

showed carbonyl absorption at 5.87 μ and strong absorption for the nitro groups at 6.58 and 7.42 μ .¹⁰ The n.m.r. spectrum exhibited a singlet at 1.59 p.p.m. for three methyl hydrogens, several peaks between 2.33 and 3.38 p.p.m. representing the one methinyl and four methylene hydrogens, and two groups of peaks between 6.90 and 7.90 p.p.m. for eight aromatic hydrogens.

Anal. Calcd. for $C_{17}H_{15}N_2O_5$: C, 62.19; H, 4.91; N, 8.51. Found: C, 62.20; H, 4.91; N, 8.48.

The semicarbazone, recrystallized from ethanol-water, melted at 165–166°.

Anal. Calcd. for $C_{18}H_{19}N_3O_5$: C, 56.10; H, 4.97; N, 18.17. Found: C, 56.27; H, 5.07; N, 18.16.

Synthesis of Ketone VI.—A mixture of 22.6 g. (0.22 mole) of acetylacetone, 17.5 g. (0.1 mole) of α,α' -dichloro-*p*-xylene, and 31.2 g. (0.2 mole) of anhydrous potassium carbonate in anhydrous ethanol was refluxed for 16 hr. The ethanol was removed, water was added, and the mixture was extracted with ether. The ethereal solution was dried and evaporated; the residue was recrystallized from methanol to afford 10.9 g. (50%) of 4,4'-phenylenedi-2-butanone, m.p. 53.5–55°, lit.¹² m.p. 55–56°. The bissemicarbazone, recrystallized from ethanol, melted at 208–210°, lit.²¹ m.p. 209°. The infrared spectrum showed carbonyl absorption at 5.80 μ .

(21) A. Seolomina, *Zh. Obshch. Khim.*, **36**, 1225 (1904).

Aldolization of 1,1-Diphenylpropanone by Grignard Reagents¹

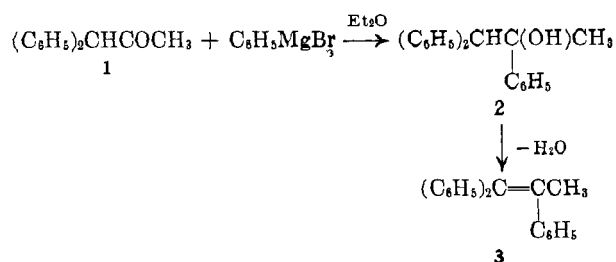
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The reaction of a series of organometallic compounds with 1,1-diphenylpropanone (1) has been investigated. Whereas methylmagnesium iodide, phenyllithium, and methyl bromoacetate in the presence of zinc added "normally" to ketone 1, both phenyl- and cyclohexylmagnesium bromide aldolized 1 to 1,1,5,5-tetraphenyl-4-methyl-3-penten-2-one (4). Chemical and spectral evidence for structure 4 is presented. The facile oxidative cleavage of 1,1-diphenylpropanone (1) to benzophenone in basic solution is also described.

In connection with our study of the mechanism of the rearrangement accompanying the addition of fluorine to 1,1-diarylethylenes,² it was necessary to prepare 1,1,2-triphenyl-1-propene (3). Although the synthesis of 3 had been described previously,³ we chose to prepare it by a different method starting with 1,1-diphenylpropanone (1). We planned to convert 1 to 1,1,2-triphenyl-2-propanol (2) with phenylmagnesium bromide and then dehydrate the carbinol to the desired propene 3. This two-step sequence was particularly attractive since, unlike the published procedure, it appeared readily adaptable to the preparation of a number of derivatives of 3 which would be required in a later investigation.



When 1,1-diphenylpropanone (1) was allowed to react with an approximately equimolar amount of ethereal phenylmagnesium bromide, the expected carbinol, 1,1,2-triphenyl-2-propanol (2), was obtained in only 8% yield; accompanying 2 was a new compound which was isolated in 30% yield. On the basis of its molecular formula, $C_{30}H_{26}O$, and the well-known ability of Grignard reagents to effect aldol condensations of ketones under certain circumstances,⁴ it appeared likely that this new material was the dehydration product of the ketol formed by self-condensation of 1. This

possibility was confirmed by the following chemical and spectral evidence which shows conclusively that the compound is 1,1,5,5-tetraphenyl-4-methyl-3-penten-2-one (4).

Compound 4 exhibited an intense band in the infrared at 5.95 μ , attributable to a conjugated carbonyl group, and its ultraviolet spectrum had λ_{max} 248 m μ (ϵ 12,900). The n.m.r. spectrum of 4 showed the presence of 20 aromatic protons centered at τ 2.82, two nonequivalent benzhydrylic protons at τ 5.20 and 4.98, and one olefinic and three methyl protons at τ 4.09 and 7.82, respectively. The α,β -unsaturated ketone 4 slowly afforded a 2,4-dinitrophenylhydrazone, decolorized both bromine and potassium permanganate solutions, and, as expected, gave no coloration with tetranitromethane.⁵

Hydrogenation of 4 in ethanol or glacial acetic acid with 10% palladium on charcoal invariably resulted in reduction to 1,1,5,5-tetraphenyl-4-methyl-2-pentanone (5) in 77–85% yield (see Chart I) regardless of whether the reaction was run for 2.5 or 24 hr. Ketone 5 displayed a band at 5.82 μ in the infrared and, although the compound did form an oxime, it appeared to contain a hindered carbonyl group as evidenced by its complete resistance to both 2,4-dinitrophenyl- and *p*-nitrophenylhydrazone formation and to attempted Clemmensen reduction.

