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TRICYCLO[$2^{3,6}$.1.1.0]PYRAN-2-ONE

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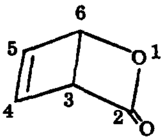
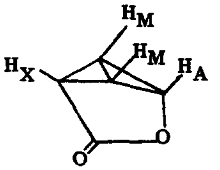
Bicyclo[2.2.0]pyran-2-one (1), the major product from ultraviolet irradiation of 2-pyrone (1), undergoes a novel rearrangement when dissolved in aprotic solvents such as acetonitrile, methylene chloride, or methyl iodide and stored for 12-16 hr at 25°. Removal of solvent at 0° and fractional molecular distillation (25°, <0.1 mm) affords a liquid substance of greater volatility than 1 which polymerizes rapidly at 25° when neat but which may be kept unchanged for weeks at -78°. The rearrangement product, to which we assign structure 2, was shown to be an isomer of 1 through combustion analysis and molecular weight determinations [calcd. for $C_6H_4O_2$: C, 62.50; H, 4.19; mol. wt. 96; found: C, 62.36; H, 4.19; mol. wt. 96 (mass spectrometric), 94.5 (osmometric)]. The isomerization product exhibits infrared absorption at 5.50 and 5.57 μ (carbon tetrachloride) and an ultraviolet maximum at 278 mμ (ε 37) (in ether). The nmr spectrum (deuteriochloroform, internal TMS) consists of a doublet of triplets (δ, ppm downfield, 4.72, one H), a doublet of doublets (δ 3.50, two H), and a doublet of triplets (δ 2.45, one H), in excellent accord with the assignment as tricyclo[$2^{3,6}$.1.1.0]pyran-2-one (2). Analysis of the AM_2X nmr pattern provides the following parameters.



1

$\delta H_A = 4.72$ ppm
$\delta H_M = 3.50$ ppm
$\delta H_X = 2.45$ ppm

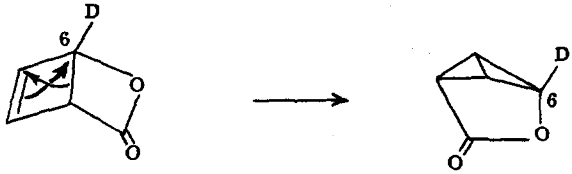


2

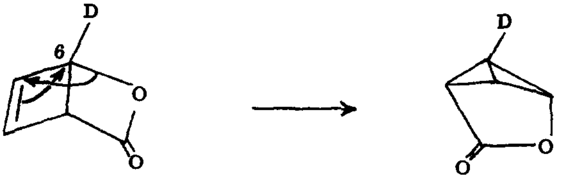
$J_{AX} = 5.2$ Hz
$J_{AM} = 1.6$ Hz
$J_{MX} = 1.4$ Hz

The appreciable long-range coupling constant (J_{AX} 5.2 Hz) has considerable precedence; other strained systems exhibit significant long-range coupling as well (2,3,4).

Two general types of pathways for the rearrangement 1 → 2 can be formulated, the first (eq. 1) not involving carbon-oxygen bond breaking and the second (eq. 2) with carbon-oxygen bond



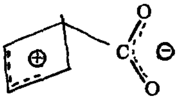
eq. 1



eq. 2

breaking. Deuterium labeling experiments suffice to distinguish between these alternative pathways.

The nmr spectrum of the deuteriated tricyclic lactone produced upon rearrangement of bicyclo-[2.2.0]pyran-2-one-6-d (prepared by irradiation of 2-pyrone-6-d) shows three equal-area multiplets at δ 4.72, 3.50, and 2.45. Obviously, deuterium originally at position 6 in bicyclic 1 finds itself at the bicyclobutane fusion in the tricyclic structure 2, a label distribution which supports the pathway involving carbon-oxygen bond cleavage (eq. 2). A reasonable intermediate for this rearrangement might be dipolar ion 3 which could well exist as an intramolecular ion pair in the comparatively nonpolar solvents which suffice for this rearrangement. The cyclization of 3 to 2, which represents an unusual mode of nucleophilic attack on an allylic cation, might be favored by a contribution from or an isomerization to 4.



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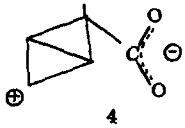

4

The 2-pyrone-6-d used for the labeling study was prepared by the zinc-acetic acid-d reduction of 6-iodo-2-pyrone, prepared in situ by treatment of 6-chloro-2-pyrone (5) with anhydrous sodium iodide. The nmr, infrared, and mass spectra of 2-pyrone-6-d thus prepared are in accord with the proposed structure (6).

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