deuterioethanol containing sodium ethoxide, prepared by addition of 10 mg of sodium to the alcohol, was heated under reflux for 7 min. Distillation of the solvent (in about 5 min) to reduce the volume to 5 ml, followed by chilling at −15°, led to 100 mg of hexadeuterio **2b**, mp 165–169°. Dimer **2b** was found to be much less stable than isomer **2a** in refluxing ethanolic sodium ethoxide. Heating under the above conditions for periods longer than 30 min resulted in destruction of dimer **2b**. However, complete deuterium exchange of all enolizable hydrogens occurred very rapidly within 5–10 min with isomers **2a** and **2b** under the conditions described. The nmr spectrum of hexadeuterio **2b** was different from that of hexadeuterio **2a**. The phenyl protons appeared as a τ 2.3–2.9 multiplet with a principal signal at τ 2.53, the two ring benzyl protons as singlets at τ 6.18 and 6.30, and the two isopropyl methine protons as a multiplet centered at *ca.* τ 8.3; the remainder of the spectrum is discussed in the text. As with hexadeuterio **2a**, proton signals of all six enolizable protons were absent in the spectrum of hexadeuterio **2b**.

Attempts to prepare deuterio derivatives of cyclic dimer **2c** and acyclic dimer **3a** were unsuccessful. Cyclic dimer **2c** rapidly exchanged and epimerized into dimer **2b**, and acyclic dimer **3a** was converted quantitatively into hexadeuterio **2a** under the deuterium-exchange conditions (refluxing deuterioethanol–sodium methoxide for *ca.* 5–10 min). Trimer **4** was readily destroyed under these reaction conditions. However, a low yield of a sample was recovered after 5-min heating on the steam bath, mp 138–140°, which contained deuterium; almost complete exchange of hydrogen for deuterium of the C-6 ring methylene protons (d, τ 7.18), and side-chain methylene protons (multiplets at τ 7.83 and 8.25) occurred, as evidenced by the disappearance of these peaks in the recovered sample; the remaining enolizable protons were incompletely exchanged.

3,5-Diphenyl-2-isopropyl-2-cyclohexen-1-one (7).—To styryl isobutyl ketone (18.8 g, 0.10 mol) and acetophenone (12.0 g, 0.10 mol) dissolved in 100 ml of absolute ethanol was added a solution of sodium ethoxide prepared from 0.46 g of sodium dissolved in 15 ml of absolute ethanol. The solution was allowed to stand at 25° for 17 hr, then heated under reflux for 24 hr. The red-orange solution was neutralized with acetic acid and concentrated to dryness. The gummy residue was extracted with methylene chloride and the extracts were concentrated to yield 22.8 g of viscous red oil; crystallization from ethanol gave 1.24 g of crude cyclic dimer **2a**, mp 175–195°. The filtrate was distilled to yield 1.0 g of recovered acetophenone. The residue (19.7 g) was crystallized from hexane-cyclohexane to yield 2.0 g of additional **2a**, mp 170–200°. The filtrate was concentrated and the residue dissolved in benzene containing 0.1 g of camphorsulfonic acid; the solution was then heated under reflux for 16 hr. The solution was concentrated and the residue dissolved in hot hexane, treated with decolorizing charcoal (Darco G-60), filtered, and cooled to −15°. The gummy crystals (4.62 g) which were deposited were fractionally crystallized from hexane to yield 0.50 g of cyclohexenone **7**: mp 88–90°; recrystallization from hexane raised the melting point to 90–91°; $\nu_{\mathrm{KBr}}^{\mathrm{cm}^{-1}}$ 1640 (C=O), 1600 (C=C); $\lambda_{\max}^{\mathrm{EtOH}}$ 204 mμ (ϵ 17,900), 260 (9800).

Anal. Calcd for $C_{21}H_{22}O$: C, 86.85; H, 7.64; mol wt, 290.4. Found: C, 87.20; H, 7.60; mol wt, 321 (vapor osmometry).

3,5-Diphenyl-2-isopropyl-4-(3-methylbutanoyl)phenol (5).—A 0.4-g sample of cyclic dimer **2b** and 0.05 g of 10% palladium–charcoal were mixed and heated in a nitrogen atmosphere at 280–290° for 15 min, and at 300–310° for 5 min. The cooled residue was extracted with methylene chloride and the filtrates were concentrated to yield 0.37 g of residue which was crystallized from ethanol to yield 80 mg (20%) of dimer **2a** as long needles, mp 200–203° (when mixed with an authentic sample of **2a** the melting point was not depressed). No **2b** could be recovered. The filtrate was concentrated to dryness and the residue crystallized from benzene to yield 20 mg (5%) of crude **5**, mp 190–200°; recrystallization gave **5**, rhombic prisms, mp 200–201°; when mixed with an authentic sample, mp 202–203°, the melting point was not depressed (lit.[9c] mp 202–203°).

