Before sealing a tube there was inserted 1 g of compound **11**, and 2 ml of trifluoroacetic acid-*d* (10% solution). The tube was placed in an oil bath for 24 hr at 100°, after which the contents were made basic by pouring into 10% sodium carbonate solution followed by extraction with ether. After drying ($MgSO_4$) and removing the ether, the nmr spectrum of the residue was taken. Upon comparison of the area, τ 7.3–8.2, with the undeuterated spectrum it was concluded that essentially one hydrogen was exchanged.

Registry No.—**1** (n = 4), 25090-34-0; **1** (n = 5), 25090-35-1; **1** (n = 6), 25090-36-2; **11**, 25111-12-0; **11** 2,4-DNP, 25111-13-1.

Exalted n–π* Transitions for Substituted Phenylacetones

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As the alkyl group in 1-phenylcyclopropyl alkyl ketones was changed in the series Me, Et, *i*-Pr, *t*-Bu, strong absorption due to conjugation of the phenyl group with the cyclopropane ring appeared. This conjugation produced absorption tailings which led to false exaltations in the n–π* region. A method is presented which aids in detection of such cases. The stronger acetyl–cyclopropane conjugation is suggested only for the methyl ketone and a value of 2 kcal appeared suitable. Although α′-alkylation of α-phenylacetones did not increase the ketonic absorption, α-alkylation appeared to do so and the possible reasons for this are discussed. The addition of methyllithium to diphenylacetic acids is not a satisfactory synthesis of diphenylacetones.

The fact that α-phenylacetone showed an increase of extinction coefficient (ε 150, EtOH) in the n–π* region (280–290 mμ) has received various interpretations. Cookson[1] originally proposed that such exaltations arose most significantly when the plane of the carbonyl group faced the plane of the benzene ring ($\theta = \psi = 90°$ as in Figure 1b). In contrast, it was proposed somewhat later[2] that there was involvement of the n electrons of oxygen. This leads, at least by the LCAO method, to a prediction that the oxygen should nearer the β,γ unsaturation for maximum exaltation. Still later,[3] a computer program, which calculated angular populations as a function of hydrogen–hydrogen repulsions and then evaluated several proposals for explaining exaltations, supported the Cookson view. The best equation (not stated explicitly in ref 3) was $\epsilon = 30 + 810 \sin^2\theta \sin^2\psi$, wherein ε is the observed extinction coefficient of an unstrained α-phenyl ketone in ethanol solution and the angles are those defined in Figure 1. Of the ketones examined, only 1-acetyl-1-phenylcyclopropane proved to be an exception. The present paper deals with the source of this difficulty and sets forth additional factors concerning application of the Cookson proposal.

Discussion of Results

The computer program gave no recognition to the fact that the acetyl group and the cyclopropane ring show conjugation in the bisected structure ($\psi = 0°$ or 180°). Such conjugation for cyclopropanecarboxaldehyde was estimated to be in excess of 2 kcal by Bartell.[4a] Such a conjugation term was inserted using the simple expression[4b] $E = -2.0 \cos^2\psi$ and found to yield acceptable results. Greater or lesser values of the maximum conjugation energy were less satisfactory: 0 kcal (ϵ_{calcd} 213.5), 1 (102.9), 1.5 (87.7), 2.0 (76.7), 2.5 (69.4). In an effort to obtain further support for this interpretation, there has been prepared a series of ketones with larger alkyl groups. These were expected to show increasing exaltations of the ketonic absorption due to adoption of conformation **1b** (90–90°). The numerical data of Table III (Experimental Section) seem to support such a result. Sought in the following paragraph, however, is a numerical method of deducing the correctness of such a conclusion. Such a method would be of use with literature reports which usually give only spectral values. When complete spectra are at hand, visual examination often suffices for estimation of the existence of a tailings contribution to the n–π* region. For this reason, complete spectra are given in Figure 2 for the four 1-acyl-1-phenylcyclopropanes. This figure suggests that true exaltations of the n–π* region are not obtained in the three new cases. Rather, extinction coefficients in both the benzenoid and carbonyl portions of the spectra are elevated by tailings of strong absorption in the 200-220-mμ region. Absorption in this region increased as R of RCO– was changed in the series Me, Et, *i*-Pr, *t*-Bu. This is due to increasing conjugation of the phenyl group with the cyclopropane ring. Thus, it is proposed that the conformation of the methyl ketone lies toward that with angles $\psi = 180°$, $\theta = 90°$ (Ac in the bisected structure), while that for the *t*-butyl ketone lies heaviest toward that with angles $\psi = 90° = 270°$, $\theta = 0°$ (Ph in the bisected structure). The small bathochromic shift of the ketonic band of the methyl ketone supports the former interpretation. The increased absorption shown by the four ketones in the 200-mμ region is interpreted as being due to increased phenyl–cyclopropane conjugation.[5] This proposal of an angular dependence seems at variance with the conclusion of Eastman[6] who observed little difference in the log ε plots for compounds of fixed geometry. It must be recalled, however, that the angular departures from the bisected structure

