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Synthesis of Ketones of the Type $\text{CH}_3\text{COCH}_2\text{R}$ from Acetylacetone and Halides with Ethanolic Potassium Carbonate. An Alkylation–Cleavage Process¹

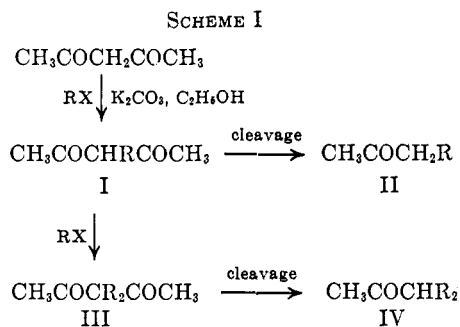
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A number of ketones of the type $\text{CH}_3\text{COCH}_2\text{R}$, where R is alkyl, aralkyl, or a related group, were prepared in good yield from acetylacetone and appropriate halides by means of ethanolic potassium carbonate. This alkylation–cleavage process appears more convenient than earlier procedures. Other courses of reaction were observed with certain halides. One of these involved dialkylation and cleavage to give the ketone of the type $\text{CH}_3\text{COCHR}_2$; this process was useful when R was *m*-nitrobenzyl. Twofold monoalkylation and cleavage occurred with α,α' -dichloro-*p*-xylene to form 4,4'-phenylenedi-2-butanone.

It is well known that acetylacetone can be alkylated with an alkyl halide by means of a suitable base² and that the resulting alkyl derivative can be cleaved by an alcoholic base.³ We have effected such an alkylation–cleavage process to form ketones of type II in a single procedure by means of ethanolic potassium carbonate; in certain cases a dialkylation–cleavage process to form ketones of type IV was also observed (Scheme I).



The general procedure involved refluxing approximately equal molecular equivalents of acetylacetone, halide, and potassium carbonate in ethanol for 16 hr.⁴ The results with most of the halides studied are summarized in Tables I–III. Table I shows that the yields of ketones of type II were generally satisfactory (52–79%). The products on which the yields were based were indicated to be pure by v.p.c. or sharp melting point. This method is useful for the synthesis of a number of ketones II, especially those in which R is a substituted benzyl, a methallyl, or a phenacyl group. However, the reactions with *o*- and *p*-nitrobenzyl chloride afforded black mixtures, from which the corresponding ketones II were isolated only as their semicarbazones (see Table I and Experimental Section).⁵

Six of the ketones II listed in Table I are known compounds; they were identified by infrared spectra (for the carbonyl group) and by essential agreement of their melting or boiling points and also of those of derivatives with the reported values.⁶ The present one-stage procedure appears more convenient than the earlier, two-stage procedures involving alkylation of acetoacetic ester followed by cleavage,⁷ and the Claisen–Schmidt condensation of acetone with the appropriate aldehyde followed by reduction of the resulting α,β -unsaturated ketone⁸ (see Table I). Also the present synthesis of II (R = $\text{CH}_2\text{COC}_6\text{H}_5$) seems preferable to that involving the Friedel–Crafts acylation of benzene with levulinyl chloride.⁹

The other 10 ketones II listed in Table I appear to be new compounds. Their structures were supported by analyses (Table II) and by absorption spectra. The infrared spectra of all of the ketones showed the expected carbonyl absorption near 5.85μ , and those of the nitro ketones also exhibited nitro absorptions near 6.5 and 7.4μ ¹⁰ (see Table I). The n.m.r. spectra, which were determined on five of the new ketones II (Table III), showed the expected singlet for the methyl hydrogen and appropriate peaks for the aromatic hydrogens. The spectra of the *meta*- and *para*-substituted benzyl ketones II exhibited collapsed A_2B_2 systems and that of *o*-bromobenzyl ketone II a complex A_2B_2 system for the respective ethylene groups ($-\text{CH}_2\text{CH}_2-$).

As indicated in Scheme I, intermediate I may undergo not only cleavage to form ketones II, but also further alkylation to give III which may be cleaved to afford ketones IV. The latter course of reaction apparently

(1) This investigation was supported by National Science Foundation Research Grant No. NSF GP 2274 and by Public Health Service Research Grant No. CA 04455-06.

(2) See A. W. Johnson, E. Markham, and R. Price, *Org. Syn.*, **42**, 75 (1962).

(3) See R. G. Pearson and E. A. Mayerle, *J. Am. Chem. Soc.*, **73**, 926 (1951).