3,5-Diphenyl-2-isopropylphenol (6).—A mixture of 1.0 g of 3,5-diphenyl-2-isopropyl-2-cyclohexen-1-one (7) and 0.3 g of 10% palladium on charcoal was heated under gentle reflux in a nitrogen atmosphere for 10 min. The mixture was extracted with hot chloroform, filtered, and the filtrate concentrated to dryness. Crystallization of the residue from hexane gave 0.44 g (44%) of crude phenol **6**, mp 105–108°. Recrystallization from hexane gave needlelike prisms: mp 111–114° (lit.[9c] mp 114–115°); when mixed with an authentic sample, mp 114–115°, the melting point was not depressed; $\lambda_{\max}^{\mathrm{EtOH}}$ 206 mμ (ϵ 38,000), 235 (27,000), 264 (16,500), 300 (4450).

Anal. Calcd for $C_{21}H_{20}O$: C, 87.46; H, 6.99. Found: C, 87.57; H, 7.05.

Registry No.—**1**, 2892-18-4; **2a**, 18346-83-3; hexadeuterio **2a**, 18366-75-1; **2b**, 18346-82-2; hexadeuterio **2b**, 18366-76-2; **2c**, 18366-77-3; **3a**, 10596-48-2; **4**, 18366-78-4; **6**, 18354-80-8; **7**, 18354-81-9.

Acknowledgment.—The authors are indebted to Drs. Wayne R. Carpenter and Thomas G. Archibald for assistance in securing the mass spectra and for helpful discussions.

Photorearrangement of β,γ-Unsaturated Ketones. Application to the Synthesis of Bridged Bicyclic Ketones

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Department of Chemistry, The Ohio State University, Columbus, Ohio 43210

Received March 14, 1968

Ultraviolet irradiation of β,γ-unsaturated ketones such as **3**, **5**, and **7** in which the double bond occupies an exocyclic position with respect to the carbonyl group has been found to give rise exclusively to unsaturated bridged bicyclic ketones. The photorearrangements were shown to be completely reversible, the apparent photostationary states lying substantially in favor of **3**, **5**, and **7**. Although ketones **4**, **6**, and **8** do not predominate at equilibrium, isolation can be achieved by preparative-scale gas chromatography. These conversions therefore provide synthetic entry to previously unknown and otherwise difficultly accessible carbonyl compounds. The spectra and physical properties of these ketones are presented in some detail.

Light-induced transformations of β,γ-unsaturated ketones have been the subject of recent intensive study. The capability of such formally nonconjugated molecules for photochemical excitation and subsequent chemical change is linked to the enhanced n → π* absorption generally associated with the β,γ-unsaturated carbonyl chromophore.[2] In brief, it is now recognized that cyclic and acyclic β,γ-unsaturated ketones may undergo three general types of phototransformation depending upon the structure of the

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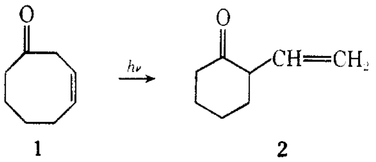
[1] The Ohio State University Postdoctoral Fellow, 1967–1968.

[2] (a) A. Moskowicz, K. Mislow, M. A. W. Glass, and C. Djerassi, *J. Amer. Chem. Soc.*, **84**, 1945 (1962); (b) D. E. Bays, R. C. Cookson, and S. Mackenzie, *J. Chem. Soc., B*, 215 (1967).

particular molecule: carbon monoxide expulsion,[3] Norrish type-I cleavage, often accompanied by allylic rearrangement,[4] and conjugated cyclopropyl ketone formation.[5] Photoreduction of a β,γ-unsaturated ketone has been observed in one instance.[6]

The molecular change involved in the allyl migration of an acyl radical as seen, for example, in the conversion of **1** into **2**[4l,m] is unprecedented in ground-state chemistry and suggests several diverse synthetic applications. The present paper describes the photorearrangement of bicyclic ketones in which the β,γ-olefinic linkage occupies an exocyclic position with respect to the carbonyl group.



1 **2**

Results

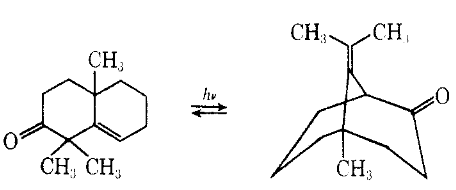
Irradiation of **3** in dilute pentane solution with a Hanovia 450-W mercury arc and Vycor optics led to the rapid establishment of a photostationary state consisting of the starting ketone **3** and a single photoproduct (see Table I).[7a] Further irradiation (beyond 60 min) did not appear to alter the ratio of the two components but gave a poorer recovery of the ketones presumably because of polymer formation. Preparative-scale vpc served to provide pure samples of the liquid photoketone which was characterized as its semicarbazone derivative. In agreement with structure **4**, this photoisomer exhibited an intense infrared (ir) band (in CCl_4) at 5.84 μ and an ultraviolet (uv) spectrum in isooctane solution [λ_{max} 286 mμ (ε 145) and 300 sh (125)] suggestive of a nonplanar β,γ-unsaturated ketone.[2] The nuclear magnetic resonance (nmr) spectrum, which is fully compatible with this structural assignment, displays, *inter alia,* a high field singlet at δ 1.43 assigned to the saturated methyl group at C-5, singlets at 1.68 and 1.92 attributable to the isopropylidine methyl groups, and a broad pattern (1 H) at 3.37 indicative of an allylic α-keto proton.[8-10] The substance does not exhibit absorption below δ 3.4. Final evidence that **3** and **4** are interrelated structurally by a noncomplicated photorearrangement process was obtained by irradiation of purified samples of **4**. A

