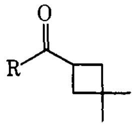
standable in terms of biradical **10** and eq 1. Formation of an alternative biradical **11** from **2** is also conceivable, and collapse of this species could lead to cyclobutanol **12** and possibly to 4,4-dimethyl-2-isobutylcyclohexanone (**13**). It is noteworthy that we found neither of these possible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



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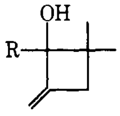

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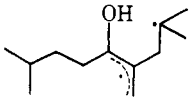
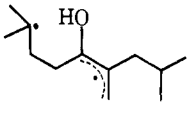


10

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



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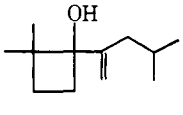

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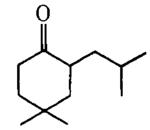

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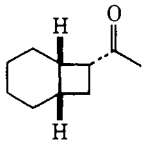
Turning to synthetically more interesting examples, we found that photochemical isomerization of **3** (40 hr, 68% conversion) gave a 9:1 mixture of bicyclic products **14**[3] and **15**[3] in 64%[9] yield. The structures of these methyl ketones were firmly established by the following three sets of 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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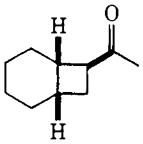

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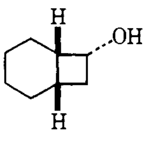

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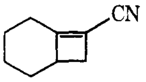

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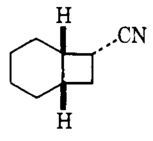

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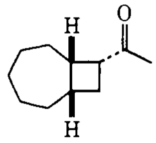
Irradiation of the cycloheptyl-substituted ketone **4** (72 hr, 90% conversion) gave similar results. In this case, however, the yield of ketones **19** and **20** (10:1) was diminished to 31%,[9] and we observed concomitant formation of at least two cyclobutanols (10%).[18] Independent synthesis of **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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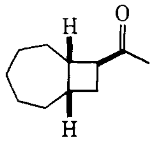

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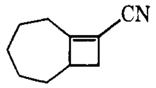

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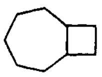

22

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

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(18) We will give details of these alcohols in our full paper.

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(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] $(+)_{589}$-$Cr(phen)_3Cl_3$ at a concentration of 0.00073 *M* in a medium of 3.00% potassium antimony D-tartrate proceeds with a

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(1) We thank the National Research Council of Canada for financial support.

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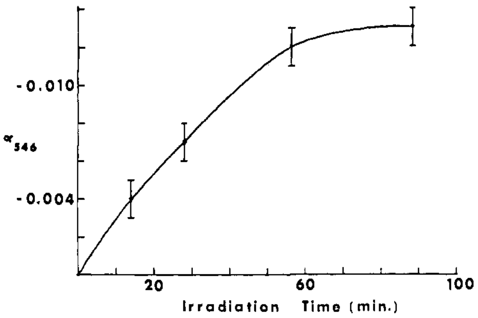

Figure 1. Observed rotation as a function of irradiation time at 25° for a solution of 0.00050 M $Cr(phen)_3Cl_3$ obtained by ion exchange separation from a solution 0.00073 M in complex containing 3% potassium antimony D-tartrate. The latter solution was the one irradiated. (The dilution was necessary to achieve complete recovery of the complex from the resin.) Note that the half-time for photoracemization of a comparable resolved sample was 27 min.

half-time of 27 min at 25° under unpolarized illumination with the 350-nm lamps of a Rayonnet photoreactor. Light intensity in the reactor was gauged by ferrioxalate actinometry.[6] The quantum yield for isomerization is approximately 0.016. Thermal racemization is entirely negligible ($t^1/_2 \simeq$ 17 days at 25°).

Figure 1 shows rotations at 546 nm achieved by irradiating comparable solutions of *racemic* $Cr(phen)_3^{3+}$ in the presence of antimony D-tartrate. These are reported as rotations of the metal complex after separation of the total sample from the dextrorotatory anion on a Dowex 1-X4 anion-exchange column (chloride form). The levorotatory isomer predominates. (In the absence of irradiation, the work-up yields inactive solutions.) Figure 1 indicates that the system approaches a steady-state rotation after 88 min of irradiation, which corresponds to three racemization half-lives for resolved $Cr(phen)_3Cl_3$. The steady-state rotation corresponds to a 1.7% resolution. An essentially identical degree of photoresolution was achieved using an initial complex concentration of 0.0004 M. This is consistent with the absence of a specific chloride counterion effect on photoisomerization.[4] A slightly higher percentage resolution was obtained in 6% antimony D-tartrate (2.4%).

Table I shows the steady-state specific rotations compared to a resolved sample at the several wavelengths available on the Perkin-Elmer 141 polarimeter used in this study. They are consistent with the attribution of steady-state rotation to Cr $(phen)_3^{3+}$. Further, the partially photoresolved samples undergo photoracemization in times similar to photoracemization of the conventionally resolved complex.