(4) The reaction with *o*-chlorobenzyl chloride was mentioned without details in footnote 12 of a recent paper: T. M. Harris and C. R. Hauser, *J. Org. Chem.*, **29**, 1391 (1964).

(5) Although such alkylations have generally been assumed to involve an $\text{S}_{\text{N}}2$ mechanism, a radical-anion process has been proposed recently for carbon alkylation of the anion of 2-nitropropane with *m*- and *p*-nitrobenzyl halides: R. C. Kerber, G. W. Urry, and N. Kornblum, *J. Am. Chem. Soc.*, **86**, 3904 (1964).

(6) That II [R = $\text{CH}_2\text{C}(\text{CH}_3)=\text{CH}_2$] had not isomerized to the possible α,β -unsaturated ketone, 5-methyl-3-hexen-2-one, was further supported by the failure of its infrared spectrum to show a conjugated carbonyl (see Table I).

(7) See C. S. Marvel and F. D. Hager, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1932, p. 243; J. R. Johnson and F. D. Hager, *ibid.*, p. 343.

(8) See N. L. Drake and P. Allen, Jr., ref. 7, p. 69; J. Frederick, J. Dippy, and R. L. Lewis, *Rec. trav. chim.*, **56**, 1000 (1937).

(9) J. H. Helberger, *Ann.*, **522**, 269 (1936).

(10) See L. J. Bellamy, "The Infrared Spectra of Complex Organic Molecules," John Wiley and Sons, Inc., New York, N. Y., 1960, p. 298.

TABLE I
 SYNTHESIS OF KETONES II FROM ACETYLACETONE AND HALIDES WITH ETHANOLIC POTASSIUM CARBONATE^a

Halide	R	Ketone II		B.p. (mm.) or m.p., °C.		Semicarbazone m.p., °C.	
		Yield, ^b %	Infrared C=O, μ	Found	Lit.	Found	Lit.
Benzyl chloride	CH ₂ C ₆ H ₅	73 ^c	5.85	105-107 (7)	112 (15) ^d	140-141	141-142 ^d
<i>o</i> -Bromobenzyl bromide	CH ₂ C ₆ H ₄ Br- <i>o</i>	75	5.80	139-140 (10)	...	187-188	...
<i>m</i> -Bromobenzyl bromide	CH ₂ C ₆ H ₄ Br- <i>m</i>	78	5.81	145 (10)	...	160-161	...
<i>o</i> -Chlorobenzyl chloride	CH ₂ C ₆ H ₄ Cl- <i>o</i>	78	...	90-94 (0.4)	164-168 (25) ^e	171-172	172.5-173.5 ^e
<i>m</i> -Chlorobenzyl bromide	CH ₂ C ₆ H ₄ Cl- <i>m</i>	65	5.81	119-120 (4)	...	150-151	...
<i>p</i> -Chlorobenzyl chloride	CH ₂ C ₆ H ₄ Cl- <i>p</i>	62	5.83	107 (0.5)	...	164-165.5	...
<i>m</i> -Fluorobenzyl chloride	CH ₂ C ₆ H ₄ F- <i>m</i>	60	5.85	71-72 (2)	...	156-157	...
<i>o</i> -Nitrobenzyl chloride	CH ₂ C ₆ H ₄ NO ₂ - <i>o</i>	10 ^f	216-217	...
<i>m</i> -Nitrobenzyl chloride	CH ₂ C ₆ H ₄ NO ₂ - <i>m</i>	65	5.86 ^g	44	...	198	...
<i>p</i> -Nitrobenzyl chloride	CH ₂ C ₆ H ₄ NO ₂ - <i>p</i>	65 ^f	214-215	...
α -Chloromethylnaphthalene	CH ₂ C ₁₀ H ₇ - α	61	5.83	124 (1)	124 (1) ^h	176-177	176-177 ^h
Methallyl chloride	CH ₂ C(CH ₃)=CH ₂	50	5.82	148-150 (760)	147-149 (760) ⁱ	137-138	136.5-137.5 ⁱ
			5.81				
Phenacyl chloride	CH ₂ COC ₆ H ₅	55	5.91	119 (0.5)	109 (0.35) ^j	103-104 ^k	104 ^k
<i>n</i> -Butyl iodide	<i>n</i> -C ₄ H ₉	60	...	150-152 (760)	150.2 (760) ^l	125-126	121-123 ^m
<i>n</i> -Butyl bromide	<i>n</i> -C ₄ H ₉	28 ⁿ	...	150-152 (760)	150.2 (760) ^l	125-126	121-123 ^m

