citation of **3** (10^{-2} M in benzene; λ_{max} 370 nm (ϵ 63))[7] using a Corning 7380 glass filter (transmitting $\lambda >$ 340 nm) and an external 275-W sun lamp gave, in addition to extensive polymer formation, two new photoproducts **4** and **5** in a ratio of 1:7 after 24–48 hr. These products could be isolated in approximately 10% yield by passage of the crude photolysate through a short neutral alumina column (chloroform eluent); final separation of **4** and **5** was achieved by means of preparative vapor-phase chromatography (70% recovery).[8] Photolysis using *tert*-butyl alcohol–benzene (80:20) as solvent under otherwise identical conditions led to a **4**:**5** ratio of 5:1; employment of methanol, hexane, or acetonitrile afforded virtually complete polymer formation.

Photoproducts **4**, mp 67.5–68.5°, and **5**, mp 147–150°, were shown to be isomeric with starting material by means of elemental analysis and mass spectrometry. Their structures were assigned on the basis of spectral data, hydrogenation studies, mechanistic consideration, their thermal interconversion, and finally, in the case of **4**, on a single-crystal X-ray structure determination.

Distinguishing spectral features of **4** which support its structure are the following: a 5.72-μ carbonyl ir stretch,[9] a two-proton vinyl hydrogen multiplet centered at τ 4.15, and a broad uv absorption (MeOH) at 293 nm (ϵ 17, n $\rightarrow$ π^*). Hydrogenation over palladium on charcoal gave the dihydro derivative:[10] bp 55° (0.05 mm); ir ($CHCl_3$) 5.71 (C=O) μ; uv max (MeOH) 288 nm (ϵ 48, n $\rightarrow$ π^*).

Crystals of tricyclo[4.4.0.$0^{3,7}$]dec-8-ene-2,5-dione (**4**) are monoclinic, a = 6.806 (1), b = 15.171 (1), c = 7.667 (1) Å, β = 92.18 (1)°, Z = 4, space group $P2_1/n$. The structure was determined with Cu Kα scintillation counter data by direct methods (symbolic addition procedure programmed by Long[11]), and refined by full-matrix least squares, the final R being 0.046 for 984 observed reflections. Anisotropic thermal factors were used for C and O; H atoms were refined isotropically. Bond lengths are normal, and the associated angles show slight deviations from the expected values[12] which may be related to the bridged structure. Intermolecular contacts correspond to van der Waals interactions. A complete report of the crystallographic analysis will be published separately.[13]

The structure of photoproduct **5** was indicated by infrared (KBr) carbonyl stretching frequencies at 5.68 and 5.80 μ and by uv (MeOH) n $\rightarrow$ π^* absorptions at 296 (ϵ 260) and 310 nm (ϵ 230) characteristic of β,γ-unsaturated ketones.[14] The 220-MHz nmr spectrum, while complex, supported structure **5**. The vinyl hydrogens appeared essentially as triplets centered at τ 3.39 and 4.07 with a mutual coupling of 8 Hz. The C_4 methylene protons (τ 6.90 and 7.69) were basically doublets with a geminal coupling of 17 Hz; the large exo–endo chemical-shift difference is similar to that observed for the α-methylene protons of camphor.[15] The C_{10} methylene protons appeared at τ 8.04 and 8.40 with a geminal coupling of 12 Hz; both were essentially doublets with smaller vicinal couplings. The C_6 methine appeared as a clean triplet, J = 7 Hz, at τ 6.66. The remaining methine protons gave complex multiplets centered at τ 6.81, 7.37, and 7.56. Hydrogenation of **5** over palladium on charcoal gave the dihydro derivative:[10] mp 151–152°; ir ($CHCl_3$) 5.70 and 5.81 (C=O) μ; uv max (MeOH) 292 nm (ϵ 55, n $\rightarrow$ π^*); and no vinyl hydrogens in the nmr.