On the other hand, Wolff-Kishner reduction of 5 was successful and afforded 1,1,5,5-tetraphenyl-2-methylpentane (6) in 46% yield. This reaction, however, took an unexpected course when the Huang-Minlon modification was employed; only diphenylmethane and 4,4-diphenyl-3-methylbutyric acid (7) were produced. Acid 7 was identical with an authentic sample whose preparation is described in a later section of this paper. Undoubtedly, the acid and diphenylmethane resulted from basic cleavage of 5, since these same products were obtained when the re-

(1) Supported by a research grant (NSF-G22020) of the National Science Foundation.

(2) J. Bornstein, M. R. Borden, F. Nunes, and H. I. Tarlin, *J. Am. Chem. Soc.*, **85**, 1609 (1963).

(3) D. Y. Curtin and M. J. Hurwitz, *ibid.*, **74**, 5381 (1952).

(4) Cf. S. O'Brien and D. C. C. Smith [*J. Chem. Soc.*, 2905 (1963)] for a recent example of such an occurrence.

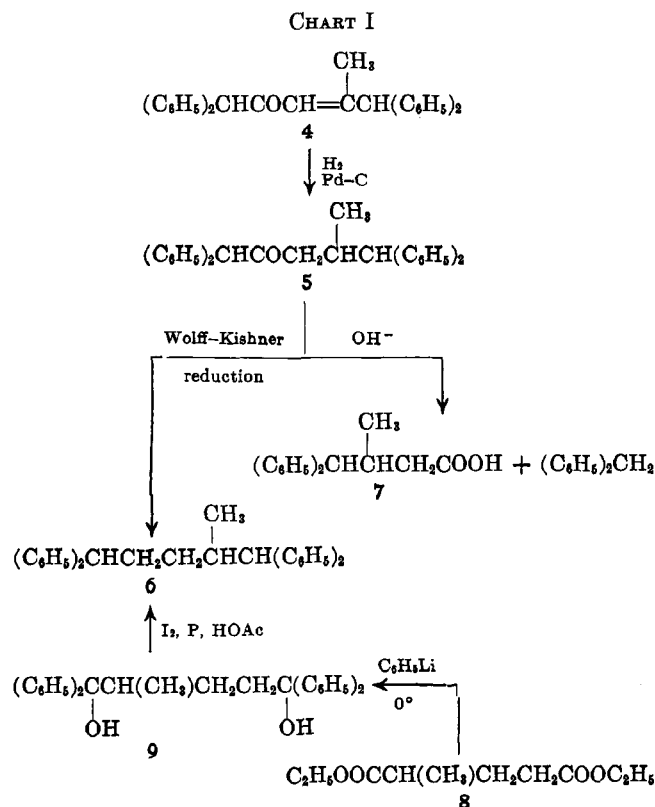
(5) H. Roth in Houben-Weyl, "Methoden der Organischen Chemie," Vol. II, 4th Ed., Georg Thieme Verlag, Stuttgart, 1953, p. 281.

TABLE I
REACTION OF 1,1-DIPHENYLPROPANONE WITH ORGANOMETALLIC COMPOUNDS^a

Reagent	Time, hr.	Addition product	Yields, % ^b	
			Addition	Aldolization to 4
CH ₃ MgI	1	(C ₆ H ₅) ₂ CHC(OH)(CH ₃) ₂ (10)	63	0
C ₆ H ₅ MgBr	1	(C ₆ H ₅) ₂ CHC(OH)(CH ₃)C ₆ H ₅ (2)	8	30
C ₆ H ₅ Li	1	(C ₆ H ₅) ₂ CHC(OH)(CH ₃)C ₆ H ₅ (2)	26	0
C ₆ H ₁₁ MgBr	1	...	0	14 ^c
BrZnCH ₂ COOCH ₃	3	(C ₆ H ₅) ₂ CHC(OH)(CH ₃)CH ₂ COOCH ₃ (11)	51 ^d	0

^a All reactions were carried out with approximately equimolar amounts of reactants in ether at reflux temperature. ^b Unless otherwise noted, per cent yields refer to purified products. ^c Cf. ref. 11. ^d Percentage is for the crude product, m.p. 54–57°; an analytical sample, recrystallized twice from ligroin, had m.p. 56.2–57.8°.

action was subsequently repeated in the absence of hydrazine hydrate.



A comparison sample of 1,1,5,5-tetraphenyl-2-methylpentane (**6**) was synthesized in over-all yield of 36% by reduction with phosphorus and iodine of 1,1,5,5-tetraphenyl-2-methylpentane-1,5-diol (**9**), which had been obtained by treatment of diethyl 2-methylglutarate (**8**) with an excess of ethereal phenyllithium in the cold. This compound was identical in all respects with the hydrocarbon prepared from **5** by Wolff-Kishner reduction.