TABLE I

TIME-COMPOSITION DATA FOR THE PHOTOREARRANGEMENTS OF **3**, **5**, AND **7**

Irradiation period, min	**3**, ratio **3**:**4**[a]	**5**, ratio **5**:**6**[a]	**7**, ratio **7**:**8**[a]
15	13.0:1	4.2:1	7.3:1
25		4.0:1	
30	10.0:1		6.7:1
35		3.8:1	
45	9.9:1		
55		3.9:1	
60			6.6:1

[a] Only two components were seen in each series of experiments.



3 **4**

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(3) (a) J. E. Starr and R. H. Eastman, *J. Org. Chem.*, **31**, 1393 (1966); (b) P. Dowd and K. Sachdev, *J. Amer. Chem. Soc.*, **89**, 715 (1967); (c) L. D. Hess and J. N. Pitts, *ibid.*, **89**, 1973 (1967).

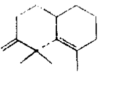
(4) (a) G. Büchi and E. M. Burgess, *ibid.*, **82**, 4333 (1960); (b) P. E. Eaton, *Tetrahedron Lett.*, 3695 (1964); (c) R. Criegee and J. Furrer, *Chem. Ber.*, **97**, 2949 (1964); (d) D. I. Schuster, M. Axelrod, and J. Auerbach, *Tetrahedron Lett.*, 1911 (1963); (e) G. O. Schenk and R. Steinmetz, *Chem. Ber.*, **96**, 520 (1963); (f) R. L. Cargill, M. E. Beckham, A. E. Seibert, and J. Dorn, *J. Org. Chem.*, **30**, 3647 (1965); (g) N. C. Yang and D. M. Thap, *Tetrahedron Lett.*, 3671 (1966); (h) E. Baggiolini, E. G. Herzog, S. Iwasaki, R. Schorta, and K. Schaffner, *Helv. Chim. Acta*, **50**, 297 (1967); (i) E. F. Kiefer and D. A. Carlson, *Tetrahedron Lett.*, 1617 (1967); (j) L. D. Hess, J. L. Jacobson, K. Schaffner, and J. N. Pitts, Jr., *J. Amer. Chem. Soc.*, **89**, 3684 (1967); (k) W. F. Erman and H. C. Kretschmar, *ibid.*, **89**, 3842 (1967); (l) L. A. Paquette and R. F. Eizember, *ibid.*, **89**, 6205 (1967); (m) J. K. Crandall, J. P. Arrington, and J. Hen, *ibid.*, **89**, 6208 (1967); (n) D. E. Bays and R. C. Cookson, *J. Chem. Soc., B*, 226 (1967); (o) R. G. Carlson and J. H. Bateman, *Tetrahedron Lett.*, 4151 (1967); (p) M. Fischer and B. Zech, *Chem. Ber.*, **101**, 2360 (1968); (q) L. A. Paquette, R. F. Eizember, and O. Cox, *J. Amer. Chem. Soc.*, **90**, 5153 (1968).

(5) (a) L. P. Tenney, D. W. Baykin, Jr., and R. E. Lutz, *ibid.*, **88**, 1835 (1966); (b) J. R. Williams and H. Ziffer, *Chem. Commun.*, 194 (1967); (c) J. R. Williams and H. Ziffer, *ibid.*, 469 (1967); see also ref 4q.

(6) R. L. Cargill, J. R. Damewood, and M. M. Cooper, *J. Amer. Chem. Soc.*, **88**, 1330 (1966).

(7) (a) The percentage compositions cited in Tables I and II were determined with a Varian-Aerograph Hy-Fi gas chromatograph[7b] and the values are uncorrected for differences in flame ionization response of the isomeric ketone pairs. This type of analysis was deemed most satisfactory, albeit that the values are not precisely correct, in view of the low concentrations of the bridged bicyclic ketones early in the irradiation experiments with **3**, **5**, and **7**. The internal consistency of the technique is obvious from the data in the two tables. (b) On the other hand, the values given in the text are product composition values derived from preparative-scale reactions (see Experimental Section), analysis of which has been made by thermal conductivity vapor phase chromatography (vpc). Because differences in thermal conductivity response are generally minimal, the photostationary-state values obtained by this technique are considered more accurate.

(8) A referee has raised the question that the ir, uv, and nmr spectra of this photoproduct may be abnormal, thereby allowing for several alternative structural possibilities such as i–iii. Although we have not been successful in our varied attempts to degrade or to synthesize in unequivocal fashion the bridged bicyclic ketones (see footnote 9), this point does not seem well taken since the nmr chemical shift data completely rule out such alternative formulations. It is also difficult to reconcile the complete reversibility of the photoisomerization (*vide infra*) with these alternatives. Furthermore, we are not prepared to accept the premise that the spectral properties of the photoisomers need be abnormal (see particularly ref 10).



