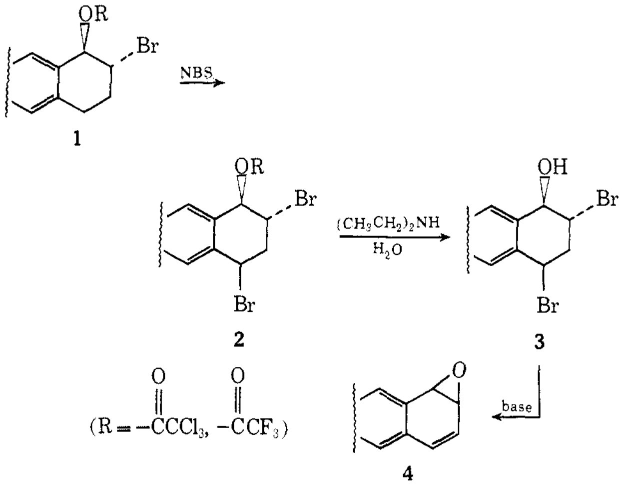
the procedure is limited to K-region oxides.[9] Dehydrohalogenation routes have been utilized for the preparation of non-K-region arene oxides.[10,11] The major difficulty is the instability of a typical intermediate, such as tetralin 1,2-epoxide, under the conditions of bromination with *N*-bromosuccinimide.[12] We have now solved this problem by using halohydrin esters which are stable to the bromination conditions.

The ester blocking groups of choice were trichloro- and trifluoroacetates which allowed their facile removal in the presence of the highly reactive benzylic bromine. Subsequent base treatment introduced both the unsaturation and the epoxide ring in a single step.



Naphthalene 1,2-oxide was prepared with great ease and in excellent yield by this procedure, starting with 1-hydroxy-2-bromotetralin which was acetylated with trifluoroacetic anhydride in $CHCl_3$ to yield **1** (bp 100–105° (0.2 mm), 84%),[13] convertible with surprising ease[14] and in excellent yield (with *N*-bromosuccinimide) to the dibromide **2** (mp 89–90° from petroleum ether, 87%) which was hydrolyzed with aqueous diethylamine in acetonitrile to **3** (mp 109–110° from petroleum ether, 90%). On treatment with dry $NaOCH_3$ in tetrahydrofuran, both the epoxide ring and the double bond were generated in one step to yield naphthalene 1,2-oxide (yield 97%).[15] The overall yield in this procedure is 65% for four steps compared with 14% for three steps by the earlier route from the same starting material.[12,14]

The value of the new method was further proven by the successful preparation of the dibromo ester precursors to the unknown 1,2- and 3,4-oxides of phenanthrene from the corresponding halohydrin trichloroacetates of **1**; yields for the *N*-bromosuccinimide reaction to produce the analogs of **2** were 53 and 82%, respectively. For the sequence leading to phenanthrene 3,4-oxide, the dibromo ester **2** was hydrolyzed with aqueous diethylamine in acetonitrile to the alcohol **3** which, without purification, was converted to the desired oxide[16] by diazabicyclononene[12] in overall yield of 70% for the two steps. Attempts to prepare the 3,4-oxide by the conventional route, *viz.*, bromination of 3,4-epoxy-1,2,3,4-tetrahydrophenanthrene, have been completely without success owing to the instability of the tetrahydroepoxide.

However, phenanthrene 1,2-oxide could not be prepared by the new procedure because the bromine in the 4 position of the trichloroacetate ester **2** is too reactive and undergoes side reactions prior to hydrolysis at C-1.[17] Fortunately, 1,2-epoxy-1,2,3,4-tetrahydrophenanthrene is readily brominated at the hindered, benzylic 4 position. Dehydrohalogenation[12] of the crude material gave the desired 1,2-oxide[18] in 61% overall yield for the two steps. The old and the new routes to these two new arene oxides of phenanthrene complement each other to advantage.

A report has appeared describing routes to the 7,8- and 9,10-oxides of the carcinogen benzo[*a*]pyrene[19] by an adaption of the original synthesis of naphthalene oxide.[12] The products obtained were highly impure and could only be characterized tentatively. The synthesis of these oxides by the present procedure is in progress.