It is noteworthy that the catalysts commonly used to effect the aldol condensation of aldehydes and ketones failed to bring about the self-condensation of 1,1-diphenylpropanone (**1**). Thus, in our hands, treatment of **1** with aluminum *t*-butoxide,⁶ potassium hydroxide, magnesium ethoxide, sodium ethoxide, sodium hydride, sulfuric acid, and dry hydrogen chloride gave none of the desired α,β -unsaturated ketone **4**; only unchanged starting ketone was recovered. When **1** was treated with sodium methylsulfinyl carb-

anion in dimethyl sulfoxide⁷ for 28 hr. at 100°, 50% of unchanged ketone was recovered along with a 20% yield of diphenylmethane, apparently formed by basic cleavage of the ketone; no aldolization was observed in this attempt, however.

In view of the unexpected aldolization of 1,1-diphenylpropanone (**1**) by phenylmagnesium bromide, it was of some interest to examine the action of other organometallic reagents on this ketone. Accordingly, a study was carried out with methylmagnesium iodide, phenyllithium, cyclohexylmagnesium bromide, and methyl bromoacetate in the presence of zinc. The reactions were conducted in ether under conditions comparable with those used with phenylmagnesium bromide. The results of these experiments are summarized in Table I. As Table I shows, methylmagnesium iodide and phenyllithium as well as methyl bromoacetate under conditions of the Reformatsky reaction gave only the corresponding 1,2-addition products, namely, 1,1-diphenyl-2-methyl-2-propanol (**10**), 1,1,2-triphenyl-2-propanol (**2**), and methyl 4,4-diphenyl-3-methyl-3-hydroxybutyrate (**11**),⁸ respectively. In contrast, the reaction of cyclohexylmagnesium bromide with **1** resulted exclusively in aldolization to **4**—a finding that is not surprising in the light of the observations made earlier with the comparatively less bulky aryl Grignard reagent.⁹ Actually, the α,β -unsaturated ketone **4** isolated in this instance was of poorer quality than that obtained originally with phenylmagnesium bromide. Whereas chromatographic analysis of the crude product from the reaction of cyclohexylmagnesium bromide failed to reveal the presence of any 1,2-addition product, it did uncover less than 1% of a substance melting at 187.2–188.4°. Its sharp melting point and elemental analysis led us to believe initially that this material was a pure compound. However, mass spectrometric analysis indicated that this material was a complex mixture.¹⁰ This finding coupled with a scarcity of material prompted us to discontinue our efforts to identify this contaminant.¹¹

(7) M. Chaykovsky and E. J. Corey, *J. Org. Chem.*, **28**, 254 (1963); C. Walling and L. Bollyky, *ibid.*, **28**, 256 (1963).

(8) Ester **11** proved especially useful since on saponification it afforded 4,4-diphenyl-3-methyl-3-hydroxybutyric acid, (C₆H₅)₂CHC(OH)(CH₃)CH₂COOH (**12**), which on reduction with phosphorus and iodine furnished an authentic sample of acid **7**, identical in all respects with the acid obtained earlier from the basic cleavage of ketone **5**. Acid **7** has been prepared by a different sequence by K. Ziegler, F. Crössmann, H. Kleiner, and O. Schäfer [*Ann.*, **473**, 25 (1929)].

(9) C. G. Gauerke and C. S. Marvel, *J. Am. Chem. Soc.*, **50**, 1178 (1928).

(10) We are indebted to Dr. Roland Gohlke, Dow Chemical Co., Wayland, Mass., for this analysis.

(11) The presence of this difficultly separable contaminant may possibly account for the low yield (14%) of purified **4** (Table I). Considerable difficulty and losses were experienced during the purification of **4**. In contrast, the purification of **4**, prepared from **1** and phenylmagnesium bromide was trouble free.

(6) We followed the procedure of W. Wayne and H. Adkins ["Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 367] who prepared dypnone from acetophenone with this catalyst.

The results of the present investigation strongly suggest that the greater steric bulk of the cyclic Grignard reagents is primarily responsible for the aldolization of 1,1-diphenylpropanone (1). Apparently, as the rate of addition to the hindered carbonyl group of 1 is decreased by the increasing steric requirements of the organometallic addend, enolization of 1 becomes the predominant reaction and aldolization may then ensue.¹²

It is worth pointing out that throughout this investigation small amounts of benzophenone were constantly encountered during the work-up of the reaction mixtures produced by reaction of the organometallic reagents with 1,1-diphenylpropanone (1). We believe the benzophenone arises from 1 by an autoxidative process, which probably proceeds by a base-catalyzed mechanism of the type proposed recently by Huffman and Elliott¹³ to explain the oxidative cleavage of diphenylacetaldehyde. Support for this pathway was obtained by passing a slow stream of oxygen through a dilute solution of 1 in 2% ethanolic potassium hydroxide for 15 hr.; benzophenone was formed in 37–42% yield.

