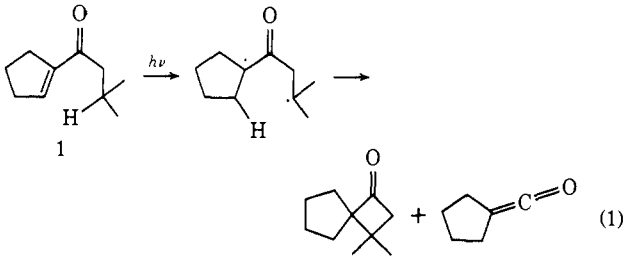
Photochemical Reactions of 3-Substituted Cyclopentenyl Ketones

Amos B. Smith, III, and William C. Agosta*

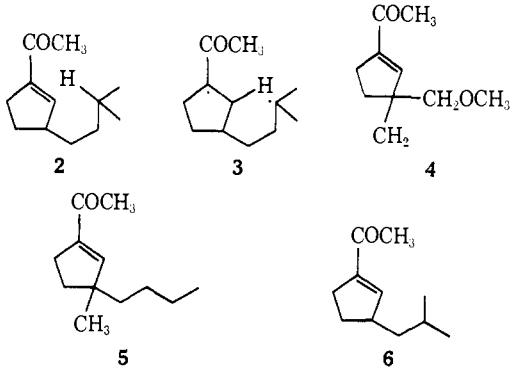
Contribution from the Laboratories of The Rockefeller University, New York, New York 10021. *Received December 3, 1973*

Abstract: Photolysis of four 3-substituted cyclopentenyl ketones (**2**, **4**–**6**) has been investigated. The observed products can be explained by 1,5-hydrogen transfer from the side chain to the β-carbon atom of the unsaturated ketone with formation of a biradical intermediate (as **3** and **14**), which then reacts in one of three ways: transfer of a second hydrogen atom to the ring (**7**, **19**), collapse (**12**), or 1,6 transfer of hydrogen from ring to side chain (**8**, **13**, **20**, and **23**). Labeling experiments with **24** and **25** provide strong support for this pathway to **8** and **13**.

Photolysis of alkyl cyclopentenyl ketones such as **1** leads to products most readily rationalized as arising from an intermediate biradical formed on intramolecular 1,5-hydrogen transfer (eq 1).[1] In view of this, as

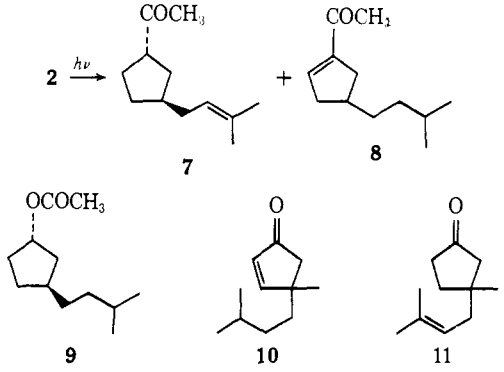


(1)



well as earlier related observations involving cyclic ketones,[2,3] it seemed interesting to inquire whether similar transformations would occur in 3-substituted cyclopentenyl ketones such as **2**. Irradiation of these compounds might furnish biradical intermediates (as **3**), the fate of which could not be predicted with certainty. We have investigated this matter through preparation and photolysis of ketone **2** as well as the related compounds **4**, **5**, and **6**. The reactions observed can indeed be explained by intermediates such as **3** and are reported below. Photochemical results are described first, followed by preparative experiments.

Irradiation of **2** in benzene solution (~0.006 *M*, λ > 3380 Å) led to two products: isopentenyl ketone **7**



(50%[4]) and the isomeric conjugated ketone **8** (15%). The latter product was identified by comparison with an authentic sample; its formation from **2** is discussed in a later section. The structure of the major product **7** is consistent with its ir and nmr spectra. The indicated trans stereochemistry is that expected if **7** arises from biradical **3**, since the second intramolecular transfer of hydrogen, from side chain to the ring radical center of **3**, should deliver this hydrogen cis to the alkyl side chain and lead to the trans compound shown. This stereochemistry was substantiated by hydrogenation of the double bond of **7** and subsequent Baeyer–Villiger oxidation using peroxytrifluoroacetic acid[5] to furnish *trans*-3-isopentylcyclopentyl acetate (**9**), which was identical with an authentic sample prepared as later described. Formation of **7** from **2** is closely analogous to the known[3] photoisomerization of 4-isopentyl-4-methylcyclopentenone (**10**) to the isopentenyl ketone **11**.

Photolysis of **4** also led to two interesting rearrangements. Isomerization of the double bond within the ring took place once again, giving this time **13** (45%), which was identical with an authentic sample. The other product isolated was **12** (44%), which clearly can be accounted for by collapse of the postulated intermediate biradical **14**. The structure of **12** rests on spectroscopic data and Wolff–Kishner reduction to bicyclic ether **15**, which was also available through independent stepwise synthesis.[6] The isomerization of **4**

(1) A. B. Smith, III, and W. C. Agosta, *J. Amer. Chem. Soc.*, **95**, 1961 (1973).

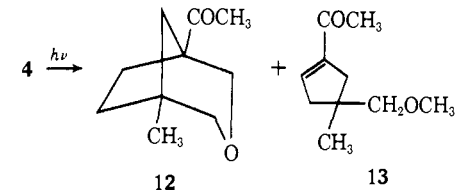
(2) W. Herz and M. G. Nair, *J. Amer. Chem. Soc.*, **89**, 5474 (1967); D. Bellus̆, D. R. Kearns, and K. Schaffner, *Helv. Chim. Acta*, **52**, 971 (1969); R. Reinfried, D. Bellus̆, and K. Schaffner, *ibid.*, **54**, 1517 (1971); W. C. Agosta and A. B. Smith, III, *J. Amer. Chem. Soc.*, **93**, 5513 (1971); J. A. Turner, V. Iyer, R. S. McEwen, and W. Herz, *J. Org. Chem.*, **39**, 117 (1974).

(3) S. Wolff, W. L. Schreiber, A. B. Smith, III, and W. C. Agosta, *J. Amer. Chem. Soc.*, **94**, 7797 (1972).

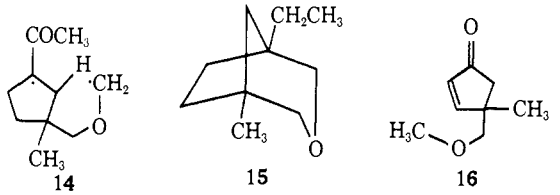
(4) All yields are based on converted starting material and were determined by calibrated vapor phase chromatography (vpc).

(5) W. D. Emmons and G. B. Lucas, *J. Amer. Chem. Soc.*, 77, 2287 (1955). Retention of stereochemistry in this oxidation has been demonstrated in numerous instances; references are given by H. O. House, "Modern Synthetic Reactions," 2nd ed, W. A. Benjamin, Menlo Park, Calif., 1972, p 324.

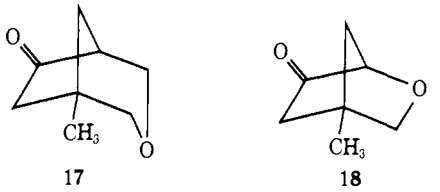
(6) S. Wolff, A. B. Smith, III, and W. C. Agosta, *J. Org. Chem.*, in press.



