composition of starting material) indicates that under these conditions *ca.* 94 ± 3% of **2** is formed *via* a [4 + 2] cycloaddition.

The position of the label in tricyclic product after heating **6** under a variety of conditions was determined using dmr spectroscopy.[12,13] The results based on the intensity ratio $D_f$:$D_{ex}$, 100:0 (184°, 21 hr), 93:7 (193°, 33.5 hr), and 70:30 (203°, 36.5 hr)[14] indicate that at 184° (21 hr) the formation of **2** proceeds exclusively by a [4 + 2] mechanism, but at higher temperatures at least one other pathway intervenes to scramble the label. Assuming that no more than 1% of **2b** is formed at 184°, the [4 + 2] pathway is kinetically favored by at least $-RT \ln k_2/k_1 = 4.576\ (457.2) \log (99) = -4.1$ kcal/mol.[15]

Although the lower energy pathway to **2** must involve a [4 + 2] cycloaddition of **1**, several interpretations of the scrambling of the label between $H_{en}$–$H_{ex}$ and $H_f$–$H_g$ proton pairs are possible. Extensive commentary on the scrambling must await the full paper but suffice it to say that the raw kinetic data can encompass a diradical mechanism for this process involving the formation of **7** from **1** (or **2**) followed by rapid coupling to give tricyclic product.[17]

Studies are continuing to test for the involvement of a [$_\pi 4_s + _\pi 2_a$] cycloaddition in the primary formation of **2** and to obtain precise activation parameters for the reactions in this system.

**Acknowledgment.** Acknowledgment is made to the Research Foundation and the Graduate School of the State University of New York at Stony Brook, to the Research Corporation, and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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(12) Dmr spectra were taken on a Bruker HFX-90 nmr spectrometer with a measuring frequency of 13.82 MHz by Mr. W. Schittenhelm of Bruker Scientific Inc., Elmsford, N. Y., to whom I am indebted. Integrations were performed electronically with the aid of a Fabri-Tek 1080 computer.

(13) The $D_g$ and $D_{en}$ resonances coincided in the 13.82-MHz dmr spectra but their combined intensities always equalled the sum of the intensities of the resolved $D_f$ and $D_{ex}$ signals. No other signals were detectable in the dmr spectra of cyclized **6**.

(14) After heating **6** for 36.5 hr at 203°, recovered dideuterio-5-allylcyclohexa-1,3-diene contained 14% of the label in the $\gamma$ position of the allyl side chain.

(15) Since factors which stabilize products may be important in stabilizing the activated complex leading to products, the [2 + 2] reaction which produces cyclobutanes is usually disadvantaged compared to the [2 + 4] case and the usual reaction course favoring formation of cyclohexenes can be explained without regard to the theory of Woodward and Hoffmann.[16] However, the present result makes clear that even in a competition where the same product could have been formed from either pathway the [4 + 2] cycloaddition is still kinetically favored.

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

(17) The experimentally derived value for the initial rate of formation of **2** (due primarily to a [4 + 2] cycloaddition) at 193° is $k = 6.16 \times 10^{-6}$ sec$^{-1}$. The computed value of 39.4 ± 3 kcal/mol[18] for the activation energy of formation of **2** from **1** coupled with an *A* factor estimated[18] at $10^{11.5 \pm 0.5}$ gives $k = 10^{-7}$ sec$^{-1}$ for the slower diradical mechanism.

(18) These parameters were estimated by group additivity methods described by (a) S. W. Benson in "Thermochemical Kinetics," Wiley, New York, N. Y., 1968; (b) S. W. Benson and H. E. O'Neal in "Kinetic Data on Gas Phase Unimolecular Reactions," NSRDS-NBS-21, 1970, U. S. Government Printing Office, Washington, D. C.; (c) H. M. Frey and R. Walsh, *Chem. Rev.*, **69**, 103 (1969), and will be discussed in detail in the full paper.

