diketone and its copper chelate.[19]



The keto alcohol VII was formed by the interaction of the enolate with p-chlorobenzaldehyde. Attempted dehydration of this keto alcohol VII resulted in a reverse aldol reaction. When a pure sample of the adduct VII was heated at 175° for two hours in the presence of air, p-chlorobenzoic

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(4) P. N. Craig and I. H. Witt, *J. Am. Chem. Soc.*, **72**, 4925 (1950).

(5) G. Cauquil and J. Rouzard, *Compt. rend.*, **237**, 1720 (1953).

(6) W. B. Bennet and A. Burger, *J. Am. Chem. Soc.*, **75**, 84 (1953).

(7) R. E. Lyle, H. L. Fielding, G. Cauquil, and J. Rouzaud, *J. Org. Chem.*, **20**, 623 (1955).

(8) R. E. Lyle and R. A. Covey, *J. Am. Chem. Soc.*, **75**, 4973 (1953).

(9) R. E. Lyle, N. B. Martin, Jr., and H. L. Fielding, *J. Am. Chem. Soc.*, **75**, 4089 (1953).

(10) A. Burger and W. B. Bennet, *J. Am. Chem. Soc.*, **72**, 5414 (1950).

(11) G. Cauquil, J. Rouzaud, R. E. Lyle, H. L. Fielding, and G. G. Lyle, *Bull. soc. chim. France*, 513 (1955).

(12) H. E. Zaugg, M. Friefelder, and B. W. Horrom, *J. Org. Chem.*, **15**, 1191 (1950).

(13) E. P. Kohler, R. C. Fuson, and J. F. Stone, Jr., *J. Am. Chem. Soc.*, **49**, 3181 (1927).

(14) R. C. Fuson and R. W. Hill, *J. Org. Chem.*, **19**, 1575 (1954).

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

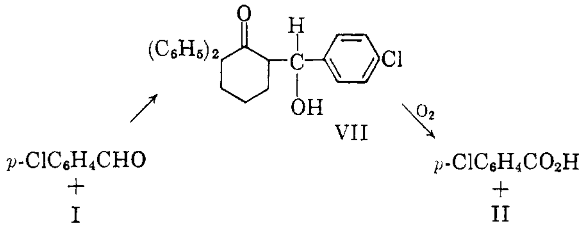
(16) S. M. Malmgren, *Ber.*, **35**, 3910 (1902).

(17) J. Colonge and S. Grenet, *Bull. soc. chim. France*, 1953, [10], C41.

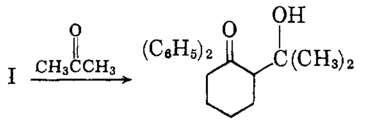
(18) C. H. Fisher, H. R. Snyder, and R. C. Fuson, *J. Am. Chem. Soc.*, **54**, 3665 (1932).

(19) H. F. Holtzclaw, Jr., and J. P. Collman, *J. Am. Chem. Soc.*, **79**, 3318 (1957).

acid and 2,2-diphenylcyclohexanone (II) were formed. A trace of base present on the porcelain reaction vessel may have catalyzed this transformation. The *p*-chlorobenzaldehyde was probably autoxidized to *p*-chlorobenzoic acid.

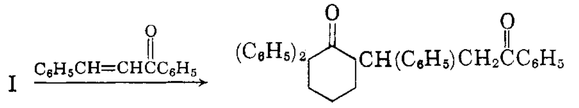


The enolate was found to add to acetone in a similar manner to form the keto alcohol VIII in a 58% yield. The infrared spectrum of this substance exhibits a carbonyl frequency at 1693 cm.$^{-1}$ This low value is probably a manifestation of intramolecular hydrogen-bonding.



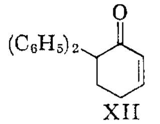
VIII

The enolate added to chalcone in the conjugate manner. The unsymmetrical 1,5-ketone IX was isolated in a 40% yield. The infrared spectrum of this substance shows carbonyl absorption bands at 1676 cm.$^{-1}$ and 1705 cm.$^{-1}$ which are assignable to the conjugated and the unconjugated carbonyl groups, respectively.