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

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

[3] S. MacKenzie, S. F. Marsocci, and H. C. Lampe, *J. Org. Chem.*, **30**, 3328 (1965).

[4] (a) L. S. Bartell, B. L. Carroll, and J. P. Gillory, *Tetrahedron Lett.*, 705 (1964). (b) A similar equation was used to express the conjugation energy of twisted acetophenones: E. A. Braude and F. Sondheimer, *J. Chem. Soc.*, 3754 (1955).

[5] S. G. Beech, J. H. Turnbull, and W. Wilson, *ibid.*, 4686 (1952), reported for 1-methyl-2-phenylcyclopropane values of 230 mμ (ε >2500), 254 (1000), and 275 (320, EtOH). The energy of the phenyl–cyclopropane conjugation was given as 1.4 kcal by G. L. Closs and H. B. Klinger, *J. Amer. Chem. Soc.*, **87**, 3265 (1965).

[6] A. L. Goodman and R. H. Eastman, *ibid.*, **86**, 908 (1964).

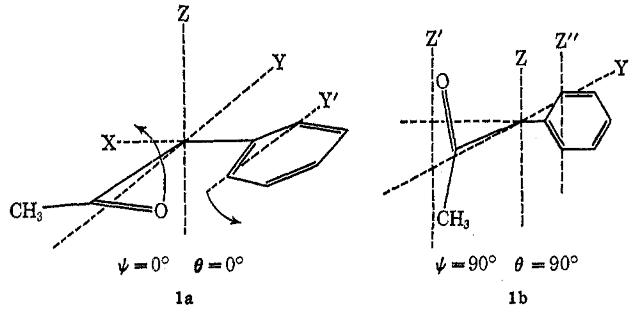


Figure 1.—In structure **1a** all carbon atoms lie in the XY plane. Positive angles are defined as counterclockwise departures from this reference position, each axis of rotation being viewed from the group toward the origin of axes. Structure **1b** shows the proposed position which leads to the maximum exaltation of the n–π^* transition.

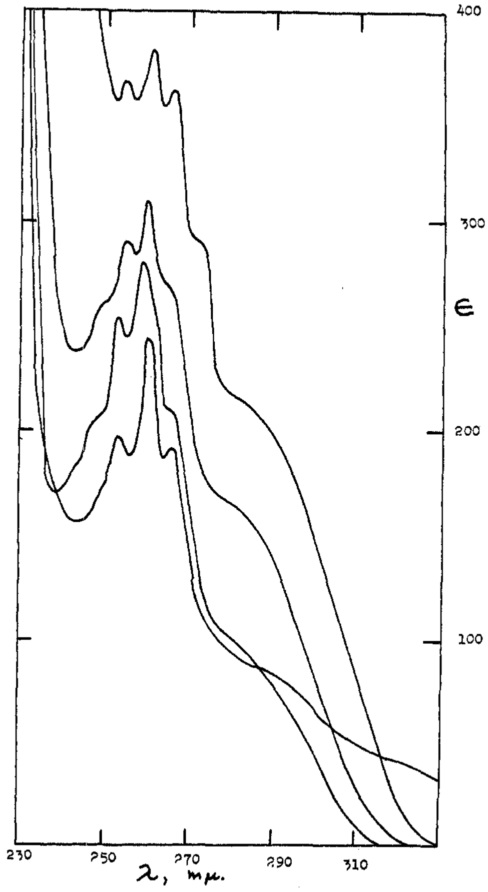
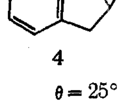