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(8) See the examples in ref 7 as well as E. Boyland and P. Sims, *Biochem. J.*, **97**, 7 (1965).

(9) Attempts in this laboratory to cyclize α-chloromuconic dialdehyde to 3-chlorobenzene oxide and *o*-formylcinnamaldehyde to naphthalene oxide with the phosphine reagent have been without success.

(10) E. Vogel and H. Gunther, *Angew. Chem., Int. Ed. Engl.*, **6**, 385 (1967).

(11) For further examples, see R. M. DeMarinis and G. A. Berchtold, *Chem. Commun.*, 810 (1971); N. Kaubisch, J. W. Daly, and D. M. Jerina, *Biochemistry*, **11**, 3080 (1972); R. Schubart, Ph.D. Thesis, Universität zu Köln, 1967.

(12) E. Vogel and F. G. Klärner, *Angew. Chem., Int. Ed. Engl.*, **7**, 374 (1968).

(13) Unless otherwise stated, all new compounds were obtained analytically pure and had satisfactory nmr (Varian 60 MHz) and mass spectra (Hitachi RMU-7, 70 eV). Yields are based on material which showed no detectable impurities by nmr.

(14) The reported yield[12] for the bromination of tetralin 1,2-epoxide with *N*-bromosuccinimide is 23%. While somewhat higher yields (*ca.* 30%) have been observed in this laboratory, very often the reaction fails to initiate and an undefined polymer along with 2-tetralone, *via* rearrangement of the starting oxide, result. Cyclization of **1** (R = H) to tetralin 1,2-epoxide with sodium ethoxide proceeds in ~75% yield of distilled product.

(15) No impurities could be detected by nmr, and the material was identical in all respects with an authentic sample.

(16) The synthesized phenanthrene 3,4-oxide (crystallized from ether–petroleum ether) gave an elemental analysis within 0.2% of theory and an nmr spectrum (CS_2 solvent) which was assigned as 1 H_3, 4.07, 1 H_4 5.02, 1 H_2 6.44, 1 H_1 6.80, and six aromatic protons 7.10–8.30; $^3J_{1,2}$ = 9.0, $^3J_{2,3}$ = 3.5, $^3J_{3,4}$ = 3.5, and $^4J_{2,4}$ = 1.5 Hz. The high instability of this material at room temperature precluded measurement of its mass spectrum or melting point.

(17) The more labile trifluoroacetate also proved unsatisfactory.

(18) The synthesized phenanthrene 1,2-oxide (mp 110–111° from ether) gave an elemental analysis within 0.2% of theory, a mass spectrum with the molecular ion (*m/e* 194) as the base peak and fragments resulting from loss of 18 and 29, and an nmr spectrum ($CDCl_3$ solvent) which was assigned as 1 H_2 4.25, 1 H_1 4.67, 1 H_3 6.63, and 1 H_4 and six aromatic protons 7.30–8.40; $^3J_{1,2}$ = 4.0, $^3J_{2,3}$ = 4.0, $^3J_{3,4}$ = 10, and $^4J_{2,4}$ = 1.5 Hz.

(19) J. F. Waterfall and P. Sims, *Biochem. J.*, **128**, 265 (1972).

Haruhiko Yagi, Donald M. Jerina*
Laboratory of Chemistry
National Institute of Arthritis, Metabolism, and Digestive Diseases
National Institutes of Health, Bethesda, Maryland 20014

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Photochemistry of α-Pyrone in Argon at 8 °K[1]

Sir:

Physical evidence for the electrocyclic opening of the α-pyrone ring system is marginal.[2] With this in mind we have reexamined this system.

Irradiation (Pyrex filter) of α-pyrone matrix isolated in argon (1 : 400) at 8 °K leads rapidly to formation of the aldehyde–ketene (Figure 1). Under these conditions

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(1) Photochemical Transformations. XLVII. See also R. G. S. Pong and J. S. Shirk, *J. Amer. Chem. Soc.*, **95**, 248 (1973).

