group protons on 1-methylnaphthalene (τ 7.25). The only discrepancy might be expected for the 4-methyl group protons in 4-methyl-1,5-naphthyridine, where the 5-nitrogen atom might influence the 4-methyl group protons by the anisotropic effect of its unshared pair of electrons and/or by its inductive effect. We do indeed observe that the chemical shifts of the various 4-methyl group protons are as predicted, except for an increased deshielding (0.1 ppm) of the methyl group protons in 4-methyl-1,5-naphthyridine.

The nmr data are therefore in agreement with the predictions of the HMO calculations and we can suggest (if there is indeed a correlation between ring current and aromaticity) that the resonance energies of the naphthyridines are essentially the same as the resonance energy of naphthalene, and that the replacement of two sp^2 carbon atoms by two sp^2 nitrogen atoms does not greatly alter the resonance stabilization of these bicyclic heteroaromatic compounds.

Experimental Section[11]

4-Methyl-1,6-naphthyridine.—To a solution of 70 ml of Sulfo-mix,[12] 25 ml of water, and 23.5 g (0.25 mole) of 4-aminopyridine, warmed to 115°, was added dropwise over 1 hr, 18.0 g (0.26 mole) of methyl vinyl ketone. The bath temperature was raised to 120° and the reaction mixture was stirred for 5 hr. The cooled solution was made basic with aqueous sodium hydroxide and steam distilled. The distillate (1 l.) was adjusted to pH 4 with phosphoric acid and extracted with five 50-ml portions of chloroform. The combined extracts were dried and on evaporation to dryness a clear oil remained which solidified after some time to form clusters. Chromatography on neutral grade 3 alumina yielded 0.36 g (1%) of 4-methyl-1,6-naphthyridine: mp 68–69°; λ_{max}^{MeOH} 203 mμ (log ϵ 481), 208 (4.53), 220 sh (4.44), 254 (3.48), 263 sh (3.45), 275 sh (3.28), 295 sh (3.30), 305 (3.44), 317 (3.43). The infrared out-of-plane vibrations of the free base in chloroform are 870, 850, 820 cm^{-1} as expected[4] for a 4-substituted 1,6-naphthyridine.

The sample was converted to the monopicrate for elemental analysis (picrate mp 184–185°).

Anal. Calcd. for $C_{15}H_{11}N_5O_7$: C, 48.25; H, 2.97; N,18.76. Found: C, 48.27; H, 3.20; N, 18.80.

2-Methyl-1,6-naphthyridine.—The same procedure was used as for the preparation of 4-methyl-1,6-naphthyridine, except that 50 g (0.60 mole) of crotonaldehyde was substituted for the methyl vinyl ketone. The yield of 2-methyl-1,6-naphthyridine was 0.18 g (0.5%): mp 60–61°; λ_{max}^{MeOH} 205 mμ (log ϵ 4.78), 225 (4.56), 230 sh (4.44), 298 (3.53), 311 (3.52). The infrared out-of-plane vibrations of the free base in chloroform are: 895, 840 cm^{-1} as expected[4] for a 2-substituted 1,6-naphthyridine. Monopicrate (mp 173–174°).

Anal. Calcd for $C_{15}H_{11}N_5O_7$: C, 48.26; H, 2.97; N, 18.76. Found: C, 48.00; H, 3.04; N, 18.90.

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[11] Melting points are corrected. Nmr spectra were obtained with a Varian A-60 spectrometer. The microanalyses were performed by Mrs. S. De Boer of this department.

[12] W. P. Utermohlen, Jr., *J. Org. Chem.*, **8**, 544 (1943).

Pyrolysis of 1-Methyl-3- isopropylidenecyclobutene

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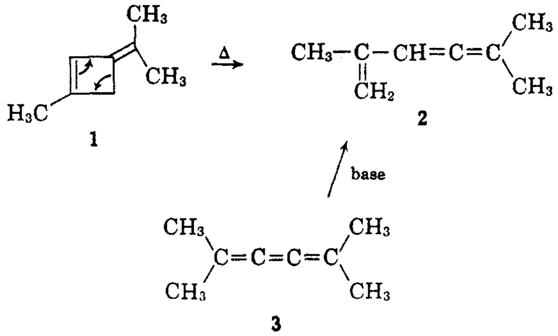
In connection with another problem,[1] we sought a convenient synthesis of the vinylallene 2, to confirm its presence as a rearrangement product from cumulene 3. An attractive route appeared to be pyrolysis of the known cyclobutene 1,[2] which by a cyclobutene to butadiene rearrangement would give 2 directly. A study of the rearrangement also seemed of interest in view of recent attention to such isomerizations.[3]



A sample of purified 1 was made available through the generosity of Dr. W. H. Sharkey. The compound indeed undergoes the isomerization at temperatures above 175° to give isomer 2 in reasonable yield. From a preparative point of view the pyrolysis was best carried out in the injector (340°) of a gas chromatograph with 2 being collected in 45 to 55% yield.