^a For 16 hr. ^b All distilled ketones II were shown to be pure by v.p.c. ^c The yield was unchanged by refluxing 3 or 96 hr. ^d L. Birkofer, *Chem. Ber.*, **80**, 83 (1947). ^e J. F. Bunnett and J. A. Skorcz, *J. Org. Chem.*, **27**, 3836 (1962). ^f Yield of semicarbazone. ^g Nitro absorption: 6.60 and 7.45 μ. ^h M. S. Newman and T. J. O'Leary, *J. Am. Chem. Soc.*, **68**, 258 (1946). ⁱ W. Kimel and A. C. Cope, *ibid.*, **65**, 1992 (1943). ^j R. M. Adams and C. A. Vanderwerf, *ibid.*, **72**, 4318 (1950). ^k 1-(*p*-Nitrophenyl)-2-methyl-5-phenylpyrrole: M. Fetizon and P. Baranger, *Compt. rend.*, **236**, 1428 (1953). ^l M. Sherrill, *J. Am. Chem. Soc.*, **52**, 1982 (1930). ^m W. S. Rapson and R. G. Shuttleworth, *J. Chem. Soc.*, 99 (1940). ⁿ The yield was 30% after refluxing for 96 hr.

 TABLE II
 ANALYSES FOR NEW KETONES II AND THEIR SEMICARBAZONES

R	Formula	Ketone II						Semicarbazone								
		Calcd., %						Calcd., %								
		C	H	N, Cl, or Br	C	H	N, Cl, or Br	Formula	C	H	Cl or Br	N	C	H	Cl or Br	N
CH ₂ C ₆ H ₄ Br- <i>o</i>	C ₁₀ H ₁₁ BrO	52.89	4.88	35.19	52.74	4.71	35.05	C ₁₁ H ₁₄ BrN ₃ O
CH ₂ C ₆ H ₄ Br- <i>m</i>	C ₁₀ H ₁₁ BrO	52.89	4.88	35.19	52.64	4.97	35.45	C ₁₁ H ₁₄ BrN ₃ O	46.49	4.97	14.79	28.12	46.24	4.91	14.83	28.26
CH ₂ C ₆ H ₄ Cl- <i>m</i>	C ₁₀ H ₁₁ ClO	65.59	6.05	19.41	65.74	5.94	19.26	C ₁₁ H ₁₄ ClN ₃ O	55.12	5.89	14.79	17.95	55.11	5.83	14.76	17.71
CH ₂ C ₆ H ₄ Cl- <i>p</i>	C ₁₀ H ₁₁ ClO	65.59	6.05	19.41	65.67	5.94	19.44	C ₁₁ H ₁₄ ClN ₃ O	55.12	5.89	14.79	17.95	55.24	6.01	14.65	17.70
CH ₂ C ₆ H ₄ F- <i>m</i> ^a	C ₁₀ H ₁₁ FO	72.27	6.67	...	72.35	6.73	...	C ₁₁ H ₁₄ FN ₃ O	59.18	6.32	...	18.82	59.06	6.18	...	18.94
CH ₂ C ₆ H ₄ NO ₂ - <i>o</i>	C ₁₁ H ₁₄ N ₄ O ₃	52.79	5.64	...	22.39	52.71	5.71	...	22.47
CH ₂ C ₆ H ₄ NO ₂ - <i>m</i>	C ₁₀ H ₁₁ NO ₃	62.16	5.74	7.25	61.94	5.80	7.23	C ₁₁ H ₁₄ N ₄ O ₃	52.79	5.64	...	22.39	52.85	5.67	...	22.55
CH ₂ C ₆ H ₄ NO ₂ - <i>p</i>	C ₁₁ H ₁₄ N ₄ O ₃	52.79	5.64	...	22.39	53.08	5.82	...	22.10

^a 2,4-Dinitrophenylhydrazone m.p. 127-128. *Anal.* Calcd. for C₁₆H₁₅FN₄O₄: C, 55.49; H, 4.37; N, 16.18. Found: C, 55.65; H, 4.53; N, 16.15.