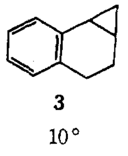
Figure 2.—Ultraviolet spectra for alkyl 1-phenylcyclopropyl ketones (curves are, in ascending order at 260 mμ, for R = Me, Et, i-Pr, t-Bu).

shown by **2**, **3**, and **4** are comparatively small in terms of $\cos^2\theta$. Moreover, inspection of the spectra of Eastman in the region of 230 mμ shows that the values of ϵ are highest for **2** and **3**, somewhat less for **4**, and definitely lower for phenylcyclopropane. It is therefore felt that the data of the present paper is not at variance with that of Eastman. The apparent difference lies mainly in the fact that the four ketones of the present work all have the same monosubstituted phenyl group and the small bathochromic shifts resulting from increased phenyl–cyclopropane conjugation are more easily seen.


4

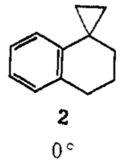
$\theta = 25°$

$\cos^2\theta = 0.82$


3

10°

0.97


2

0°

1.00

Measurement of spectra in both cyclohexane and ethanol has been helpful in detection of other cases wherein spurious elevations of the n–π^* transition might arise. A term Δ is defined as $\epsilon_{\mathrm{EtOH}} - \epsilon_{\mathrm{C_6H_{12}}}$. For any ketone, two values are easily obtainable, Δ_{260} and Δ_{290}. The former, the solvent response of ϵ in the benzenoid region, is theoretically always zero and hence becomes useful for criticism of the latter.

$\Delta_{260} < \Delta_{290} > 0$.—The positive value of Δ_{290} is typical of n–π^* transitions exalted by reason of an accompanying charge-transfer transition around 200 mμ. The lower value of Δ_{260} gives assurance that the problem of tailings is minor. The majority of the ketones in Table I show such behavior.

$\Delta_{260} > \Delta_{290} > 0$.—If the charge-transfer absorption is at a longer than usual wavelength, tailings from such may cause spurious elevations. Such is the case for bis(1-phenylcyclopentyl) ketone and probably for benzobicyclo[2.2.2]octenones.

$\Delta_{260} \leqslant 0 \geqslant \Delta_{290}$.—The inference here is that any exaltation seen is not caused by the polar transitions described above. Data for the 1-phenylcyclopropyl alkyl ketones, where the alkyl group is Et, i-Pr, or t-Bu, fit in this group.

$\Delta_{260} > 0 > \Delta_{290}$.—This special case, seen in Table I only for 1-hydroxy-1,1-diphenyl-2-propanone, is assumed to arise when the polar solvent disrupts strongly a conformation preferred in cyclohexane because of hydrogen bonding. This might be seen for all α-hydroxy-α-phenylalkanones and study of this point is underway.

Data for ketones having spectral values in the first group were analyzed by the computer program which calculated, as a function of atomic repulsions, a 13 × 25 matrix of mole fractions, representing the populations at the possible angular positions. Also as before, each mole fraction was multiplied by $\sin^2\theta\,\sin^2\psi$ and the sum represented as $\Sigma\,\sin^2\theta\,\sin^2\psi$ in Table I. Values of this summation were not calculated for ethyl, isopropyl, or t-butyl ketones. The programs, requiring optimum fitting of the higher alkyl group at each angular position, are prohibitively complex. It is worthy of note, however, that such α' substitution on an α-phenyl ketone normally has little effect on ϵ for ketones with exalted n–π^* transitions. Three pairs of ketones in Table I illustrate this[7] and also suggest a lower per cent solvent sensitivity ($\%\ \Delta_{290} = 100\Delta_{290}/\epsilon_{\mathrm{EtOH}}$) for the higher ketone of each pair. Also of lower per cent solvent sensitivity are cycloalkanones and polyphenylacetones. This observation forced reexamination of data for triphenylacetone in cyclohexane, a solvent in which the ketone is only slightly soluble. Change of ϵ from 261[8] to 297 resulted. Values for $\epsilon_{\mathrm{C_6H_{12}}}$, not ϵ_{EtOH} as in the previous study, are plotted in Figure 3

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[7] Seen earlier for phenylacetone and ethyl benzyl ketone by D. Biquard, *Bull. Soc. Chim. Fr.*, **1941**, 55.

[8] S. MacKenzie, S. F. Marsocci, and P. R. Santurri, *J. Org. Chem.*, **28**, 717 (1963).