Sealed tube thermolysis of **5** at 200° gave complete conversion to **4** within 4 hr, further substantiating the former's sutructure. This thermolysis did not occur under the vpc conditions employed[8] in the separation of **4** and **5** nor were **4** and **5** sensitive to the photolysis conditions.

The mechanism we currently favor for the conversion of the butadiene–benzoquinone adduct to **4** and **5** is shown in Scheme I. This involves n $\rightarrow$ π^* excitation of **3** followed by β-hydrogen abstraction through a five-membered transition state[16] giving resonance-stabilized diradical **6** which may close to either **7** or **8** followed by ketonization to afford **4** and **5**, respectively. It is tempting to speculate that the failure of adducts **1**, n = 1 and 2, to undergo this rearrangement is due to the bridgehead character of the radical which would necessarily be formed by β-hydrogen abstraction.

Diradical **6** in its ketonized form is a likely intermediate in the thermolysis of **5** to **4** in view of the steric requirements of the concerted process.[17]

Further product and mechanistic studies with a variety of quinone–diene adducts are in progress.

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(7) The n $\rightarrow$ π^* nature of this absorption was verified by its progressive blue shift in solvents of increasing polarity: hexane, 370 nm; ether, 367 nm; ethyl acetate, 365 nm; acetone, 364 nm; acetonitrile, 362 nm; methanol, 358 nm.

(8) Vapor-phase chromatography isolation was achieved using a 5 ft × 1/4 in. stainless steel column packed with 20% DEGS on 60–80 Chromosorb W at a temperature of 170° and a helium flow rate of 140 ml/min.

(9) This value is in accord with the 5.72-μ carbonyl band observed for 2-norbornanone. See Sadtler Standard Infrared Spectra Catalog 20, No. 20280, Sadtler Research Laboratories, Inc., Philadelphia, Pa., 1962.

(10) All new compounds gave satisfactory elemental analyses.

(11) R. E. Long, Ph.D. Thesis, University of California at Los Angeles, 1965.

(12) L. E. Sutton, Ed., *Chem. Soc., Spec. Publ.*, No. 11 (1958); No. 18 (1965).

(13) J. Trotter and C. S. Gibbons, manuscript in preparation.

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

(15) P. V. Demarco, D. Doddrell, and E. Wenkert, *Chem. Commun.*, 1418 (1969).

(16) Intramolecular hydrogen abstractions of this type through cyclic five-membered transition states, although rare, have been previously observed; see A. Padwa and W. Eisenhardt, *J. Amer. Chem. Soc.*, 93, 1400 (1971).

(17) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969); J. A. Berson, *Accounts Chem. Res.*, **1**, 152 (1968).

(18) National Research Council Predoctoral Fellow, 1968–present.

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Photochemical Isomerization of 4-Isopentyl-4-methylcyclopentenone

Sir:

We wish to describe briefly the photochemical isomerization of 4-isopentyl-4-methylcyclopentenone (**1**) and to point out that the transformations observed can be best explained by assuming intramolecular abstraction of hydrogen by the β-carbon atom of the α,β-unsaturated ketone system.

Cyclopentenone **1** was prepared from known[1] diethyl

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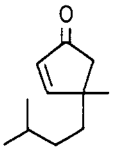
(1) G. L. Handley, E. R. Nelson, and T. C. Somers, *Aust. J. Chem.*, **13**, 129 (1960).

