for 3 hr using a Pyrex filter resulted in an almost quantitative conversion (>92%) to **20a**.

C. **Quenching Experiment.**—A 0.1 *M* solution of piperylene in ether (200 ml) failed to quench the photoisomerization of **19a** (164 mg) to **20a**. The photolysis was carried out for 3 hr using a Vycor filter, and the products were isolated by column chromatography (see Table II).

Photolysis of 2-Allyl-1,2-benzisoxazolinone (19b).—A degassed solution of 175 mg of **19b** in 180 ml of acetone was photolyzed 3 hr using Pyrex-filtered uv light. The residue obtained after acetone evaporation was chromatographed on a silica gel column. Elution with 15–20% ethyl acetate in petroleum ether yielded 143 mg (82%) of **20b**.

Photolysis of 2-*tert*-Butyl-1,2-benzisoxazolinone (19c).—A degassed solution of 191 mg of **19c** in 180 ml of acetone was photolyzed with Corex-filtered uv light for 6 hr. Elution through a silical gel column with 2–4% ethyl acetate in petroleum ether separated 95 mg (50%) of **20c**: mp 74–75°; ir (KBr) 1750 cm^{-1} (C=O); nmr (CCl$_4$) 1.72 (s, 9 H) and 6.85–7.35 ppm (m, 4 H); parent ion at *m/e* 191. *Anal.* Calcd for $C_{11}H_{13}NO_2$: C, 69.09; H, 6.85. Found: C, 68.90; H, 6.79.

Further elution with 5–15% ethyl acetate in petroleum ether yielded 75 mg (39%) of **19c**.

Photolysis of 3-Methylbenzoxazolinone (20a).—A solution of 0.5 g of **20a** in 160 ml of pentane containing ~20 ml of ether was degassed and irradiated with Vycor-filtered uv light for 3 hr. A large amount of dark, insoluble material was obtained. Extensive chromatography of the photolysate on a column of silica gel yielded **20a** (375 mg, 65%) as the only elutable product.

Irradiation of 3-Methoxy-1,2-benzisoxazole (22).—A degassed solution of 149 mg of **22** in 180 ml of ether was photolyzed with Vycor-filtered uv light for 6 hr. The products were isolated by chromatography on a silica gel column. Elution with 5–10% ethyl acetate in petroleum ether yielded 33 mg of an oil whose nmr spectrum was consistent with a 6:1 mixture of **22** and **23**. Compound **24** was obtained by eluting with 15–25% ethyl acetate in petroleum ether, mp 74.5–76° (from pentane). The mass spectrum of **24** showed a molecular ion at *m/e* 151, and its ir and nmr spectra were identical with those of authentic **24**. Irradiation of **22** under identical conditions in absolute methanol followed by chromatography of the photolysate yielded 27 mg (18%) of **22**, 16 mg (11%) of **24**, and 36 mg (24%) of **23**. The mass spectrum of **23** had a parent ion at *m/e* 149, and its ir and nmr spectra were identical with those of authentic **23**. Irradiation of **22** (148 mg) in acetone 180 ml for up to 9 hr using a Pyrex filter resulted in a quantitative recovery of starting material.

Registry No.—**3,** 21725-69-9; **4,** 59-49-4; **19a,** 24963-20-0; **19b,** 26384-70-3; **19c,** 26384-71-4; **20a,** 21892-80-8; **20b,** 13444-14-9; **20c,** 26384-73-6; **22,** 26384-74-7; **23,** 26384-75-8; **24,** 26384-76-9.

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The Photochemistry of 4-Methyl-4-alkoxy-2-pentanones

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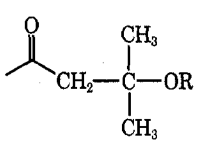
The mechanism of the formation of five-membered ring ethers by irradiation of β-alkoxy ketones has been investigated using deuterium labeling. A pathway involving δ-hydrogen abstraction by electronically excited carbonyl is implicated.

The photoreaction of aliphatic ketones to give smaller ketones and olefins, known as the Norrish type II photocleavage, is one of the most extensively studied areas of photochemistry. The field has been reviewed recently[1-3] and remains a subject of current interest.[4-6]

It is now well established that the reaction proceeds *via* γ-hydrogen abstraction to give 1,4 diradicals which can either cleave to olefins,[1] ring close to cyclobutanes,[1] or return to starting material.[4] Recent work of Turro and Weiss[7] has established that the geometry of the species which precedes hydrogen abstraction resembles that of a cyclic olefin; *i.e.*, γ hydrogens which lie in the plane of the carbonyl group, are easily transferred. The increased strain energy of the five and seven carbon cyclic olefins over that of cyclohexene (4.5 and 4.0 kcal/mol, respectively)[8] clearly accounts, at least qualitatively, for the high selectivity toward γ abstraction.