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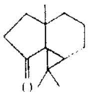

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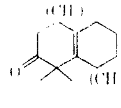
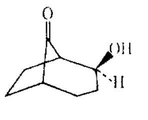


iii

(9) Despite this disadvantage, the photoisomerization pathway appears to be the only available route to such bridged ketones (with the exception of **9**) at the present time. We have tried without success to convert by means of a variety of reactions the ketols iv [N. A. LeBel and L. A. Spurlock, *J. Amer. Chem. Soc.*, **84**, 4360 (1962)] and v [A. C. Cope, D. L. Nealy, P. Scheiner, and G. Wood, *ibid.*, **87**, 3130 (1965)] and the diketone vi [J. R. Hargreaves and P. W. Hickmott, *Tetrahedron Lett.*, 4173 (1966)] into the desired β,γ-unsaturated ketones. Further, efforts to degrade **6** to vi by means of the ozonolysis procedure of Meinwald and Gassman [*J. Amer. Chem. Soc.*, **82**, 5445 (1960)] were to no avail, further degradation to more highly oxygenated material being observed.



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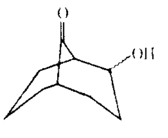

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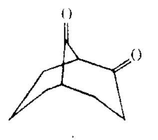


vi

(10) C. H. DePuy and P. R. Story, *J. Amer. Chem. Soc.*, **82**, 627 (1960).

Table II

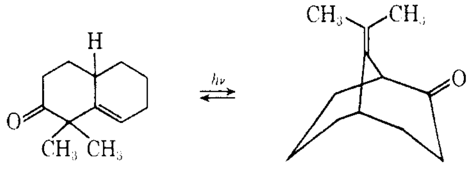
Time–Composition Data for the Photorearrangements of **4**, **6**, and **8**

Irradiation period, min	**4**, ratio **3**:**4**[a]	**6**, ratio **5**:**6**[a]	**8**, ratio **7**:**8**[a]
10	1.4:1	0.9:1	0.6:1
20	4.3:1	2.0:1	2.4:1
30	7.6:1	3.1:1	5.2:1
40	9.5:1	3.7:1	6.8:1
50	9.7:1	3.8:1	6.9:1
60	9.7:1		

[a] Only two components were seen in each series of experiments.

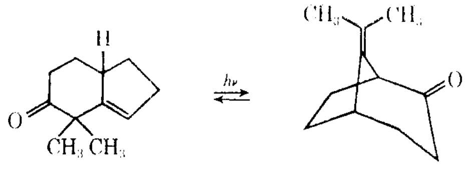
photostationary state which was virtually identical with that observed when proceeding from **3** was rapidly attained (see Table II).[7a]

Similarly, ketone **5** was found to give rise to **6** when irradiated under identical conditions; again, a photostationary state was rapidly established (see Table I). It is interesting that the nonbridged ketone **5** predominates to the extent of approximately 77%, whereas in the case of **3** the product distribution is such that **3** is present to the extent of about 94%.[7b] Photoketone **6** exhibited a 5.84-μ carbonyl band in the ir which is characteristic[11] of a cyclohexanone. The uv spectrum (isooctane) [λ_{max} 293 mμ (ϵ 130), 302 (130), and 311 sh (100)] is characteristic of a β,γ-unsaturated carbonyl chromophore.[2,10] The 60-MHz nmr spectrum showed the isopropylidene methyl groups as singlets at δ 1.73 and 1.66. In addition, the allylic α-keto proton was seen at δ 3.25 and the allylic bridgehead proton at 3.07; this is to be compared with the nmr spectrum of **4** which lacks the latter absorption because of the presence of a methyl group at that position.



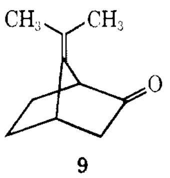
5 6

Irradiation of tetrahydroindanone **7** in dilute pentane solution again rapidly effected the establishment of a photoequilibrium with a lone photoketone which also displayed 5.83-μ ir carbonyl absorption characteristic of a six-membered ring ketone. The nmr spectrum was very similar to that of **6** with three-proton singlets at δ 1.75 and 1.62 and broadened one-proton signals centered at 3.30 and 3.03. The uv spectrum in isooctane exhibited maxima at 288 mμ sh (ϵ 360), 296 (420), 305 (390), and 317 (225). These data and analogy to the rearrangement of **3** and **5** indicated that this photoketone is 8-isopropylidenebicyclo[3.2.1]octan-2-one (**8**).



7 8

In the case of **8**, there is observed an increase in λ_{max} and also in the extinction coefficient over that for its two higher homologs, **4** and **6**. These data suggest somewhat improved interaction between the carbonyl group and the double bond in **8**, in full agreement with the observation of such interaction in Dreiding models of **4**, **6**, and **8** and with the spectral parameters previously reported for congener **9** [λ_{max} 308 mμ (ϵ 423)].[10]



9

The photostationary state in this last instance was found to consist of approximately 88% **7** and 12% **8**,[7b] independent of the direction from which the equilibrium was approached (Tables I and II).