12 13



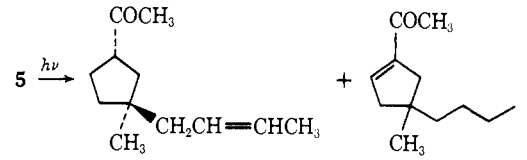
14 15 16



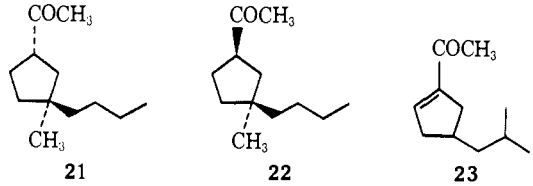
17 18

to **12** has good analogy in cyclopentenone photochemistry, since photolysis of **16** yields the corresponding bicyclic product **17**.[3] Indeed, comparison of the 220-MHz nmr spectra of these two keto ethers **12** and **17** provided strong initial evidence for the structure of **12**. Irradiation of **16** also affords an anomalous second product, the keto ether **18**, in which a methylene group has been lost.[7] There was no evidence for this type of unusual reaction in the photochemistry of **4**.

Parallel reactions occurred with **5**, which yielded photoproducts **19** (13%, apparently a ~9:1 mixture of



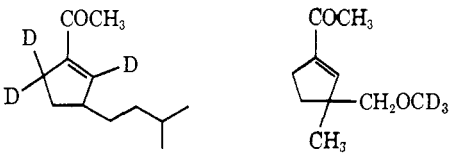
19 20



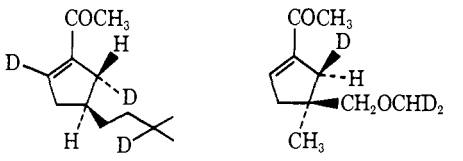
21 22 23

trans and cis olefins by ir and nmr) and **20** (52%). Hydrogenation of the double bond of **19** gave the butyl compound **21**, which was also formed (along with **22**) on hydrogenation of **20**. The stereochemistry of the acetyl group of **19** (and therefore **21**) is assigned in analogy with the configuration proved for **7** above. Irradiation of the isobutyl compound **6** led to its double bond isomer **23** (~10%) plus nonvolatile products.

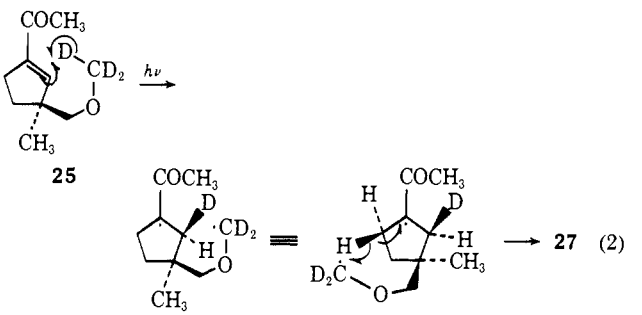
We turn now to consideration of the reaction common to **2**, **4**, **5**, and **6**, that is, the shift of the conjugated double bond within the cyclopentene ring leading to **8**, **13**, **20**, and **23**. Superficially this is a [1,3]-sigmatropic rearrangement of hydrogen.[8] It is formally related to similar transformations in various other systems,[9] for which both intermolecular and intramolecular pathways have been put forward in specific instances. In the present investigation the other photoisomers concomitantly formed are all conveniently rationalized through 1,6-biradical intermediates, a circumstance suggesting that these biradicals may play a role in isomerization of the double bond within the ring. We have investigated this possibility through preparation and photolysis of **24** and **25**, suitable deuterium labeled versions of **2**



24 25



26 27



25 28

and **4**. Photolysis of these substrates yielded products with no loss of label and no scrambling of deuterium in recovered starting material. Nmr spectra of the ketones isolated require the labeling patterns depicted in **26** and **27**. The stereochemical assignments follow from the chemical shift effects expected of vicinal substituents; in **8** allylic hydrogen cis to the adjacent isopentyl group should be upfield from hydrogen cis to hydrogen, and in **13** allylic hydrogen cis to adjacent methyl should be upfield from hydrogen cis to methoxymethyl.[10] In the 220-MHz spectra of **8** and **13** the four allylic hydrogens appear as two multiplet signals, each for two protons. In both **26** and **27** it is the lower field allylic multiplet that is reduced to a single proton, consonant with the stereochemistry shown. This geometry is just that expected for intramolecular abstraction of hydrogen from the side chain by the β-carbon atom of the substrate enone through the sterically most favorable six-membered intermediate. These labeling patterns of **26** and **27** provide direct evidence that isomerization of **4** to **13** involves transfer of hydrogen from the methoxyl group to the β-carbon atom of **4** and that formation of **8** from **2** involves transfer of hydrogen from the incipient β-carbon atom of **8** to the side chain tertiary center. Together the results imply for these

(7) S. Wolff and W. C. Agosta, *J. Chem. Soc., Chem. Commun.*, 502 (1973).

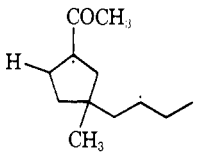
(8) R. B. Woodward and R. Hoffmann, *Angew. Chem.*, **81**, 797 (1969); *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

(9) For example, see F. J. McQuillin and J. D. Parrack, *J. Chem. Soc.*, 2973 (1956); W. G. Dauben and W. T. Wipke, *Pure Appl. Chem.*, **9**, 539 (1964); P. J. Kropp, *J. Amer. Chem. Soc.*, **89**, 3650 (1967); P. J. Kropp and H. J. Krauss, *ibid.*, **89**, 5199 (1967); K. A. Burdett, D. H. Yates, and J. S. Swenton, *Tetrahedron Lett.*, 783 (1973); N. P. Peet, R. L. Cargill, and J. W. Crawford, *J. Org. Chem.*, **38**, 1222 (1973).

(10) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, Oxford, 1969, pp 234–236, and references cited therein.

isomerizations a two-step process most simply accommodated by the intermediacy of biradicals **3** and **14** (or **28**). This conclusion is illustrated for the conversion of **25** to **27** in eq 2.

This two-step mechanism for isomerization of the cyclopentene double bond strongly suggests that the biradical intermediate can revert to starting ketone (*e.g.*, **28** → **25** in eq 2), as well as proceed to the isomeric product, since the transition state for reversion (1,5-hydrogen transfer) should be at least as favorable as that for isomerization (1,6-hydrogen transfer). Some indication that the geometry for 1,6 transfer is actually unfavorable, at least as an initial step, comes from photolysis of ketones **8**, **13**, and **20**. In these compounds, with the cyclopentene double bond now away from the side chain, 1,6 transfer of hydrogen from side chain to ring is necessary as the initial step to reach the same biradicals that can arise from **2**, **4**, and **5** on 1,5 transfer. However, irradiation of **13** yielded virtually only polymer, and **20** reacted apparently *via* 1,5 transfer (see **29**) rather than 1,6 shift, since the only product



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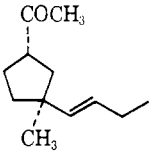
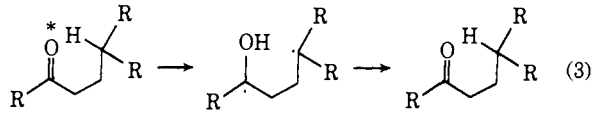


30

isolated was **30** (34%).[11] Ketone **8** gave largely polymer, with 5% of **7** the sole volatile product, and even this could result from an initial 1,5 transfer.

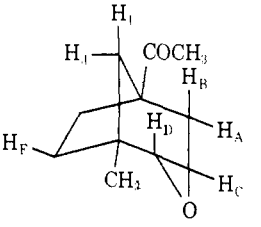
The suggestion that reversion of intermediates such as **28** to starting ketone is a favorable process implies that this may represent a significant pathway for radiationless decay in these compounds. Such a process would be analogous to the disproportionation of the biradical intermediate to ground state ketone (eq 3) which is



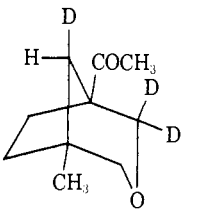
(3)

considered responsible for quantum inefficiency in the type II reaction.[12] Quantitative studies are required to evaluate the importance of such reversible transfer to the β-carbon atom as an energy wasting step in the photochemistry of α,β-unsaturated ketones. For the present we note that there are now several acylcyclopentenes and cyclopentenones in which intermolecular or intramolecular transfer of hydrogen to this center occurs in the observable photochemistry,[1-3] and this suggests a significant role for the reversible process.