IX

In anticipation of the dehydration of the β-keto alcohol VII, *p*-chlorobenzaldehyde was condensed with 2,2-diphenylcyclohexanone in the presence of alcoholic potassium hydroxide to form the benzal derivative X. Benzaldehyde reacted to produce a similar α,β-unsaturated ketone XI. An examination of the ultraviolet spectra of these α,β-unsaturated ketones confirmed the expected exocyclic position of the olefinic bonds. The ultraviolet spectrum of 2,2-diphenyl-5-cyclohexenone (XII) was reported to exhibit a single maximum at 215 mμ with a molar extinction coefficient of 13,000.[5] The ultraviolet spectra of the α,β-unsaturated ketones X and XI exhibit single maxima at 292 mμ (ϵ 13,460) and 268 mμ (ϵ 7,810), respectively.



XII

EXPERIMENTAL[20]

Enolization of 2,2-diphenylcyclohexanone (II) *with the phenyl Grignard reagent.* To a solution of the phenyl Grignard reagent, prepared from 0.48 g. (0.02 g.-atom) of magnesium and 3.5 g. (0.022 mole) of phenyl bromide, in 25 ml. of ether was added a solution of 5.0 g. (0.02 mole) of 2,2-diphenylcyclohexanone[11] (II) in 75 ml. of ether. The mixture heated itself at reflux for 2 min. and was then stirred and heated at reflux for 90 min. At the end of this time, a white suspension was present in the flask. The enolate was not isolated but was used *in situ*.

The action of magnesium on 6-bromo-2,2-diphenylcyclohexanone (III). A 10-ml. portion of a solution of 3.29 g. (0.01 mole) of 6-bromo-2,2-diphenylcyclohexanone[9] (III) was dropped on 0.24 g. (0.01 g.-atom) of magnesium and a small crystal of iodine. The mixture was heated and, after 2 min., the iodine color suddenly disappeared. The remainder of the bromo ketone solution was added over a 15-min. period. The mixture was stirred and heated at reflux for 2 hr. The mixture was decomposed with dilute hydrochloric acid and ice, the organic layer was removed, and the aqueous layer was extracted with 25 ml. of ether. The ether portions were combined and dried over sodium sulfate. Removal of the ether gave an oil which formed white crystals from heptane; yield 1.98 g. (79%); m.p. 100–101°. A mixture melting point with an authentic sample of 2,2-diphenylcyclohexanone (II) was not depressed.

Treatment of 6-bromo-2,2-diphenylcyclohexanone (III) *with the phenyl Grignard reagent.* To a solution of 0.05 mole of the phenyl Grignard reagent, prepared from 1.2 g. of magnesium and 8.0 g. of phenyl bromide, in 75 ml. of ether was added 1.0 g. (0.003 mole) of 6-bromo-2,2-diphenylcyclohexanone (III). The mixture was stirred and heated at reflux for 5 hr. At the end of this time, the mixture was decomposed with dilute hydrochloric acid and ice. The organic layer was removed, the aqueous layer was extracted with 25 ml. of ether, the combined organic portions were dried, and the ether was removed. The oil crystallized from heptane to form white crystals melting at 99–100°. A mixture melting point with an authentic sample of 2,2-diphenylcyclohexanone (II) was not depressed.

Carbonation of the enolate I. To a suspension of 0.02 mole of the magnesium enolate[21] of 2,2-diphenylcyclohexanone (I) in 100 ml. of ether was added 10 g. of crushed solid carbon dioxide. The resulting slurry was stirred for 12 hr. and then decomposed with a mixture of dilute hydrochloric acid and ice. The ether layer was removed, and the aqueous layer was extracted with two 25-ml. portions of methylene chloride. The organic solutions were combined and dried. The solvent was removed and the residue was dissolved in 20 ml. of acetone. The acetone solution was combined with 50 ml. of heptane, and the mixture was cooled to 0°. The resulting white crystals were collected by filtration; yield 3.63 g. (61%). The pure 3,3-diphenyl-2-ketocyclohexane carboxylic acid (IV) melted at 135–136° with subsequent decarboxylation.

Anal.[22] Calcd. for $C_{19}H_{18}O_3$: C, 77.53; H, 6.16. Found: C, 77.61; H, 6.33.

The infrared spectrum[23] (Nujol) of this substance exhibits strong absorption bands at 2550–2700 cm.$^{-1}$, 1723 cm.$^{-1}$, 1703 cm.$^{-1}$, 1638 cm.$^{-1}$, and 1600 cm.$^{-1}$

Decarboxylation of 3,3-diphenyl-2-ketocyclohexanecarboxylic acid (IV). A 0.39-g. sample of the keto acid IV was heated until it fused. Carbon dioxide was evolved for 2 min. Recrystallization of the resulting paste afforded white crystals

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(20) All melting points are corrected.