TABLE I

KETONES LISTED IN ORDER OF PER CENT CHANGE OF $\epsilon_{n-\pi^*}$ ON CHANGE OF SOLVENT

Compd no.	Ketone	Registry no.	Σ[a]	Δ_{260}[b]	Δ_{290}	% Δ_{290}[c]	Tailings
	Bis(1-phenylcyclopentyl) ketone			275	186	53	Strong
1	1-Acetyl-1-phenylcyclopropane[d]		0.033	40	25	33	Yes
2	1-Acetyl-1-phenylcyclobutane[d]	3972-67-6	0.384	56	103	29	No
3	Phenylacetone[e]		0.184	20	42	28	No
4	1-Acetyl-1-phenylcyclohexane[d]		0.310	42	84	27	No
5	1-Acetyl-1-phenylcyclopentane[d]		0.283	32	72	25	No
6	3-Methyl-3-phenyl-2-butanone		0.189	23	46	24	No
7	Dimethyl 1,2,3,4-tetrahydro-9-oxo-1,4-ethanoanthracene-7,8-exodicarboxylate[f]	25097-80-7	0.562		105	23	Presumed
	3-Phenyl-2-butanone			28	48	22	No
	1-Propionyl-1-phenylcyclohexane			15	63	19	No
	2,4-Dimethyl-2-phenyl-3-pentanone			20	34	17	No
	1-Propionyl-1-phenylcyclopentane			10	43	14	No
	2-Methyl-2-phenylcyclohexanone[g]				14	14	
	2,2,3-Trimethyl-5-phenylbicyclo[3.2.0]-hepten-3-one-6[h]			−47	100	13	
8	1,1,1-Triphenyl-2-propanone		0.61	23	40	12	Uncertain
	1,2,2,3-Tetramethyl-5-phenylbicyclo-[3.2.0]hepten-3-one-6[h]			44	45	10	
9	1,1-Diphenyl-2-propanone[e]		0.40	21	20	9	No
10	3,3-Diphenyl-2-butanone		0.48	40	17	5	No
11	2,2-Diphenylcyclopentanone		0.647	−17	13	4	No
	1-Pivalyl-1-phenylcyclopropane			−35	−28	−13	Yes
	1-Propionyl-1-phenylcyclopropane			−20	−20	−21	Yes
	1-Isobutyryl-1-phenylcyclopropane			−55	−61	−39	Yes
	1-Hydroxy-1,1-diphenyl-2-propanone			+142	−129	−38	Yes

[a] The first column is $\Sigma \sin^2 \theta \sin^2 \psi$ calculated by computer. For each angular setting, the value of $\sin^2 \theta \sin^2 \psi$ is multiplied by the mole fraction of ketone in that conformation, the mole fraction being based on calculated repulsion energies. [b] The term Δ is $\epsilon_{EtOH} - \epsilon_{C_6H_{12}}$ at the wavelength indicated. [c] The term % $\Delta_{290} = 100\Delta_{290}/\epsilon_{EtOH}$. [d] Reference 3. [e] Reference 8. [f] Reference 1. [g] Reference 13. [h] D. E. Bays and R. C. Cookson, *J. Chem. Soc. B*, 226 (1967).

against computer calculated values of $\Sigma \sin^2 \theta \sin^2 \psi$. Two lines are shown. The upper line has points for α-phenyl ketones which have at least one α-alkyl group. On the lower line are points for ketones without this feature. To explain this situation, two arguments can be advanced. Firstly, it can be assumed that the repulsion equations in the computer program do not correctly treat the forces between the rotors and an alkyl group on the same carbon. The computer program provides no flexibility or fitting of such groups. If this first explanation is correct, compounds with fixed ketone groups should have data falling on the lower line. This seems to be the case for 2,2-diphenylcyclopentanone.[9] For compounds with the benzobicyclo[2.2.2]octenone skeleton, data are inconclusive. Those for the compound of Cookson[1] (Table I) seem to lie closer to the upper line but for the parent compound was reported[10] 297 mμ (313, hexane) which would fall approximately between the two lines. However, the increased substitution of the phenyl ring and the tailings problem make these cases of questionable relevance. The value of $\Sigma \sin^2 \theta \sin^2 \psi$ for cyclohexanone with an axial phenyl (0.183 for ψ fixed at 120°) is too small to provide a clear decision between the two lines nor are spectral data altogether uniform.[11] A second explanation for the existence of two lines proposes that an α-alkyl group on an α-phenylketone increases the tendency of the phenyl group to interact with the ketone group.[12] This may result from a light decrease of the bond angle between Ph and Ac or from an inductive effect. This explanation suggests that the value of