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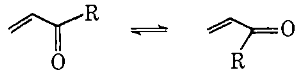
## A Simple Method for Assigning Vibrational Frequencies to Rapidly Equilibrating Rotational Isomers

*Sir:*

Continuing interest in the conformations of organic molecules and related spectral properties[1] prompts us to report a novel and simple method based upon the matrix isolation technique for assigning vibrational frequencies to rapidly equilibrating rotational isomers. Previous workers have employed temperature-dependent infrared spectroscopic studies of gaseous and liquid samples, Raman spectroscopy, and infrared studies of the crystal[2-4] in the determination of vibrational patterns of individual conformers. In our method an immobilized mixture of conformers in an argon matrix at 20.4°K is prepared by rapid freezing of a room temperature equilibrated gas-phase sample. The conformer ratio is then perturbed by photochemical irradiation. Under the conditions of the experiment infrared bands are highly resolved, and the low temperature and rigidity of the matrix prohibit thermal interconversion of conformers corresponding to local energy minima.[5] If the conformer ratio is displaced photochemically, analysis of the changes in the relative intensities of bands allows assignments to be made to the components of the mixture.

The method is illustrated for but-3-en-2-one (**1**) which has been studied spectroscopically and is thought to exist primarily in the s-cis and s-trans forms.[2,6-8] The enthalpy difference between the two rotamers is approximately 0.5 kcal/mol favoring the s-trans form.



s-cis s-trans

**1**, R = $CH_3$
**2**, R = H

Photoirradiation of **1** in an Ar matrix ($M/R$ = 800) with nickel sulfate filtered light from a medium pressure mercury arc for periods up to 4.16 hr produced only changes in the relative intensities of bands as shown for a representative region of the infrared spectrum in Figure 1. A number of bands which included the carbonyl absorption at 1690 cm$^{-1}$ previously assigned to the s-trans conformer upon irradiation decreased at identical rates, whereas another set showed a corresponding increase in intensity. The observation of a reciprocal relationship between two sets of bands

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(1) (a) N. Oi and J. F. Coetzee, *J. Amer. Chem. Soc.*, **91**, 2473, 2478 (1969); (b) G. J. Karabatsos and D. J. Fenoglio, *ibid.*, **91**, 1124, 3572, 3577 (1969); (c) A. J. Bowles, W. O. George, and D. B. Cunliffe-Jones, *Chem. Commun.*, 103 (1970); (d) W. E. Stewart and T. H. Siddall, III, *Chem. Rev.*, 70, 517 (1970); (e) D. J. Chadwick, J. Chambers, G. D. Meakins, and R. L. Snowden, *Chem. Commun.*, 624, 625 (1971); (f) I. Juchnovski and J. Kaneti, *Tetrahedron*, 27, 4269 (1971); (g) D. D. Faulk and A. Fry, *J. Org. Chem.*, **35**, 364 (1970); (h) R. B. Birge, W. C. Pringle, and P. A. Leermakers, *J. Amer. Chem. Soc.*, **93**, 6715 (1971).

(2) K. Noack and R. N. Jones, *Can. J. Chem.*, **39**, 2201 (1961).

(3) R. Mecke and K. Noack, *Chem. Ber.*, **93**, 210 (1960).

(4) R. L. Erskine and E. S. Waight, *J. Chem. Soc.*, 3425 (1960).

(5) At 20°K thermally induced unimolecular reactions with *A* factors in the range of $10^{13}$ sec$^{-1}$ and activation energies greater than 1 or 2 kcal/mol would not be observable on the time scale of the experiment.

(6) A. J. Bowles, W. O. George, and W. F. Maddams, *J. Chem. Soc. B*, 810 (1969). (As these authors point out, it is possible that the conformer referred to as s-cis is actually skew or nonplanar.)

(7) P. D. Foster, V. M. Rao, and R. F. Curl, Jr., *J. Chem. Phys.*, **43**, 1064 (1965).

(8) W. G. Fately, R. K. Harris, F. A. Miller, and R. E. Witkowski, *Spectrochim. Acta*, **21**, 231 (1965).