(2) O. L. Chapman and C. L. McIntosh, *ibid.*, **95**, 247 (1973).

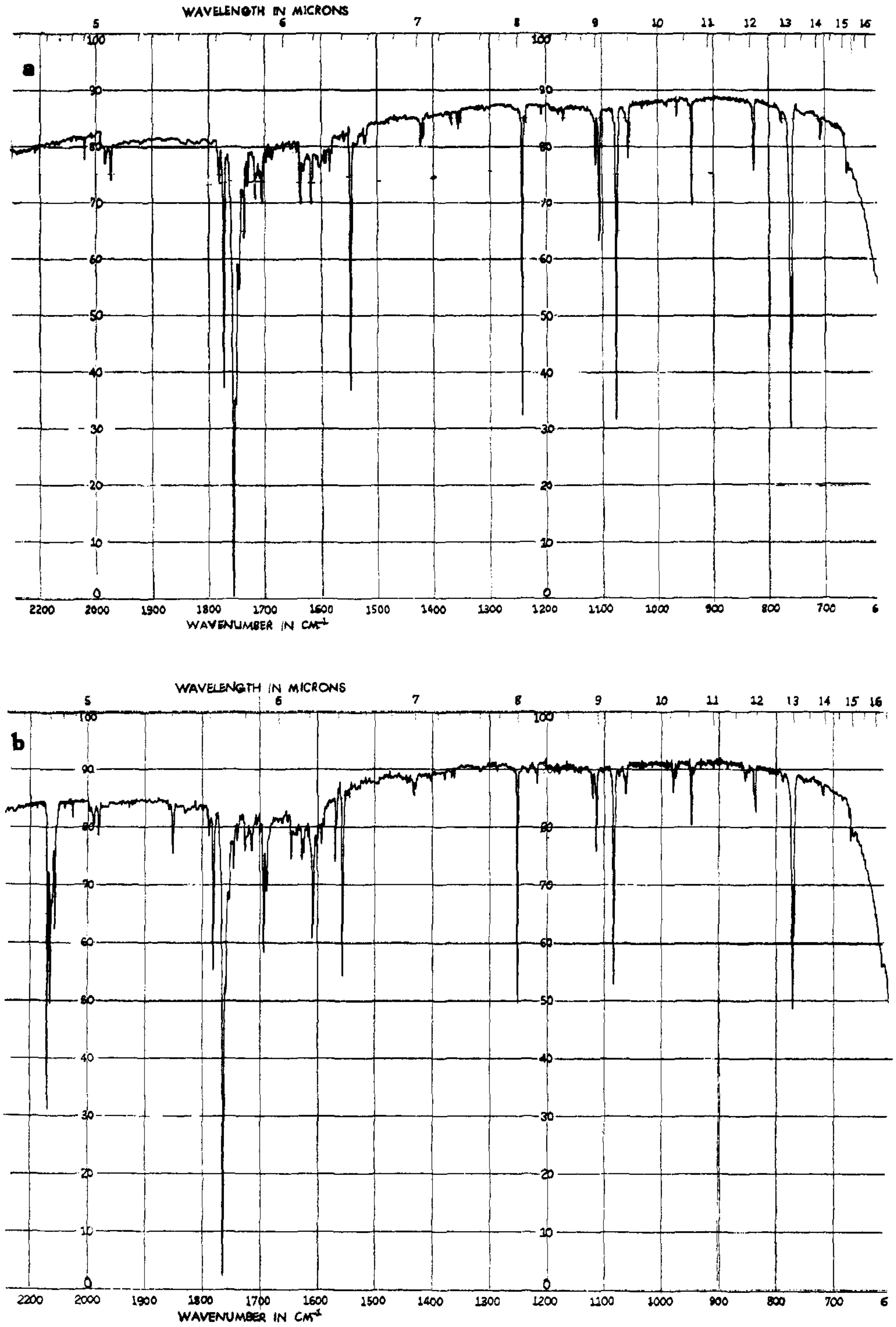


Figure 1. (a) α-Pyrone matrix isolated in argon at 8 °K before irradiation. The three small bands in the 1950–2050-cm^{-1} range are due to a trace of iron tricarbonyl–cyclobutadiene complex in the vacuum system. (b) α-Pyrone matrix isolated in argon at 8 °K after 4 min of irradiation with a Pyrex-filtered 1000-W mercury arc lamp.