3-isopentyl-3-methylglutarate (**2**), available *via* Guareschi condensation on 5-methyl-2-hexanone. Reductive cyclization of **2** using sodium in liquid ammonia[2] gave acyloin **3** [oil; ir 3450 (broad), 1752 (s) cm^{-1}; nmr δ (0.91 (d, J = 5 Hz), 1.10 (s), 9 H), 1.10–2.60 (m, 9 H), (3.80 (broad, exchanges with D_2O), 4.20 (m), 2 H)].[3] Esterification of **3** with methanesulfonyl chloride in pyridine yielded the mesylate **4** [mixture of epimers, mp 53–57°; ir 1765 (s), 1365 (s), 1175 (s) cm^{-1}; nmr δ 0.91 (d, J = 5 Hz, 6 H), 1.15 (s, 3 H), 1.20–2.70 (m, 9 H), 3.10 (s, 3 H), 4.90 (m, 1 H)],[3] which readily lost methanesulfonic acid in hot hexamethylphosphoramide[4] to furnish **1** [oil; ir 1723 (s) cm^{-1}; nmr δ (0.88 (d, J = 5 Hz), 1.20 (s), 0.80–2.20 (m), 16 H), 5.95 (d, J = 5.5 Hz, 1 H), 7.30 (d, J = 5.5 Hz, 1 H)].[3]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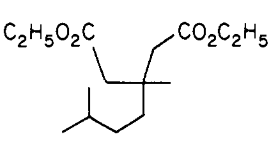

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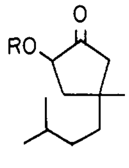
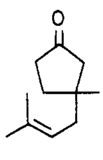


3, R = H
4, R = CH3SO2

Irradiation[5] of ketone **1** (1 mg/ml) in benzene solution afforded a mixture of three isomeric products in the approximate yields indicated: 62% **5** [oil; ir 1750 (s), 1675 (w), 840 (w) cm^{-1}; δ 1.05 (s, 3 H), (1.15–2.40 (m), 1.62 (broad s), 1.74 (broad s), 14 H), 5.16 (m, 1 H)],[3] 24% **6** [oil; ir 3060 (w), 1750 (s), 1650 (m), 880 (ms) cm^{-1}; nmr δ 1.08 (s, 3 H), (1.30–2.50 (m), 1.74 (broad s), 13 H), 4.66 (m, $w_{1/2}$ = 4 Hz, 2 H)],[3] and 11% **7** [oil; ir 1745 (s) cm^{-1}; nmr δ 0.95 (s, 3 H), 1.00 (s, 3 H), 1.13 (s, 3 H), 1.20–2.00 (m, 9 H)].[3] With pentane as solvent the overall reaction was faster but led to reduced yields: 44% **5**, 8% **6**, and 10% **7**. The three products were separated and purified by preparative vpc.[6] Taken with satisfactory analytical and spectroscopic data, the following transformations firmly establish the structures assigned to these compounds. Catalytic hydrogenation of both **5** and **6** led to cyclopentanone **8** [oil; ir 1748 (s) cm^{-1}; nmr δ 0.90 (d, J = 5 Hz, 3 H), 1.02 (s, 3 H), 1.12–1.92 (m, 7 H), 1.94 (s, 2 H), 2.13–2.43 (m, 2 H)],[3] which was also available on reduction[7] of mesylate **4** with calcium in liquid ammonia. Bicyclic ketone **7** suffered rapid type I cleavage on irradiation[5] in methanol to form methyl ester **9** [oil; ir 1740 cm^{-1}; nmr δ (0.90 (s), 1.00 (s), 9 H), 1.10–1.70 (m, 8 H), 2.20 (s, 2 H), 3.63 (s, 3 H)],[3] presumably by way of the expected[8] ketene intermediate. Saponification of **9** gave the corresponding carboxylic acid **10** [mp 47.5–48.5°; ir 3400–2400 (m), 1710 (s) cm^{-1}; nmr δ (0.93 (s), 1.08 (s), 1.0–2.0 (m), 17 H), 2.18 (s, 2 H), 12.01 (s, 1 H)],[3] which was identical with an authentic sample prepared by a known procedure from 4,4-dimethylcyclohexanone.[9]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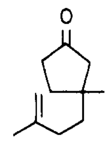
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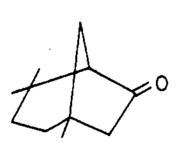
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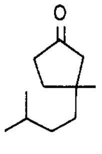
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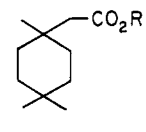
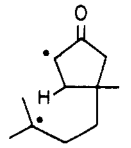
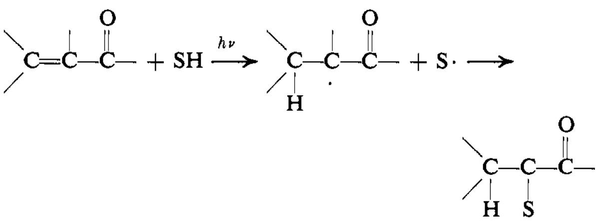