We have investigated the photochemistry of several ethers of diacetone alcohol (**1a–c**) in an attempt to understand those features which might lead to hydrogen abstraction *via* seven-membered ring transition states (δ abstraction) and wish to report these results below.



1a, R = CH_3
b, R = CH_2CH_3
c, R = CD_3

Results and Discussion

When irradiated in pentane, both **1a** and **1b** yield mesityl oxide **2**, an alcohol **3**, and a tetrahydrofuranol **4** (see Scheme I). In these systems γ-hydrogen abstraction enjoys a two- or threefold statistical advantage over δ abstraction. Despite this and the fact that no obvious geometrical constraints are operative,[9] *no* products of γ-hydrogen abstraction (acetone, olefin, or cyclobutanol) could be found. This result, first reported by

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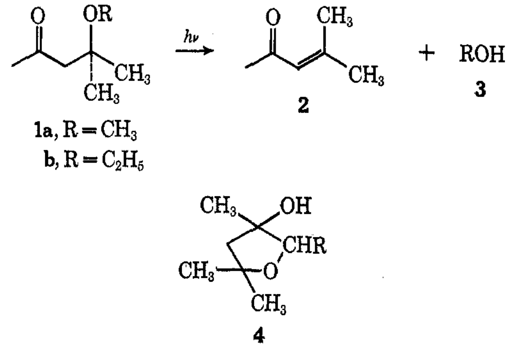
[1] P. J. Wagner and G. S. Hammond, *Advan. Photochem.*, **5**, 21 (1968).
[2] J. G. Calvert and J. N. Pitts, "Photochemistry," Wiley, New York, N. Y., 1966, pp 382–427.
[3] J. N. Pitts, Jr., *J. Chem. Educ.*, **34**, 112 (1957).
[4] N. C. Yang and S. P. Elliot, *J. Amer. Chem. Soc.*, **91**, 7550 (1969).
[5] L. M. Stephenson, P. R. Cavigli, and J. L. Parlett, *ibid.*, in press.
[6] P. J. Wagner and A. E. Kemppainen, *ibid.*, **90**, 5896 (1968).
[7] N. J. Turro and D. S. Weiss, *ibid.*, **90**, 2185 (1968).
[8] S. W. Benson "Thermochemical Kinetics," Wiley, New York, N. Y., 1968.
[9] N. C. Yang reports similar finding in systems where the γ hydrogens are sterically inaccessible; see "Reactivity in Photoexcited Organic Molecules," Interscience, New York, N. Y., 1967, pp 145.

SCHEME I

PHOTOREACTIONS OF 4-METHYL-4-ALKOXY-2-PENTANONES



Coyle, Peterson, and Heicklen[10] for **1a** and more recently encountered by Yates and Pal,[11] is unique in alkyl ketone photochemistry.[2]

In considering the formation of the cyclic ether **4**, it seemed entirely possible that the primary photoprocess involves γ abstraction. Subsequent hydrogen atom migrations would then form the 1,5 diradical **6** which could ring close to the product (see Scheme II). 1,4 diradicals, such as **5**, have been the subject of several recent studies, and lifetimes sufficiently long to allow such processes have been found.[12] To test this hypothesis the products of the photolysis of trideuteriomethyl ether (**1c**) were examined.

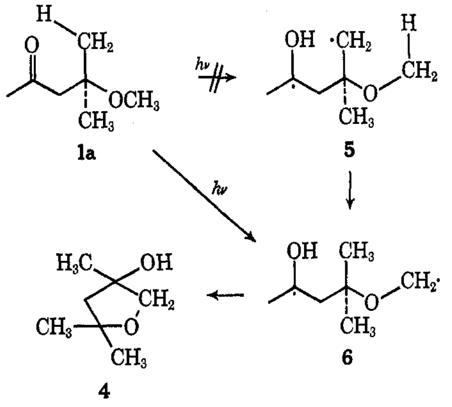
Analysis of the cyclic ether derived from the photolysis of **1c** showed that, within the error limits of our method (nmr integration, $\pm 5\%$), no deuterium incorporation into the methyl groups could be demonstrated. After H_2O exchange, mass spectral analysis showed 2.00 ± 0.10 excess deuterium atoms. Additionally, starting material recovered after 75% complete photolysis showed no deuterium scrambling, and the mesityl oxide isolated from the reaction showed no excess deuterium.

