step and/or the reaction of the excited state with a ground-state molecule.

Experimental Section

Melting points are uncorrected. The infrared spectra were recorded on a JASCO DS-402G spectrophotometer; the ultraviolet spectra were obtained with a Hitachi 124 spectrophotometer; the nmr spectra were measured with a JEOLCO C-60HL spectrometer using tetramethylsilane as an internal standard; the mass spectrum was recorded on a Hitachi RMU-6E spectrometer; the molecular weight was determined by a Hitachi 115 molecular weight measuring apparatus.

4-Thiapyrone (I).—4-Thiapyrone was prepared by the method of Arndt and Bekir,[12] which gave a colorless needle after recrystallization from carbon tetrachloride, mp 110° (lit.[12] 110°). The uv and nmr spectra are consistent with the reported spectra.[13,14]

Direct Irradiation of I.—A solution of 2 g of I in 200 ml of acetonitrile was irradiated for 50 hr with a 100-W medium pressure mercury arc through a quartz filter. Purified nitrogen was passed through the solution during irradiation. After removal of solvent under vacuum the residual solid was chromatographed on a silica gel with benzene–chloroform eluent to yield 40 mg of II. After isolation of II 95% of I was recovered. II, a colorless solid, was recrystallized from acetone: mp 248° dec; uv $\lambda_{\max}^{\mathrm{CH_3CN}}$ 307 nm (ϵ *ca.* 100); ir (KBr) 1710 cm^{-1} ($\nu_{\mathrm{C=O}}$); nmr (DMSO-d_6) δ 3.45–3.70 (m, 4 H) and 4.55–4.80 (m, 4 H); the principal peaks of mass spectrum at *m/e* (rel intensity) 224 (48.5), 149 (23.5), 137 (16.0), 113 (60.0), 112 (100.0), 86 (44.0), 84 (61.7), 58 (37.8), and 57 (22.7).

Anal. Calcd for $C_{10}H_8O_2S_2$: C, 53.55; H, 3.59; O, 14.27; S, 28.59. Found: C, 53.45; H, 3.71; O, 14.40; S, 28.38.

Photosensitized Reaction of I.—A 200-ml benzene solution of 2 g of I and 1 g of benzophenone was irradiated for 50 hr with a 100-W medium-pressure mercury lamp filtered by a Pyrex glass. After similar work-up described above, 42 mg of II was isolated.

Registry No.—I, 1003-41-4; II, 32538-05-9.

Acknowledgments.—The authors are grateful to Professor K. Teramura for his interest in this work.

[12] F. Arndt and N. Bekir, *Chem. Ber.*, **63**, 2393 (1930).

[13] J. Jones, W. Derbyshire, and H. S. Gutowsky, *J. Phys. Chem.*, **69**, 1 (1965).

[14] R. Mayer, W. Brey, and R. Zahradnik, *Advan. Heterocycl. Chem.*, **8**, 249 (1967).

Rearrangement of the Grignard Reagent from 5-Chloro-1-pentene-*5,5*-d_2[1]