 TABLE III
 N.M.R. SPECTRA OF NEW KETONES II

R	Type of hydrogen	P.p.m.	Peak character	No. of hydrogens (peak ratio)
CH ₂ C ₆ H ₄ Br- <i>o</i>	Methyl	2.00	Singlet	3 (0.69)
	Methylene	2.43-3.13	A ₂ B ₂ system	4 (0.90)
	Aromatic	6.77-7.57	Several peaks	4 (1.0)
CH ₂ C ₆ H ₄ Br- <i>m</i>	Methyl	1.97	Singlet	3 (0.71)
	Methylene	2.55-2.80	Collapsed A ₂ B ₂ system	4 (0.99)
	Aromatic	6.95-7.35	Several peaks	4 (1.0)
CH ₂ C ₆ H ₄ Cl- <i>m</i>	Methyl	1.98	Singlet	3 (0.72)
	Methylene	2.52-2.75	Collapsed A ₂ B ₂ system	4 (0.94)
	Aromatic	6.82-7.19	Several peaks	4 (1.0)
CH ₂ C ₆ H ₄ Cl- <i>p</i>	Methyl	2.01	Singlet	3 (0.78)
	Methylene	2.59-2.78	Collapsed A ₂ B ₂ system	4 (0.96)
	Aromatic	6.85-7.27	Single peak	4 (1.0)
CH ₂ C ₆ H ₄ NO ₂ - <i>m</i>	Methyl	2.17	Singlet	3 (0.75)
	Methylene	2.85-3.11	Collapsed A ₂ B ₂ system	4 (1.0)
	Aromatic	7.45-8.39	Two groups of peaks	4 (1.0)

occurred generally to a small extent, as residues were left on distilling the ketones II. Moreover, in an experiment with benzyl chloride on a relatively large scale, the corresponding ketone IV and intermediate III were isolated each in 2% yield.¹¹ In an experiment with *p*-chlorobenzyl chloride, another type of by-product, the corresponding enol ether of acetylacetone,

was isolated in 1% yield. Incidentally, such minor products were readily separated from the desired ketones II.

It seemed possible to increase the relative yield of the ketone IV by employing 2 molecular equiv. of the halide to one of acetylacetone. At least with benzyl chloride, however, these proportions of reactants increased the yield of IV to only 15%, II being obtained in 68% yield.

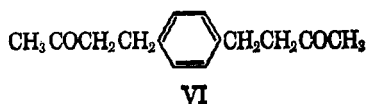
Whereas *m*-nitrobenzyl chloride and most of the other halides listed in Table I afforded mainly the corresponding ketone II, *m*-nitrobenzyl bromide, which is more reactive than the chloride, produced largely (70%) the corresponding ketone IV even when only equal molecular equivalents of the reactants were employed. Actually this dialkylation-cleavage process furnishes a convenient method of synthesis of IV (R = CH₂C₆H₄NO₂-*m*), which appears to be new. Its structure was supported by analysis and absorption spectra (see Experimental Section).

(11) In a similar experiment with methallyl chloride, the residue left on distilling ketone II [R = CH₂C(CH₃)=CH₂] was indicated by v.p.c. to contain three components, which, on the assumption that these were I, IV, and III [R = CH₂C(CH₃)=CH₂], were obtained in yields of 4, 5, and 12%, respectively.

Although the reaction with *n*-butyl iodide afforded ketone II ($\text{R} = n\text{-C}_4\text{H}_9$) in 60% yield, that with the less reactive *n*-butyl bromide produced this ketone in only 28% yield (see Table I). Apparently the starting β -diketone, acetylacetone, underwent cleavage, as the yield of II was only 30% after prolonged refluxing.

In contrast to the other halides studied, benzhydryl chloride reacted preferentially with the solvent to form benzhydryl ethyl ether in 80% yield.

Besides the monohalides considered above, the dihalide, α, α' -dichloro-*p*-xylene, was employed under the usual conditions to give diketone VI in 50% yield. Evidently a twofold monoalkylation-cleavage process occurred. This method appears more convenient than an earlier, condensation-reduction procedure.¹²



Discussion

The halides employed according to Scheme I may be classified conveniently in the following four groups: group I, halides that afford mainly ketones II; group II, halides that yield largely ketones IV; group III, halides that alkylate so slowly that the acetylacetone undergoes appreciable cleavage; and group IV, halides that react preferentially with the solvent. Although only single examples are given for the halides in each of the last three groups, other examples could presumably be found.