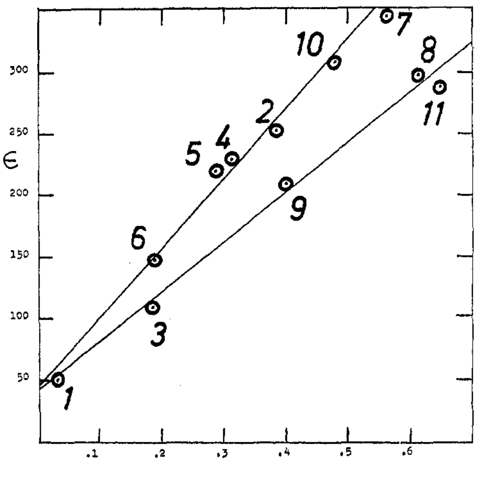

Figure 3.—A plot of $\epsilon_{C_6H_{12}}$ against the value of $\Sigma \sin^2 \theta \sin^2 \psi$: (1) 1-acetyl-1-phenylcyclopropane, (2) 1-acetyl-1-phenylcyclobutane, (3) phenylacetone, (4) 1-acetyl-1-phenylcyclohexane, (5) 1-acetyl-1-phenylcyclopentane, (6) 2-methyl-2-phenyl-3-butanone, (7) a benzobicyclo[3.2.0]octenone (see Table I), (8) triphenylacetone, (9) diphenylacetone, (10) 2,2-diphenyl-3-butanone, (11) 2,2-diphenylcyclopentanone.

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(9) Obtained through the courtesy of R. T. Conley, *Recl. Trav. Chim. Pays Bas*, **81**, 198 (1962).

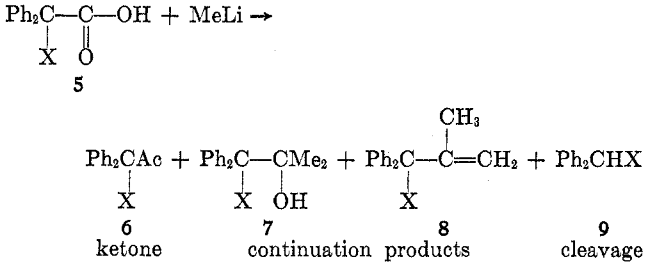
(10) K. Kitahonoki and Y. Takano, *Tetrahedron Lett.*, **24**, 1597 (1963).

(11) R. C. Cookson and J. Hudec, *J. Chem. Soc.*, **1962**, 429.

(12) When such a methyl group is directly on the donor, as in certain β,γ-unsaturated ketones, exaltations are increased.[1]

$\Sigma \sin^2 \theta \sin^2 \psi$ for 2,2-diphenylcyclopentanone is erroneous owing to the programming of the cyclopentane ring as planar. Puckering of the ring would lower the value toward that for the cyclohexane system. If, following this accomodation, the remaining values of $\Sigma \sin^2 \theta \sin^2 \psi$ are increased 15% for each alkyl group, a tolerably good agreement with linear behavior is obtained (plot not shown). Evidence favorable to this explanation exists. For example, 2-methyl-2-phenylcyclohexanone has a value of ϵ (100, EtOH)[13] almost as high as that for a cyclohexanone with a fixed axial phenyl,[14] this in spite of the fact that the main conformation should be equatorial phenyl and axial methyl. In a second example, a steroid which had an equatorial methyl in addition to an axial phenyl had the higher amplitude of its rotatory dispersion curve[11] although values of the extinction coefficients had the reversed order. This explanation led to reexamination of certain ketones useful in the present work. Values of ϵ (150, 160, EtOH) quoted[15] for 3-phenyl- and 3-methyl-3-phenyl-2-butanone have been revised upward (226, 193, EtOH) and that for 3,3-diphenyl-2-butanone (410, hexane)[15] revised downward (307, C_6H_{12}; 324, EtOH). The new data have been used in the tables and in Figure 3. Which of the two explanations represents the major factor is not, at present, known but this uncertainty should not lead, in our view, to the abandonment of the Cookson proposal. Other new evidence in favor of it can, after all, be cited. Observed[16] for 2-keto-2,3-paracyclophane were bands at 222 (15,300), 275 (380), and 307 (197) and for 2-keto-2,4-paracyclophane bands at 217 (13,100) and 285 (709). According to models, the latter compound can achieve a conformation near that shown by Figure 1b (90–90°) and the $n-\pi^*$ band is strong. The former compound has a stronger charge-transfer band but a weaker $n-\pi^*$ band. The angle ψ for the ketone group must be greater than 90° and is probably nearer to 120–150°. Consequently, the theory based on participation of the n electrons of oxygen, which calls for the greatest charge-transfer absorption at angular positions near 90–90° and the greatest $n-\pi^*$ absorption at positions near 60–60°, may be wrong on both counts.