Isomer 2, C_8H_{12}, exhibits infrared absorption at the expected positions, including 1941 cm^{-1} (allene) and 876 cm^{-1} (terminal methylene). The ultraviolet spectrum of 2 exhibits a λ_{max}^{EtOH} at 218 mμ (ϵ 22,000).[4] The nmr spectrum of 2 was quite informative showing a 6-proton singlet at δ 1.70 (allenic methyls), a broadened 3-proton singlet at δ 1.75 (vinyl methyl), a 2-proton multiplet at δ 4.78 (terminal methylene) and a one 1-proton multiplet at δ 5.67 (allenic hydrogen). Catalytic hydrogenation resulted in the uptake of 3 moles of hydrogen to give 2,5-dimethylhexane, identical with an authentic sample. The thermal rearrangement product was identical in all respects with 2 obtained from 3.[1,5]

For the kinetic runs, small samples of 1, dissolved in *n*-hexane (as an internal standard), were sealed, and the reactions run in a constant-temperature Woods metal bath. Unfortunately, similarity in the ultraviolet spectra of 1 and 2 required that the disappearance of 1 be followed by gas chromatography. Formation of 2 did not quite parallel disappearance of 1, most likely due to dimerization.[6] From the rates at 200° and 220°, the activation energy shown in Table I was calculated. Also shown are the data for two related isomerizations.

It is noted from the data in Table I that the isomerization of 1 is much slower than that of the nonconju-

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[1] F. T. Bond and D. E. Bradway, *J. Am. Chem. Soc.*, **87**, 4977 (1965).

[2] J. K. Williams and W. H. Sharkey, *ibid.*, **81**, 4269 (1959).

[3] See for example: (a) M. A. Battiste and M. E. Burns, *Tetrahedron Letters*, 523 (1966); (b) R. Criegee, D. Seebach, R. E. Winter, B. Barritzu, and H. A. Brune, *Chem. Ber.*, **98**, 2339 (1965); (c) H. M. Frey, D. C. Marshall, and R. F. Skinner, *Trans. Faraday Soc.*, **61**, 861 (1965), and earlier references cited therien.

[4] *Cf.* vinylallene itself shows infrared absorption at 1940 cm^{-1} and λ_{max}^{EtOH} 216.5 mμ: E. R. H. Jones, H. H. Lee, and M. C. Whiting, *J. Chem. Soc.*, 341 (1960).

[5] A compound assigned structure **2** has been reported previously: A. F. Thompson and E. N. Shaw, *J. Am. Chem. Soc.*, **64** 363 (1942).

[6] H. Fischer, "The Chemistry of Alkenes," S. Patai, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, p 1064.

TABLE I

ACTIVATION ENERGIES FOR CYCLOBUTENE ISOMERIZATIONS

Compd	E_A (kcal/mole)	Ref
1	39	This work
	32.5	*a*
	33	*b*

[a] W. Cooper and W. D. Walters, *J. Am. Chem. Soc.*, **80**, 4220 (1958). [b] See ref 3c.

gated cyclobutenes. Presumably this reflects the conjugated nature of **1**, and the relative instability of **2** compared with more typical butadienes. While the additional ring strain in **1** should work in the opposite direction, it is not surprising that this effect is relatively small.

Experimental Section[7]

A. **2,5-Dimethylhexa-1,3,4-triene (2). From 1-Methyl-3-isopropylidenecyclobutene.**—Samples of **1** (*ca.* 20 μl) were introduced by syringe into the injector (340°) of an Aerograph A-90-P_2 gas chromatograph. Using a 10-ft Cyanosilicone column maintained at 60°, a single peak (retention time 9.5 min) was observed. This component was trapped in a collector held at Dry Ice–acetone temperature. From 0.285 g of **1** there was obtained 0.151 g of **2**, $n^{25}D$ 1.4617.

Anal. Calcd for C_8H_{12}: C, 88.82; H, 11.18. Found: C, 88.68; H, 11.20. Spectral properties of **2** are reported in the text.

B. **From 2,5-Dimethylhexa-2,3,4-triene.**—A freshly prepared sample of **3**[1] (100 g) was dissolved in 3 ml of carefully purified and degassed triglyme. Sodium hydride (0.08 g) was added and the suspension stirred under nitrogen for 20 min at 100°. The cooled solution was decanted and examined by glpc showing only one peak with a retention time identical with that of **2** prepared by method A. Preparative glpc of a 0.5-ml aliquot resulted in the collection of 0.009 g of **2** which showed infrared and ultraviolet absorption identical with that of **2** prepared by method A.