The behavior of α,β-unsaturated cyclic ketones under conditions of electron impact has been the subject of considerable study.[12] It is now recognized that such systems often undergo mechanistically interesting alkyl and aryl rearrangements. Because β,γ-unsaturated ketones have been little studied, and particularly in view of the isomeric nature of the three ketone pairs **3**–**8**, we were led to examine their mass spectra (see Table III). The mass spectra of ketones **3**, **5**, and **7** differ markedly from those of their bridged bicyclic isomers. Not only do these ketones give rise to abundant molecular ions, but fragmentations involving M − 43 and M − 55 ions occur to a significant extent. In contrast, bridged bicyclic ketones **6** and **8** exhibit very weak molecular ions and considerable fragmentation to low molecular weight ions. The base peak in both cases is found at *m/e* 43. The mass spectrum of **4** is quite complicated. From such data it is clear that electron-impact fragmentation (70 eV) of the two ketone pairs does not proceed exclusively by α-keto cleavage to afford identical allylic radical cations. Thus, although a number of organic compounds display parallel behavior on electron impact and pyrolysis,[13] such a comparison apparently cannot be extended in the present case to include photolysis.

Discussion

The photochemical interconversion of ketone pairs **3**-**8** unquestionably involves initial n → π^* excitation of the carbonyl group and cleavage of the allylic α-carbonyl bond. Migration of the acyl function to the alternate terminus of the allyl moiety can proceed in concerted fashion and therefore may not involve discrete diradical intermediates. The possible concerted nature of this photochemical change finds its basis in orbital symmetry considerations of such 1,3 suprafacial[14] sigmatropic shifts.[9]

Although the present report establishes the fact that

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(11) L. J. Bellamy, "The Spectra of Complex Molecules," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1958.

(12) R. L. N. Harris, F. Komitsky, Jr., and C. Djerassi, *J. Amer. Chem. Soc.*, **89**, 4765 (1967), and pertinent references cited therein.

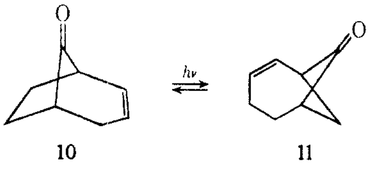
(13) M. P. Cava and R. J. Spangler, *ibid.*, **89**, 4550 (1967); D. C. DeJongh, R. Y. Van Fossen, and C. F. Bourgeois, *Tetrahedron Lett.*, 271 (1967), and references cited therein.

(14) The geometrical restraints placed upon ketones **6**–**11** by the arrangement of atoms can only lead to suprafacial shifts.

TABLE III
m/e VALUES AND PER CENT RELATIVE ABUNDANCE FOR VARIOUS FRAGMENT IONS OF KETONES **3–8**

Compd	m/e (% relative abundance)
4	39 (58), 40 (14), 41 (90), 43 (30), 51 (23), 52 (16), 53 (52), 54 (12), 55 (65), 57 (19), 65 (32), 66 (15), 67 (58), 69 (36), 77 (52), 78 (16), 79 (75), 80 (20), 81 (63), 82 (16), 91 (75), 92 (16), 93 (100), 94 (28), 95 (49), 105 (45), 106 (17), 107 (69), 108 (30), 109 (20), 110 (26), 117 (14), 119 (20), 121 (65), 122 (20), 123 (17), 131 (14), 133 (17), 135 (51), 136 (55), 137 (58), 149 (63), 150 (26), 159 (20), 163 (11), 164 (13), 177 (65), 192 (80), 193 (13)
6	41 (50), 42 (63), 43 (100), 57 (24), 71 (12), 79 (14), 123 (12), 135 (12), 178 (15)
8	39 (13), 41 (38), 42 (74), 43 (100), 56 (14), 57 (32), 71 (20), 72 (11), 164 (5)
3	39 (47), 40 (10), 41 (100), 51 (15), 53 (36), 55 (43), 57 (14), 65 (18), 67 (35), 69 (26), 77 (36), 78 (12), 79 (48), 80 (10), 81 (49), 91 (55), 92 (13), 93 (82), 94 (20), 95 (35), 105 (27), 106 (13), 107 (55), 108 (20), 109 (13), 110 (20), 120 (15), 121 (51), 122 (14), 123 (14), 133 (12), 135 (39), 136 (40), 137 (50), 149 (51), 150 (18), 159 (10), 163 (10), 164 (11), 177 (56), 192 (84), 193 (13)
5	39 (52), 41 (83), 43 (50), 51 (18), 52 (11), 53 (37), 55 (34), 65 (21), 67 (59), 69 (20), 77 (47), 78 (17), 79 (95), 80 (22), 81 (42), 91 (61), 92 (18), 93 (67), 94 (26), 95 (14), 105 (24), 106 (10), 107 (65), 108 (18), 119 (20), 121 (43), 122 (18), 123 (91), 124 (12), 135 (96), 136 (35), 163 (12), 178 (100), 179 (13)
7	39 (45), 41 (50), 43 (17), 51 (17), 52 (10), 53 (26), 55 (20), 65 (21), 66 (11), 67 (28), 77 (39), 78 (13), 79 (53), 80 (28), 81 (12), 91 (56), 92 (12), 93 (86), 94 (12), 105 (28), 107 (89), 108 (55), 109 (100), 110 (12), 120 (42), 121 (34), 122 (12), 131 (12), 136 (11), 164 (85), 165 (10)