The search for a synthesis of certain substituted diphenylacetones led to study of the addition of organolithium compounds to acids, a useful synthesis of ketones pioneered by Gilman[17] and surveyed further by Tegner.[18] The method has been employed for synthesis of monophenylacetones.[3,18,19] It has now been found that the reaction is not generally applicable to diphenylacetic acids. The yields indicated above reflect the composition of the neutral fraction and hence are based on acid consumed. In the case of benzilic acid, the purity of the ketone could be increased by use of inverse addition but in the other cases this change did not alter the product composition.



a, X = H
b, X = Me
c, X = OMe
d, X = OH

Dianion formation, %		
6	**7 + 8**	**9**
	33	67
		100
46	20	Trace

Experimental Section

All ketones were examined by nmr spectroscopy using a Varian A-60 apparatus. Elementary analyses were performed by Micro-Analysis, Inc., Wilmington, Del. Ultraviolet spectra were taken of solutions in 95% ethanol and purified cyclohexane with a Beckman DK-2 apparatus which was also used in the previous papers in this series.

New ketones are described in Table II. Certain others were prepared following literature directions: 1-phenylcyclopropyl ethyl ketone,[20] 1-phenylcyclopentyl ethyl ketone,[20] 3-phenyl-2-butanone,[21] 3-methyl-3-phenyl-2-butanone[22] and 3,3-diphenyl-2-butanone.[23] The latter three ketones were regenerated from extensively recrystallized semicarbazones. From 1-cyano-1-phenylcyclopentane[24] was obtained bis(1-phenylcyclopentyl) ketone[25] in yields of 16% (*i*-PrMgBr) and 21.5% (*i*-BuMgCl). No volatile ketones could be isolated in these cases or with 1-cyano-1-phenylcyclohexane[26] and these reagents.

2,2-Diphenylpropanoic Acid, 5b.—To 0.85 mol of methyllithium was added with stirring 0.30 mol of diphenylacetic acid, **5a**. The solution became orange. The excess lithium wire was removed and there was added 0.70 mol of methyl iodide. The solution was refluxed 3 hr and allowed to stand overnight. It was poured into water and the ether layer separated and dried. Evaporation gave a white solid (0.35 g), tetraphenylethane. Acidification of the aqueous layer gave crude **5b** (49.2 g, 77%). It was recrystallized from 2:1 ethanol–water. The final yield of colorless acid, mp 177–178°,[27] was 34.5 g or 53%. When methyl iodide was not added, diphenylacetic acid could be recovered in 80% yield by pouring the ether into water and acidifying the aqueous layer.

1-Hydroxy-1,1-diphenyl-2-propanone, 6d.—To 1500 ml of ether containing 0.975 mol of methyllithium was added a solution of 41.4 g (0.18 mol) of benzilic acid, **5d**, in 500 ml of ether. The color, momentarily gray, changed quickly to purple. The solution was allowed to stand overnight. It was poured onto ice. Acidification of the water layer gave no **5d**. Evaporation of the ether layer gave 41.1 g of liquid residue which was distilled under reduced pressure (0.1 mm). Although little change of boiling point was seen, three fractions were collected: bp 130° (18.3 g), 130° (7.9 g), and slightly above 130° (3.0 g). The third fraction

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[13] P. Colard, I. Elphimoff-Felkin, and M. Verrier, *Bull. Soc. Chim. Fr.*, 516 (1961).