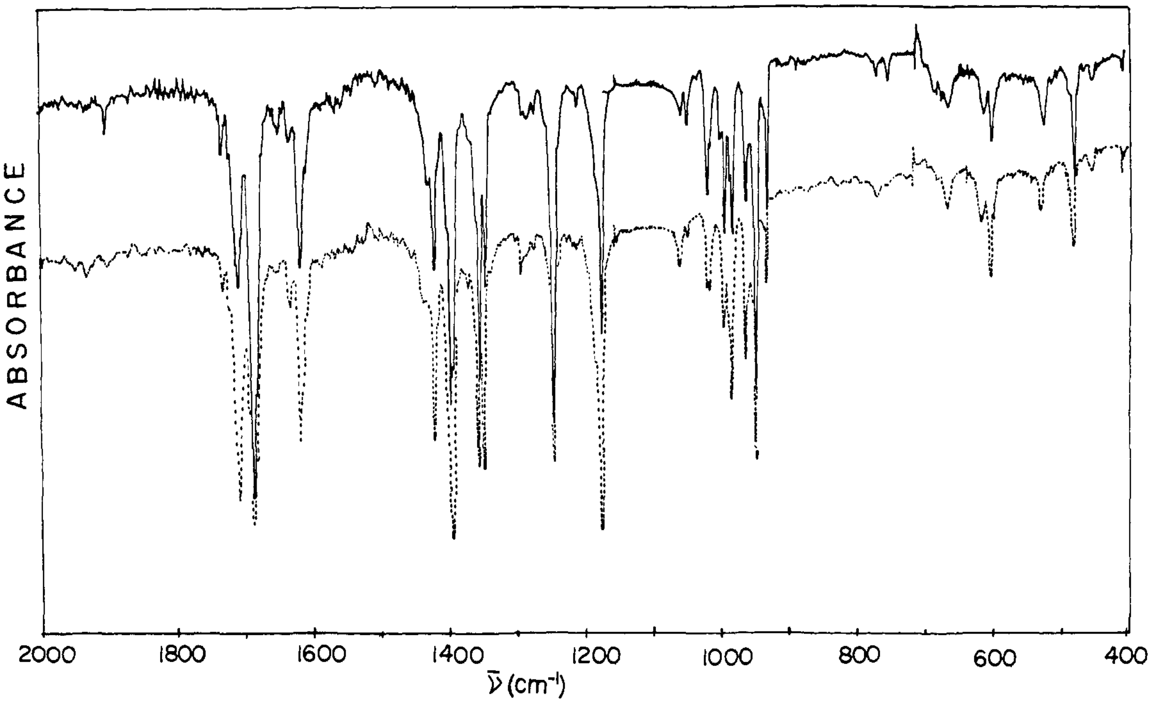

Figure 1. Infrared spectra of matrix-isolated but-3-en-2-one before (—) and after (---) 4.16 hr of photolysis.

reflects a change in the ratio of the conformers and represents an approach to a photostationary state differing from the initial condition following matrix deposition. Warming the matrix to 40°K for 0.25 hr and then cooling to 20°K does not alter the relative ratios of the two sets of bands in the spectrum of the photochemically generated mixture. After photolysis the cryotip cold window was warmed to room temperature and the sample was pumped through a liquid nitrogen cooled trap, again mixed with argon, and redeposited at 20°K. The spectrum of the redeposited sample was identical with that of starting material indicating that the photochemical change was thermally reversible at room temperature. Vibrational assignments of modes which showed resolvably different frequencies for the s-cis and s-trans conformers are listed in Table I and represent the most complete determination of such conformer-specific vibrational features to date.[2,6,8] Additional vibrational maxima which appear to be common to the two conformers were observed at 3760 (w), 3690 (vw), 3506 (vw), 3490 (w), 3472 (w), 3367 (vw), 3100 (w), 3018 (w), 3014 (w), 2975 (vw), 2920 (w), 2850 (vw), 1904 (w), 1733 (w), 1651 (w), 1635 (w), 1621 (m), 1608 (sh), 1430 (sh), 1421 (m), 1398 (s), 1394 (sh), 1273 (w), 1214 (vw), 934 (m), 681 (w), 666 (w), 526 (m), and 482 cm$^{-1}$ (m).

**Table I.** Vibrational Bands Characteristic of Either the s-cis or s-trans Conformer of But-3-en-2-one Isolated in an Argon Matrix

| Frequency, cm$^{-1a}$ s-cis | s-trans | Assignment |
|---|---|---|
| 1710 (s) | 1690 (vs) | C=O stretch |
| 1348 (s) | 1355 (s) | $CH_3$ sym deform |
| 1293 (w) | 1284 (w) | C-H rock |
| 1179 (s) | 1250 (vs) | C-C stretch |
| 1061 (w) | 1051 (w) | In-plane $CH_3$ rock |
| 1018 (m) | 1021 (m) | C-$CH_3$ stretch |
| 989 (sh) | 1003 (sh) | Out-of-plane $CH_3$ rock |
| 986 (m) | 997 (m) | Out-of-plane vinyl CH deform |
| 966 (m) | 950 (s) | $CH_2$ rock |
| 773 (w) | 756 (w) | In-plane C-$CH_3$ deform |
| 603 (m) | 616 (w) | Out-of-plane CH=$CH_2$ deform |

[a] vs = very strong, s = strong, m = medium, w = weak, sh = shoulder.