In addition to **26** and **27** discussed above there were isolated from photolysis of ketones **24** and **25** trideuterated **7** and the labeled bicyclic ketone **31**. The specific labeling pattern shown for **31** is that predicted if it (and its unlabeled version **12** (≡**12a**)) arises by way of stereospecific transfer of methoxyl hydrogen to the ring. This pattern is also in keeping with the nmr spectrum of **31**, which may be instructively compared with the spectra of both **12** and **17**. Complete analysis of the



12a



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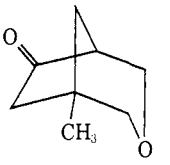

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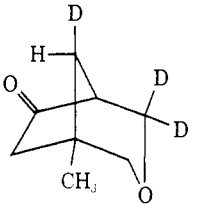
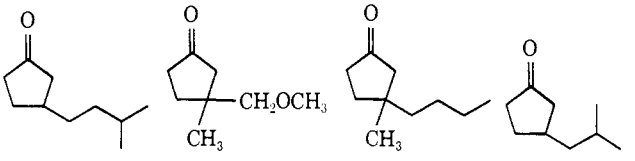


32

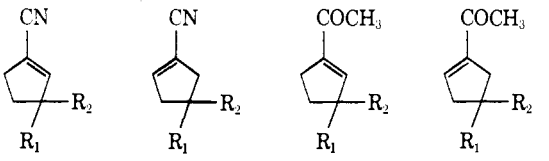
spectrum of **17** has been recorded previously.[3] The replacement of one pair of geminal carbinyl protons (H_A and H_B) in **31** is apparent in the spectrum, and the signal for H_C [δ 3.34 ppm (dd, J_{CD} = 10, J_{CJ} = 2 Hz)] points to the stereospecific retention of H_J in **31**. The specific long-range couplings H_C–H_J and H_A–H_J are seen in **17** as well as other bicyclo[3.2.1]octanes.[13] We reported earlier similar conclusions regarding the labeling pattern of **32** and its origin from **16**-OCD_3.[7]

Previous experience[1-3] all implicates a triplet state as the origin of these various hydrogen-transfer reactions. In agreement with expectation we have found that isomerization of **4** to **12** and **13** is efficiently sensitized by propiophenone and quenched by low concentrations of 2,3-dimethyl-1,3-butadiene.

Preparative Experiments. The eight acetylcyclopentenes were available from the related cyclopentanones **33a–d**. Of these, **33b**[3] and **33c**[14] were on hand,



33a **33b** **33c** **33d**



34 **35** **36** **37**

a, R_1 = H; R_2 = $CH_2CH_2CH(CH_3)_2$
b, R_1 = CH_3; R_2 = CH_2OCH_3
c, R_1 = CH_3; R_2 = $CH_2CH_2CH_2CH_3$
d, R_1 = H; R_2 = $CH_2CH(CH_3)_2$

while **33a** and **33d** were readily prepared by conjugate addition of isopentylmagnesium bromide and the corresponding isobutyl reagent to cyclopentenone in the presence of copper(I). Conversion of each ketone to the cyanhydrin, followed by dehydration with phosphorus oxychloride and pyridine, gave the unsaturated nitriles **34** and **35**. These underwent base-catalyzed

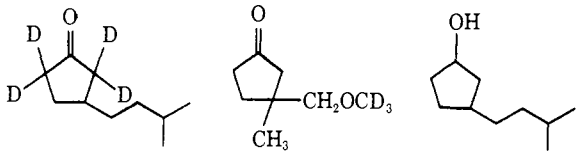
(11) Only the trans olefin shown was found. The structure and stereochemistry of **30** were proved just as outlined above for **19**.

(12) P. J. Wagner, *Accounts Chem. Res.*, **4**, 168 (1971), and references cited therein.

(13) B. Waegell and C. W. Jefford, *Bull. Soc. Chim. Fr.*, 844 (1964).

(14) Details of the preparation of **33c** by conjugate addition of lithium dibutylcuprate to 3-methylcyclopentenone will appear in a forthcoming publication of S. Wolff and W. C. Agosta.

hydrolysis in aqueous isopropyl alcohol[15] to the corresponding carboxylic acids, which reacted directly with methyllithium[16] to furnish the desired unsaturated ketones **36a–d** and **37a–d**, which correspond to **2**, **4**, **5**, **6**, **8**, **13**, **20**, and **23**. The various pairs of unsaturated nitriles could be separated and purified by preparative vpc. For preparative purposes it was more convenient, however, to carry each pair of nitriles through to the corresponding pair of methyl ketones and then effect separation of the double bond isomers at this final stage. The position of the double bond in each pair of isomeric ketones, as well as in the four pairs of nitriles, could be assigned from nmr spectra. In each pair the 3-substituted isomer, **34** or **36**, has two or three allylic protons while the 4-substituted isomer, **35** or **37**, has four allylic protons; the anticipated differences were apparent in the spectra. In addition, in each pair the 3-substituted compound, **34** or **36**, had shorter vpc retention time than the 4-substituted isomer, **35** or **37**. For the deuterated ketones **24** and **25** the same synthetic procedures were applied to **38** and **39**. The former was



38 **39** **40**

available through exhaustive exchange of **33a** using potassium carbonate in deuterium oxide–methanol-*O*-*d*, while the deuterated methoxycyclopentanone **39** was prepared by substituting iodomethane-d_3 for the ordinary reagent in the previously described[3] synthesis of **33b**.

For preparation of authentic *trans*-3-isopentylcyclopentyl acetate (**9**), ketone **33a** was reduced with lithium aluminum hydride to give a mixture of *cis*- and *trans*-3-isopentylcyclopentanol (**40**). Although neither the free alcohols nor their trimethylsilyl derivatives[17] were separable under any conditions tried, the acetates could be separated and purified by vpc. The stereochemical assignment follows from the fact that hydride reduction of both 3-*tert*-butyl- and 3-methylcyclopentanone gives similar mixtures in which the cis alcohol predominates.[18] The minor acetate was thus assigned trans structure **9**.[18a]

Experimental Section

Materials and Equipment. Solvents for photochemical experiments were Mallinckrodt benzene (analytical reagent) and Merck methanol (anhydrous reagent). All vpc was done using a Varian Aerograph Model 200 Autoprep or Model A-90-P3 with one of the following columns: (A) 30% Carbowax 1500, 10 ft × 3/8 in.; (B) 25% Carbowax 1500, 20 ft × 3/8 in.; (C) 30% QF-1, 20 ft × 3/8 in.; (D) 15% Carbowax 20M, 40 ft × 0.25 in.; (E) 30% QF-1, 50 ft × 0.25 in.; (F) 30% SE-30, 10 ft × 3/8 in. The column oven was operated at 90–190°, and helium carrier gas flow rate was 100–120 ml/min. Unless otherwise noted, both ir and nmr spectra were obtained for CCl_4 solutions, the former on a Perkin-Elmer Model 237B spectrophotometer and the latter on a Varian Model A-60 (60 MHz) or HR-220 (220 MHz) spectrometer. Ultraviolet spectra were obtained for solutions in 95% ethanol using a Cary Model 14 PM spectrophotometer. Melting points are corrected. Solutions were dried with either anhydrous Na_2SO_4 or $MgSO_4$. All photochemical experiments were carried out with Hanovia Model L mercury lamp (No. 679A-36) in a quartz immersion well using a uranium glass (Corning No. 3320) as filter. The reaction vessel was wrapped with aluminum foil.