Since the success of the method to form ketones II appears to be dependent not only on relatively rapid alkylation but also on either facile cleavage or retarded further alkylation, the optimum time for the synthesis of II may differ with the different halides. Thus, in the reaction with benzyl chloride the alkylation-cleavage product II was obtained in 70% yield within 1 hr. (indicated by v.p.c.), whereas in that with *o*-chlorobenzyl chloride the alkylated diketone I has been isolated in 53% yield after 1.5 hr.⁴ However, in the latter case, the ketone II ($\text{R} = \text{CH}_2\text{C}_6\text{H}_4\text{Cl-}o$) was obtained in 78% yield after 16 hr. Apparently the presence of the *o*-chloro atom in the intermediate I retarded not only cleavage but also further alkylation.

The difference in the course of reaction with *m*-nitrobenzyl chloride and bromide is evidently due to the difference in the rate of further alkylation of the monoalkylation intermediate I ($\text{R} = \text{CH}_2\text{C}_6\text{H}_4\text{NO}_2\text{-}m$) as this intermediate, which may undergo either cleavage or further alkylation, is the same in the two cases.

Experimental Section¹³

Syntheses of Ketones II. A. General Procedure.—A mixture of 0.11 mole of acetylacetone, 0.10 mole each of alkyl halide and anhydrous potassium carbonate, and 100 ml. of com-

mercial anhydrous (dried over Linde 3A Molecular Sieves) ethanol was refluxed for 16 hr. The ethanol (and ethyl acetate, a by-product, identified by v.p.c.) was removed by distillation. The residue was shaken with 150 ml. of water to dissolve the salts, and the resulting mixture was extracted three times with 150 ml. of ether. The ethereal extracts were combined, and the solution was dried over anhydrous magnesium sulfate. The solvent was removed. The residue was distilled under reduced pressure or recrystallized to give the ketone II. Appropriate derivatives were prepared. The results are summarized in Tables I–III.

B. Isolation of By-products.—By-products were indicated by v.p.c. to be present in the crude liquid reaction mixtures. Certain of them were isolated as described below from the residues left on distilling the ketone II.

The liquid residue from the reaction with benzyl chloride (effected on 0.5-mole scale) was further fractionated to give 1.3 g. (2%) of α, α -dibenzylacetone, b.p. 170–176° (7 mm.); the infrared spectrum showed carbonyl absorption at 5.84 μ .^{14,15} The solid residue left after distillation was recrystallized from hexane to give 1.1 g. (2%) of α, α -dibenzylacetylacetone, m.p. 112.5–114°, lit.¹⁶ m.p. 111–112°. The n.m.r. spectrum exhibited a singlet at 2.13 p.p.m. for six methyl hydrogens, a singlet at 3.30 p.p.m. for four methylene hydrogens, and several peaks between 6.93 and 7.50 p.p.m. for 10 aromatic hydrogens.

Anal. Calcd. for $\text{C}_{13}\text{H}_{20}\text{O}_2$: C, 81.39; H, 7.19. Found: C, 81.28; H, 7.03.

The liquid residue from the reaction with *p*-chlorobenzyl chloride was further fractionated to give 1.3 g. (1%) of the *p*-chlorobenzyl enol ether of acetylacetone, m.p. 94.5–95° after recrystallization from hexane. The n.m.r. spectrum showed two singlets at 2.13 and 2.37 p.p.m. for six methyl hydrogens, a singlet at 4.83 p.p.m. for two methylene hydrogens, a singlet at 5.49 p.p.m. for one vinyl hydrogen, and a single peak at 7.35 p.p.m. for four aromatic hydrogens.

Anal. Calcd. for $\text{C}_{12}\text{H}_{13}\text{ClO}$: C, 64.16; H, 5.81; Cl, 15.78. Found: C, 63.92; H, 5.94; Cl, 15.68.

The dark liquid residue from the reaction with phenacyl chloride was further fractionated to sublime in the distillation column 1 g. of a substance, m.p. 135–137°, which was neither 2-methyl-5-phenylfuran, lit.¹⁷ m.p. 42°, nor 3-phenyl-2-penten-1-one, lit.¹⁷ m.p. 82°. This product was not further investigated.

C. Reactions with *o*- and *p*-Nitrobenzyl Chloride.—In these reactions dark mixtures were obtained. Removal of the solvent left black, tarry residues that resisted recrystallization.¹⁸ These semisolids were refluxed with mixtures of semicarbazine hydrochloride, sodium acetate, 95% ethanol, and water to give, after cooling and recrystallizing the resulting solid from ethanol, the corresponding semicarbazones (see Tables I and II).