Since deuterium substitution should retard the rate of hydrogen abstraction, these findings rigorously exclude the intervention of intermediate **5** in the mechanism shown in Scheme II. Thus *direct* abstraction of δ hydrogen is implicated as the route to the cyclic ethers.[13]

Simple thermochemical reasoning indicates that this would not be the anticipated result. If the formation of cyclic ether involves δ-hydrogen abstraction, the limit of our ability to detect Norrish type II products ($<0.1\%$) implies that δ-hydrogen abtraction is more favorable than γ- by ~4 kcal/mol. Assuming, in addition, that cyclohexene and cycloheptene are adequate strain models for the two transition states leading to abstraction requires that the hydrogen transfer from $-OCH_3$ be more favorable than that from $-CH_3$

SCHEME II

MECHANISMS FOR CYCLIC ETHER FORMATION



by ~8 kcal/mol. Oxygen substitution lowers C–H bond dissociation energies 3–5 kcal/mol;[14] however, very fast reactions such as these in general show rate differences which reflect only a small fraction of the total bond dissociation energy differences.[15] On this basis we anticipated significant amounts of γ-hydrogen abstraction.

The difficulty with the analysis above doubtless rests with the model chosen for strain evaluation.[16] The calculations clearly indicate, however, that substituents capable of radical stabilization are expected to have profound effects on the primary site of these intramolecular hydrogen abstractions. In certain cases such reactions might offer convenient synthetic routes to five and larger membered ring compounds.

The mechanism of the equally interesting photoelimination of methanol is also under investigation. The reverse of this reaction has potential synthetic applicability as a 1,3 difunctionalization route and work on this aspect of the problem is in progress.

Experimental Section

All nuclear magnetic resonance spectra (nmr) were taken on a Varian T-60 spectrometer in $CDCl_3$ solvent using TMS as an internal standard. Mass spectral analyses were performed on an Atlas C-4 mass spectrometer at ionizing voltages of 70 eV.

Preparation of Ethers 1a–c.—Mesityl oxide was distilled before use; 12 g (0.12 mol) was added to 0.24 mol of the appropriate alcohol containing 1 cc of concentrated sulfuric acid. After 4 days, standing at room temperature, the dark reaction mixture was poured slowly into excess aqueous bicarbonate solution. This mixture was extracted with ether, and the organic layer was dried ($MgSO_4$) and concentrated. The products were distilled to give clear liquids: methyl ether, trideuteriomethyl ether [bp 57° (15 mm), ~10 g (70%)], and ethyl ether [bp 68° (15 mm), 11 g (59%)]. Each of these products contained a small amount of mesityl oxide ($<10\%$) which was removed by preparative vapor phase chromatography (vpc) on 20% SE-30 liquid phase. The nmr spectrum of the trideuteriomethyl ether (**1c**) show $<1\%$ protio impurity in the δ 3.0–3.4 ppm region.

Photolysis of 1a–c.—Solutions of ethers **1a–c**, 10% in pentane, were irradiated in Pyrex equipment using the light from a medium-pressure mercury arc. The reaction mixture was moni-

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[10] D. J. Coyle, R. V. Peterson, and J. Heicklen [*J. Amer. Chem. Soc.*, **86**, 3850 (1964)] first studied the photochemistry of **1a** and reported small yields of acetone and olefin. More recent work of Yates and Pal[11] on both Ia and Ib report no Norrish type II products in these photolyses, in agreement with this work.

[11] P. Yates and J. M. Pal, *Chem. Commun.*, 553 (1970).

[12] L. M. Stephenson and J. I. Brauman, *J. Amer. Chem. Soc.*, in press. In the case of 1,4 diradicals derived from triplet state precursors, lifetimes of 10^{-4}–10^{-6} sec have been estimated.

[13] While this work was in progress, Yates and Pal[11] reported their study of β-alkoxy ketone photochemistry. While this work did not exclude the mechanistic possibility shown in Scheme II, their results and conclusions agree completely with those developed in this paper.

[14] F. K. Cruickshank and S. W. Benson, *ibid.*, **91**, 1289 (1969).

[15] In the hydrogen atom abstraction reactions of benzophenone excited triplet state, for example, C. Walling and M. J. Gibian [*J. Amer. Chem. Soc.*, **87**, 3361 (1965)] report that 2-propanol is only 3.5 times as reactive as cyclohexane as a hydrogen donor.

[16] Since hydrogen eclipsing interactions contribute a substantial amount to ring strain energies, the presence of two oxygens and a hydrogen in seven-membered ring species probably make our estimate too high.

tored and examined analytically by vpc using 10 ft × 0.25 in. columns packed with 15% SE-30 on Chromosorb P. At the conclusion of the photolysis,[17] the pentane was removed and the mixture of mesityl oxide, starting material, and cyclic ether was separated by preparative vpc using a 14 ft × 3/8 in. column containing 20% SE-30 on Chromosorb P. Nmr analyses confirmed their structures which were in accord with prievious work.[10,11]

Registry No.—**1a**, 107-70-0; **1b**, 27921-36-4; **1c**, 27921-37-5.

Acknowledgment.—This work was supported through the generosity of the Dupont Young Professors Fund.

