field[2] and a coordination sphere of five bonded oxygen atoms.[6] Work is in progress to ascertain the relationship of the solid species reported here to the species formed in solution. In addition, the effect of dehydration on the structure is being determined, and efforts are being made to prepare a comparable compound from basic media.

Acknowledgment. The authors wish to express their gratitude to the National Science Foundation (No. GU-2632) and E. R. Squibb and Sons, Inc., for financial assistance to support this and subsequent studies.

(9) (a) Address requests for reprints and for information on the preparation and properties of the compound to this author; (b) address requests for information on the X-ray structure determination to this author.

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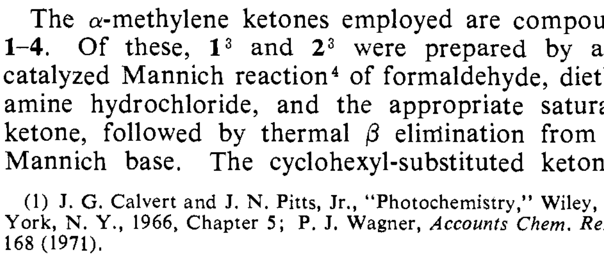
Photochemical Formation of Cyclobutanes from α-Methylene Ketones

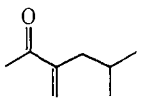
Sir:

We describe here a photochemical cyclization of α-methylene ketones to form the related, isomeric cyclobutanes. Under the simple conditions used this process is the predominant chemical transformation observed, and it furnishes synthetically useful yields of cyclobutyl ketones. We suggest that the isomerization results from formation of the familiar type II biradical[1] and its subsequent closure on the carbon atom of the methylene group to yield the cyclobutyl ketone as its enol. In some cases we have also isolated in smaller amount the expected[1] cyclobutanols, which arise from alternative closure of the biradical on the carbonyl carbon atom. The suggested pathway is shown in eq 1, where for convenience the biradical is depicted as an allylically stabilized species.[2]



(1)

The α-methylene ketones employed are compounds **1–4**. Of these, **1**[3] and **2**[3] were prepared by acid-catalyzed Mannich reaction[4] of formaldehyde, diethylamine hydrochloride, and the appropriate saturated ketone, followed by thermal β elimination from the Mannich base. The cyclohexyl-substituted ketone **3** was synthesized from known[5] ethyl 2-cyclohexylacetoacetate (**5**). This keto ester was converted to its ethylene ketal (**6**) and then reduced with lithium aluminum hydride; the alcohol **7** thus formed was treated directly with acid to furnish **3**[3] in an overall yield of 78%. The cycloheptyl homolog **4**[3] was available (88%) by a similar sequence from ethyl 2-cycloheptylacetoacetate,[3] itself prepared by alkylation of the potassium salt of acetoacetic ester with cycloheptyl iodide[6] in diglyme. Each of these ketones (**1–4**) was purified by preparative vpc,[7] and characterized by ir and nmr spectroscopy.



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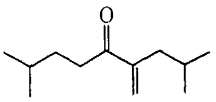

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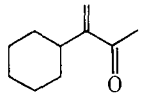

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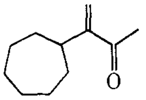

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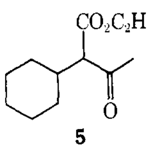

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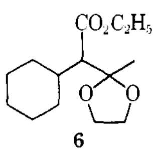

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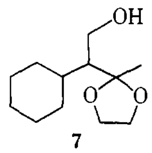

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Irradiation[8] of **1** in pentane for 64 hr caused destruction of 89% of the starting material and formation of two products. The major of these (68%[9]) was 3,3-dimethylcyclobutyl methyl ketone (**8a**),[3] identical with a sample prepared by reaction[10] of 3,3-dimethylcyclobutanecarboxylic acid (**8c**)[11] with methyllithium in ether. The minor photochemical product (19%[9]) was recognized as the type II cyclobutanol **9a**[3] [oil; ir 3620 (m), 3475 (w), 3070 (w), 2960 (s), 2865 (m), 1680 (w),[12] 880 cm^{-1}; nmr δ 1.02 (s) and 1.07 (s) (6 H), 1.22 (s, 3 H), 1.55 (s, 1 H, exchanges with D_2O), 2.12 (m, 2 H), 4.77 (m, 1 H), 5.02 (m, 1 H)].

