mentation, not represent the true ratios of loss of CS and CO. Nevertheless, the trend is obvious and invites the hypothesis that the more stable isomers,[9] thiapyran-2-one and 4-methylthiapyran-2-one, having sulfur in the ring, do not rearrange and lose solely CO. However, 4,6-dimethylpyran-2-thione, which cannot rearrange by the thermal mechanism because of the blocking methyl group in position 6 (see ref 3), loses CS almost exclusively. By analogy, 4-methoxy-6-methylpyran-2-thione is expected to lose only CS. This occurs predominately (98.6%).[10] Intermediate in behavior are the molecular ions of pyran-2-thione, 5-bromopyran-2-thione, 3-methylpyran-2-thione, and 4-methylpyran-2-thione, which, by this criterion, appear to rearrange substantially prior to fragmentation.

The simplest rationalization of the preceding results is that decarbonylation is several times faster than the rearrangement sequence for 2-pyrone molecular ions but several times slower for thio-2-pyrone molecular ions unless the rearrangement of the latter is blocked by a substituent in position 6. The failure of 2-pyrone to scramble the oxygen label requires the operation of some alternate process to scramble the 3 and 5 deuteriums. Whether this deuterium scrambling occurs before or after decarbonylation is unknown nor is it known whether it occurs via a symmetric ion or through dynamic scrambling. Hence, speculation on the source of the deuterium scrambling is presently unwarranted.

Experimental Section

Oxygen-18-Labeled 2-Pyrone. 2-Ethoxypyrylium fluoroborate[4] (0.17 g) was added to 0.07 g of water containing 30.0% oxygen-18 and 41.2% deuterium. After 3 hr at room temperature and 18 hr of storage at −20°, the sample was distilled at 80° (7 Torr). ^1H NMR showed the resulting pale yellow oil to be 2-pyrone, water, and ca. 1% of an ethoxyl-containing impurity. The sample was dissolved in methylene chloride and dried over anhydrous potassium carbonate. Vacuum evaporation of the solvent afforded 2-pyrone with an impurity with a significant ion at *m/e* 66. The impurity was removed by liquid chromatography on silica, eluting with 50:50 methylene chloride–pentane, to give 2-pyrone containing 24.5% oxygen-18 (Table I).

To assess the limits of acid-catalyzed exchange, an attempt was made to label 2-pyrone by HCl-catalyzed exchange with water containing 30.0% oxygen-18 (pH ca. 2). This experiment gave no oxygen-18 incorporation either after 32 days at room temperature or after 1 hr in a steam bath.

Acknowledgment. Mass spectrometric analyses were performed by Mr. J. Wrona on a Varian MAT CH-5 spectrometer. The mass spectral data processing equipment was provided by NIH Grants CA 11388 and GM 16864, from the National Cancer Institute and the National Institute of General Medical Sciences, respectively.

Registry No.—2-Pyrone, 504-31-4; 2-pyrone-2-thione, 23639-33-0.

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Methyl Hyponitrite

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Several of the lower molecular weight alkyl hyponitrites were synthesized by Partington and Shah,[1] Zorn,[2a] and Holden and Kutschke.[2b] The parent member of the series has been mentioned in the patent literature[3] but apparently has not been synthesized, probably because safety considerations outweighed the need. Methyl hyponitrite is an attractive, low-temperature source of methoxy radicals, and we were interested in the compound for use in connection with studies of gas-phase reactions leading to photochemical smog.

Reaction of silver hyponitrite[4] with excess methyl bromide at 0° according to Traylor's procedure[5] gave a solution that was fractionated at low pressure and temperature to remove methyl bromide. Methyl hyponitrite was obtained as a colorless, fragrant liquid at 25° that formed ice-like crystals when condensed from the gas phase onto the walls of a tube at −196°.

The ester was prepared twice without incident. A third preparation of ca. 1 g, however, exploded violently during a *second* bulb-to-bulb distillation from an 8-mm tube. The glass was pulverized into dust so fine that no damage was done to the vacuum system, although the operator sustained superficial cuts from particles that penetrated clothing.[6]

We suspected that "bumping" of the boiling liquid caused the detonation, but a 0.5-g sample in a wide, shallow-bottomed tube later exploded as it was being frozen in a Dewar flask containing liquid nitrogen. Since there was no obvious reason in this case, handling of the neat ester appears to be exceptionally unpredictable. Our experience is in accord with highly disparate accounts in the literature concerning the stability of lower alkyl hyponitrites.

A modified preparation with mineral oil as a diluent proceeded without incident. The ester was handled as a gas and cocondensed with excess 1,4-cyclohexadiene. The resulting solution was diluted with benzene-d_6. Portions were transferred to two NMR tubes for product study. The tubes were degassed and sealed off. One was placed in a bath at 100° for 5 min; a signal at δ 3.06 (CH_3OH) was the only resonance observed other than those from 1,4-cyclohexadiene (δ 2.6 and 5.8) and benzene (δ 7.2). The latter was initially present as an impurity, although it was also an expected product from H abstraction.

A second tube containing 0.9 ± 0.2 *M* hyponitrite was placed in a preheated ^1H NMR probe at 70°. The area of the resonance at δ 3.5 decreased 88% in 50 min, with $t_{1/2}$ 17 ± 5 min.