Experimental Section¹⁴

Reaction of 1,1-Diphenylpropanone (1) with Phenylmagnesium Bromide. Formation of 1,1,5,5-Tetraphenyl-4-methyl-3-penten-2-one (4) and 1,1,2-Triphenyl-2-propanol (2).—To a stirred Grignard solution, prepared from 2.8 g. (0.115 g.-atom) of magnesium turnings and 20.0 g. (0.128 mole) of bromobenzene in 50 ml. of ether, was added in a nitrogen atmosphere and at reflux temperature during the course of 45 min. a solution of 21.0 g. (0.10 mole) of 1,1-diphenylpropanone in 100 ml. of ether. The resulting mixture was heated under reflux for 1 hr. and then cooled in an ice bath while 100 ml. of a saturated solution of ammonium chloride in ice-water was added slowly with stirring. The ether layer was removed and the aqueous phase was extracted twice with 40-ml. portions of ether. The combined ethereal extracts were washed with water, dried, and concentrated under reduced pressure to give 23.9 g. of a light yellow, semisolid residue. One recrystallization of this material from ethanol yielded 7.82 g. (39%) of crude 1,1,5,5-tetraphenyl-4-methyl-3-penten-2-one (4) as white crystals melting at 129–132°. A second recrystallization from the same solvent afforded 6.1 g. (30%) of 4: m.p. 132.8–134.0°; λ_{\max} 5.95 μ ; λ_{\max} 248 m μ (ϵ 12,900); n.m.r. (deuteriochloroform), τ 2.82 (20H), 5.20 (1H), 4.98 (1H), 4.09 (1H), 7.82 (3H).

Anal. Calcd. for C₃₀H₂₈O: C, 89.51; H, 6.51; mol. wt., 402.5. Found: C, 89.7; H, 6.6; mol. wt. (Rast), 386.

Treatment of a saturated ethanolic solution of ketone 4 with an equal volume of 2,4-dinitrophenylhydrazine reagent¹⁵ at room temperature for 20 hr. afforded the 2,4-dinitrophenyl-

hydrazone, m.p. 180–182°. The analytical sample, m.p. 183.2–184.0°, was isolated as deep yellow crystals after two recrystallizations from a 1:1 mixture of glacial acetic acid–ethanol.

Anal. Calcd. for C₂₆H₂₆N₄O₂: N, 9.62. Found: N, 9.81.

A 3.9-g. portion of the concentrated mother liquor from which 4 had crystallized was chromatographed on a column (30 X 2.5 cm.) of neutral alumina using successively hexane and mixtures of hexane–benzene and benzene–ethanol of increasing polarity as eluents. Thirty fractions were collected. Fractions 28–29 afforded 2.4 g. of a viscous oil from which 0.68 g. (8.3%) of 1,1,2-triphenyl-2-propanol (2), m.p. 83–85° (lit.¹⁶ m.p. 86–87°), λ_{\max} 2.74 μ , was isolated after two recrystallizations from hexane. Unchanged ketone 1 (13.5%, fractions 22–26), biphenyl (114 mg., fractions 10–11), and traces of benzophenone were also isolated.

1,1,2-Triphenyl-1-propene (3).—Dehydration of 2 was effected by heating under reflux for 6 hr. a 100-mg. quantity of the compound in 10 ml. of aqueous 20% sulfuric acid. The reaction mixture was cooled to room temperature, diluted with 10 ml. of water, and extracted with two 15-ml. portions of ether. The combined ether extracts were washed with water and dried. Removal of the solvent under reduced pressure gave 56 mg. of a white solid, m.p. 73–75°, after two recrystallizations from methanol. Chromatography of this material on neutral alumina using in succession hexane and hexane–benzene mixtures as eluents followed by one recrystallization from methanol raised the melting point of the 1,1,2-triphenyl-1-propene (3) to 87.0–88.0° (lit.³ m.p. 86–89°). The infrared spectrum of this compound was identical with the published spectrum.³

Hydrogenation of 4. Formation of 1,1,5,5-Tetraphenyl-4-methyl-2-pentanone (5).—A solution of 1.5 g. (3.73 mmoles) of 4 in 270 ml. of glacial acetic acid, to which 654 mg. of 10% palladium on charcoal had been added, was shaken with hydrogen at an initial pressure of 34 p.s.i. at room temperature for 4 hr. The mixture was filtered and the filtrate was heated to 80° and held at this temperature while sufficient water was added to develop a faint turbidity. After the mixture had been allowed to stand at room temperature for 36 hr., the white needles were collected by filtration and washed with water several times. The yield of 1,1,5,5-tetraphenyl-4-methyl-2-pentanone (5) was 1.28 g. (86%), m.p. 127.0–128.0°, λ_{\max} 5.82 μ . An analytical sample was obtained after two recrystallizations from ethanol, m.p. 128.2–129.2°.

Anal. Calcd. for C₃₀H₂₈O: C, 89.07; H, 6.97. Found: C, 89.19; H, 7.17.

The oxime of 5 had m.p. 158.6–160.0° after several recrystallizations from ethanol.

Anal. Calcd. for C₃₀H₂₉NO: N, 3.34. Found: N, 3.24.