General Procedure for Irradiations. A solution of the 1-acylcyclopentene (1 mg/ml) in benzene or methanol was flushed with dry nitrogen for 15–30 min and then irradiated for the stated time at about 15° under nitrogen with magnetic stirring. Benzene photolyses were monitored by ir using 1.0-mm cells. Photolyses in benzene were worked up by distillation through a long Vigreux column to yield the product as an oil. All products were obtained as colorless oils unless otherwise indicated.

Photolysis of 3-Isopentyl-1-cyclopenten-1-yl Methyl Ketone (2). A solution of 60 mg of **2** in 75 ml of benzene was irradiated for 17 hr. Vpc on column C indicated destruction of 83% of **2** and formation of two products. The first (50%) was shown to be **7**: ir 2955 (s), 2925 (s), 2860 (m), 1712 (vs), 1445 (m), 1370 (m), 1355 (m), 1162 (m) cm^{-1}; nmr (220 MHz) δ 1.05–1.41 (m, 3 H), 1.50–2.01 with br s at 1.59 and 1.68 (m, 12 H), 2.06 (s, 3 H), 2.84 (m, 1 H), 5.08 (m, 1 H); mass spectrum *m/e* 180.1506 (M^+, calcd for $C_{12}H_{20}O$, 180.1514).

The second (15%) was shown to be **8** by comparison of ir, nmr, and vpc retention time with authentic **8** described below.

Photolysis of 3-Methoxymethyl-3-methyl-1-cyclopenten-1-yl Methyl Ketone (4). A solution of 149.3 mg of **4** in 200 ml of benzene was irradiated for 10 hr. Vpc on column A indicated almost complete destruction of **4** and the formation of two products. Preparative vpc gave a pure sample of each product. The first (45%) was shown to be **13** by comparison of ir, nmr, and vpc retention times with those of authentic **13**. The second (44%) was shown to be **12**: ir 2950 (s), 2930 (m), 1705 (vs), 1455 (m), 1348 (m), 1095 (m) cm^{-1}; nmr (220 MHz) δ 0.945 (s, 3 H, CH_3), 1.36–1.53 (m, 2 H), 1.69–1.94 (m, 4 H), 2.02 (s, 3 H, $COCH_3$), 3.13 (dd, J_{CD} = 10, J_{DF} = 1 Hz, H_D), 3.32 (dd, J_{CD} = 10, J_{CJ} = 2 Hz, 1H, H_C), 3.34 (d, J_{AB} = 10 Hz, 1 H, H_B), 3.72 (dd, J_{AB} = 10, J_{AJ} = 2 Hz, 1 H, H_A).

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.37; H, 9.78.

Photolysis of 3-Butyl-3-methyl-1-cyclopenten-1-yl Methyl Ketone (5). A solution of 40 mg of **5** in 40 ml of benzene was irradiated for 8 hr. Vpc on column E indicated destruction of ~90% of **5** and the formation of two products. Preparative vpc gave a sample of each. The first (13%) was **19**: ir 3025 (w), 2950 (s), 2850 (w), 1715 (vs), 960 (m) cm^{-1}; nmr (220 MHz) δ 0.942 (s, 3 H), 1.32–2.00 (m, 11 H), 2.05 (s, 3 H), 2.28–2.54 (m, 1 H), 5.40 (m, 2 H); this sample appeared to contain ~12% of the cis olefin as indicated by a singlet at δ 0.918; mass spectrum *m/e* 188.1516 (M^+, calcd for $C_{12}H_{20}O$, 188.1514).

The second (52%) was **20** as shown by comparison of ir and vpc retention time with those of authentic **20**.

Photolysis of 3-Isobutyl-1-cyclopenten-1-yl Methyl Ketone (6). A solution of 43 mg of **6** in 45 ml of benzene was irradiated for 22 hr. Vpc on column D indicated destruction of 80% of **6** and formation of **23** (10%) as shown by comparison of ir and vpc retention times with those of authentic **23**.

Photolysis of 3-Isopentyl-1-cyclopenten-1-yl Methyl Ketone-2,5,5-d_3 (24). A solution of 200 mg of **24** in 200 ml of benzene was irradiated for 11 hr. Vpc on column C indicated almost complete destruction of **24** and the formation of two products with the same vpc retention times as **7** and **8**, respectively. The first was **7**-d_3: nmr (220 MHz) δ 1.05–1.41 (m, 2 H), 1.59 (br s, 3 H), 1.68 (br s, 3 H), 1.75–2.00 (m, 4 H), 2.06 (s, 3 H), 2.84 (br d, J = 10 Hz, 1 H), 5.08 (m, 1 H).

The second was **26** (15%): nmr (220 MHz) δ 0.85 (br s, 6 H), 1.09–1.50 (m, 5 H), 2.00–2.32 with s at 2.19 (m, 5 H), 2.54–2.78 (m, 1 H).

Photolysis of 3-Methoxymethyl-3-methylcyclopenten-1-yl Methyl Ketone-d_3 (25). A solution of 96.9 mg of **25** in 80 ml of benzene was irradiated for 10 hr. Vpc on column C indicated destruction of ~70% of **25** and formation of two products. Preparative vpc gave a pure sample of each. The recovered **25** was unchanged, indi-

(15) Previous experience with similar hydrolyses has shown that solvent methanol, but not isopropyl alcohol, is incorporated into the acidic product, presumably through Michael addition: R. A. Cormier and W. C. Agosta, *J. Amer. Chem. Soc.*, **96**, 1867 (1974).

(16) M. J. Jorgenson, *Org. React.*, **18**, 1 (1970).

(17) J. F. Klebe, H. Finkbeiner, and D. M. White, *J. Amer. Chem. Soc.*, **88**, 3390 (1966).

(18) J.-C. Richer and C. Gilardeau, *Can. J. Chem.*, **43**, 3419 (1965); R. G. Haber and B. Fuchs, *Tetrahedron Lett.*, 1447 (1966).

(18a) NOTE ADDED IN PROOF. For a recently reported photochemical rearrangement which appears to involve abstraction by the β-carbon atom in a steroidal 5-substituted acylcyclopentene, see F. Marti, H. Wehrli, and O. Jeger, *Helv. Chim. Acta*, **56**, 2698 (1973).

cating no deuterium exchange. The first product was **27** (~25%): nmr (220 MHz) δ 1.06 (s, 3 H), 2.04–2.23 with s at 2.20 (m, 5 H), 2.60 (ddd, $J_1 = 3$, $J_2 = 3$, $J_3 = 19$ Hz, 1 H), 3.10 (s, 2 H), 3.26 (m, 1 H), 6.98 (dd, $J_1 \sim J_2 \sim 2$ Hz, 1 H).

The second was **31**: nmr (220 MHz) δ 0.945 (s, 3 H, CH_3), 1.36–1.53 (m, 1 H), 1.69–1.94 (m, 4 H), 2.02 (s, 3 H, $COCH_3$), 3.14 (dd, $J_{CD} = 10$, $J_{DF} = 1$ Hz, H_D), 3.34 (dd, $J_{CD} = 10$, $J_{CJ} = 2$ Hz, 1 H, H_C). Proton designations are given in **12a**.

Photolysis of 4-Isopentyl-1-cyclopenten-1-yl Methyl Ketone (8). A solution of 58 mg of **8** in 80 ml of benzene was irradiated for 35 hr. Vpc on column C indicated destruction of 78% of **8** and formation of 5% of **7**, which was identified by ir spectrum and vpc retention time.