the concentration of the ketene is much higher than at 77 °K, and several features of the infrared spectrum can be observed. The most striking feature of the spectrum of the photoproduct is the complexity of the ketene region. Four bands can be clearly identified by time *vs.* intensity plots as due to primary products. In addition, two aldehyde bands due to primary products can be observed. The β-lactone initially reported by Corey and Streith[3] is also a primary product (1850 cm^{-1}) although formed slowly. The richness of the spectrum particularly in the ketene region is most remarkable. The large number of bands is due to the fact that excited α-pyrone gives rise to several rotamers of the aldehyde–ketene which do not thermally interconvert at 8 °K. This interpretation is confirmed by warming the sample to 35 °K. The rotamers equilibrate during the warming, and this equilibration produces dramatic changes in the ketene and aldehyde carbonyl absorptions (Figure 2). At 35 °K less than 3 kcal/mol of activation energy is available. In a separate experiment,

(3) E. J. Corey and J. Streith, *J. Amer. Chem. Soc.*, **86**, 950 (1964).

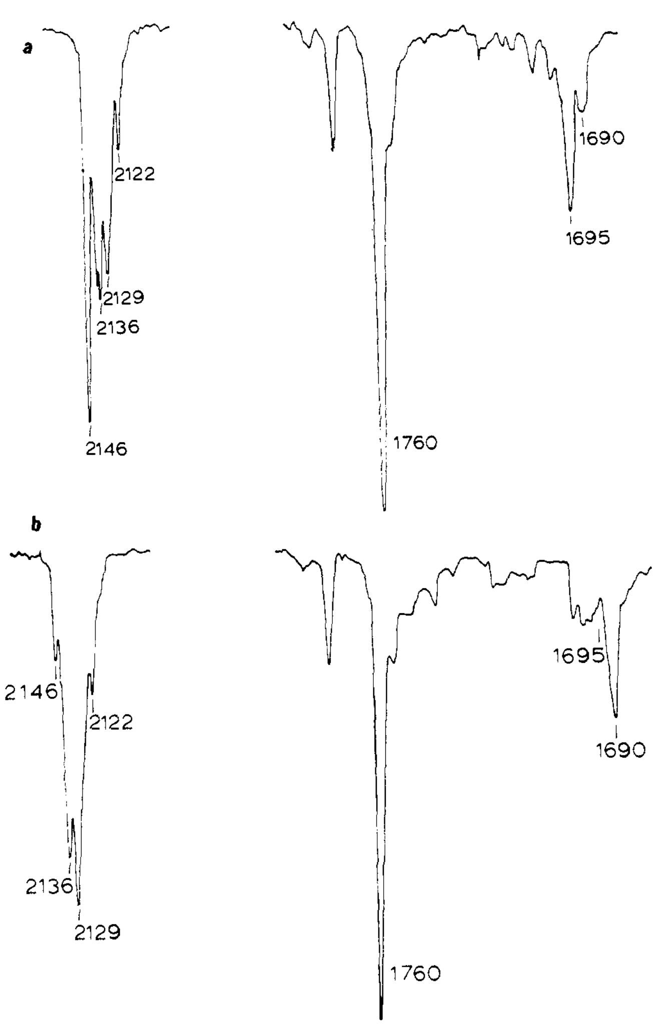
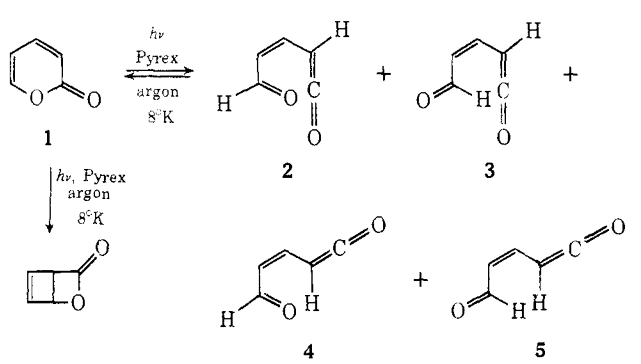


Figure 2. (a) Expanded scale view of the carbonyl region of α-pyrone matrix isolated in argon at 8°K after 32 min of irradiation with a Pyrex-filtered 1000-W mercury arc lamp. (b) The sample shown in Figure 2a after warming to 35°K for 5 min.