Wolf-Kishner Reduction of 5. Formation of 1,1,5,5-Tetraphenyl-2-methylpentane (6).—A mixture of 350 mg. (0.87 mmole) of 5, 2.5 ml. of 85% hydrazine hydrate, and 10 ml. of triethylene glycol was stirred at 100–110° for 21 hr. The temperature of the reaction mixture was then raised slowly to 200° (ca. 2 hr.) while 2–3 ml. of distillate was collected. The clear solution was cooled to 100°, 287 mg. of sodium hydroxide pellets was added, and the resulting mixture was heated to 200–220° and held at this temperature for 22 hr. The reaction mixture was then cooled, diluted with an equal volume of water, and acidified with dilute hydrochloric acid. The resulting milky suspension was extracted with three 30-ml. portions of ether, and the combined ether extracts were washed successively with 30 ml. of 5% sodium hydroxide (in order to remove a small amount of acid 7) and water. Removal of the solvent from the dried ether extract gave 260 mg. of a colorless oil which solidified on standing overnight at room temperature. Recrystallization of the solid residue from methanol yielded 140 mg. (46%) of 1,1,5,5-tetraphenyl-2-methylpentane (6), m.p. 57–59°. A second recrystallization from the same solvent gave the analytically pure hydrocarbon, m.p. 58.2–60.0°, as white crystals.

Anal. Calcd. for C₃₀H₃₀: C, 92.26; H, 7.74. Found: C, 92.47; H, 7.60.

Compound 6 was shown by a mixture melting point determination and infrared spectral comparison to be identical with an authentic specimen whose preparation is described below.

Acidification with dilute hydrochloric acid of the sodium hydroxide extract from above precipitated 28 mg. (13%) of 4,4-diphenyl-3-methylbutyric acid (7), m.p. 116.0–117.5°, identical in all respects with the comparison sample prepared below.

(12) The enolization and aldolization of ketones by Grignard reagents are reviewed at length in M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall, Inc., New York, N. Y., 1954, p. 166.

(13) J. W. Huffman and R. P. Elliott, *Chem. Ind.* (London), 650 (1963).

(14) Melting points are corrected and boiling points are uncorrected. Thin layer chromatography was done with silica gel as adsorbent; iodine vapor was used to detect the various compounds. Gas chromatography was carried out on an F & M Model 500 gas chromatograph using a 2-ft. silicone gum rubber column with helium as the carrier gas. Infrared spectra were recorded on a Perkin-Elmer Model 137 Infracord and, unless otherwise specified, carbon tetrachloride was used as solvent. The ultraviolet spectra were obtained with a Perkin-Elmer Model 202 spectrometer with absolute ethanol as solvent. N.m.r. spectra were determined with a Varian Model A-60 spectrometer using tetramethylsilane as an internal standard. Sodium sulfate was employed as drying agent. 1,1-Diphenylpropanone (1), supplied by Matheson Coleman and Bell, was recrystallized from petroleum ether (b.p. 30–60°) and had m.p. 60–61° [E. M. Schultz and S. Mickey (ref. 6, p. 343) reported m.p. 60–61° for this ketone]. Elemental analyses were performed by Dr. S. M. Nagy of Massachusetts Institute of Technology and by Galbraith Laboratories, Inc., Knoxville, Tenn.

(15) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p. 111.

(16) J. Levy, *Bull. soc. chim. France*, [4] 29, 892 (1921).

Basic Cleavage of 5 to 4,4-Diphenyl-3-methylbutyric Acid (7) and Diphenylmethane.—A mixture of 600 mg. (1.48 mmoles) of **5**, 660 mg. of sodium hydroxide pellets, 6.0 ml. of 85% hydrazine hydrate, and 20 ml. of triethylene glycol was stirred successively at 100–110° for 2 hr. and at 195–200° for 40 hr.¹⁷ The cooled reaction mixture was diluted with water, acidified with dilute hydrochloric acid, and extracted with ether. The ether solution was washed once with water and then extracted with two 30-ml. portions of 5% sodium hydroxide. Acidification of the combined alkaline extracts with dilute hydrochloric acid precipitated 309 mg. (82%) of 4,4-diphenyl-3-methylbutyric acid (**7**), m.p. 117–118° (lit.⁸ m.p. 113°), which was shown by a mixture melting point determination and infrared spectral comparison to be identical with an authentic sample whose preparation is described below.

Concentration of the dried ether extract from above gave 33 mg. of a light yellow oil, the main component of which was shown by gas chromatography to be diphenylmethane. Thin layer chromatography (4:1 mixture of hexane–ethyl acetate developer) of the oil furnished additional evidence for the presence of this hydrocarbon.

When ketone **5** was heated at 120° for 2 hr. with sodium hydroxide in triethylene glycol in the absence of hydrazine hydrate both acid **7** and diphenylmethane were formed. However, this reaction, unlike the one carried out in the presence of hydrazine hydrate, gave lower yields of these products, which were of inferior quality.

1,1,5,5-Tetraphenyl-2-methylpentane-1,5-diol (9).—This reaction was carried out in an atmosphere of dry nitrogen. Phenyllithium, prepared from 9.6 g. (1.38 g.-atoms) of lithium wire, 102.0 g. (0.65 mole) of bromobenzene, and 300 ml. of ether, was cooled with stirring to 0° in an ice–salt bath and treated over a 30-min. period with a solution of 10.0 g. (0.050 mole) of diethyl 2-methylglutarate¹⁸ in 75 ml. of ether. The mixture was stirred an additional 2 hr. at 0° and then overnight at room temperature. The resultant suspension was filtered through glass wool onto cracked ice and the aqueous layer was separated and extracted with three 50-ml. portions of ether. The combined ether solutions were washed with water and dried. Removal of the ether gave 33.0 g. of an amber-colored, viscous oil, which was chromatographed twice on neutral alumina using in succession hexane and hexane–benzene and benzene–ethanol mixtures as eluents. 1,1,5,5-Tetraphenyl-2-methylpentane-1,5-diol (**9**) was obtained as a faint yellow glass, which successfully resisted all attempts to induce crystallization, yield 18.9 g. (89%), λ_{\max} 2.72 μ .