4, **6**, and **8** can be synthesized photochemically from readily available precursors, it was disappointing to observe that these bridged ketones do not exceed their nonbridged counterparts at the apparent photostationary states.[15] Germane to this question of product distribution is the recent report by Erman and Kretschmar[4k] that the more strained cyclobutanone **11** predominates over **10** at photoequilibrium (1.7:1). Two other examples studied by these workers followed the same course. However, the examples presented herein and earlier[4] demonstrate unequivocally that product distribution is determined solely by the photochemical properties of the molecules in question and is not related to their relative thermodynamic stabilities. In particular, utmost caution should be exercised in attempts to correlate wavelength and intensity of n → π^* absorption bands of such β,γ-unsaturated ketones with product distribution, particularly when broad spectrum light sources are employed. The precise output of such lamps at the different wavelengths is frequently difficult to assess; therefore, correlations with available uv absorption data cannot be made justifiably. Whether product distribution will be predictable when appropriate monochromatic light sources are used under strictly controlled conditions remains to be determined.



10 **11**

Experimental Section[16]

1,1,4a-Trimethyl-1,3,4,4a,5,6,7-heptahydronaphthalen-2-one (**3**).—This ketone was prepared in the manner described by Marshall and Hochstetler[17] and Yanagita, Hirakura, and Saki.[18] From 10.0 g of 4a-methyl-3,4,4a,5,6,7,8-heptahydronaphthalen-2-one[19] there was obtained 8.24 g of a colorless liquid, bp 73.5–75.5° (0.5 mm), which was a mixture of two components in the ratio 8.05:1. Pure **3** was obtained by regeneration (pyruvic acid) of the recrystallized (*sec*-butyl alcohol) semicarbazone: mp 222–224° dec. The purified ketone displayed mp 32–33.5° (lit.[18] mp 31.5–32.5°); $\lambda_{\max}^{\text{isooctane}}$ 228 mμ (ϵ 35), 296 sh (35), and 305 sh (30); $\delta_{\text{TMS}}^{\text{CCl}_4}$ 5.51 (triplet, J = 4.3 Hz, 1 H, vinyl proton), 2.6–1.4 (complex pattern, 10 H, methylene protons), 1.17 (singlet, 6 H, C-1 dimethyl protons), and 0.98 (singlet, 3 H, C-4a methyl group).

9-Isopropylidene-5-methylbicyclo[3.3.1]nonan-2-one (**4**).—A solution of 2.00 g (10.4 mmol) of **3** in 600 ml of pentane was irradiated for 30 min under a nitrogen atmosphere with a 450-W medium-pressure Hanovia Type L mercury arc in a quartz immersion well apparatus fitted with a Vycor filter. Removal of the solvent *in vacuo* at 25° gave a colorless oil (1.96 g) which was shown by vpc (column A,[20] 155°) to be a mixture of unchanged **3** and a single photoproduct (**4**) in the ratio 14.4:1. This mixture was subjected to preparative-scale vpc separation (column A,[20] 140°) to afford 1.53 g (76.5%) of **3** and 0.107 g (5.4%) of **4**: mp *ca.* 25°; $\lambda_{\max}^{\text{CCl}_4}$ 5.84, 6.84, 7.28, 8.00, 8.36, 8,57, 8.94, 9.15 μ; $\lambda_{\max}^{\text{isooctane}}$ 286 (ϵ 145), 300 sh mμ (ϵ 125); $\delta_{\max}^{\text{CCl}_4}$ 3.37 (broad signal, 1 H, allylic α-keto proton), 2.5–1.5 (complex pattern, 10 H, methylene protons), and 1.92, 1.68, and 1.43 (singlets, 3 H each, methyl groups). This ketone was characterized as its semicarbazone, mp 185–187° dec (from methanol).

Anal. Calcd for $C_{14}H_{23}N_3O$: C, 67.43; H, 9.30; N, 16.85. Found: C, 67.54; H, 9.24; N, 16.87.