(21) The enolate was prepared by enolization of 2,2-diphenylcyclohexanone with the phenyl Grignard reagent.

(22) The microanalyses were performed by Mr. Josef Nemeth, Miss C. Higham, and Mrs. Frederick Ju.

(23) The infrared spectra were determined by Mr. Paul McMahon and Miss Mary DeMott.

0.20 g.; m.p. 100–101°. A mixture melting point with an authentic sample of 2,2-diphenylcyclohexanone (II) was not depressed.

Condensation of the enolate I with ethyl acetate. To a suspension of 0.02 mole of the enolate[21] I in 100 ml. of ether was added a solution of 0.88 g. (0.01 mole) of ethyl acetate in 10 ml. of ether. The slurry was heated at reflux for 90 min., and then another 0.88 g. (0.01 mole) of ethyl acetate was added. The mixture was then heated at reflux for 3.5 hr. At the end of this time the mixture had become a clear solution. The solution was decomposed with ice and dilute hydrochloric acid, and the organic layer was removed. The aqueous layer was extracted with three 25-ml. portions of ether. The ether solutions were combined and dried. The ether was removed, and the residue was crystallized from methylene chloride-heptane; yield 4.12 g.

The crystalline mixture was dissolved in 35 ml. of acetone, water was added until the solution became cloudy, and then another 5 ml. of acetone was added. To this solution was added 1.5 g. of copper acetate monohydrate. The green mixture was shaken for 3 hr. and allowed to stand for 12 hr. The green solid was removed and washed with three 15-ml. portions of acetone. The green chelate was recrystallized from benzene-pentane; yield 1.89 g. (29%). The pure copper chelate of 6-acetyl-2,2-diphenylcyclohexanone (VI) melted at 264–265°.

Anal. Calcd. for $C_{40}H_{38}O_4Cu$: C, 74.36; H, 5.89. Found: C, 74.38; H, 5.96.

The infrared spectrum (chloroform) of this chelate exhibits strong absorptions at 1590 cm.$^{-1}$ and 1560 cm.$^{-1}$ No absorption band is present in the 1600 cm.$^{-1}$ to 1800 cm.$^{-1}$ region.

The acetone filtrate from the chelation reaction was distilled until half the acetone had been removed. Twenty milliliters of water was added, and the solution was cooled. The resulting white crystals were collected and dried; yield 2.6 g. (52% recovery); m.p. 96–97°. A mixture melting point with 2,2-diphenylcyclohexanone (II) was not depressed. A similar experiment with acetyl chloride gave the copper chelate (VI) of V in 6% yield.

Formation of 6-acetyl-2,2-diphenylcyclohexanone (V) *from its copper chelate.* To a suspension of 1.48 g. of the copper chelate VI in 25 ml. of ether was added 25 ml. of dilute hydrochloric acid. The mixture was shaken for 15 min. The organic layer was removed, extracted with sodium bicarbonate solution, and then extracted with water. The ether solution was dried, and the ether was removed. The solid was recrystallized from methylene chloride–heptane; yield 1.0 g. (74%). The pure 6-acetyl-2,2-diphenylcyclohexanone (V) melted at 104–104.5°.

Anal. Calcd. for $C_{20}H_{20}O_2$: C, 82.15; H, 6.89. Found: C, 82.07; H, 6.88.

The infrared spectrum (chloroform) of this substance exhibits broad absorption in the regions 1720–1700 cm.$^{-1}$ and 1625–1580 cm.$^{-1}$

Condensation of the enolate I with acetone. To a suspension of 0.02 mole of the enolate[21] I in 100 ml. of ether was added a solution of 2.32 g. (0.04 mole) of acetone in 10 ml. of ether. The slurry was heated at reflux for 14 hr. and decomposed with dilute hydrochloric acid and ice. The ether layer was removed, and the aqueous layer was extracted with 80 ml. of ether. The ether solutions were combined and dried. The ether was removed, and the white powder was recrystallized from heptane; yield 3.58 g. (58%). The pure 6-(α-hydroxyisopropyl)-2,2-diphenylcyclohexanone (VIII) melted at 93–94°.

Anal. Calcd. for $C_{21}H_{14}O_2$: C, 81.78; H, 7.84. Found: C, 81.66; H, 7.86.