A parallel reaction occurred on photolysis of **2** (40 hr, 100% conversion). In this case the major product, cyclobutyl ketone **8b**[3] (67%[9]), was independently prepared by reaction[13] of diisoamylcadmium with the acyl chloride from **8c**. The minor product (12%[9]) was cyclobutanol **9b**[3] [oil; ir 3620 (m), 3480 (w), 3070 (w), 2960 (s), 2875 (s), 1680 (w),[12] 1470 (m), 880 cm^{-1}; nmr δ 0.92 (d, $J = 5$ Hz), 1.05 (s), and 1.08 (s) (12 H), 1.4 (m, 6 H), 2.1 (m, 2 H), 4.80 (m, 1 H), 4.95 (m, 1 H)]. This isomerization of **2** to **8b** and **9b** is readily under-

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[1] J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, Chapter 5; P. J. Wagner, *Accounts Chem. Res.*, **4**, 168 (1971).

[2] Similar closure of type II biradicals from two cyclopentenones is described by W. C. Agosta and A. B. Smith, III, *J. Amer. Chem. Soc.*, **93**, 5513 (1971).

[3] This new compound gave satisfactory elemental analysis for carbon and hydrogen after purification by preparative vpc.

[4] F. F. Blicke, *Org. React.*, **1**, 303 (1942).

[5] J. T. Adams, B. Abramovitch, and C. R. Hauser, *J. Amer. Chem. Soc.*, **65**, 552 (1943).

[6] L. Ruzicka, P. A. Plattner, and H. Wild, *Helv. Chim. Acta*, **28**, 395 (1945).

[7] Vapor phase chromatography (vpc) was carried out under conditions similar to those described in ref 2.

[8] Irradiations were carried out on dilute (1 mg/ml) solutions with a Hanovia Model L mercury lamp (No. 679A-36) in a quartz immersion well using a Corning No. 3320 uranium glass filter (λ >3300 Å). Benzene was solvent unless otherwise indicated.

[9] Reported yields were obtained by calibrated vpc measurements and are based on converted starting material.

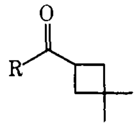
[10] M. J. Jorgenson, *Org. React.*, **18**, 1 (1970).

[11] K. C. Brannock, A. Bell, R. D. Burpitt, and C. A. Kelly, *J. Org. Chem.*, **29**, 801 (1964).

[12] The methylene stretching frequency is known to be a sensitive function of environment; this value is typical of methylenecyclobutanes: L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen, London, 1958, Chapter 3; "Advances in Infrared Group Frequencies," Methuen, London, 1968, Chapter 2.

[13] D. A. Shirley, *Org. React.*, **8**, 28 (1954).

standable in terms of biradical **10** and eq 1. Formation of an alternative biradical **11** from **2** is also conceivable, and collapse of this species could lead to cyclobutanol **12** and possibly to 4,4-dimethyl-2-isobutylcyclohexanone (**13**). It is noteworthy that we found neither of these possible products ($<1\%$).



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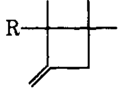

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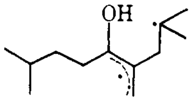

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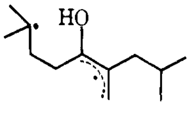
a, R = Me
b, R = $CH_2CH_2CHMe_2$
c, R = OH



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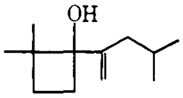

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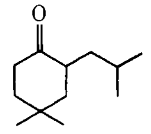

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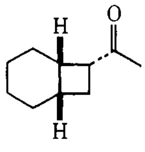
Turning to synthetically more interesting examples, we found that photochemical isomerization of **3** (40 hr, 68% conversion) gave a 9:1 mixture of bicyclic products **14**[3] and **15**[3] in 64%[9] yield. The structures of these methyl ketones were firmly established by the following three sets of experiments. First, Baeyer-Villiger oxidation[14] of **14** with trifluoroperacetic acid and subsequent saponification gave *endo-cis*-bicyclo[4.2.0]octan-7-ol (**16**). The ir spectra of this alcohol from **14** and of its derived phenylurethane (mp 119–120.5°) were identical with those of authentic[15] **16** and its derivative (mp 119.5–120°). Second, **14** was independently prepared from the known[16] unsaturated nitrile **17**. Hydrogenation of **17** over palladium on carbon gave **18**,[3] which on reaction with methylmagnesium bromide followed by hydrolysis yielded **14**. Third, base-catalyzed equilibration of **14** and **15** gave identical mixtures of the two ketones, with the exo isomer **15** predominating (5:1). Preferential formation of the less stable endo isomer **14** in the photochemical reaction is consistent with kinetically controlled protonation[17] of an initially formed enol (see eq 1) from the less hindered exo side.