1,1-Dimethyl-1,3,4,4a,5,6,7-heptahydronaphthalen-2-one (**5**).—This compound was prepared according to the method of Marshall and Andersen.[21] From 10.0 g of 3,4,4a,5,6,7,8-heptahydronaphthalen-2-one[22] there was obtained 11.7 g of crude product which by vpc analysis (column B,[20] 150°) was a mixture of two major components in the ratio 2.5:1. Purification of **5** was achieved by means of the semicarbazone, mp 185.5–187° (from methanol), to give a colorless oil: bp 86–87° (0.7 mm) [lit.[21] bp 62–64° (0.25 mm)]; $n^{25}\text{D}$ 1.5045; $\lambda_{\max}^{\text{isooctane}}$ 289 mμ (ϵ 80), 297 (85), 306 (75), and 317 (40); $\delta_{\text{TMS}}^{\text{CCl}_4}$ 5.53 (doublet of triplets, $J_{8,7}$ = 3.9 Hz, $J_{8,4a}$ = 1.7 Hz, 1 H, vinyl proton), 2.9–1.3 (complex pattern, 11 H, methylene protons), and 1.21 and 1.13 (singlets, 3 H each, methyl groups).

9-Isopropylidenebicyclo[3.3.1]nonan-2-one (**6**).—Irradiation of a solution of 1.50 g (8.45 mmol) of **5** in 450 ml of pentane in the above apparatus for 30 min afforded, after concentration *in vacuo* at 0°, 1.48 g of a yellow oil which was shown by vpc (column A,[20] 130°) to be a mixture of unchanged **5** and a single photoproduct **6** in the ratio 3.4:1. Preparative-scale vpc separation (column B,[20] 135°) of this mixture afforded 0.592 g (39.5%) of **5** and 0.104 g (6.9%) of **6**: $\lambda_{\max}^{\text{CCl}_4}$ 5.84, 6.92, 7.30, 7.55, 8.14, 9.16 μ; $\lambda_{\max}^{\text{isooctane}}$ 293 mμ (ϵ 130), 302 (130), and 311 sh (100); $\delta_{\text{TMS}}^{\text{CCl}_4}$ 3.25 and

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(15) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 2511 (1965).

(16) Melting points were determined with a Thomas–Hoover melting point apparatus and are corrected. Ir spectra were recorded with a Perkin-Elmer Infracord Model 137 spectrometer fitted with sodium chloride prisms. Uv spectra were determined with a Cary 14 recording spectrometer. Nmr spectra were obtained with a Varian A-60 spectrometer purchased with funds made available through the National Science Foundation. The mass spectra were measured with an AEI MS-9 mass spectrometer at an ionizing energy of 70 eV. The microanalyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

(17) J. A. Marshall and A. R. Hochstetler, *Chem. Commun.*, 732 (1967).

(18) M. Yanagita, M. Hirakura, and F. Saki, *J. Org. Chem.*, **23**, 841 (1958).

(19) J. A. Marshall and W. I. Fanta, *ibid.*, **29**, 2501 (1964).

(20) Column A: 0.25 in. × 5.5 ft aluminum column packed with 20% SE-30 on 60/80 mesh Chromosorb W. Column B: 0.25 in. × 5.5 ft aluminum column packed with 20% SF-96 on 60/80 mesh Chromosorb W. All preparative gas chromatographic work was accomplished with Varian-Aerograph A-90P3 gas chromatographs fitted with thermal conductivity cell detectors.

(21) J. A. Marshall and N. H. Andersen, *J. Org. Chem.*, **31**, 667 (1966).

(22) G. S. Stork, A. Brizzolara, H. Landesman, J. Szmuszkovicz, and R. Terrell, *J. Amer. Chem. Soc.*, **85**, 207 (1963).

3.07 (broad signals, 1 H each, bridgehead protons), 2.9–1.5 (complex pattern, 10 H, methylene protons), and 1.73 and 1.66 (singlets, 3 H each, isopropylidene methyl groups). This ketone was characterized as its semicarbazone, mp 205–207° dec (from methanol).

Anal. Calcd for $C_{13}H_{21}N_3O$: C, 66.35; H, 9.00; N, 17.86. Found: C, 66.46; H, 8.98; N, 17.74.

4,4-Dimethyl-4,6,7,7a-tetrahydroindan-5-one (**7**).—Treatment of 10.0 g of 3,6,7,7a-tetrahydroindan-5-one[22] according to the procedure of Marshall, Andersen, and Johnson[23] gave 5.43 g of a colorless liquid, bp 52–55° (0.5 mm), which contained approximately 77% **7**. Purification was achieved *via* its semicarbazone, mp 209–210.5° dec (from methanol), to give **7**: bp 55.5–56.5° (0.6 mm); $n^{25}\text{D}$ 1.4935; $\lambda_{\max}^{\text{isooctane}}$ 289 mμ (ε 90), 298 (95), 308 (85), and 319 (45); $\delta_{\text{TMS}}^{\text{CCl}_4}$ 5.34 (doublet of doublets, $J_{3,2}$ = 2 Hz, $J_{3,7a}$ = 2 Hz, 1 H, vinyl proton), 3.0–1.3 (complex pattern, 9 H, methylene protons), and 1.22 and 1.20 (singlets, 3 H each, methyl groups).