Anal. Calcd. for C₃₀H₃₀O₂: C, 85.28; H, 7.14. Found: C, 85.24; H, 6.99.

The foregoing preparation was unsuccessful when phenylmagnesium bromide was used in place of phenyllithium. A considerable amount of carbonyl-containing material was always isolated when the reaction of the diester with the Grignard reagent was carried out under a variety of conditions.

Reduction of 9 to 1,1,5,5-Tetraphenyl-2-methylpentane (6).—A mixture of 8.8 g. (0.021 mole) of **9**, 7.95 g. of red phosphorus, and 3.86 g. of iodine in 120 ml. of glacial acetic acid containing 1 ml. of water was heated under reflux for 24 hr. The resulting suspension was cooled to room temperature and filtered through Celite, and the filtrate was treated with 125 ml. of 10% sodium bisulfite to destroy excess iodine. The canary yellow mixture was extracted three times with 75-ml. portions of ether. The combined extracts were washed successively with three 50-ml. portions of 2.5% sodium bisulfite, two 50-ml. portions of 5% sodium hydroxide, and, finally, with water. Concentration of the dried extract gave 7.23 g. of a colorless viscous oil, a 4.5-g. portion of which was chromatographed on a column of neutral alumina using hexane and hexane–benzene mixtures as eluents. This operation gave 4.4 g. of colorless oil which was taken up in 35 ml. of absolute ethanol. Refrigeration of this solution for 2 days afforded 2.1 g. (41.5%) of 1,1,5,5-tetraphenyl-2-methylpentane (**6**), m.p. 58–60°, identical in all respects with the hydrocarbon obtained by Wolff–Kishner reduction of **5** as described above.

Reaction of 1,1-Diphenylpropanone (1) with Methylmagnesium Iodide. Formation of 1,1-Diphenyl-2-methyl-2-propanol (10).—The reaction of 5.25 g. (0.025 mole) of 1,1-diphenylpro-

panone in 30 ml. of ether with methylmagnesium iodide, prepared from 0.7 g. (0.029 g.-atom) of magnesium turnings, 4.55 g. (0.032 mole) of methyl iodide, and 25 ml. of ether, was effected in an atmosphere of nitrogen under the same conditions described above for the reaction of the ketone with phenylmagnesium bromide. The crude reaction product (5.6 g.), which was found by infrared analysis to contain some starting ketone, was distilled under reduced pressure through a semimicro column. The yield of 1,1-diphenyl-2-methyl-2-propanol (**10**), b.p. 135–139° (3.5 mm.), n_D^{20} 1.5718, λ_{\max} 2.74 μ , was 3.6 g. (63%). Brodhag and Hauser¹⁹ report b.p. 151–152° (5.5 mm.) and n_D^{20} 1.5722 for carbinol **10**, prepared from benzhydrylmagnesium chloride and acetone. Thin layer chromatographic analysis (4:1 mixture of hexane–ether developer) of our crude reaction product indicated that no aldol product **4** was present.

Dehydration of **10** was effected by heating under reflux for 2.5 hr. a 2.4-g. quantity in 15 ml. of 20% aqueous sulfuric acid. Work-up of the reaction mixture by the procedure used with compound **3** afforded a colorless oil which was distilled through a semimicro column. The yield of 1,1-diphenyl-2,2-dimethylethylene, b.p. 95–97° (0.5 mm.), n_D^{25} 1.5812 [lit.¹⁹ b.p. 153–154° (16 mm.), n_D^{20} 1.5871], was 923 mg. (40%). This product was shown by infrared spectral comparison to be identical with an authentic sample of the ethylene.²⁰

Reaction of 1,1-Diphenylpropanone (1) with Phenyllithium. Formation of 1,1,2-Triphenyl-2-propanol (2).—To 19.0 ml. of 1.70 *N* phenyllithium in ether was added with stirring in an atmosphere of dry nitrogen a solution of 5.9 g. (0.028 mole) of 1,1-diphenylpropanone in 30 ml. of ether. The addition of ketone required 15 min. and was accompanied by a mildly exothermic reaction. The resulting mixture was heated under reflux for 1 hr. and was then cooled in an ice bath while 20 ml. of a cold, saturated solution of ammonium chloride in water was added slowly with stirring. The ether layer was separated and the aqueous phase was extracted with two 30-ml. portions of ether. The combined ether solutions were washed with water and dried. Removal of the solvent under reduced pressure gave 7.03 g. of a viscous yellow oil. Chromatography of a 2.63-g. portion of this oil on neutral alumina (hexane, hexane–benzene, benzene, and benzene–ethanol as eluents) gave 85 mg. of biphenyl, 650 mg. of unchanged ketone **1**, traces of benzophenone, and 1.25 g. of crude 1,1,2-triphenyl-2-propanol (**2**). Recrystallization of **2** from hexane yielded 0.78 g. (26%) of white crystals, m.p. 82–85°, identical with the carbinol obtained from the action of phenylmagnesium bromide on 1,1-diphenylpropanone. Both thin layer chromatography and infrared analysis of the crude reaction product failed to reveal the presence of 1,1,5,5-tetraphenyl-4-methyl-3-penten-2-one (**4**).