Preliminary studies of matrix isolated $\alpha,\beta$-unsaturated aldehydes were conducted with acrolein (**2**) which is thought to exist almost exclusively in the s-trans form.[6,9] Irradiation of **2** as above ($M/R$ = 500) for periods up to 2.5 hr caused bands to grow at 2848 (m), 2756 (m, formyl C-H stretch), 1616 (s, C=C stretch), 1406 (sh), 1402 (s, vinyl $CH_2$ in-plane deformation), 995 (m, vinyl CH out-of-plane deformation), 970 (m, formyl CH out-of-plane deformation), 918 (m, $CH_2$ out-of-plane deformation), and 547 cm$^{-1}$ ($\angle$CCO bending). Noack and Jones[2] and Erskine and Waight[4] have pointed out that the ratio of the band intensities of the C=O to the C=C stretching vibrations is considerably larger for s-trans than for s-cis $\alpha,\beta$-unsaturated ketones. Noack has also observed that there is a greater frequency separation between C=O and the C=C stretching bands of the cisoid conformation than of the transoid species.[2]

Interestingly, for this aldehyde, the new C=C stretching frequency at 1616 cm$^{-1}$ is considerably more intense than the corresponding band at 1623 cm$^{-1}$ in starting material, whereas there is a slight but progressive diminution in the intensity of the carbonyl absorption at 1709 cm$^{-1}$. Photolyzing small amounts (<18 mm) of acrolein ($M/R$ = 850) did not result in the production of a new carbonyl band under conditions where the intensity of new bands characteristic of a terminal methylene unit at 995 and 918 cm$^{-1}$

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(9) R. Wagner, J. Fines, J. W. Simmons, and J. H. Goldstein, *J. Chem. Phys.*, **26**, 634 (1957); S. Dzhessati, V. I. Tuylin, and V. M. Tatevskii, *Moscow Univ. Chem. Bull.*, **22**, 8 (1971).

increased beyond those at 1000 and 912 cm$^{-1}$ attributed to the transoid conformer. Evaporation and redeposition in an argon matrix of photolyzed **2** as in the case of **1** caused the spectrum to reverse to that of starting material.

All these changes are consistent with the production of the previously undetected s-cis conformer. The fact that no new peaks attributable to carbonyl stretching were observed is consistent with the interpretation that the stretching frequencies of the carbonyl band of the cisoid and transoid forms of **2** are coincident within the limits of resolution (0.1 cm$^{-1}$).

We are continuing matrix-isolation studies by various spectroscopic methods toward the determination of spectral parameters and barriers to rotation of conformers and the production of new chemical species.

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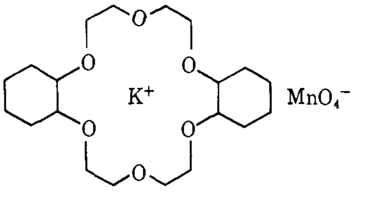
## Crown Polyether Chemistry. Potassium Permanganate Oxidations in Benzene[1]

*Sir:*

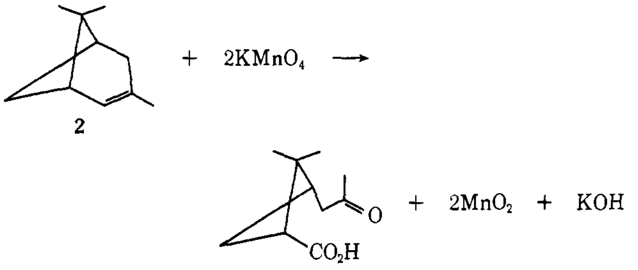
The crown polyethers and their ability to complex metal salts have aroused interest because of the possibility of increased salt solubility and increased anion reactivity in organic solvents.[2] Yet, few synthetic applications of these ethers have been reported. We have found that potassium permanganate can be solubilized in benzene by complexing with dicyclohexyl-18-crown-6 to provide a convenient and efficient oxidant, **1**,



**1**

for organic compounds under mild conditions. Thus far we have demonstrated oxidations of olefins, alcohols, aldehydes, and alkylbenzenes as shown in Table I. In the absence of the crown ether, potassium permanganate has no detectable solubility in benzene, and no reaction occurs with organic substrates.

