solution which had contained no lithium benzoate was transferred to a 1-mm, quartz cell and placed on the reference side of a Perkin-Elmer spectrophotometer, while a sample of the other solution was placed in the sample beam. The ultraviolet spectrum was then scanned. It was previously determined by vapor phase chromatography that the products of the solvolysis under these conditions were the same in the presence of the salt as in its absence within ±1%. Consequently, absorptions owing to 2-phenylpropene [λ_{max} 245 mμ (ϵ 1.09 $\times$ 10^4)], ethyl phenyldimethylcarbinyl ether [λ_{max} *ca.* 220 mμ (ϵ *ca.* 2.5 $\times$ 10^3)], and any phenyldimethylcarbinyl *p*-nitrobenzoate [λ_{max} 263 mμ (ϵ 1.33 $\times$ 10^4)] which may have remained were cancelled by the presence of the same amounts of these compounds in the reference sample and thus, the slight absorption (0.038) observed at 230 mμ in the spectrum of the sample which had contained lithium benzoate was due to phenyldimethylcarbinyl benzoate [λ_{max} 230 mμ (ϵ 1.53 $\times$ 10^4)]. The addition to the sample solution of an amount of phenyldimethylcarbinyl benzoate corresponding to 0.05% of the *p*-nitrobenzoate reacting to form the benzoate increased the absorption from 0.038 to 0.070, indicating that in the original analysis there was an amount of phenyldimethylcarbinyl benzoate remaining which corresponded to less than 1% of the original amount of the *p*-nitrobenzoate. A rate constant of 1.53 $\times$ 10^{-4} $\sec^{-1}$ was obtained for the disappearance of phenyldimethylcarbinyl benzoate in ethanol at 100° in the presence of a four to one molar excess of lithium benzoate. From this rate constant it may be calculated that 43% of the phenyldimethylcarbinyl benzoate formed from phenyldimethylcarbinyl *p*-nitrobenzoate and excess lithium benzoate had reacted in 10 hr, the time allowed for the reaction. Thus, less than 1% of the original phenyldimethylcarbinyl *p*-nitrobenzoate had reacted with the four molar excess of lithium benzoate in ethanol at 100°.

The products of the solvolysis of phenyldimethylcarbinyl thionbenzoate in ethanol at 25° were determined in the presence of a four molar excess of lithium *p*-methoxythiobenzoate, prepared as previously described. In this experiment 0.5280 g of phenyldimethylcarbinyl thionbenzoate, 0.4760 g of 2,6-lutidine, and 2.0084 g of 90% lithium *p*-methoxythiobenzoate were dissolved in 200 ml of ethanol in a volumetric flask. The solution was deoxygenated in the usual manner and placed in a water bath at 25.0° ± 0.01° for 24 hr (*ca.* 10 half-lives of the thionbenzoate reaction in ethanol at 25°). Into the resulting solution was dissolved 0.1075 g of chlorobenzene and 0.0990 g of methyl 2-nitro-3-methylbenzoate, this solution was extracted in the usual manner, and the products were analyzed by vapor phase chromatography. The products were the same (±2%) as those observed for the solvolysis of the thionbenzoate in the absence of lithium *p*-methoxythiobenzoate, except for an additional peak in the chromatograph following phenyldimethylcarbinyl thiolbenzoate. A comparison of the integrations of this peak, before and after the addition to the sample solution of an amount of authentic phenyldimethylcarbinyl *p*-methoxythiolbenzoate corresponding to the thion ester forming 1% of *p*-methoxythiol ester, showed that the integration had nearly doubled after the addition of the authentic phenyldimethylcarbinyl *p*-methoxythiolbenzoate. This indicated that less than 1% of the original amount of phenyldimethylcarbinyl thionbenzoate had reacted with the excess lithium *p*-methoxythiobenzoate to form phenyldimethylcarbinyl *p*-methoxythiolbenzoate.