Reaction of 1,1-Diphenylpropanone (1) with Cyclohexylmagnesium Bromide. Formation of 1,1,5,5-Tetraphenyl-4-methyl-3-penten-2-one (4).—The Grignard reagent prepared from 0.70 g. (0.029 g.-atom) of magnesium turnings, 5.22 g. (0.032 mole) of redistilled cyclohexyl bromide, and 10 ml. of ether was allowed to react with a solution of 5.25 g. (0.025 mole) of 1,1-diphenylpropanone in 40 ml. of ether under the conditions described above for phenylmagnesium bromide. The crude product (5.85 g.) was a colorless, viscous oil which solidified when scratched. Recrystallization from ethanol gave 2.5 g. (50%) of impure 1,1,5,5-tetraphenyl-4-methyl-3-penten-2-one (**4**), m.p. 106–114°. Three additional recrystallizations from the same solvent yielded 0.72 g. (14%) of **4**, m.p. 130.5–133.0°, shown by infrared spectral comparison and a mixture melting point determination to be identical with the α,β -unsaturated ketone isolated from the reaction of **1** with phenylmagnesium bromide.

A 1.7-g. portion of the concentrated mother liquors from which **4** had crystallized was chromatographed on a column (22 \times 3.0 cm.) of neutral alumina using successively hexane, hexane–benzene, benzene, and benzene–ethanol as eluents. From this operation there was isolated 25% of starting ketone **1**, traces of a compound believed to be bicyclohexyl, traces of benzophenone, and less than 1% of a material which showed strong absorption at 2.72 μ in the infrared and had m.p. 187.2–188.4° after two recrystallizations from ethanol.

Anal. Calcd. for C₃₀H₂₈O: C, 89.07; H, 6.98. Found: C, 89.10; H, 7.07.

(17) Huang-Minlon, *J. Am. Chem. Soc.*, **68**, 2487 (1946).

(18) R. S. Livshits, N. A. Preobrazhenskii, and M. S. Bardinskaya, *J. Gen. Chem. USSR*, **15**, 836 (1945); *Chem. Abstr.*, **41**, 709 (1947).

(19) A. Brodhag and C. R. Hauser, *J. Am. Chem. Soc.*, **77**, 3024 (1955).

(20) P. Sabatier and M. Murat, *Compt. rend.*, **186**, 1433 (1913).

Mass spectrometric analysis¹⁰ showed that the above material was a mixture.

Reformatsky Reaction of 1,1-Diphenylpropanone (1) with Methyl Bromoacetate. Formation of Methyl 4,4-Diphenyl-3-methyl-3-hydroxybutyrate (11).—This reaction was carried out in an atmosphere of dry nitrogen. To a stirred suspension of 1.96 g. (0.03 g.-atom) of zinc shot (20 mesh) in 10 ml. of ether containing a few crystals of iodine was added at reflux temperature in the course of 30 min. a mixture of 5.25 g. (0.025 mole) of 1,1-diphenylpropanone and 3.83 g. (0.025 mole) of methyl bromoacetate. Reaction commenced after 1.5 hr. of heating and the reaction mixture was held at reflux for an additional 3 hr. The reaction mixture was cooled in an ice bath and hydrolyzed with 50 ml. of 5% aqueous sulfuric acid. The aqueous phase was separated and extracted with three 25-ml. portions of ether. The combined ether solutions were washed with 5% sodium bicarbonate and then with water. Removal of the solvent from the dried solution afforded 6.4 g. of a mobile oil which was evaporatively distilled (210° at 1 mm.). This effected separation of the more volatile, unreacted 1,1-diphenylpropanone (1.50 g., 29% recovery), whose infrared spectrum revealed the presence of a small amount of benzophenone. The nonvolatile residue was chromatographed on a 22 × 3.0 cm. basic alumina packed column using successively hexane, hexane-benzene, benzene, and benzene-ethanol as eluents. Thirty-five fractions were collected. Fractions 28-29 contained 3.59 g. (51%) of methyl 4,4-diphenyl-3-methyl-3-hydroxybutyrate (11), m.p. 54-57°. Two recrystallizations from ligroin gave an analytical sample, m.p. 56.2-57.8°, λ_{\max} 2.82 and 5.81 μ .

Anal. Calcd. for $C_{18}H_{20}O_3$: C, 76.03; H, 7.09. Found: C, 76.27; H, 7.01.

Saponification of 11 to 4,4-Diphenyl-3-methyl-3-hydroxybutyric Acid (12).—Saponification of crude ester 11 was carried out by heating under reflux a 2.95-g. quantity for 4 hr. with 15 ml. of 5% ethanolic potassium hydroxide. The resulting yellow solution was diluted with 15 ml. of water and acidified with dilute hydrochloric acid. The milky suspension was extracted twice with ether and the combined ether extracts were extracted, in turn, with 5% sodium hydroxide. Acidification of the alkaline extract caused a yellow oil to separate. This suspension was extracted with ether and the ether extract was washed with water and dried. Removal of the solvent under reduced pressure afforded 1.46 g. (53%) of 4,4-diphenyl-3-methyl-3-hydroxybutyric acid (12) as an oil, which solidified on standing overnight at room temperature, m.p. 127-130°. Recrystallization of this material from 40 ml. of ligroin containing 2 ml. of ethanol gave, after refrigeration for 48 hr., 990 mg. of white crystals, m.p. 131.0-132.0°, $\lambda_{\max}^{CHCl_3}$ 2.87 (broad) and 5.90 μ .