Photolysis of 4-Methoxymethyl-4-methyl-1-cyclopenten-1-yl Methyl Ketone (13). A solution of 100 mg of **13** in 83 ml of benzene was irradiated for 20 hr. Vpc on column A indicated destruction of 76% of **13**. No products were detected in greater than about 2% yield.

Photolysis of 4-Butyl-4-methyl-1-cyclopenten-1-yl Methyl Ketone (20). A solution of 71 mg of **20** in 70 ml of benzene was irradiated for 40 hr. Vpc on column D gave **30** (34%): ir 3025 (w), 2960 (s) 2870 (m), 1718 (vs), 965 (m) cm^{-1}; nmr (220 MHz) δ 0.974 (t, $J = 7$ Hz, 3 H), 1.06 (s, 3 H), 1.36–2.09 with s at 2.05 (m, 11 H), 2.77–2.99 (m, 1 H), 5.34 (m, 2 H); mass spectrum *m/e* 180.1508 (M^+, calcd for $C_{12}H_{22}O$, 180.1514).

***trans*-3-Isopentylcyclopentyl Methyl Ketone from Hydrogenation of 7.** A solution of 60 mg of **7** in 2 ml of methanol was hydrogenated over 10 mg of 5% palladium on carbon at about 1 atm. Work-up and isolation gave the desired product: ir 2950 (s), 2925 (s), 2870 (m), 2850 (m), 1712 (s), 1465 (m), 1360 (m), 1350 (m), 1160 (m) cm^{-1}; nmr (220 MHz) δ 0.865 (d, $J = 6$ Hz, 6 H), 1.00–2.09, 2.04 (m, s, 15 H), 2.72–2.82 (m, 1 H); mass spectrum *m/e* 182.1672 (M^+, calcd for $C_{12}H_{22}O$, 182.1670).

***trans*-3-Isopentylcyclopentyl Acetate (9). A. From Baeyer-Villiger Oxidation.** To 500 μl of peroxytrifluoroacetic acid[5] and 159 mg of Na_2HPO_4 in 1 ml of CH_2Cl_2 was added 50 mg of the ketone described immediately above in 1 ml of CH_2Cl_2. This mixture was heated at reflux for 30 min and worked up with water and ether. Vpc on column D gave the major product (70%) as an oil. This was identical with authentic **9** prepared below by nmr and vpc retention time.

B. From Reduction of 33a. Reduction of 485 mg of **33a** with $LiAlH_4$ in ether in the usual manner gave 486 mg of an oil which was a 3:2 mixture (nmr) of two products. This mixture was acetylated using acetic anhydride in pyridine and then separated by vpc on column D. The major product was *cis*-3-isopentylcyclopentyl acetate: ir 2955 (s), 2925 (s), 2870 (m), 1730 (vs), 1460 (m), 1455 (m), 1450 (m), 1240 (s), 1010 (m), cm^{-1}; nmr (220 MHz) δ 0.869 (d, $J = 7$ Hz, 6 H), 1.05–1.83 (m, 11 H), 1.93 (s, 3 H), 2.09–2.28 (m, 1 H), 4.94–5.04 (m, 1 H).

Anal. Calcd for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18. Found: C, 72.64; H, 11.16.

The second and minor product was **9**: ir 2955 (s), 2925 (s), 2870 (m), 1735 (vs), 1240 (s), 1010 (m) cm^{-1}; nmr (220 MHz) δ 0.869 (d, $J = 7$ Hz, 6 H), 1.05–2.09, 1.93 (m, s, 15 H), 5.00–5.12 (m, 1 H).

Anal. Calcd for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18. Found: C, 72.79; H, 11.18.

1-Ethyl-5-methyl-3-oxabicyclo[3.2.1]octane (15). To a mixture containing 23 mg of sodium hydride, 0.30 ml of hydrazine (97%), and 1 ml of freshly distilled ethylene glycol was added 5.6 mg of **12**. The resultant mixture was heated at 195° in a sealed tube for 8 hr. It was then added to water and extracted with pentane. After washing and drying, the solvent was carefully reduced to 0.20 ml through a Vigreux column. Vpc analysis on column C indicated the formation of one product. Preparative vpc gave a pure sample which was identical with authentic **15**[6] by comparison of ir and nmr spectra and vpc retention time.

***trans*-3-Butyl-*cis*-3-methylcyclopentyl Methyl Ketone (21). A. From Hydrogenation of 19.** A solution of 11.6 mg of **19** in 2 ml of methanol was hydrogenated over 11 mg of 5% palladium on carbon. Work-up and isclation gave a pure compound which was shown to be **21** by comparison of nmr, ir, and vpc retention time with that of material described below.

B. From Hydrogenation of 30. A 20.5-mg sample of **30** was reduced as described for **19** and the sole product identified, in the same way, as **21**.

C. From Hydrogenation of 20. A solution of 157 mg of **20** in 5 ml of methanol was hydrogenated over 24 mg of 5% palladium on carbon. Work-up, isolation and vpc analysis on column D indicated two products, in the ratio of 1:2. Preparative vpc gave a pure sample of each. The first was **22**: ir 2955 (s), 2925 (s), 2870 (m), 2860 (m), 1715 (s), 1460 (m), 1350 (m), 1160 (m) cm^{-1}; nmr (220 MHz) δ 0.91 (t, $J = 7$ Hz with s at 0.927, 6 H), 1.14–1.64 (m, 10 H), 1.73–1.95 (m, 2 H), 2.06 (s, 3 H), 2.82–3.04 (m, 1 H); mass spectrum *m/e* 182.1660 (M^+, calcd for $C_{12}H_{22}O$, 182.1670). The second was **21**: ir 2955 (s), 2925 (s), 2870 (m), 2860 (m), 1715 (s), 1460 (m), 1350 (m), 1160 (m) cm^{-1}; nmr (220 MHz) δ 0.91 (t, $J = 6$ Hz with s at 0.936, 6 H), 1.09–2.00 (m, 12 H), 2.05 (s, 3 H), 2.77–2.95 (m, 1 H); mass spectrum *m/e* 182.1665 (M^+, calcd for $C_{12}H_{22}O$, 182.1670).

Sensitization and Quenching Experiments with 4. Sensitization, quenching, and control samples were irradiated simultaneously through uranium glass in a revolving turntable apparatus. Irradiation of a 0.00359 *M* solution of **4** in benzene for 6.5 hr gave 71% conversion to **12** and **13** in the ratio of 0.79:1, respectively. An identical sample which contained 11.2 mol equiv of propiophenone, which absorbs 81% of the light, gave 100% conversion.

Irradiation of a 0.0036 *M* solution of **4** in benzene for 10 hr gave 87% conversion to **12** and **13**. Identical samples which contained 0.021 and 0.077 *M* 2,3-dimethyl-1,3-butadiene gave 36 and 19% conversion, respectively.

3-Isopentylcyclopentanone (33a).[19] A solution of isopentylmagnesium bromide was prepared from magnesium (1.32 g, 0.055 g-atom) and isopentyl bromide (4.10 g, 0.050 mol) in 50 ml of ether. The reaction mixture was cooled to 0°, and tetrakisiodo(tributylphosphine)copper[20] (1.575 g, 0.004 mol) was introduced with ether (10 ml), followed by dropwise addition of cyclopentenone (4.1 g, 0.050 mol) in 25 ml of ether. Upon the completion of the addition, the reaction mixture was poured into a solution of saturated NH_4Cl containing a few milliliters of NH_4OH. Extraction with ether drying, and removal of the solvent yielded 8.49 g. A short-path distillation (70–100° (1.0 Torr)) gave 1.917 g (22%) of **33a**, which was purified on column C: ir 2960 (s), 2925 (s), 2860 (m), 1748 (vs), 1465 (m), 1400 (m), 1380 (w), 1362 (w), 1150 (m) cm^{-1}); nmr (220 MHz) δ 0.887 (d, $J = 7$ Hz, 6 H), 1.14–1.32 (m, 2 H), 1.36–1.82 (m, 5 H), 1.91–2.36 (m, 5 H).