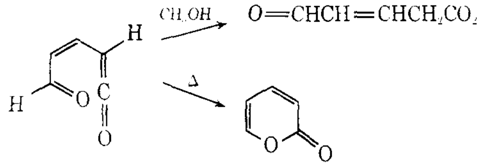
α-pyrone, matrix isolated in argon at 8°K, was irradiated (Pyrex filter) without warming. The initial ketene bands changed in intensity on continued irradiation and new ketene bands appeared. In the end, the ketene bands and the α-pyrone bands decreased almost to zero, and the ultimate product was the β-lactone.

These results can be understood in terms of the following model. Electronically excited α-pyrone undergoes electrocyclic opening, and in the process of demotion and thermal equilibration a nonthermodynamic mixture of four rotamers is formed. It is no accident that four rotamers are observed. This is the number of planar forms available by rotation about carbon-carbon single bonds. Warming equilibrates the rotamers and increases the concentration of the more stable rotamers (**4** and **5**) relative to the less stable rotamers (**2** and **3**). The direct observation of a mixture of rotamers formed in a photochemical reaction appears to be the first such observation.[4] It is quite surprising that this much movement occurs in argon at 8°K. It is interesting also that there is a substantial temperature effect on the position of the photostationary state between the ketene and the pyrone. At 77°K the ketene is barely detectable while at 8°K the ketene bands are very prominent. The existence of a photostationary state makes it clear that the α-pyrone and the ketenes are photochemically interconverting. In fact, the changes in the intensity of the ketene bands on continued irradiation probably reflect differences in the relative absorption by the rotamers of the ketene.



Irradiation (Pyrex filter) of 4,6-dimethyl-2-pyrone in Argon at 8°K also gave a mixture of ketene rotamers and ultimately the β-lactone. The ketene formed at a slower rate and the photostationary state had less ketene than in the case of α-pyrone.

Characterization of the aldehyde-ketene from α-pyrone shows unequivocally that de Mayo's suggestion[2,3] concerning ketene formation from pyrones is correct. It leaves the problem whether or not ketenes are involved in the formation of methyl esters at room temperature. Flash photolysis results at room temperature (10^{-3} M α-pyrone in hexane) show that the aldehyde-ketene half-life is less than 50 μsec. The half-life is presumably determined by recyclization to α-pyrone in the absence of nucleophiles. In the presence of nucleophiles a competition exists between nucleophilic attack and electrocyclic closure. The result of the competition will depend on the relative thermal coefficients of the reactions. A similar competition exists in the cyclization of *cis*-diene-ketenes.[5,6]



It is known that formation of ester products from 4,6-dimethyl-2-pyrone involves photochemical addition of methanol to the pyrone rather than thermal addition of methanol to a ketene. It may well be that this is the general case and that ketene formation at room temperature is simply an energy wasting process.

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(4) Photochemical interconversions of rotamers at 20°K have been reported: A. Krantz, T. D. Goldfarb, and C. Y. Lin, *J. Amer. Chem. Soc.*, **94**, 4022 (1972).

(5) O. L. Chapman, *Proc. XXIIIrd Int. Congr. Pure Appl. Chem., Spec. Lect.*, **1**, 311 (1971).

(6) J. D. Hobson, M. M. Al Holly, and J. R. Malpass, *Chem. Commun.*, 764 (1968).

O. L. Chapman,* C. L. McIntosh, J. Pacansky
Department of Chemistry, Iowa State University
Ames, Iowa 50010

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