The infrared spectrum (chloroform) of this substance exhibits absorption bands at 3520 cm.$^{-1}$ and 1693 cm.$^{-1}$

Condensation of the enolate I with p-chlorobenzaldehyde. To a suspension of 0.02 mole of the enolate[21] I in 100 ml. of ether was added a solution of 2.8 g. (0.02 mole) *p*-chlorobenzaldehyde in 50 ml. of ether at a rate to maintain boiling. Ten minutes were required for the addition. The resulting clear solution was heated at reflux for 1 hr. and decomposed with dilute hydrochloric acid and ice. Fifty milliliters of methylene chloride was added; the organic layer was removed and dried. The solvent was removed, and the white solid was recrystallized from ethanol-methylene chloride; yield 6.06 g. (76%). The pure 6-(α-hydroxy-*p*-chlorobenzyl)-2,2-diphenylcyclohexanone (VII) melted at 156–157.5°.

Anal. Calcd. for $C_{25}H_{23}O_2Cl$: C, 76.83; H, 5.89. Found: C, 76.73; H, 5.99.

The infrared spectrum (Nujol) of this substance shows strong absorption bands at 3520 cm.$^{-1}$ and 1697 cm.$^{-1}$

Pyrolysis of 6-(α-hydroxy-p-chlorobenzyl)-2,2-diphenylcyclohexanone (VII). A 1.0-g. sample of the adduct VII was placed in a porcelain dish which was covered with a watch glass and heated at 200° for 2 hr. When the system was cooled, white crystals were found on the watch glass. A light brown solid remained in the dish.

The white crystals were washed with 20 ml. of a 10% potassium carbonate solution. The basic filtrate was acidified with hydrochloric acid, cooled, and the white crystals were collected; yield 0.15 g.; m.p. 242–243°. A mixture melting point with an authentic sample of *p*-chlorobenzoic acid was not depressed.

The residue remaining in the dish was recrystallized from heptane; yield 0.29 g.; m.p. 100–101°. A mixture melting point with an authentic sample of 2,2-diphenylcyclohexanone (II) was not depressed.

1,4-Addition of the enolate I to chalcone. To a suspension of 0.02 mole of the enolate[21] I in 100 ml. of ether was added a solution of 4.16 g. (0.02 mole) of chalcone in 50 ml. of benzene. The mixture became a clear, light-yellow liquid and heated itself under reflux spontaneously for 3 min. The solution was heated at reflux for 1 hr. and decomposed by pouring on crushed ice and dilute hydrochloric acid. To the resulting slurry was added 50 ml. of methylene chloride, and the organic layer was removed. The organic solution was dried and the solvent removed. The oily residue was crystallized by dissolving it in 25 ml. of ether, adding pentane until an oil began to form and then adding 5 ml. of ethanol. The white crystals were collected and dried; yield 3.6 g. (40%). The pure β-(3,3-diphenyl-2-ketocyclohexyl)-β-phenylpropiophenone (IX) melted at 110–111°.

Anal. Calcd. for $C_{33}H_{30}O_2$: C, 86.46; H, 6.55. Found: C, 86.62; H, 6.60.

The infrared spectrum (chloroform) of this substance exhibits strong carbonyl absorption bands at 1705 cm.$^{-1}$ and 1676 cm.$^{-1}$

Condensation of p-chlorobenzaldehyde with 2,2-diphenylcyclohexanone (II). A mixture of 6.16 g. (0.04 mole) of *p*-chlorobenzaldehyde and 10.0 g. (0.04 mole) of 2,2-diphenylcyclohexanone (II) was dissolved in 100 ml. of hot ethanol. To this solution was added 30 ml. of a 4% solution of potassium hydroxide in ethanol. The mixture was allowed to stand at room temperature for 12 hr. The resulting suspension was cooled to 0° and filtered; the light yellow crystals were washed with 25 ml. of cold ethanol; yield 12.6 g. (84%). The pure 6-(*p*-chlorobenzylidene)-2,2-diphenylcyclohexanone (X) melted at 146–149°.

Anal. Calcd. for $C_{25}H_{21}OCl$: C, 80.54; H, 5.64. Found: C, 80.33; H, 5.74.

The infrared spectrum (chloroform) of this substance shows an absorption band at 1677 cm.$^{-1}$ assignable to the conjugated carbonyl group.

The ultraviolet spectrum (ethanol) shows a single absorption maximum at 292 mμ with a molar extinction coefficient of 13,460.