Anal. Calcd for $C_{10}H_{18}O$: C, 77.86; H, 11.76. Found: C, 78.04; H, 11.82.

3-Isobutylcyclopentanone (33d). Preparation and purification of **33d** was according to the procedure given above for **33a**, but using isobutyl bromide: ir 2960 (s), 2940 (m), 2900 (s), 2870 (m), 1740 (vs), 1465 (m), 1400 (m), 1380 (m), 1365 (m), 1150 (s) cm^{-1}; nmr (220 MHz) δ 0.905 (d, $J = 7$ Hz), 0.915 (d, $J = 7$ Hz) (6 H), 1.23–1.77 (m, 5 H), 1.86–2.36 (m, 5 H).

Anal. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 77.21; H, 11.49.

3-Isopentylcyclopentanone-*2,2,5,5-d*$_4$ (38). A mixture of 5.10 g of 3-isopentylcyclopentanone (**33a**), 5 ml of D_2O, 5 ml of ethanol-*O-d*, and 100 mg of K_2CO_3 was stirred at room temperature under nitrogen for 24 hr. The solvent was then removed on the rotary evaporator. This procedure was repeated three times, with a final stirring period of 1 week. Isolation and drying gave 2.86 g. Preparative vpc on column A gave a pure sample: ir 2960 (s), 2925 (s), 2865 (m), 2190 (vw), 2110 (vs), 1748 (vs), 1465 (m), 1380 (w), 1362 (w) cm^{-1}; nmr (220 MHz) δ 0.887 (d, $J = 7$ Hz, 6.00 H), 1.14–2.36 (m, 8.06 H).

3-Methoxymethyl-3-methycyclopentanone-*d*$_3$ (39). This ketone was prepared following the procedure for **33b**[8] but using iodomethane-d_3. Vpc retention time and nmr (except for methoxy signal) were identical with those of **33b**.[21]

General Procedure for Synthesis of 3- and 4-Substituted 1-Cyclopentene-1-carbonitriles. The appropriate 3-substituted cyclopentanone (0.032 mol) was added to NaCN (0.130 mol) dissolved in 20 ml of H_2O. This mixture was then cooled to −5° and $NaHSO_3$ (0.065 mol) dissolved in 20 ml of H_2O was added over a period of 30 min. After 2 hr at 5°, 30 ml of ether was added and the mixture vigorously stirred for 5 min. After separation of the phases, the aqueous phase was extracted several times with ether. The combined ether fractions were dried over $MgSO_4$ without further washing. Removal of the solvent yielded the appropriate cyanohydrin as a colorless liquid. On several occasions complete conversion to the cyanohydrin (as monitored by ir) required a second cycle of the above procedure.

The crude cyanohydrin was dissolved in 15 ml of benzene and 15 ml of pyridine. This mixture was cooled to 0° and a mixture of 15

(19) I. S. David and C. Imer, *Bull. Soc. Chim. Fr.*, 634 (1951).
(20) J. Hooz and R. B. Layton, *Can. J. Chem.*, **48**, 1626 (1970).
(21) Ketone **39** was first prepared by Dr. Steven Wolff in this laboratory (*cf.* ref 7).

ml of $POCl_3$ and 15 ml of pyridine was added dropwise over a period of 30 min. This mixture was allowed to stir at room temperature overnight and then heated on a steam bath for 30 min. After cooling it was poured onto ice and extracted several times with ether. The combined ether fraction was washed and dried. Removal of solvent gave a mixture (~1:2) of the 3- and 4-substituted 1-cyanocyclopentene. The over-all yield was 80–90%. The isomeric nitriles were separated by vpc and are listed below in order of their retention times.

General Procedure for Synthesis of 3- and 4-Substituted 1-Cyclopentene-1-yl Methyl Ketones. To the appropriate mixture of 3- and 4-substituted nitriles (0.068 mol) a solution of 50 ml of 10% (*w/v*) KOH and 50 ml of 2-propanol was added. The resultant mixture was heated at reflux under nitrogen for 4–5 days and then added to water and extracted several times with ether. These ether fractions were washed several times with water and then dried over $MgSO_4$. Removal of solvent gave a mixture of 3- and 4-substituted 1-cyclopentene-1-carboxylic acids as a light yellow oil. Yields ranged from 60 to 80%.

This mixture of carboxylic acids (0.0280 mol) was dissolved in 100 ml of ether and cooled to −50° under nitrogen. To this solution was added over 30 min 36 ml (0.0572 mol) of a 1.6 *M* ethereal solution of methyllithium. After addition was complete, the mixture was allowed to stir for 1.5 hr at −5°. After this period, the mixture was poured onto ice and the phases separated. The aqueous phase was extracted several times with ether, and the combined ether fractions were washed and dried. Removal of solvent gave the mixture of ketones as a light yellow oil. The yields ranged from 75 to 98%. Isomeric ketones were purified by vpc.

3-Isopentyl- and 4-Isopentyl-1-cyclopentene-1-carbonitrile (34a and 35a). Preparative vpc on column A gave a pure sample of each nitrile. The first was **34a**: ir 2960 (s), 2930 (s), 2880 (m), 2220 (m), 1612 (w), 1465 (w), 1380 (w), 1360 (w), 860 (w) cm^{-1}; nmr (220 MHz) δ 0.891 (d, J = 7 Hz, 6 H), 1.09–1.68 (m, 6 H), 2.08–2.28 (m, 1 H), 2.50–2.81 (m, 3 H), 6.45 (m, 1 H).

Anal. Calcd for $C_{11}H_{17}N$: C, 80.92; H, 10.52; N, 8.58. Found: C, 81.18; H, 10.80; N, 8.31.

The second was **35a**: ir 2955 (s), 2925 (s), 2865 (m), 2845 (m), 2210 (m), 1620 (w), 1465 (m), 1430 (w), 1380 (w). 1365 (w), 962 (w) cm^{-1}; nmr (220 MHz) δ 0.882 (d, J = 7 Hz, 6 H), 1.09–1.25 (m, 2 H), 1 35–1.59 (m, 3 H), 2.04–2.46 (m, 3 H), 2.56–2.82 (m, 2 H), 6.45 (m, 1 H).

Anal. Calcd for $C_{11}H_{17}N$: C, 80.92; H, 10.52; N, 8.58. Found: C, 81.08; H, 10.43; N, 8.42.

3-Methoxymethyl-3-methyl- and 4-Methoxymethyl-4-methyl-1-cyclopentene-1-carbonitrile (34b and 35b). Preparative vpc on column A gave a pure sample of each nitrile. The first was **34b**: ir 2955 (s), 2930 (s), 2875 (s), 2820 (s), 2220 (m), 1620 (w), 1455 (m), 1445 (m), 1380 (m), 1175 (m), 1110 (vs), 1095 (vs), 875 (m), 865 (m) cm^{-1}; nmr (220 MHz) δ 1.09 (s, 3 H), 1.55–1.73 (m, 1 H), 1.86–1.93 (m, 1 H), 2.54–2.68 (m, 2 H), 3.16 (m, 2 H), 3.30 (s, 3 H), 6.35 (m, 1 H); mass spectrum *m/e* 151.0984 (M^+, calcd for $C_9H_{13}NO$, 151.0997).