Product Stability Determinations.—In a typical experiment 0.1148 g of 2-phenylpropene, 0.2090 g of 2,6-lutidine, and 5 ml of 0.20 *M* ethanolic hydrochloric acid (prepared by bubbling hydrogen chloride through ethanol) were dissolved in 100 ml of ethanol in a volumetric flask. This solution was then treated as described for product analysis, 0.1051 g of chlorobenzene being added. Analysis showed 0.1138 g (99.1% yield) of 2-phenylpropene present. All products were shown by this method to be stable within a average deviation of ±2.6% under the reaction conditions as described. Commercial *p*-nitrobenzoic acid, thiobenzoic acid, and silver nitrate were employed in the appropriate experiments. In most runs infinity titers were obtained and the first-order rate constants were calculated using a FORTRAN program and an IBM-7094 digital computer. This program calculates the best-fit, least-square line through the points of a plot of ln *Y* *vs.* time. The points are weighted in proportion to the relative magnitude of *Y* values.

Registry No.—Ethyl phenyldimethylcarbinyl ether, 1712-74-9; phenyldimethylcarbinyl chloride, 934-53-2; phenyldimethylcarbinyl *p*-nitrobenzoate, 7429-06-3; phenyldimethylcarbinyl thionbenzoate, 7429-19-8; *p*-methylphenyl dimethylcarbinyl thiobenzoate, 7429-18-7; *p*-trifluoromethylphenyldimethylcarbinyl thionbenzoate, 7429-15-4; *p*-methylphenyldimethylcarbinol, 1197-01-9; phenyldimethylcarbinyl thiolbenzoate, 7429-01-8; lithium *p*-methoxythiobenzoate, 7429-02-9; *p*-methoxythiobenzoic acid, 6279-44-3; phenyldimethylcarbinyl *p*-methoxythiolbenzoate, 7429-05-2.

The Electron-Impact Fragmentation of 4-Thiapyrone and N-Methyl-4-pyridone

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The mass spectra of 4-thiapyrone (1) and N-methyl-4-pyridone (3) are analyzed by comparison with the spectra of isotopically substituted derivatives. The doublet shape of the metastable peak associated with the loss of carbon monoxide from the molecular ion is attributed to fragmentation with loss of kinetic energy.

The empirical analysis of the electron-impact fragmentation process of the fundamental functional types has received considerable attention in recent years.[2] Although the structures proposed in such analyses must be regarded as convenient rationales, the utility of these assignments in further structural work has been amply demonstrated. For example, the principal pathways in the fragmentation of 4-pyrone[3] correlate well with the major fragmentation processes in natural products containing this nucleus.[4,5] In order to assess the generality of the fragmentation processes observed with 4-pyrone[3] for similar structure types we have analyzed the mass spectra of 4-thiapyrone (1), N-methyl-4-pyridone (3), and their isotopically substituted

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[1] (a) Standard Oil of California Fellow, 1964–1965; (b) National Institutes of Health Fellow, 1966–1967.

[2] (a) F. W. McLafferty, "Determination of Organic Structures by Physical Methods," Vol. 2, F. C. Nachod and W. D. Phillips, Ed., Academic Press Inc., New York, N. Y., 1962, p 29; (b) K. Biemann, "Mass Spectrometry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962; (c) J. H. Beynon, "Mass Spectrometry," Elsevier Publishing Co., Amsterdam, 1960; (d) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Interpretation of Mass Spectra of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1964; (e) F. W. McLafferty, Ed., "Mass Spectrometry of Organic Ions," Academic Press Inc., New York, N. Y., 1963.

[3] P. Beak, T. H. Kinstle, and G. Carls, *J. Am. Chem. Soc.*, **86**, 3833 (1964).

[4] (a) R. I. Reed and J. M. Wilson, *J. Chem. Soc.*, 5949 (1963); (b) C. S. Barnes and J. L. Occolowitz, *Australian J. Chem.*, **17**, 975 (1964); (c) M. M. Badawi, M. B. E. Fayez, T. A. Bryce, and R. I. Reed, *Chem. Ind.* (London), 498 (1966).

[5] However, internal consistency in a series and chemical intuition do not establish the validity of a structural assignment. W. H. Pirkle [*J. Am. Chem. Soc.*, **87**, 3022 (1965)] has elegantly shown that the fragment formed by loss of carbon monoxide in the mass spectrum of 2-pyrone is not a cyclic furan ion.