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[17] The conversion rate generally slowed considerably after 50–75% conversion, presumably due to competitive absorption by product mesityl oxide. In no run did the extent conversion exceed 75%.

Quantitative Studies in Stereochemistry. XV. Photochemistry. VIII.[1a] The Photochemical Interconversion of Diastereomeric Acetophenone Pinacols Induced by Shorter Wavelength Ultraviolet Irradiation[1b,c]

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meso- and *dl*-acetophenone pinacols, stable to wavelengths above 3000 Å, are interconverted essentially quantitatively on irradiation in benzene solution by light of predominantly 2537 Å to produce an equilibrium mixture containing the two diastereomers in a *dl/meso* ratio of 2.05. This value stands in contrast to the corresponding ratio of 1.09 observed in a number of solvents for the photopinacolization of acetophenone. Irradiation of the pinacols in other solvents (2-propanol, $CHCl_3$, CCl_4, CS_2) led to recovered pinacols (incompletely interconverted), acetophenone, and unidentified decay products. A tightly bound radical pair is invoked to explain the results.

An earlier report[2] from this laboratory described the stereochemistry accompanying the photopinacolization of acetophenone. Employing ultraviolet radiation peaking at approximately 3500 Å with a negligible component below 3000 Å, ratios of the *dl*- to *meso*-pinacol in the range of 1.06–1.14 were consistently obtained in neutral or acidic 2-propanol. The stereochemistry appeared to be independent of time, concentration, the initial presence of oxygen, and certain variations in solvent (*e.g.*, cyclohexane). The pinacols proved individually stable to the reaction medium. A continuous stream of oxygen through the reaction mixture did, however, completely inhibit the formation of pinacol.

Accompanying the earlier report were certain inconsistent, nonreproducible data that arose when the photopinacolization was induced either by a Hanovia broad-spectrum source or by predominantly 2537-Å radiation. The two sources gave erratic but generally higher *dl/meso* ratios. An analysis[2] of the spectral distribution of these two sources indicated that both had either a predominant or appreciable component below 3000 Å. Several runs qualitatively verified the tentative hypothesis that the shorter wavelength irradiation interconverted the diastereomers. The present report extends these earlier observations to include studies in a number of solvents as well as a more extensive survey of the reaction in a noninvolved solvent, benzene. This latter solvent permitted the quantitative evaluation of an equilibrium constant for the resultant photostationary state.

This purely photochemical interconversion of diastereomeric pinacols would appear to be the first of its sort to be reported.[3] The data are compiled in Tables I and II.

Results and Discussion

The results in Table I establish the background of the problem, provide some qualitative measure of the rate of the interconversion and/or decay of the pinacols, and provide some indication of the involvement of the several different solvents investigated. Runs 1–4 cover the normal pinacolization of acetophenone at 3500 Å with its consistent *dl/meso* ratio of 1.09 and constitute a stability check of the individual diastereomers (reaction times more than tenfold that required for complete photopinacolization of acetophenone) demonstrating their noninterconvertibility for these reaction conditions. Runs 5–7 show the related results when Hanovia broad-spectrum radiation is used.[4] These results clearly indicate that the maximum time employed, 72 hr, is an insufficient reaction time for the sample size utilized. Also suggested is a slightly greater rate for the interconversion starting with the *meso*-pinacol.[5] Runs 8–18 follow through with smaller samples and/or longer reaction times or alternate solvents. In an hydroxylic solvent (run 9) the pinacols are eventually completely lost in 7 days. Carbon disulfide, carbon tetrachloride, and chloroform as solvents (runs 10–18), in this order of increasing reactivity, all appeared to interact with the pinacols to produce acetophenone.[6] That interconversion was accompanying

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[1] (a) Paper VII: J. H. Stocker, R. M. Jenevein, and D. H. Kern, *J. Org. Chem.*, **34**, 2810 (1969); (b) presented in part at the Southeast Reginal Meeting of the American Chemical Society, Richmond, Va., Nov 5–7, 1969; (c) financial support from the U. S. Atomic Energy Commission under Contract AT-(40-1)-2833 is gratefully acknowledged.

[2] J. H. Stocker and D. H. Kern, *J. Org. Chem.*, **31**, 3755 (1966).

[3] Formal interconversion rather than simple cleavage is implied here. Photochemical cleavage has been reported; see, for example, ref 7.

[4] See ref 2 for spectral distribution of the several sources of radiation employed.

[5] In runs 5–7, some material has been lost to unidentified products, presumably by interaction with solvent. Acetophenone and methylphenylcarbinol were not observed but, if formed, would immediately be recycled to pinacol under the reaction conditions.

[6] Except for carbon disulfide (a known, but poor, radical trap), these interactions are readily rationalized as an intermediate ketyl radical abstracting a chlorine to produce acetophenone, HCl, and a volatile polychlorethane. The reaction mixtures proved strongly acidic on testing.