9, R = CH3
10, R = H



11

Formation of these three products (**5**, **6**, and **7**) in nearly quantitative yield suggests that in the reactive excited state the single significant process leading to chemical reaction is abstraction of hydrogen from the side chain by the β-carbon atom through a six-membered intermediate to form **11**. A second hydrogen transfer in **11** could lead to **5** and **6**, while collapse of **11** with carbon–carbon bond formation would provide **7** directly. If the pathway involving **11** is correct, this intramolecular reaction appears to be closely related to the photochemical α-addition of solvent to unsaturated ketones,[10,11] for which an analogous course (eq 1) has been suggested.[10] Studies currently in progress with deuterium-labeled **1** should clarify this matter.[12]



$$>C{=}C{-}\overset{O}{\overset{\|}{C}}{-} + SH \xrightarrow{h\nu} >\underset{H}{C}{-}\dot{C}{-}\overset{O}{\overset{\|}{C}}{-} + S\cdot \longrightarrow >\underset{H}{C}{-}\underset{S}{C}{-}\overset{O}{\overset{\|}{C}}{-} \quad (1)$$

In addition to being interesting mechanistically, the observed photochemical isomerization of ketone **1** to **5** and **6** implies a new, synthetically attractive method for long-range activation of a hydrocarbon chain, while the closure to **7** represents a simple entry into the bicyclo[3.2.1]octane system.

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[2] The procedure used was adapted from H. Kwart and J. A. Ford, Jr., *J. Org. Chem.*, **24**, 2060 (1959).

[3] This new compound gave satisfactory elemental analysis for carbon and hydrogen.

[4] This elimination reaction is a simple extension to a mesylate of the dehydrohalogenation of α-halo ketones described by R. Hanna, *Tetrahedron Lett.*, 2105 (1968).

[5] Irradiations were carried out with a Hanovia Model L mercury lamp (No. 679A-36) in a quartz immersion well; filters used were Pyrex 7740 (λ >2800 Å) for **7** and Corning No. 3320 uranium glass (λ >3300 Å) for **1**.

[6] Vapor-phase chromatography (vpc) was carried out at 160° using a Varian Aerograph Model A-90-P3 equipped with a 10 ft × $^3/_8$ in. aluminum column packed with 30% QF-1 on Chromosorb W.

[7] J. H. Chapman, J. Elks, G. H. Phillipps, and L. J. Wyman, *J. Chem. Soc.*, 4344 (1956).

[8] J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, Chapter 5.

[9] The sequence employed followed closely the synthesis of 1-methylcyclohexaneacetic acid from cyclohexanone, as described by W. Parker and R. A. Raphael, *J. Chem. Soc.*, 1723 (1955).

[10] D. Belluš, D. R. Kearns, and K. Schaffner, *Helv. Chim. Acta*, **52**, 971 (1969), and references cited therein.

[11] W. C. Agosta and A. B. Smith, III, *J. Amer. Chem. Soc.*, in press.

[12] A hexacyclic photoproduct noted by W. Herz and M. G. Nair, *ibid.*, **89**, 5474 (1967), appears to arise by intramolecular hydrogen transfer and bond formation analogous to the conversion of **1** to **7**.

[13] Fellow of the Alfred P. Sloan Foundation.

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