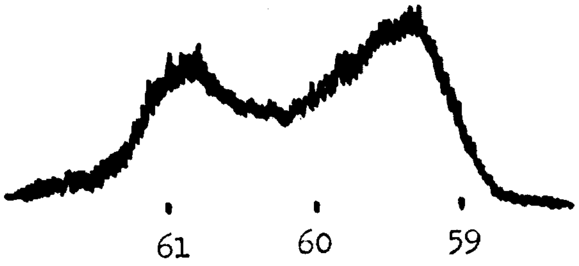
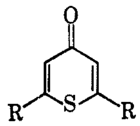
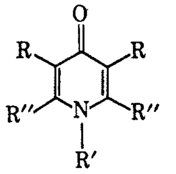


Figure 1.—Metastable peak for the loss of carbon monoxide from N-methyl-4-pyridone with an ionizing potential of 20 ev and an accelerating potential of 3 kv. The calculated value is m/e 60.2.

derivatives (**2** and **4**–**7**). The mass spectrum of 4-pyridone has been reported by Spiteller and Spiteller-Friedmann[6] to be characterized by the loss of carbon monoxide and hydrogen cyanide. Clugston and MacLean[7] have noted a loss of carbon monoxide in quinolones. Corral and Orazi[8] have recently reported the mass spectrum of a derivative of ribalinium in which fragmentations involving the N-methyl-4-pyridone nucleus are obscured by other processes.





1, R = H
2, R = D

3, R = R'' = H; R' = CH_3
4, R = R'' = H; N = N^{15}; R' = CH_3
5, R = R'' = H; R' = CD_3
6, R = H; R'' = D; R' = CH_3
7, R = D; R'' = H; R' = CH_3

Results and Discussion

The partial mass spectra of the 4-thiapyrones and N-methyl-4-pyridones studied are summarized in Tables I and II. In all cases the molecular ion (M) is an intense peak with the doubly charged molecular ion appearing as an ion of low intensity. The expulsion of carbon monoxide from the molecular ion to give an M − 28 ion is a general process for these molecules as shown by appropriate shifts of the fragment ions and metastable peaks in the spectra of the isotopically substituted species. Analogous losses of carbon monoxide have been observed in the mass spectra of cyclic ketones,[9] tropones,[10] 4-pyridone,[5-7] and 4-pyrones.[3,4]

TABLE I
PEAK INTENSITIES IN THE MASS SPECTRA OF THE 4-THIAPYRONES

m/e	1	2
116		2
115		3
114	1	25
113	2	
112	25	
89		1
88	1	2
87	1	17
86	17	8
85	1	1
84	9	
61		1
60	1	1
59	1	12
58	15	3
57	6	3
56	1	
54		2
53	2	
46		2
45	3	
41		1
40		1
39	2	

TABLE II
PEAK INTENSITIES IN THE MASS SPECTRA OF THE N-METHYL-4-PYRIDONES

m/e	3	4	5	6	7
113			3		
112			34	3	3
111		3		34	34
110	3	34			
109	34				
85			2		
84			11	1	
83		3		10	10
82	2	8	4	6	4
81	9	5			
80	5				
58			3		
57			1		
56		2	2	3	3
55	3	1	1	3	2
54	2	2	1	2	1
53	3	3	2	1	2
45			9		
43		7		7	
42	9				8
41					3
40				2	
39	3	2	3		

The metastable peaks associated with the loss of carbon monoxide from the molecular ions of **1**–**7** were centered at the expected value, but had a broadened doublet shape (Figure 1). Analogous metastable peaks have been ascribed[11,12] to fragmentations which occur with a release of kinetic energy. In the present case the observed peak widths are consistent with an energy release of 0.4 ± 0.1 ev.[13] Although the factors

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[6] G. Spiteller and M. Spiteller-Friedmann, *Monatsch. Chem.*, **93**, 1395 (1962).

[7] D. M. Clugston and D. B. MacLean, *Can. J. Chem.*, **44**, 786 (1966).

[8] R. A. Corral and O. O. Orazi, *Tetrahedron*, **21**, 909 (1965).

[9] (a) J. H. Beynon, G. R. Lester, and A. E. Williams, *J. Phys. Chem.*, **63**, 1861 (1959); (b) J. H. Beynon, R. A. Saunders, and A. E. Williams, *Appl. Spectry.*, **14**, 95 (1960); (c) E. Schumacher, *Helv. Chim. Acta.*, **46**, 1295 (1963).