Anal. Calcd. for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71; neut. equiv., 270.3. Found: C, 75.47; H, 6.64; neut. equiv., 271.0.

Reduction of 12 to 4,4-Diphenyl-3-methylbutyric Acid (7).—A suspension of 200 mg. (0.74 mmole) of hydroxy acid 12, 1.52 g. of red phosphorus, and 550 mg. of iodine in 10 ml. of glacial acetic acid to which 10 drops of water had been added was heated under reflux for 20 hr. The cooled reaction mixture was filtered through Celite and excess iodine was destroyed by treating the orange filtrate with 40 ml. of 2.5% sodium bisulfite. The tan solid which precipitated was collected by filtration, washed with water, and dried (180 mg., m.p. 105-113°). Recrystallization from hexane yielded 130 mg. (69%) of 4,4-diphenyl-3-methylbutyric acid (7), m.p. 115.0-117.5°. A second recrystallization from ethanol-water raised the melting point to 118.2-119.4° (lit.⁸ m.p. 113°).

Anal. Calcd. for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.21; H, 7.15.

Oxidative Cleavage of 1,1-Diphenylpropanone (1) to Benzophenone.—Oxygen from a cylinder was passed at the rate of 1 bubble/sec. for 15 hr. through a solution of 300 mg. of 1,1-diphenylpropanone in 6 ml. of 2% ethanolic potassium hydroxide. The solvent was removed under reduced pressure, the residue was taken up in ether, and the resulting solution was washed with water until neutral. Removal of the ether from the dried solution gave 209 mg. of a light yellow oil which was found to contain 111 mg. (42%) of benzophenone by quantitative infrared analysis.²¹ The benzophenone was further characterized by conversion to the corresponding 2,4-dinitrophenylhydrazone. Treatment of an ethanolic solution of the oily residue with 2,4-dinitrophenylhydrazine reagent¹⁸ afforded 215 mg. (41%) of the derivative, m.p. 233-239°, which was collected by filtration within 5 min. of its formation in order to avoid contamination by the more slowly formed dinitrophenylhydrazone of 1,1-diphenylpropanone. Recrystallization from glacial acetic acid afforded 190 mg. (37%) of benzophenone 2,4-dinitrophenylhydrazone, m.p. 240-242° (lit.²² m.p. 238-239°), which was shown to be identical with an authentic specimen by a mixture melting point determination and infrared spectral comparison.

(21) The analysis was done on a 56.5-mg. aliquot of the crude oily product diluted to a volume of 1.0 ml. with CCl_4 . The intensities of the absorption bands characteristic of the ketone at 6.02, 10.63, and 10.88 μ were compared with a calibration curve obtained from the spectra of an authentic sample (2, 5, 10, 20, 35, and 50 mg./ml. of carbon tetrachloride solution) of benzophenone.

(22) E. H. Huntress and S. P. Mulliken, "Identification of Pure Organic Compounds," Order I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 363.

Quantitative Confirmation of the Cookson Rule for α -Phenyl Ketones

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It is suggested that the exaltation of absorption in the region of 280 $m\mu$ shown by α -phenyl ketones is unrelated in the main to any orbital overlap between the carbon orbitals of the phenyl ring and the n orbital of the oxygen atom of the carbonyl group. Such exaltations appear to be primarily a result of orbital overlap between the carbon of the carbonyl group and the β -carbon of the β,γ -unsaturated system as previously proposed by Cookson. Data for ketones of fixed geometry and for ketones with groups rotatable to a degree are combined in a single uniform treatment and afford the opportunity of examining the nearest-neighbor suggestion and the accuracy of equations for π and σ overlap of bond orbitals.

After examination of a substantial list of β,γ -unsaturated ketones, Cookson proposed² that spectral exaltations in the region of 280-290 $m\mu$ arose most significantly when the p orbital on the carbon of the carbonyl group pointed toward the p orbital on the β -carbon of the β,γ -unsaturated system; *i.e.*, S_1 is a

maximum in Figure 1. Subsequent to this, Labhart and Wagniere³ proposed that exalted $n-\pi^*$ transitions derived their strength from a charge-transfer band, the derivation being proportional to the square of the overlap integral (S_3) of the n orbital on the oxygen of the carbonyl group with the p orbital of the β -carbon of the β,γ -unsaturated system. If only the β -orbital of the β,γ -unsaturated system is involved (the "nearest-

(1) (a) To whom inquiries should be addressed. (b) From the Ph.D. thesis of S. F. Marsocci. (c) Acting Director, University of Rhode Island Computer Laboratory.

(2) R. C. Cookson and N. S. Wariyar, *J. Chem. Soc.*, 2302 (1956).

(3) H. Labhart and G. Wagniere, *Helv. Chim. Acta*, **42**, 2219 (1959).