[14] For 2,2-diphenylcyclohexanone 125 was reported (EtOH): W. B. Bennet and A. Burger, *J. Amer. Chem. Soc.*, **75**, 84 (1954).

[15] Extracted from small-scale graphs by the authors of ref 1.

[16] D. J. Cram and R. C. Hegeson, *J. Amer. Chem. Soc.*, **88**, 3515 (1966).

[17] H. Gilman and P. R. Van Ess, *ibid.*, **55**, 1258 (1933).

[18] C. Tegner, *Acta Chem. Scand.*, **6**, 782 (1952).

[19] K. Mislow and C. L. Hamermesh, *J. Amer. Chem. Soc.*, **77**, 1590 (1955).

[20] P. Läuger, M. Prost, and R. Charlier, *Helv. Chim. Acta.*, **42**, 2394 (1959).

[21] C. M. Suter and A. W. Weston, *J. Amer. Chem. Soc.*, **64**, 535 (1942).

[22] W. D. Kumler, L. A. Strait, and E. L. Alpen, *ibid.*, **72**, 1463, 4558 (1950).

[23] K. Sisido and H. Nozaki, *ibid.*, **70**, 776 (1948).

[24] C. H. Tilford, M. G. Van Campen, and R. S. Shelton, *ibid.*, **69**, 2902 (1947).

[25] While this work was in progress, a detailed study of this ketone was reported: J. W. Wilt, H. Philip, and D. G. Shultenover, *J. Org. Chem.*, **33**, 1666 (1968).

[26] A. W. Weston, *J. Amer. Chem. Soc.*, **68**, 2345 (1946).

[27] D. E. Batemen and C. S. Marvel, *ibid.*, **49**, 2914 (1927), reported 173–174°.

TABLE II

KETONES FROM NITRILES AND RMgX

$(CH_2)_{n-1}CPhCOR$	Registry no.	Yield, %	Bp or mp (mm), °C	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N
$n = 3$, R = Et		56	*a*						
Semicarbazone	25097-58-9		164–165	67.50	7.40	18.16	67.43	7.44	17.97
$n = 3$, R = *i*-Pr		40	62–64 (0.1)	82.93	8.56		83.10	8.35	
Semicarbazone	25097-59-0		194–195	68.54	7.70	17.13	68.60	7.67	16.99
$n = 3$, R = *t*-Bu		20	70–72 (0.1)	83.12	8.97		82.79	8.96	
$n = 6$, R = Et		69	91–92 (0.1)	83.29	9.32		83.20	9.19	
$Me_2CPhCOi\text{-}Pr^b$	25097-60-3	32	80–82 (0.1)	82.05	9.53		82.18	9.38	

[a] Reference 20. [b] Did not form a semicarbazone.

TABLE III

SPECTRAL VALUES FOR PHENYLATED ACETONES AND CYCLOALKANONES[a]

Ketone	Registry no.	C_6H_{12}		95% EtOH	
$(CH_2)_{n-1}CPhCOR$					
$n = 3$, R = Me[b]	1007-71-2	260 (205)	288 (50)	260 (245)	289 (75)
R = Et	25097-62-5	259 (296)	285 (114)	259 (276)	285 (94)
R = *i*-Pr	25097-63-6	261 (366)	285 (216)	260 (311)	285 (155)
R = *t*-Bu	25097-64-7	267 (396)	285 (238)	266 (361)	285 (210)
$n = 5$, R = Me[b]	4046-09-7	260 (220)	296 (220)	260 (252)	291 (292)
R = Et	17206-41-6	261 (239)	295 (268)	260 (249)	292 (311)
$n = 6$, R = Me[b]	3183-57-1	260 (208)	298 (230)	260 (250)	290 (314)
R = Et	2886-61-5	258 (225)	294 (274)	259 (240)	293 (337)
Bis(1-phenylcyclopentyl)	15811-02-6	261 (515)	295 (164)	261 (790)	290 (350)
		223 (18000)		225 (13800)	
$AcCH_2Ph^c$	103-79-7	260 (235)	289 (108)	258 (255)	283 (150)
AcCH(Ph)Me	769-59-5	258 (210)	289 (177)	258 (238)	283 (226)
$AcC(Ph)Me_2$	770-85-4	261 (211)	292 (147)	258 (234)	285 (193)
i-$PrCOC(Ph)Me_2$	25097-60-3	260 (215)	295 (164)	258 (235)	292 (198)
Ph_2CHAc^c	781-35-1	260 (485)	292 (210)	260 (506)	287 (230)
Ph_2CMeAc	2575-20-4	260 (460)	298 (307)	260 (500)	292 (324)
$Ph_2C(OH)Ac$	4571-02-2	259 (355)	284 (468)	258 (497)	290 (339)[d]
Ph_3CAc	795-36-8	261 (912)	300 (297)	260 (935)	295 (337)
2,2-Diphenylcyclopentanone	15324-42-2	260 (582)	305 (288)	259 (565)	305 (301)