[10] (a) J. B. McCollum and S. Meyerson, *J. Am. Chem. Soc.*, **85**, 1739 (1963); (b) J. M. Wilson, M. Osashi, H. Budzikiewicz, and C. Djerassi, *Tetrahedron*, **19**, 2247 (1963); (c) O. L. Chapman, T. H. Kinstle, and M. T. Sunn, *J. Am. Chem. Soc.*, **88**, 2618 (1966).

[11] J. H. Beynon, R. A. Saunders, and A. E. Williams, *Z. Naturforsch.*, **20a**, 180 (1965).

[12] (a) W. Higgins and K. R. Jennings, *Chem. Commun.*, 99 (1965); (b) M. C. Flowers, *ibid.*, 235 (1965); (c) T. W. Shannon, F. W. McLafferty, and C. R. McKinney, *ibid.*, 478 (1966).

[13] The alternative possibility that the doublet shape is due to two overlapping metastable transitions, for **3** (Figure 1) at m/e 60.2 (m/e 109 → m/e 81 + CO) and m/e 58.7 (m/e 109 → m/e 80 + CHO) may be ruled out by consideration of the spectrum of N-methyl-d_3-4-pyridone (**5**) which would have corresponding peaks at m/e 63.0 (m/e 112 → m/e 84 + CO) and m/e 60.1 (m/e 112 → m/e 82 + CDO). The observed broadened metastable in the mass spectrum of **5** is centered at m/e 63.0 and extends from m/e 62 to 64. Moreover the breadth of the peaks appears to be inversely proportional to the accelerating voltage in accord with previous work[11] although the limited range of accelerating voltages available (2–3 kv) makes this a qualitative observation. The slit width which can make determination of the kinetic energy imprecise, corresponds to the conditions shown to give reliable results.[12c]

leading to metastable transitions of this type are not yet apparent, the possibility that these peaks may be structurally diagnostic is of interest and requires further investigation.

Formulation of the ions produced by decarbonylation of the molecular ions **1** and **3** as the thiophene (a) and pyrrole (b) ions, respectively, provides an economical but tentative[5,14] rationale for a large portion of the remaining fragmentations and for the peak shifts in the isotopically substituted compounds.[15-17]

The "retro-Diels-Alder"[2b] process which is competitive with the loss of carbon monoxide in the fragmentation of 4-pyrones[3,4] is an important fragmentation pathway for 4-thiapyrone (**1**) but not for N-methyl-4-pyridone (**3**). In the case of **1** the loss of carbon monoxide from the resultant ion (*m/e* 86) followed by loss of a hydrogen atom would account for the intense peak at *m/e* 58 and 57 as well as for the isotope shifts in the spectrum of **2**. The predominance of decarbonylation of the molecular ion of **1** over "retro-Diels-Alder" cleavage is observed at lower ionizing potentials analogous to the case of 4-pyrone.[3]

In summary the fragmentation of 4-pyrone appears to provide an adequate model for the fragmentation of 4-thiapyrone (**1**) but not for N-methyl-4-pyridone (**3**). The spectrum of the latter is generally consistent with fragmentation by loss of carbon monoxide followed by further fragmentation of the pyrrole ion.

Experimental Section

The spectra were obtained on an Atlas CH 4 mass spectrometer using a variable-temperature vacuum lock inlet system and 70 ev as the ionizing potential. In an attempt to minimize spectral variations owing to changes in the total ionization, light spot recordings requiring 5–10-sec scan times were employed. The partial spectra in the tables have been corrected for the presence of isotopic impurities over those of natural abundance and the spectra have been normalized to the spectra of the parent molecule except for **2**. The following isotopically substituted mixtures were used: **2**, 3% C_5H_3DSO, 91% $C_5H_2D_2SO$, and 6% C_5HD_3SO; **6**, 12% C_6H_6DNO and 88% $C_6H_5D_2NO$; **7**, 20% C_6H_6DNO and 80% $C_6H_5D_2NO$. The partial spectra for **1** and **2** are reported as $\%\Sigma_{24}$ and those for **3**, **4**, **5**, **6**, and **7** as $\%\Sigma_{20}$.