Condensation of benzaldehyde with 2,2-diphenylcyclohexanone (II). A mixture of 2.6 g. (0.024 mole) of benzaldehyde and 5.0 g. (0.02 mole) of 2,2-diphenylcyclohexanone (II) was condensed in the usual manner; yield 4.23 g. (62%). The pure 6-benzylidene-2,2-diphenylcyclohexanone (XI) melted at 109–110°.

Anal. Calcd. for $C_{25}H_{22}O$: C, 88.72; H, 6.55. Found: C, 88.67; H, 6.58.

The infrared spectrum (chloroform) of this substance shows absorption at 1677 cm.$^{-1}$ assignable to the conjugated carbonyl group.

The ultraviolet spectrum (ethanol) shows a single absorption maximum at 268 mμ with a molar extinction coefficient of 7810.

URBANA, ILL.

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

Some Condensation Reactions of Isopropylidene Malonate[1]

JOHN A. HEDGE,[2] CARL W. KRUSE,[3] AND H. R. SNYDER

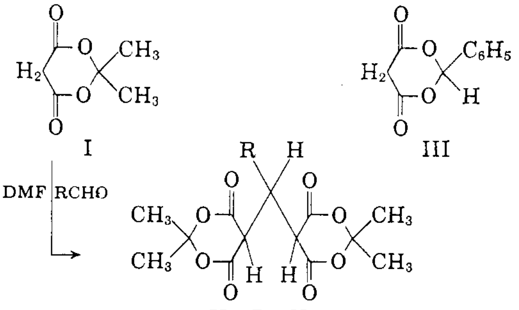
Received August 11, 1960

Isopropylidene malonate undergoes condensation with formaldehyde, acetaldehyde and benzaldehyde in dimethylformamide at room temperature with no added catalyst to give the corresponding aldol-Michael products in excellent yields. The condensation of isopropylidene malonate with other carbonyl compounds is also discussed.

Isopropylidene malonate (I) contains a methylene group of unusually great acidity and an ester group that undergoes hydrolysis under extremely mild conditions. These features make it appear an attractive alternative to malonic ester as a reagent for the synthesis of compounds containing very sensitive functions that might be altered under the conditions of the ordinary malonic ester syntheses. Some reactions of the reagent I with carbonyl compounds and alkyl halides have been reported[4-7]; in this paper several new aldol and Michael condensation products of isopropylidene malonate and of the similar ester, benzylidene malonate[8] (III) are described.

Although the structure of isopropylidene malonate (I) has been proved conclusively,[4] benzylidene malonate has been regarded[8,9] as a carboxy-β-lactone as recently as 1954, this formulation being patterned after the "Meldrum's Acid" structure originally suggested[10] for I. To make certain that III is the analog of I, its infrared spectrum was examined; the absence of carboxyl bands confirmed the structure III.

Condensations of I with aqueous formaldehyde, with acetaldehyde, and with benzaldehyde, all in dimethylformamide (DMF) at room temperature and with no added catalyst, gave nearly quantitative yields of the aldol-Michael products II. The product IIb from acetaldehyde was also obtained in moderate yield from crotonaldehyde, obviously as the result of the occurrence of a reverse aldol reaction. Benzylidene malonate and formaldehyde also reacted readily to form the product similar to IIa.



I

III

IIa. R = H
b. R = CH_3
c. R = C_6H_5

When the reaction of benzaldehyde and isopropylidene malonate was carried out in dimethyl sulfoxide (DMSO) or glacial acetic acid, a mixture of the aldol-Michael product (IIc) and the unsaturated (aldol) product, isopropylidene benzalmalonate, was formed. These solvents evidently are less favorable to the Michael reaction than is dimethylformamide. The same solvent effect also was noted in the reaction of isopropylidene malonate with the less reactive aldehyde, *p*-nitrobenzaldehyde. With this combination in dimethyl sulfoxide only the unsaturated product, isopropylidene *p*-nitrobenzalmalonate, was obtained (74%), but in dimethylformamide a mixture of this substance and the Michael product formed. In dimethylformamide cinnamaldehyde reacted to form only the aldol product, isopropylidene cinnamalmalonate (82%). It is interesting that in this experiment, unlike that with crotonaldehyde, there was no indication of the formation of products resulting from a reverse aldol reaction. The reaction

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(3) Phillips Petroleum Co. Fellow, 1956-57.

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