Catalytic Reduction of 2.—A sample (0.100 g) of pyrolytically prepared **2** was dissolved in 3 ml of 95% ethanol and hydrogenated for 1 hr in a microapparatus using 0.100 g of 5% Pd–C catalyst. The uptake of hydrogen was 106% of that calculated for three double bonds. The filtered solution was taken up in 10 ml of pentane, washed four times with water, and dried. Most of the pentane was removed through a Vigreux column. Preparative glpc of the residue afforded 0.041 g of 2,5-dimethylhexane, the infrared and nmr spectra of which were identical with those of an authentic sample.

Kinetics of the Pyrolysis.—Carefully washed and dried capillary tubes were filled with dilute (3%) solutions of **1** in carefully purified *n*-hexane. The tubes were cooled, purged with purified nitrogn, and sealed. Pyrolyses were carried out in a thermostated Woods metal bath (±0.3°). For analysis, samples were removed, cooled, opened, and the amount of **1** (relative to *n*-hexane standard) remaining determined by the areas of the relative glpc peaks. The injector and detector of the glpc for analysis were maintained at 120° and the 10-ft cyanosilicone column at 60°, conditions which were shown not to isomerize **1**. Rates obtained from good first-order plots were $k_{200°} = 1.58 \times 10^{-4}$ sec^{-1} and $k_{200°} = 8.60 \times 10^{-4}$ sec^{-1}.

Acknowledgment.—This work was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society. We are extremely grateful to Dr. W. H. Sharkey for the sample of **1** which made this study possible.

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[7] The analysis was by Galbraith Laboratories Inc. Infrared spectra were run on a Beckman IR-8, ultraviolet spectra on a Cary 15, and nmr spectra on a Varian A-60 instrument in carbon tetrachloride using TMS as an internal standard.

The Oxidative Decarboxylation of α-Halo Acids by Pyridine N-Oxide. A Degradative Method for Carboxylic Acids[1]

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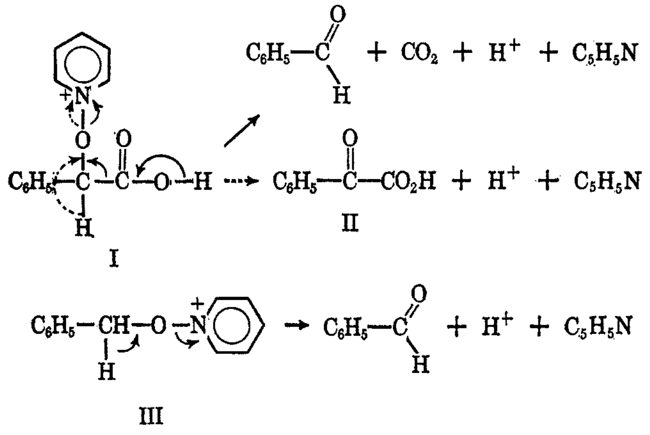
It has been reported that a number of carboxylic acid anhydrides can be oxidatively decarboxylated to aldehydes and ketones by pyridine N-oxide.[2,3] In order to account for the benzaldehyde and the small quantity of phenylglyoxylic acid (II) produced in the oxidative decarboxylation of phenylacetic acid, it was postulated that a key reaction intermediate is the N-(α-carboxybenzyloxy)pyridinium ion (I).[2] The β elimination of a proton and a pyridine nucleus, as shown (dotted arrows) would produce phenylglyoxylic acid. This reaction is directly analogous to the base-promoted decomposition of the N-benzyloxypyridinium ion (III) which produces benzaldehyde.[4] The ion I could also decompose in the carboxylogous[5] fashion (solid arrows) to yield benzaldehyde, carbon dioxide, and the elements of the pyridinium ion.



This scheme suggests that the nucleophilic attack of pyridine N-oxide on α-bromophenylacetic acid should produce benzaldehyde and phenylglyoxylic acid *via* the intermediate I. This postulated reaction sequence has in fact been realized. The reaction of excess pyridine N-oxide with α-bromophenylacetic acid in refluxing benzene produces benzaldehyde (49% yield), carbon dioxide (46%), and phenylglyoxylic acid (5%). Pyridine is produced but was not quantitatively determined. In refluxing toluene, the yields are improved to 58%, 58%, and 11%, respectively.

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[1] (a) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. (b) Taken from the Ph.D. thesis of I. H. Song, University of Pittsburgh, 1966.

[2] T. Cohen, I. H. Song, and J. H. Fager, *Tetrahedron Letters*, 237 (1965).

[3] C. Rüchardt, S. Eichler, and O. Krätz, *ibid.*, 233 (1965); T. Koenig, *ibid.*, 3127 (1965).

[4] W. Feely, W. L. Lehn, and V. Boekelheide, *J. Org. Chem.*, **22**, 1135 (1957).

[5] This convenient term takes cognizance of the fact that for most reactions which involve proton removal there are analogous reactions of the corresponding carboxylic acid which involve loss of both a proton and carbon dioxide. The latter reactions, which are carboxylogs of the former, invariably occur more rapidly.