The second was **35b**: ir 2955 (m), 2920 (m), 2860 (m), 2810 (m), 2220 (m), 1618 (w), 1105 (vs) cm^{-1}; nmr (220 MHz) δ 1.09 (s, 3 H), 2.07–2.36 (m, 2 H), 2.45–2.72 (m, 2 H), 3.12 (s, 2 H), 3.30 (s, 3 H), 6.40 (m, 1 H).

Anal. Calcd for $C_9H_{13}NO$: C, 71.49; H, 8.67; N, 9.26. Found: C, 71.69; H, 8.74; N, 9.23.

3-Butyl-3-methyl- and 4-Butyl-4-methyl-1-cyclopentene-1-carbonitrile (34c and 35c). Preparative vpc on column A gave a sample of each nitrile. The first was **34c**: ir 2955 (s), 2930 (s), 2850 (m), 2210 (m), 1620 (w), 1465 (m), 1455 (m), 1375 (w), 870 (m) cm^{-1}; nmr (220 MHz) δ 0 91 (t, J = 6 Hz, 3 H), 1.08 (s, 3 H), 1.14–1.50 (m, 6 H), 1.62–1.95 (m, 2 H), 2.54–2.68 (m, 2 H), 6.42 (m, 1 H). The second was **35c**: ir 3050 (w), 2950 (s), 2925 (s), 2865 (m), 2850 (m), 2210 (m), 1615 (w), 1462 (m), 1426 (m), 1370 (m), 875 (w) cm^{-1}; nmr (220 MHz) δ 0.91 (t, J = 7 Hz, 3 H), 1.07 (s, 3 H), 1.14–1.47 (m, 6 H), 2.14–2.54 (m, 4 H), 6.52 (m, 1 H); mass spectrum *m/e* 163.1343 (M^+, calcd for $C_{11}H_{17}N$, 163.1368).

3-Isobutyl- and 4-Isobutyl-1-cyclopentene-1-carbonitrile (34d and 35d). Preparative vpc on column B gave a pure sample of each nitrile. The first was **34d**: nmr (220 MHz) δ 0.895 (d, J = 7 Hz, with d, J = 7 Hz, at 0.925, 6 H), 1.07–1.73 (m, 4 H), 2.04–2.25 (m, 1 H), 2.46–2.61 (m, 2 H), 2.73–2.95 (m, 1 H), 6.45 (m, 1 H); mass spectrum *m/e* 149.1191 (M^+, calcd for $C_{10}H_{15}N$, 149.1204).

The second was **35d**: nmr (220 MHz) δ 0.895 (d, J = 7 Hz, 6 H), 1.25–1.36 (m, 2 H), 1.25–1.68 (m, 1 H), 2.04–2.29 (m, 2 H), 2.32–2.77 (m, 3 H), 6.56 (m, 1 H); mass spectrum *m/e* 149.1224 (M^+, calcd for $C_{10}H_{15}N$, 149.1204).

3-Isopentyl- and 4-Isopentyl-1-cyclopentene-1-carbonitrile-2,5,5-d_3 (34a-d_3 and 35a-d_3). To a solution of 7.89 g (0.161 mol) of NaCN dissolved in 20 ml of D_2O and cooled to −5° was added 6.30 g (0.0398 mol) of 3-isopentylcyclopentanone-2,2,5,5-d_4 (**38**). To this mixture 7.60 g (0.040 mol) of $Na_2S_2O_5$ dissolved in 20 ml of D_2O was added over a period of 30 min. After an additional 2 hr at −5° the reaction was treated as above to give a mixture of **34a**-d_3 and **35a**-d_3. Preparative vpc on column A gave a pure sample of each nitrile. The first was **34a**-d_3: nmr (220 MHz) δ 0.877 (d, J = 6 Hz, 6 H), 1.09–1.64 (m, 6 H), 2.06–2.22 (m, 1 H), 2.68–2.84 (m, 1 H). The second was **35a**-d_3: nmr (220 MHz) δ 0.877 (d, J = 6 Hz, 6 H), 1.09–1.23 (m, 2 H), 1.34–1.58 (m, 3 H), 2.14 (dd, J_1 = 6, J_2 = 18 Hz, 1 H), 2.22–2.40 (m, 1 H), 2.64 (dd, J_1 = 8, J_2 = 18 Hz, 1 H).

3-Isopentyl- and 4-Isopentyl-1-cyclopenten-1-yl Methyl Ketone (2 and 8). Preparative vpc on column A gave a pure sample of each ketone. The first was **2**: ir 3045 (w), 2960 (s), 2925 (s), 2870 (m), 2850 (m), 1675 (vs), 1620 (m), 1465 (m), 1365 (m), 1265 (m); nmr (220 MHz) δ 0.891 (d, J = 6 Hz, 6 H), 1.09–1.64 (m, 5 H), 2.00–2.32 with s at 2.19 (m, 6 H), 2.54–2.78 (m, 2 H), 2.46–2.55 (m, 1 H).

Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 80.24; H, 11.15.

The second was **8**: ir 3050 (w), 2955 (s), 2920 (s), 2860 (m), 2840 (m), 1675 (vs), 1620 (m), 1465 (m), 1370 (m), 1360 (m), 1230 (m) cm^{-1}; nmr (220 MHz) δ 0.876 (d, J = 6 Hz, 6 H), 1.09–1.64 (m, 5 H), 2.04–2.36 with s at 2.22 (m, 6 H), 2.55–2.83 (m, 2 H), 6.50 (m, 1 H).

Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.94; H, 11.17.

3-Methoxymethyl-3-methyl- and 4-Methoxymethyl-4-methyl-1-cyclopenten-1-yl Methyl Ketone (4 and 13). Preparative vpc on column A gave a pure sample of each ketone. The first was **4**: ir 3050 (w), 2950 (m), 2920 (m), 2860 (m), 2820 (m), 1675 (vs), 1620 (m), 1365 (m), 1110 (s), 1095 (s) cm^{-1}; nmr (220 MHz) δ 1.09 (s, 3 H), 1.56 (ddd, $J_1 = J_2 = 3, J_3 = 5$ Hz, 1 H), 1.79 (ddd, $J_1 = J_2 = 3, J_3 = 5$ Hz, 1 H), 2.21 (s, 3 H), 2.47 (dd, $J_1 = J_2 = 3$ Hz, 1 H), 2.48 (dd, $J_1 = J_2 = 3$ Hz, 1 H), 3.14 (s, 2 H), 3.26 (s, 3 H), 6.32 (m, 1 H).

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.35; H, 9.56.

The second was **13**: ir 3060 (w), 2950 (m), 2915 (m), 2855 (m), 2810 (m), 1675 (vs), 1620 (m), 1370 (m), 1235 (m), 1110 (s) cm^{-1}; nmr (220 MHz) δ 1.06 (s, 3 H), 2.04–2.68 with s at 2.20 (m, 7 H), 3.10 (s, 2 H), 3.26 (s, 3 H), 6.44 (m, 1 H).

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.42; H, 9.48.

3-Butyl-3-methyl- and 4-Butyl-4-methyl-1-cyclopenten-1-yl Methyl Ketone (5 and 20). Preparative vpc on column C gave a pure sample of each ketone. The first was **5**: ir 3050 (w), 2960 (s), 2925 (s), 2855 (m), 1675 (vs), 1615 (m), 1460 (m), 1450 (m), 1370 (m), 1360 (m), 1265 (m) cm^{-1}; nmr (220 MHz) δ 0.91 (t, J = 6 Hz, 3 H), 1.04 (s, 3 H), 1.11–1.86 (m, 8 H), 2.20 (s, 3 H), 2.49 (m, 2 H), 6.37 (dd, $J_1 = J_2 = 1$ Hz, 1 H); mass spectrum *m/e* 180.1533 (M^+, calcd for $C_{12}H_{20}O$, 180.1514).