8-Isopropylidenebicyclo[3.2.1]octan-2-one (**8**).—A solution of 1.50 g (9.15 mmol) of **7** in 450 ml of pentane was irradiated for 30 min under the predescribed conditions. Removal of the solvent *in vacuo* at 25° gave 1.49 g of a light yellow oil which was shown by vpc (column A or B,[20] 130°) to be a mixture of unchanged **7** and a single photoproduct **8** in the ratio 7.6:1. Preparative vpc (column B,[20] 130°) of this mixture led to the isolation of 0.874 g (58%) of **7** and 0.130 g (8.7%) of **8**: $\lambda_{\max}^{\text{CCl}_4}$ 5.83, 6.89, 7.04, 7.28, 7.65, 8.10, 9.74 μ; $\lambda_{\max}^{\text{isooctane}}$ 288 sh mμ (ε 360), 296 (420), 305 (390), and 317 (225); $\delta_{\text{TMS}}^{\text{CCl}_4}$ 3.30 and 3.03 (broad signals, 1 H each, bridgehead protons), 2.7–1.75 (complex pattern, 8 H, methylene protons), and 1.75 and 1.62 (singlets, 3 H each, isopropylidene methyl groups). This ketone was characterized as its semicarbazone, mp 205–206° dec (from methanol).

Anal. Calcd for $C_{12}H_{19}N_3O$: C, 65.12; H, 8.65; N, 18.99. Found: C, 65.18; H, 8.64; N, 19.06.

Photoequilibration Experiments.—Solutions (*ca.* 1%) of ketones **3–8** in pentane were placed under a nitrogen atmosphere in quartz test tubes, affixed to the exterior of the quartz well, and irradiated in the manner described above. The progress of the reactions were monitored by vpc analysis on a Varian-Aerograph Hy-Fi Model 600D gas chromatograph. Aliquots were obtained by piercing the septum-sealed test tubes with a syringe of the proper size.

Registry No.—**3**, 4668-61-5; **3** semicarbazone, 18366-32-0; **4**, 18346-76-4; **4** semicarbazone, 18346-77-5; **5**, 2020-07-7; **5** semicarbazone, 5164-39-6; **6**, 18346-78-6; **6** semicarbazone, 18346-79-7; **7**, 18366-35-3; **7** semicarbazone, 18366-36-4; **8**, 18346-80-0; **8** semicarbazone, 18346-81-1.

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[23] J. A. Marshall, N. H. Andersen, and P. C. Johnson, *J. Amer. Chem. Soc.*, **89**, 2748 (1967).

Notes

Ferrocene Studies. II.

The Reaction of Ferrocenyllithium with Aromatic Aldehydes[1]

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In general, organometallic compounds react with aromatic aldehydes to give secondary alcohols. A recent exception is the reported formation of 2-aroylpyrroles from the reaction of pyrrylsodium with aromatic aldehydes.[2] This reaction was proposed by Raines to proceed through an alkoxide reduction involving a second mole of the aldehyde.

We now wish to report that the reaction of ferrocenyllithium (I) with aromatic aldehydes in tetrahydrofuran gave aryl ferrocenyl ketones (II). Thus *p*-chlorbenzaldehyde, tolualdehyde, anisaldehyde, and ferrocenecarboxaldehyde gave the appropriate aryl ferrocenyl ketone (II) and no secondary alcohol when either a 3:1 or 1:1 *M* ratio of the aldehyde was added to ferrocenyllithium (I) in tetrahydrofuran. The expected alcohol was obtained (together with the ketone) only when benzaldehyde was allowed to react in a 1:1 molar ratio. With an excess of aldehyde, benzaldehyde also gave rise to ketone and no alcohol.

This reaction apparently follows a course similar to that proposed by Raines[2] in the pyrrole series. Thus when phenylferrocenylmethanol (III) was treated with *n*-butyllithium, alkoxide IV was formed as indicated by the formation of the ether V upon the addition of methyl iodide. When benzaldehyde was added to IV benzoylferrocene (II, Ar = C_6H_5) was obtained (Scheme I).

The ferrocenyllithium (FcLi) was prepared from bromoferrocene in tetrahydrofuran.[3] That complete lithiation of the bromoferrocene had occurred was checked by direct carbonation to form ferrocenecarboxylic acid. In all cases liquid aldehydes were purified by distillation under a nitrogen atmosphere before use and the tetrahydrofuran was distilled freshly from lithium aluminum hydride. In all cases a significant amount of ferrocene appears as a product of the reaction. This could arise by a simple proton abstraction from impurities or solvent, as a product from some mechanistic pathway, or more likely as the result of hydrolysis of unused ferrocenyllithium which had not reacted with the aldehyde. The later reasoning would

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[1] Part I.: F. D. Popp and J. A. Kirby, *J. Chem. Eng. Data*, **8**, 604 (1963). We should like to thank the Norwich Pharmacal Co. for financial support of a portion of this work.

[2] S. Raines, *J. Org. Chem.*, **32**, 227 (1967).

[3] H. Rosenburg, J. M. Barton, and M. M. Hollander, Abstracts of 2nd Annual International Symposia on Organometallic Chemistry, Madison, Wis., Aug 30–Sept 3, 1965. We should like to thank Dr. Rosenberg for his helpful comments in regard to this preparation.