Reaction with Benzhydryl Chloride.—The reaction with this halide by the general procedure afforded benzhydryl ethyl ether, b.p. 124–128° (1.6 mm.), lit.¹⁹ b.p. 160–161° (19 mm.), yield 85%. The infrared spectrum of the product showed absorption at 9.05 μ for C–O–C.²⁰ The same product was obtained in 85% yield when benzhydryl chloride was refluxed with ethanol alone for 16 hr.

Synthesis of Ketone IV ($\text{R} = \text{CH}_2\text{C}_6\text{H}_4\text{NO}_2\text{-}m$).—This reaction was effected as described above for the synthesis of ketones II employing 0.11 mole of acetylacetone and 0.1 mole each of *m*-nitrobenzyl bromide and potassium carbonate. The reaction mixture, on removal of the solvent and addition of water, afforded 19 g. of crude solid product. A 2.0-g. sample of this crude product was refluxed with a mixture of semicarbazide hydrochloride, sodium acetate, and ethanol–water to give immediately 0.2 g. (10%) of the semicarbazone of ketone II, $\text{R} = \text{CH}_2\text{C}_6\text{H}_4\text{NO}_2\text{-}m$ (see Table II). The remainder of the crude product was recrystallized from cyclohexane–ethanol to afford 11.8 g. (70%, based on the halide) of ketone IV ($\text{R} = \text{CH}_2\text{C}_6\text{H}_4\text{NO}_2\text{-}m$) as light brown needles, m.p. 90.5–92°. The infrared spectrum

(14) C. Cherrier, *Compt. rend.*, **225**, 997 (1947).

(15) The oxime, recrystallized from ethanol, melted at 75–76°; J. M. Conia [*Ann. chim.* (Paris), **8**, 709 (1953)] reported m.p. 75°.

(16) H. Adkins, W. Kutz, and D. D. Coffman, *J. Am. Chem. Soc.*, **56**, 3212 (1930).

(17) M. Julia and M. Fétizon, *Compt. rend.*, **240**, 1109 (1955).

(18) A dark residue was also obtained in the reaction with *m*-nitrobenzyl chloride, but it was readily recrystallized from hexane–ethanol to give the pure product (see Table I).

(19) G. Stanikov, *Ber.*, **57**, 7 (1924).

(20) See ref. 10, p. 116.

(12) P. Ruggli and E. Girod, *Helv. Chim. Acta*, **27**, 1464 (1944).

(13) Melting points, which were taken on a Mel-Temp capillary melting point apparatus, and boiling points are uncorrected. Infrared spectra were determined with a Perkin-Elmer Model 137 or 237 Infracord with potassium bromide pellets of solids and neat samples of liquids on sodium chloride plates. N.m.r. spectra were obtained with a Varian A-60 spectrometer using tetramethylsilane as an internal reference point and carbon tetrachloride as solvent. Elemental analyses were by Dr. I. A. Schoeller, Mikro-Labor, Kronach, West Germany, by Galbraith Laboratories, Knoxville, Tenn., and by Triangle Chemical Laboratories, Chapel Hill, N. C.

showed carbonyl absorption at $5.87\ \mu$ and strong absorption for the nitro groups at 6.58 and $7.42\ \mu$.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 $C_{17}H_{15}N_2O_6$: 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 $5.80\ \mu$.

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

Aldolization of 1,1-Diphenylpropanone by Grignard Reagents¹

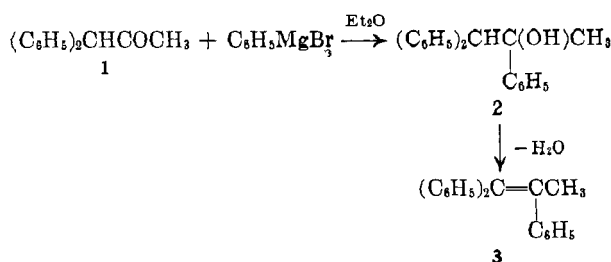
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The reaction of a series of organometallic compounds with 1,1-diphenylpropanone (1) has been investigated. Whereas methylmagnesium iodide, phenyllithium, and methyl bromoacetate in the presence of zinc added "normally" to ketone 1, both phenyl- and 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

(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.

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 $5.95\ \mu$, 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 benzylic 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 $5.82\ \mu$ 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-

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