Table I. Comparison of Steady-State Specific Rotation with $(+)_{589}$-$Cr(phen)_3Cl_3$

λ, nm	436	546	578	589
[α](steady state)	−53.1	−28.4	−24.0	−21.9
[α]((+)-$Cr(phen)_3Cl_3$)	+3460	+1716	+1402	+1320

Irradiation of solutions for periods considerably longer than those shown in Figure 1 results in photosubstitution of resolving agent for a coordinated phenanthroline. Under these conditions, a highly levorotatory orange solution is obtained after separation on the anion resin. The relative rotations at the Perkin-Elmer wavelengths available are markedly different from those shown in Table I. In addition, this species was not observed to photoracemize.

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Received July 19, 1971

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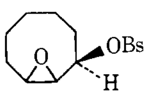
(6) C. G. Hatchard and C. S. Parker, *Proc. Roy. Soc., Ser. A*, **235**, 518 (1956).

Evidence for a Change in Rate-Determining Step in the Acid-Catalyzed Hydrolysis of a Vinyl Ether

Sir:

During the past few years there has been intense interest in the detailed mechanisms of the acid-catalyzed hydrolyses of acetals[1] and vinyl ethers.[2] Part of this interest stemmed from a desire to understand catalytic processes in detail,[1a,2a-g] while renewed interest in the mechanism of acetal hydrolysis has been stimulated by the resemblance of their hydrolytic processes to the action of certain glycosidic enzymes.[1a,b]

In this communication we wish to report the synthesis of 9-methoxyoxacyclonon-2-ene[3] (IIIb), and the kinetic investigation[4] of its hydrolysis in wholly aqueous buffered solutions. In acid solutions, this material can potentially hydrolyze by two main mechanisms, *i.e.*, initial protonation on endocyclic or exocyclic oxygen atoms of IIIb followed by rate-determining cleavage to a stabilized oxonium ion[1] (A-1 mechanism, Scheme I), or



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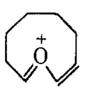

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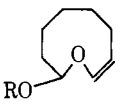
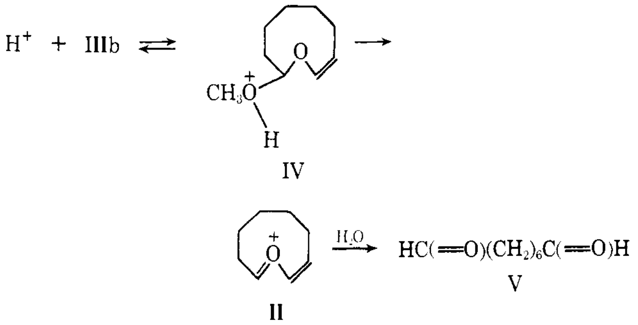


IIIa, R = H
b, R = CH_3

Scheme I. A-1 Hydrolysis Mechanism



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(1) (a) E. H. Cordes, *Progr. Phys. Org. Chem.*, **4**, 1 (1967); (b) E. Anderson and T. H. Fife, *J. Amer. Chem. Soc.*, **93**, 1701 (1971); (c) H. G. Bull, K. Koeler, T. C. Pletcher, J. J. Ortiz, and E. H. Cordes, *ibid.*, **93**, 3002 (1971), and references contained therein.

(2) (a) A. J. Kresge, H. L. Chen, Y. Chiang, E. Murrill, M. A. Payne, and D. S. Sagatys, *ibid.*, **93**, 413 (1971); (b) A. J. Kresge and Y. Chiang, *J. Chem. Soc. B*, 53, 58 (1967); (c) M. M. Kreevoy and R. Eliason, *J. Phys. Chem.*, **72**, 1313 (1968); (d) V. Gold and D. C. A. Waterman, *J. Chem. Soc. B*, 839 849 (1969); (e) T. H. Fife, *J. Amer. Chem. Soc.*, **87**, 1084 (1965); (f) T. Okuyama, T. Fueno, H. Nakatsujii, and J. Furakawa, *ibid.*, **89**, 5826 (1967); (g) G. Lienhard and T. C. Wang, *ibid.*, **91**, 1146 (1969); (h) P. Salomaa, A. Kankaanperä, and M. Lajunen, *Acta Chem. Scand.*, **20**, 1790 (1966).

(3) The Hantzsch–Widman method for naming IIIb is 2-methoxy-2,3,4,5,6,7-hexahydrooxonine, IUPAC 1957 Rules for Nomenclature of Organic Chemistry, *J. Amer. Chem. Soc.*, **82**, 5445 (1960), Section B-1.

(4) The kinetics were followed spectrophotometrically with a Gilford Model 2400 spectrophotometer by monitoring the disappearance of starting material at 210–225 nm.