[a] Values are wavelength in mμ and, in parentheses, molar extinction coefficient at maxima. Certain literature values are used without alteration and reference is accordingly made. [b] Reference 3. [c] Reference 8. [d] Quite close to the value for an ethanol solution given in ref 13.

solidified after a few days. The solid was recrystallized three times from cyclohexane to give colorless crystals, mp 91–92°, 0.5 g, with an nmr spectrum with four bands: 7.2 (10 complex), 2.70 (1 s), 2.08 (1 s), and 1.20 (6 s). The melting point reported for 1,1-diphenyl-2-methylpropanediol-1,2 is 91–92°.[28] Nmr analysis of fraction 1 using the upfield bands for methyl hydrogens indicated that the ratio of ketone to glycol was about 3:1. The ratio for fraction 2 was 2:1. These two fractions were combined and refluxed 14 hr with hydroxylamine hydrochloride (8.0 g) and sodium acetate trihydrate (15.7 g) in 200 ml of 50% ethanol. About 50% of the solvent was removed by distillation. The crude residue (23 g), obtained slowly by cooling, was recrystallized from 500 ml of ligroin. The crystals weighed 9.6 g. These were recrystallized from 250 ml of 60% ethanol. The yield of pure oxime, mp 165° (lit.[29] 159–160°), was 8.2 g. In contrast to the oxime prepared by inverse addition described below, it did not yellow slightly in air. The oxime was mixed with 250 ml of water and 3.5 g of pyruvic acid and refluxed 5 hr. The cooled solution was extracted with ether which was washed with sodium bicarbonate solution, dried, and evaporated. Vacuum distillation gave 3.9 g of ketone which soon solidified. Crystallization from ligroin gave massive crystals, mp 64–65° (lit.[30] 63.5°). The nmr spectrum had three bands: 7.02 (10 s), 4.60 (1 s), and 1.83 (3 s). Inverse addition of 0.206 mol of methyllithium to 0.069 mol of **5d** gave 7.1 g of recovered **5d** and 6.1 g of a pale yellow oil, bp 130° (0.1 mm). Spectral examination suggested that this oil contained no glycol but did contain some benzophenone. The oil gave the oxime as before, but this yellowed in air.

Addition of Methyllithium Solution to Diphenylmethoxyacetic Acid, 5c.—No difference was seen between forward and inverse addition. Methyllithium (0.122 mol) was added to 0.06 mol of **5c**. There was obtained 8.0 g of recovered **5c** and 2.9 g of a pale yellow oil which contained about 40% 1,1-diphenylethanol, 35% methyl benzhydryl ether, and up to 35% benzophenone. The first two compounds were isolated by chromatography followed by crystallization.

Addition of 2,2-Diphenylpropanoic Acid to Methyllithium.—A solution of 0.136 mol of MeLi was added to 0.068 mol of **5b**. There was obtained 10.2 g of recovered **5b** and 2.8 g of a yellow oil. Analysis of the nmr spectrum suggested that this oil was comprised of 67% 1,1-diphenylethane, 22% 3,3-diphenyl-2-methyl-2-butanol, and 11% 3,3-diphenyl-2-methyl-1-butene. A portion of the 1,1-diphenylethane was isolated by chromatography. Neither continuation product was isolated.

Registry No.—1,2,2,3-Tetramethyl-5-phenylbicyclo[3.2.0]hepten-3-one-6, 25097-81-8; 2-methyl-2-phenylcyclohexanone, 17206-54-1; 2,2,3-trimethyl-5-phenylbicyclo[3.2.0]hepten-3-one-6, 25097-78-3.

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