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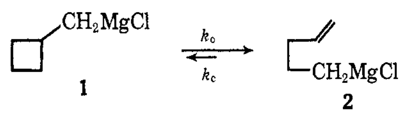
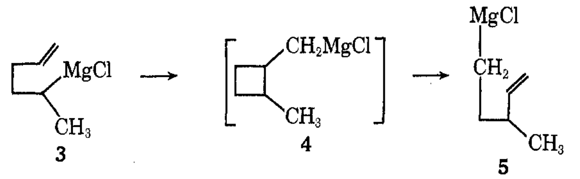
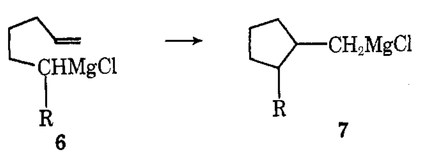
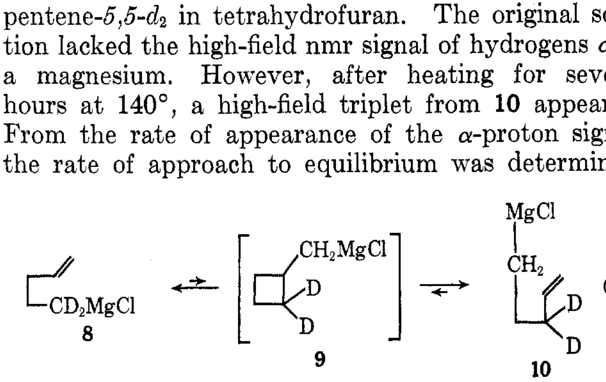
In previous work, it has been shown that the Grignard reagent **1** from cyclobutylmethyl chloride undergoes a ring-cleavage rearrangement to **2**.[2] In addition, rearrangement of Grignard reagent **3** to **5** was observed, the cyclized reagent **4** being proposed as an intermediate.[2a] In the latter case, the reaction most probably has as its driving force the conversion of a secondary Grignard reagent into a more stable primary one. Ring closure to a five-membered ring has also been observed[3] (eq 3). It thus appeared desirable to demonstrate directly the reversibility implied in eq 1.


(1)


(2)


(3)

A Grignard reagent was prepared from 5-chloro-1-pentene-*5,5*-d_2 in tetrahydrofuran. The original solution lacked the high-field nmr signal of hydrogens α to a magnesium. However, after heating for several hours at 140°, a high-field triplet from **10** appeared. From the rate of appearance of the α-proton signal, the rate of approach to equilibrium was determined.


(4)

After correction for Grignard reagent destroyed by reaction with the solvent (see Experimental Section), approximate rate constants of 3×10^{-6} sec^{-1} at 140° and 3.5×10^{-5} sec^{-1} at 160° were determined. If possible secondary isotope effects on the rates and equilibria are ignored, the rate of ring closure equals the rate of approach to equilibrium: each act of ring closure would produce a molecule of **9**, which on cleavage, has an equal probability of yielding isomer **8** or **10**.

1-Pentene, isolated from hydrolysis of a solution heated for several half-lives, was examined by nmr. Integration showed that about 40% of the 1-pentene had the deuterium distribution corresponding to **10**.

Extrapolation of rate constants for the *cleavage* of the cyclobutylmethyl Grignard reagent (see Experimental Section) yields a value of 7.5×10^{-3} sec^{-1} at 140°. With the ring closure rate, an equilibrium constant of 2.5×10^3 is derived for eq 1. In principle, it should be possible to derive ΔH for eq 1 from the temperature dependence of this equilibrium constant, and hence an estimate of the strain energy of the cyclobutane ring. Because of the competing reaction with solvent, the present kinetics are insufficiently precise to allow this approach. However, by an alternative approach, ΔG and an estimate of ΔS[4] for eq 1 may be combined to yield $\Delta H = -2.1$ kcal/mol.

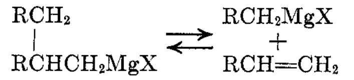
[1] This research was supported in part by a grant from the Petroleum Research Fund, administered by the American Chemical Society.

[2] (a) E. A. Hill, H. G. Richey, Jr., and T. C. Rees, *J. Org. Chem.*, **28**, 2161 (1963); (b) E. A. Hill and J. A. Davidson, *J. Amer. Chem. Soc.*, **86**, 4663 (1964).

[3] H. G. Richey, Jr., and T. C. Rees, *Tetrahedron Lett.*, 4297 (1966); E. A. Hill, R. J. Theissen, R. A. Doughty, and R. Miller, *J. Org. Chem.*, **34**, 3681 (1969).

[4] This estimate, 10.6 eu at 140°, uses the gas-phase entropy change of the model reaction methylcyclobutane ⇆ 1-pentene. The entropy of methylcyclobutane was obtained by adjustments from the published value for cyclobutane: G. W. Rathjens, Jr., N. K. Freeman, W. D. Gwinn, and K. S. Pitzer, *J. Amer. Chem. Soc.*, **75**, 5634 (1953). The authors may be consulted for further details.