The products of the oxidation reactions are ketones or potassium salts of carboxylic acids and are obtained in high yields without using excess oxidant. Intermediate products of consecutive oxidations were not obtained. For example, diols were not observed from olefins but aldehydes were detected and could be isolated from olefins and primary alcohols when the oxidations were carried to low conversion. The potassium salts of the acids are usually insoluble in benzene, and this is advantageous not only for product isolation but also because the salts are not subject to further oxidation. This is exemplified by the oxidation of $\alpha$-pinene (**2**) to *cis*-pinonic acid (**3**) in 90% yield by this method.



In contrast, aqueous potassium permanganate oxidation of $\alpha$-pinene gives pinonic acid in 40–60% yield.[3]

The reagent is prepared by stirring equimolar amounts of dicyclohexyl-18-crown-6 and potassium permanganate in benzene at 25° to give a clear, purple solution with concentrations of potassium permanganate as high as 0.06 *M*.[4] This is one of the few examples where an insoluble salt can be dissolved in a nonpolar solvent like benzene simply by adding crown ether. Normally, a more polar solvent (methanol) is needed to solubilize the salt followed by solvent exchange.[2a] Complex **1** can be isolated as a purple solid but is more stable in benzene (half-life (25°) ~48 hr). Above 50°, **1** rapidly degrades to adipic acid and other products.[5] The absorption spectrum of **1** in benzene, 508 (2330), 525 (3170), 546 (3130), and 565 nm (1810), is very similar to that of aqueous permanganate ion.[6] The $^{55}$Mn nmr spectrum of **1** in benzene is less structured and the half-line width much broader than the sharp, symmetrical resonance of aqueous permanganate ion. This is indicative of a less symmetric permanganate ion and suggests that potassium permanganate is ion paired in benzene.

The oxidations may be carried out homogeneously at 25° by mixing a solution of **1** in benzene with the compound to be oxidized. With olefins, *e.g.*, *trans*-stilbene, rapid decolorization of the reagent occurs

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[1] Presented in part at the XXIIIrd IUPAC Meeting, Boston, Mass., July 1971.

[2] (a) C. J. Pedersen, *J. Amer. Chem. Soc.*, **89**, 7017 (1967); **92**, 391 (1970); *Fed. Proc., Fed. Amer. Soc. Exp. Biol.*, **27**, 1305 (1968); (b) C. J. Pedersen and H. K. Frensdorff, *Angew. Chem., Int. Ed. Engl.*, **84**, 16 (1972); (c) J. J. Christensen, J. O. Hill, and R. M. Izatt, *Science*, **174**, 459 (1971); (d) D. J. Sam and H. E. Simmons, *J. Org. Chem.*, in preparation; (e) our preliminary observations of the crown ether–potassium permanganate oxidations of organic substrates have been mentioned in the above references.

[3] V. L. Loeblich, F. C. Magne, and R. R. Mod, *Ind. Eng. Chem.*, 47, 1569 (1955); G. W. Hedrick and R. V. Lawrence, *ibid.*, **52**, 853 (1960); and A. Poplavskaya and M. I. Goryaev, *Zh. Obshch. Khim.*, **33**, 1492 (1963).

[4] Two isomers of dicyclohexyl-18-crown-6 were obtained from hydrogenation of dibenzo-18-crown-6. One isomer (mp 61–62°) gives 5.8 × 10$^{-2}$ *M* potassium permanganate solubility in benzene while the other (mp 69–70°) gives 4.2 × 10$^{-4}$ *M* solutions. The mixture of isomers was used in the oxidations and gave approximately 0.03 *M* permanganate solutions.

[5] Oxidations of compounds such as the sterically hindered 1,1-dineopentylethylene, which is completely resistant to alkaline permanganate, proceed slowly at 25° with our method. Such resistant oxidations cannot be accelerated by heating because of the concurrent reagent degradation.

[6] M. C. R. Symons and P. A. Traveleon, *J. Chem. Soc.*, 3503 (1962); M. Smith and M. C. R. Symons, *J. Chem. Phys.*, **25**, 1074 (1965).