Syntheses.—The preparation of 4-thiapyrone (**1**),[18] N-methyl-4-pyridone (**3**), N-methyl-4-pyridone-2,6-d_2 (**6**), and N-methyl-4-pyridone-3,5-d_2 (**7**),[19] have been reported. 2,6-d_2-4-Thiapyrone was prepared in 57% yield by treatment of 4-thiapyrone with 1 *N* sodium deuterioxide in deuterium oxide at room temperature for 3 hr followed by extraction with ethyl ether and sublimation. The nmr spectrum of **2** in deuteriochloroform showed a broadened resonance at $\delta = 7.05$ ppm, comparison of this result to the spectrum of **1**, AA'XX' multiplet resonances centered at $\delta = 7.05$ ppm (protons at 3 and 5) and $\delta = 7.88$ ppm (protons at 2 and 6), and to model compounds[19,20] show that the deuteriums are incorporated in **2** on the carbons adjacent to sulfur. Mass spectral molecular weight determination at 12 ev indicated that the product was a mixture of 2.7% d_1-, 91.4% d_2-, and 5.5% d_3-thiapyrone. N-Methyl-4-pyridone-3,5-d_2 (**5**) was obtained in the present case from 4-pyrone-3,5-d_2[20] and methylamine in deuterium oxide. N^{15}-Methyl-4-pyridone (**4**) and N-methyl-d_3-4-pyridone (**5**) were prepared by the following procedure.

To an equimolar mixture of the appropriate pyrone (0.5–1.3 mmoles) and either 99.5% N^{15}-methylamine hydrochloride or methyl-d_3-amine hydrochloride (Merck Sharp and Dohme) in an open tube was added 1 equiv of 1.0 *N* sodium hydroxide. After the contents were cooled, the tube was sealed and heated for 10–14 hr at 100°. The solution was cooled, transferred to a flask, and concentrated to dryness under vacuum, and the resulting material was leached with methylene chloride. Isolation and purification procedures similar to those reported for the unlabeled and other labeled derivatives[18] were then employed. Yields of pure products with melting points comparable to those of the parent molecules ranged from 50 to 70%. The mass spectra of the N^{15} and N-methyl-d_3 derivatives were obtained at low ionizing potentials and shown to be a minimum of 99% isotopically substituted.

Registry No.—**1**, 1003-41-4; **2**, 7436-15-9; **3**, 695-19-2; **4**, 7436-16-0; **5**, 7436-17-1; **6**, 1123-67-7; **7**, 2677-19-2.

Acknowledgment.—Funds for the purchase of the mass spectrometer were provided in part by the National Science Foundation. This work was supported by the Public Health Service GM-10696, and we are grateful for this support. We wish to thank Mr. Joseph Wrona for measuring the mass spectra.

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[14] The identical symmetries of **1** and a and **3** and b preclude a test of these possibilities by the method used by W. H. Pirkle for 2-pyrone.[6]

[15] J. H. Bowie, R. Grigg, D. H. Williams, S. O. Larsen, and G. Schroll [*Chem. Commun.*, 403 (1965)] have reported an analogous reaction for acyclic ketones.

[16] In the spectrum of **1** the fragments at *m/e* 58, 45, and 39 and the metastable peak at 40 (calcd for *m/e* 84 → *m/e* 58, 40.1) may be accounted for in terms of fragmentations of a: ref 2d, p 231.

[17] In the case of **3** the ions at *m/e* 80, 55, 53, 42, and 39 and the metastable peak at 37.4 (calcd for 81 → 55, 37.3) may be rationalized by pathways previously proposed for b: (a) H. Budzikiewicz, C. Djerassi, A. H. Jackson, G. W. Kenner, D. J. Newman, and J. M. Wilson, *J. Chem. Soc.*, 1949 (1964); (b) A. M. Duffield, R. Beugelmans, H. Budzikiewicz, D. A. Lightner, D. H. Williams, and C. Djerassi, *J. Am. Chem. Soc.*, **87**, 805 (1965).

[18] F. Arndt and N. Bekir, *Ber.*, **63**, 2393 (1930).

[19] P. Beak and J. Bonham, *J. Am. Chem. Soc.*, **87**, 3365 (1965).

[20] P. Beak and G. A. Carls, *J. Org. Chem.*, **29**, 2678 (1964).