Taken with an estimate of 21.7 kcal/mol[5] for the bond cleavage process



$$\begin{array}{c}RCH_2\\ |\\ RCHCH_2MgX\end{array} \rightleftarrows \begin{array}{c}RCH_2MgX\\ +\\ RCH{=}CH_2\end{array}$$

a ring strain of 24 kcal is derived. A value of 23 kcal is obtained from data at 160°.[6]

The estimates of ring strain obtained are in approximate agreement with the heat of combustion value of 26.2 kcal/mol.[7] The discrepancy, amounting to a factor of 10 to 40 in equilibrium or rate constants, could be the summation of errors from various sources in the kinetics and the estimation procedures, or it may represent the limits of applicability of the thermochemical approach to solution reactions. It could also result from some additional stabilization of the four-membered ring in the cyclobutylmethyl Grignard reagent, or from the incidence of a new, higher activation energy mechanism at the higher temperatures.[8] In any event, the current results provide a clear example of the quantitative influence of the thermochemical strain energy of a cyclobutane ring on the equilibrium constant for a chemical reaction.

Experimental Section

Nmr spectra were obtained on a Varian Associates HA-100 nmr spectrometer. Boiling points are uncorrected.

Cyclobutylmethylmagnesium chloride in tetrahydrofuran was prepared as described previously.[2b] Samples in nmr tubes were heated for appropririate times, and the extent of rearrangement was determined by integration of the signals at δ −0.35 and −0.66 ppm, corresponding to Grignard reagents 1 and 2, respectively.[2b] Rate constants obtained were 2.55×10^{-6} sec^{-1} at 59.6°; 2.76×10^{-5} sec^{-1} at 80.2°, and 2.18×10^{-4} sec^{-1} at 99.9°. Derived activation parameters were $\Delta H^{\ddagger} = 26.55 \pm 0.2$ kcal/mol and $\Delta S^{\ddagger} = -4.6 \pm 0.5$ eu.

4-Penten-1-ol-*1,1*-d_2 was prepared by reduction of methyl 4-pentenoate with lithium aluminum deuteride in diethyl ether, bp 137–140° (lit.[9] bp 141–141.5°° for isotopically normal compound).

5-Chloro-1-pentene-*5,5*-d_2 was prepared from the alcohol with thionyl chloride and tri-*n*-butylamine in ether by a procedure similar to one described previously:[2b] bp 98–103° (lit.[9] bp 103–104° for isotopically normal compound). The nmr spectrum showed no detectable absorption (<0.5%) at δ 3.5 ppm, where the α hydrogens of the isotopically normal compound absorb.

Grignard Reagent from 5-Chloro-1-pentene-*5,5*-d_2.—A Grignard reagent was prepared from 0.679 g of the chloride and 0.21 g of magnesium in 3 ml of tetrahydrofuran, and sealed in nmr tubes. After heating for several hours at 140°, a triplet signal, J = 8 Hz, appeared at δ −0.66 ppm. Poorly defined changes occurred in the olefinic absorption, and a new signal appeared at δ 6.45 ppm, attributable to ethylene formed from attack on the solvent.[10] At long reaction times, the α-hydrogen absorption reached a maximum of about 60% of one hydrogen (relative to the olefinic protons) and then decreased in size, while the ethylene absorption continued to increase. By using the appearance of ethylene as a measure of the amount of Grignard reagent destroyed by reaction with solvent, the spectra obtained for shorter reaction times were corrected for the loss of total organometallic. The rate of loss appeared to be about 20–30% of the rearrangement rate. The best rate measurements were made using a similar sample of concentration 0.92 M supplied by H. G. Richey, Jr., and T. C. Rees.