The second was **20**: ir 3050 (w), 2955 (s), 2925 (s), 2870 (m), 1675 (vs), 1620 (m), 1462 (m), 1425 (m), 1365 (s), 1235 (s) cm^{-1}; nmr (220 MHz) δ 0.91 (t, J = 6 Hz, 3 H), 1.03 (s, 3 H), 1.14–1.45 (m, 6 H), 2.14–2.25 with s at 2.20 (m, 7 H), 6.51 (m, 1 H); mass spectrum *m/e* 180.1505 (M^+, calcd for $C_{12}H_{20}O$, 180.1514).

3-Isobutyl- and 4-Isobutyl-1-cyclopenten-1-yl Methyl Ketone (6 and 23). Preparative vpc on column B gave a pure sample of each ketone. The first was **6**: ir 3050 (w), 2955 (s), 2925 (m), 2895 (m), 2865 (m), 1675 (vs), 1615 (m), 1465 (m), 1375 (m), 1360 (m), 1260 (m) cm^{-1}; nmr (220 MHz) δ 0.919 (d, J = 7 Hz), 0.932 (d, J = 7 Hz, 6 H), 1.14–1.74 (m, 4 H), 2.00–2.16 (m, 1 H), 2.20 (s, 3 H), 2.27–2.64 (m, 2 H), 2.73–3.00 (m, 1 H), 6.47 (m, 1 H).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.92. Found: C, 79.58; H, 10.88.

The second was **23**: ir 3050 (w), 2955 (s), 2925 (m), 2900 (m), 2870 (m), 2820 (m), 1675, (vs), 1618 (m), 1465 (m), 1425 (m), 1375 (m), 1365 (m), 1230 (m) cm^{-1}; nmr (220 MHz) δ 0.89 (d, J = 7 Hz, 6 H), 1.23–1.32 (m, 2 H), 1.48–1.73 (m, 1 H), 1.95–2.23 with s at 2.19 (m, 5 H), 2.23–2.50 (m, 1 H), 2.50–2.73 (m, 2 H), 6.48 (m, 1 H).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.92. Found: C, 79.65; H, 11.13.

3-Isopentyl- and 4-Isopentyl-1-cyclopenten-1-yl Methyl Ketone-2,5,5-d_3 (24 and 8-d_3). Preparative vpc on column A gave a pure sample of each ketone. The first was **24**: ir 2950 (s), 2925 (s), 2855 (m), 2840 (m), 2275 (vw), 2190 (w), 2100 (w), 1675 (vs), 1590 (m), 1435 (m), 1360 (s) cm^{-1}; nmr (220 MHz) δ 0.886 (d, J = 6

Hz, 6 H), 1.09–1.64 (m, 6 H) 2.00–2.14 (m, 1 H), 2.20 (s, 3 H), 2.68–2.86 (m, 1 H).

The second was **8**-d_3: ir 2950 (s), 2920 (s), 2870 (m), 2850 (m), 2275 (vw), 2200 (w), 2100 (w), 1675 (vs), 1590 (m), 1465 (m), 1360 (s) cm^{-1}; nmr (220 MHz) δ 0.85 (br s, 6 H), 1.09–1.50 (m, 5 H), 2.00–2.32 with s at 2.19 (m, 5 H), 2.54–2.78 (m, 1 H).

3-Methoxymethyl-3-methyl- and 4-Methoxymethyl-4-methyl-1-cyclopenten-1-yl Methyl Ketone-d_3 (25 and 13-d_3). Ketone **39** was converted to the unsaturated nitriles **34b**-d_3 and **35b**-d_3 as above. These nitriles had vpc retention time and nmr spectra (except for absent methoxy signal) identical with **34b** and **35b**. Ketones **25** and **13**-d_3 were prepared following the general procedure and purified on column A. The first obtained was **25**: ir 3050 (w), 2955 (m), 2860 (m), 2710 (w), 2240 (w), 2180 (m), 2045 (m), 1675 (vs), 1620 (m), 1360 (m), 1120 (s) cm^{-1}; nmr (220 MHz) δ 1.09 (s, 3 H), 1.56 (ddd, $J_1 = J_2 = 3, J_3 = 5$ Hz, 1 H), 1.79 (ddd, $J_1 = J_2 = 3, J_3 = 5$ Hz, 1 H), 2.21 (s, 3 H), 2.47 (dd, $J_1 = J_2 = 3$, Hz, 1 H), 3.14 (s, 2 H), 6.31 (m, 1 H).

The second was **13**-d_3: ir 3050 (w), 2950 (m), 2925 (m), 2840 (m), 2725 (w), 2240 (w), 2170 (m), 2045 (m), 1675 (vs), 1620 (m), 1370 (m), 1230 (m), 1125 (s) cm^{-1}; nmr (220 MHz) δ 1.06 (s, 3 H), 2.04–2.68 with s at 2.20 (m, 7 H), 3.10 (s, 2 H), 6.44 (m, 1 H).

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Photochemical and γ-Ray-Induced Reactions of Nucleic Acid Constituents. Dealkylation of 8-α-Hydroxyalkyl Purines

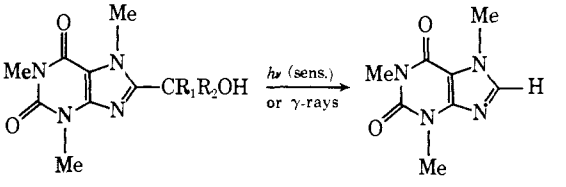
J. Salomon* and D. Elad

Contribution from the Department of Organic Chemistry, The Weizmann Institute of Science, Rehovot, Israel. *Received November 27, 1973*

Abstract: The photosensitized dealkylation of 8-α-hydroxyalkyl purines with ultraviolet light ($\lambda > 290$ nm) leads to the regeneration of the original purines in yields of up to 100%. A mechanism involving an electron transfer from the excited sensitizer to the purine molecule is proposed. The dealkylation of 8-α-hydroxyalkyl purines could also be achieved by the γ radiolysis of their aqueous solutions.

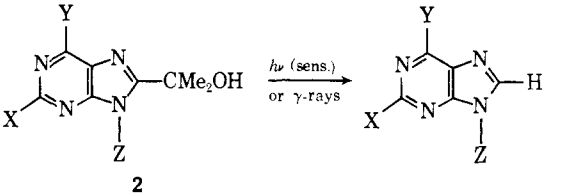
Photochemical reactions of purines from nucleic acids with a variety of organic compounds (*e.g.*, alcohols and amines) led to the substitution of the appropriate moiety for the H-8 hydrogen atom in the purine system.[1] It has further been shown that both adenine and guanine moieties in nucleic acids undergo similar photochemical reactions to yield photoproducts represented by **2** in Scheme I.[2] These modifications in the purines represent a new type of lesion in nucleic acids, the biological significance of which may depend on the existence of an appropriate repair system in the irradiated organism. In the case of pyrimidines, it is well established that the enzymic photoreactivation process involves the splitting of thymine dimers in irradiated DNA into the original monomeric moieties,[3] and preliminary studies with models indicated that the reaction may proceed through a photosensitization process.[4] It was felt that the study of photochemical reactions which will result in the restoration of the original purines from the light-modified ones may lead to a useful model for a photoreactivation process involving the repair of lesions in the purine moieties of irradiated nucleic acids. The development of a general photochemical procedure for the repair of lesions in the various moieties of DNA is also hoped for in the course of this study. The present publication includes a detailed description of photochemical reactions which result in the restoration of the

Scheme I



1

$R_1 = R_2 = H$
$R_1 = H, R_2 = Me$
$R_1 = R_2 = Me$



2

X = H, Y = NH_2, Z = H
X = H, Y = NH_2, Z = ribose
X = NH_2, Y = OH, Z = ribose

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