The area of the methanol product signal was only half of the original methyl area in the ester. We cannot account for the difference, since signals from dimethyl peroxide (δ 3.6) or low-field resonance from CH_2O were not observed. The absence of the former is consistent with a value of $k_{\text{disproportionation}}/k_{\text{recombination}} = 9.3$ reported in the gas phase,[7] and also with the small yield of di-*tert*-butyl peroxide observed from di-*tert*-butyl hyponitrite by Kiefer and Traylor[5] and by Neuman and Bussey.[8]

From group additivity[9] we estimate $\Delta H^\circ_{f,g} \cong 70$ kcal/mol for the hyponitrite, and an enthalpy change for the reaction

$$CH_3ON{=}NOCH_3(l) \rightarrow N_2(g) + CH_3OH(g) + CH_2O(g)$$

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of −139 kcal/mol, or about 1.5 kcal/g of ester. This value is comparable to that for a number of explosives and is consistent with the observed properties. The exothermicity also exceeds singlet and triplet energies of formaldehyde and other carbonyl compounds.[10] We will report our observations of solution chemiluminescence from hyponitrites later.

Experimental Section

Dry silver hyponitrite (2 g) was added at 0° to stirred methyl bromide (10 ml) that had been purified by bubbling through concentrated sulfuric acid and condensing at −78°. After 5 hr, the mixture was filtered. The excess methyl bromide was allowed to distil off at 25°; the remaining liquid was further concentrated on a vacuum line by warming repeatedly from −196° and removing vapor portionwise at low temperature. In later runs, mineral oil (1 ml/g $Ag_2N_2O_2$) was added before concentration. The fractionation was followed by means of a capillary bleed leading to a quadrupole mass spectrometer (Finnigan Model 4000). Methyl bromide displayed intense signals at *m/e* 79 and 81. Pure methyl hyponitrite froze to a white solid below 0°: ^{1}H NMR (C_6D_6) δ 3.52 ($J_{^{13}C-H}$ = 145.3 Hz); ^{13}C NMR (C_6D_6) δ 60.1 ppm downfield from internal TMS; mass spectrum (70 eV) principal *m/e* 90, 59, 31, 30, 29, 28, 15. In pure benzene-d_6 the ^{1}H NMR signal of the hyponitrite decreased 50% after 1 week at 25°. For the product study in 1,4-cyclohexadiene, the hyponitrite at 2 Torr pressure was diluted with diene to a total pressure of 6 Torr, and the mixture was condensed out at −196° and removed from the vacuum line. The magnetic resonance experiments were determined with a Varian XL-100 NMR spectrometer.

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Registry No.—Silver hyponitrite, 7784-04-5; methyl bromide, 74-83-9; methyl hyponitrite, 29128-41-4.

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Testing Proposed Reaction Mechanisms with Compounds Bound to Solid Supports

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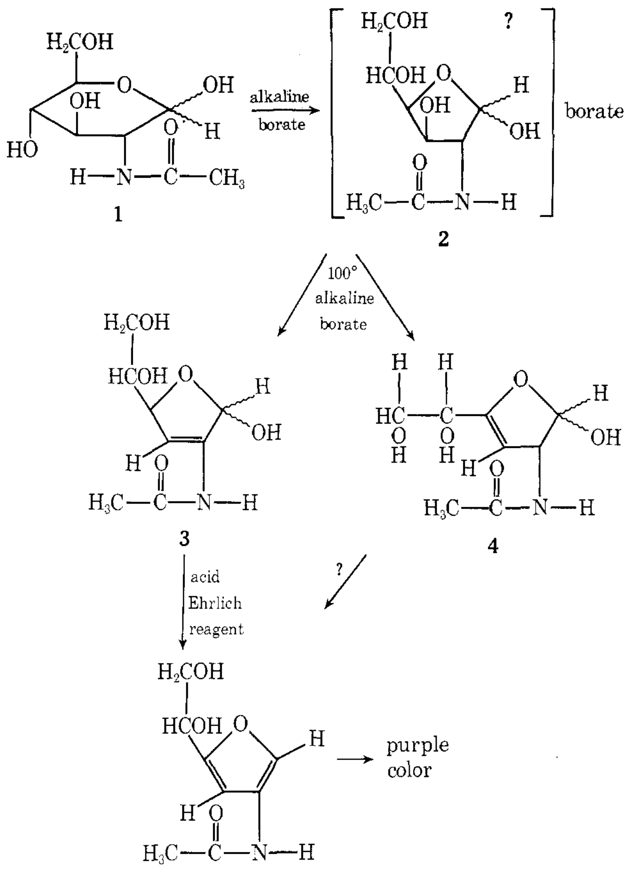
During a sequence of reactions, the fate of a functional group or side chain may be difficult to determine, particularly if one of the intermediates or the product is unstable. Determining the fate of various parts of a molecule may be facilitated if the compound can be bound to a solid support through the part of interest. This paper illustrates the value of this approach by following the fate of an *N*-acyl group through a sequence of reactions.

Scheme I



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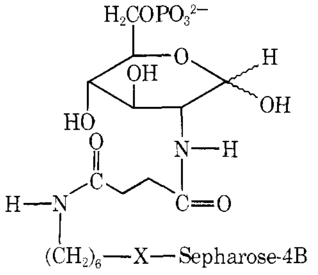

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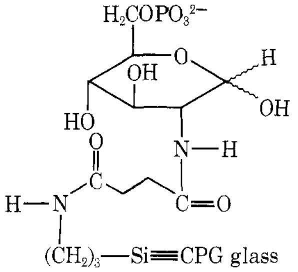

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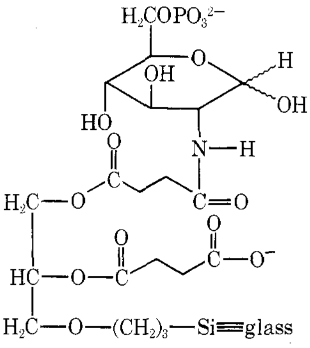

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