A sample which had been heated for four half-lives was hydrolyzed with water. The volatile materials were transferred from the residue under vacuum and gas chromatographed. The collected 1-pentene, the only detected reaction product, was analyzed by nmr. Integration yielded the following: δ 0.92 (t, 1.8, $J \cong 7.1$ Hz, CH_3 and CHD_2), 1.4 (q, 2, $J \cong 7.2$ Hz, CH_2), 2.02 (q, 1.2, $J \cong 7.2$ Hz, allylic CH_2), 4.95 (m, 2, $=CH_2$), and 5.7 ppm (m, 1, $=CH$).

Registry No.—**1**, 32251-57-3; **2**, 30090-51-8; **8**, 32251-59-5; **10**, 32251-60-8.

Acknowledgment.—We are grateful to H. G. Richey, Jr., and T. C. Rees of the Pennsylvania State University for communication of their earlier results, and for the gift of a sample of deuterated Grignard reagent used for kinetics studies.

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[5] S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, **69**, 279 (1969).

[6] It might be more valid to use only one-half of the rate of ring opening in calculating an equilibrium constant, since the observed ring cleavage is the sum of cleavages of two ring bonds. Such a treatment would lower the strain energy estimated by about 0.5 kcal/mol.

[7] S. Kaarsemaker and J. Coops, *Recl. Trav. Chim. Pays-Bas*, **71**, 261 (1952).

[8] The latter is consistent with preliminary results of T. C. Rees (Ph.D. thesis, Pennsylvania State University, communicated to us by Professor H. G. Richey, Jr.) in which no reaction was found after 170 hr at 110°.

[9] A. Juvala, *Chem. Ber.*, **63**, 1989 (1930).

[10] E. A. Hill, *J. Org. Chem.*, **31**, 20 (1966).

9-Anthroxy. A Protecting Group Removable by Singlet Oxygen Oxidation

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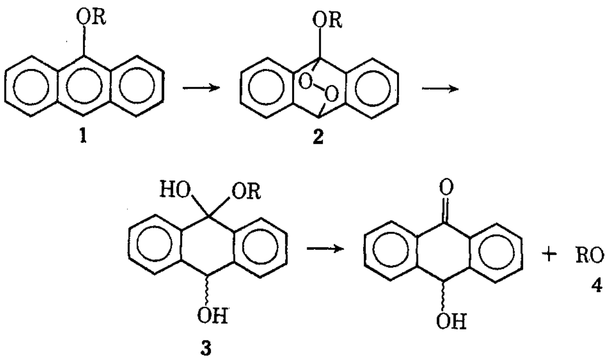
Aromatic ethers have not often[1,2] been used as protecting groups because of problems associated with attachment and removal by making and breaking the aromatic carbon–oxygen bond. We recently reported[3] that 9-anthroxy alkyl ethers **1** are useful protecting groups which can be readily cleaved at the aromatic carbon–oxygen bond by a sequence using low temperature (−30°) singlet oxygen oxidation[4] to an anthracenyl peroxide[5] (**2**) followed by mild catalytic reduction[6] of the weak oxygen–oxygen single bond. The initial reduction product is presumably the hemiketal **3**, which spontaneously eliminates the alcohol **4**. We report here some experimental details for cleaving 9-anthroxy ethers and a new method for synthesizing them.



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[1] J. F. W. McOmie in "Advances in Organic Chemistry—Methods and Results," Vol. 3, Interscience, New York, N. Y., 1963, p 191.

[2] For a listing of protecting groups devised after McOmie's review see W. Theilheimer, "Synthetic Methods," subject indexes to Vol. 24, 23, and 20.

[3] W. E. Barnett and Larry L. Needham, *Chem. Commun.*, 1383 (1970).

[4] R. W. Murray and M. L. Kaplan, *J. Amer. Chem. Soc.*, **91**, 5358 (1969).

[5] W. Bergmann and M. J. McLean, *Chem. Rev.*, **28**, 367 (1941).

[6] C. Dufraisse and J. Houpillart, *C. R. Acad. Sci.*, **205**, 740 (1937).