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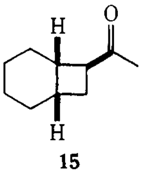

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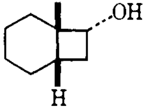

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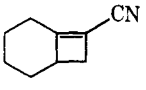

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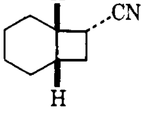
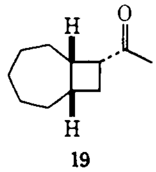


18

Irradiation of the cycloheptyl-substituted ketone **4** (72 hr, 90% conversion) gave similar results. In this case, however, the yield of ketones **19** and **20** (10:1) was diminished to 31%,[9] and we observed concomitant formation of at least two cyclobutanols (10%).[18] Independent synthesis of **19** and **20** from the previously described[16] nitrile **21** followed the path described above from **17**. This, together with base-catalyzed equilibration favoring exo isomer **20** (7:1), fully confirmed the structures assigned. We found no evidence for photochemical formation of trans fused isomers of **19** and **20**, although *cis*- and *trans*-bicyclo[5.2.0]nonane (**22**) are thought to differ little in stability.[19]



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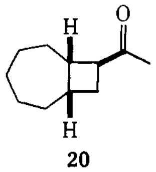

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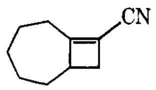

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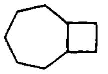

22

In the cases described this reaction provides cyclobutyl ketones conveniently and easily. Its generality and applicability to construction of more complex systems are presently under investigation.

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[14] W. D. Emmons and G. B. Lucas, *J. Amer. Chem. Soc.*, 77, 2287 (1955).

[15] A. C Cope and R. W. Gleason, *ibid.*, **84**, 1928 (1962). We are grateful to Professor Gleason, who generously provided the ir spectra of authentic 16 and its exo epimer, and of the derived phenylurethanes.

[16] I. Fleming and J. Harley-Mason, *J. Chem. Soc.*, 2165 (1964).

[17] H. E. Zimmerman, *J. Amer. Chem. Soc.*, 79, 6554 (1957), and references cited therein.

[18] We will give details of these alcohols in our full paper.

[19] N. L. Allinger, M. Nakazaki, and V. Zalkow, *J. Amer. Chem. Soc.*, **81**, 4074 (1959).

[20] Fellow of the Alfred P. Sloan Foundation and author to whom inquiries should be directed.

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Received August 16, 1971

Partial Photoresolution of Tris(1,10-phenanthroline)chromium(III) Using an Analog of the Pfeiffer Effect[1]

Sir:

Rates of thermal isomerization of enantiomeric complexes may differ in the presence of optically active counterions[2] such that the equilibrium position does not correspond to a fully racemic mixture. This is the Pfeiffer effect.[3] A recent observation that the photoracemization of Cr(phen)$_3{}^{3+}$ (phen = 1,10-phenanthroline) is sensitive to counterions[4] suggests the possibility of what we believe to be a new method of photochemical resolution. Selective intervention of an optically active counterion in the relaxation processes of excited enantiomeric complexes can lead to a photostationary state corresponding to partial resolution.

The photoracemization of resolved[5] $(+)_{589}$-Cr(phen)$_3$Cl$_3$ at a concentration of 0.00073 *M* in a medium of 3.00% potassium antimony D-tartrate proceeds with a

---

[1] We thank the National Research Council of Canada for financial support.

[2] N. R. Davies and F. P. Dwyer, *Trans. Faraday Soc.*, 50, 24 (1954).

[3] P. Pfeiffer and K. Quehl, *Chem. Ber.*, 64, 2667 (1931).

[4] N. A. P. Kane-Maguire and C. H. Langford, manuscript in preparation.

[5] C. S. Lee, E. M. Gorton, H. M. Neumann, and H. R. Hunt, *Inorg. Chem.*, 5, 1397 (1966).