Triphenylsilyl Triphenylgermyl Peroxide.—A solution of triphenylsilylamine (2.1 g), triphenylgermyl hydroperoxide,[9] and methylene chloride (150 ml) was refluxed overnight, at the end of which time the evolution of ammonia had ceased. Removal of the solvent using a rotary evaporator and recrystallization of the residue from methylene chloride produced triphenylsilyl triphenylgermyl peroxide (4 g), mp 155° (lit.[8] mp 142–142.5°). *Anal.* Calcd for $C_{36}H_{30}SiGeO_2$: C, 72.7; H, 5.08. Found: C, 72.37; H, 5.04. Active oxygen titration showed a purity of 94%.

Thermal Decomposition of Triphenylsilyl Triphenylgermyl Peroxide.—After heating (165°) the asymmetric peroxide (0.2 g) for 16 hr, the product (mp 126°) had a different ir spectrum from that of the starting material. It was dissolved in methylene chloride and hydrogen chloride was bubbled through for 10 min. Triphenylmethane and *p*-cresol were added as internal standards and glpc analysis[8] showed a 98% yield of triphenylchlorogermane and a 62% yield of phenol.

Kinetics of the Decomposition of Triphenylsilyl Triphenylgermyl Peroxide.—The thermal decomposition of a trichlorobenzene solution of the peroxide (0.01 *M*) was followed iodometrically to give the first-order rates in $sec^{-1} \times 10^5$ in Table I.

Registry No.—I, 2319-39-3; II, 31952-39-3; III, 31952-40-6; VI, 31999-36-7; IX, 27526-19-8; *p*-tolyldiphenylchlorosilane, 13868-70-5; *p*-tolyldiphenylbromosilane, 31952-43-9; *p*-tolyldiphenylsilyl hydroperoxide, 31952-44-0; *p*-anisyldiphenylchlorosilane, 18670-55-8.

Acknowledgment.—We wish to thank Dr. George Jalics for the first isolation of pentaphenylphenoxydisiloxane from the rearrangement of bis(triphenylsilyl) peroxide.

(9) R. L. Dannley and G. C. Farrant, *J. Org. Chem.*, **34**, 2428 (1969).

A Thermal Two-Carbon Ring Expansion. 2-Cyclopentenones from 3-Cyclopropyl-3-oxopropanoates

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Pyrolysis of 3-cyclopropyl-3-oxopropanoates **1a–d** (**a**, $R_1 = R_2 = H$; **b**, $R_1 = CH_3$, $R_2 = H$; **c**, $R_1 = H$, $R_2 = CH_3$; **d**, $R_1 = R_2 = CH_3$) at 500–600° (1–3 mm) gave the corresponding 2-cyclopentenones **2a–d** in 50–80% yields. The resultant substitution patterns in **2a–d** led to the conclusion that the oxo group was extruded from **1a–d**. Pyrolysis of **1a** at 760 mm gave pyrandione **10b** (R = c-C_3H_5). Pyrolysis of **10b** at 1–3 mm gave 2-cyclopentenone (**2a**). This is presented as evidence for the existence of an acylketene intermediate **11b**. The rearrangement of **1** to **2** represents a novel two-carbon ring expansion reaction of cyclopropane derivatives.

Several two-carbon thermal ring expansion reactions of cyclopropanes are known.[1-11] Of these, only the vinylcyclopropane–cyclopentene rearrangement has received more than passing interest.[1-3,12] We wish to report[13] a new thermal rearrangement of 3-cyclopropyl-3-oxopropanoate esters **1a–d** to cyclopentenones **2a–d** in moderate yields (Table I) which may prove to be of synthetic interest.

Results and Discussion

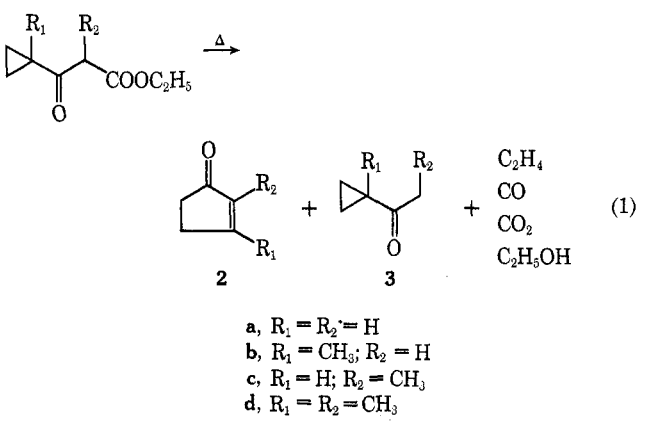
The products of pyrolysis of keto esters **1** near 500° at 1–3 mm included cyclopentenones **2**, ketones **3**, carbon monoxide, carbon dioxide, ethanol, and ethylene (eq 1).

TABLE I

PYROLYSIS OF KETO ESTERS **1a–d**

Starting material	R_1	R_2	T, °C[a]	% yield of **2a–d**, glpc[b]	T, °C	% yield of **2a–d** isolated[c]
1a	H	H	565	51	540	47
1b	CH_3	H	500	65	500	60
1c	H	CH_3	585	65	585	58
1d	CH_3	CH_3	535	81	570	68

[a] Pyrolysis temperature affording greatest glpc yield. [b] Glpc yields based upon unrecovered starting material. [c] Isolated yields based upon weight of product recovered by distillation.



(1)

a, $R_1 = R_2 = H$
b, $R_1 = CH_3$; $R_2 = H$
c, $R_1 = H$; $R_2 = CH_3$
d, $R_1 = R_2 = CH_3$

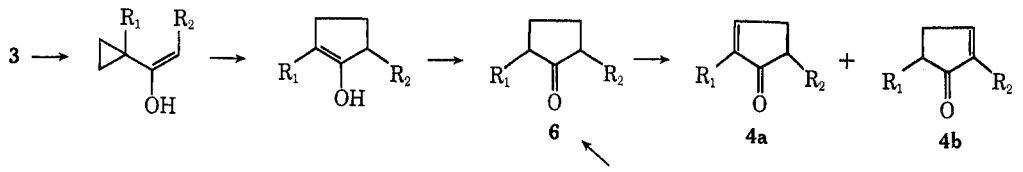
Table II presents evidence that the ratio of ketone **2a** and **3a** increased dramatically with an increase in the surface area of the pyrolysis packing material. This

(1) C. D. Gutsche and D. Redmore, "Carbocyclic Ring Expansion Reactions," Academic Press, New York, N. Y., 1968, Chapters IX, X.
(2) R. Breslow, "Molecular Rearrangements, Part I," P. de Mayo, Ed., Interscience, New York, N. Y., 1963, Chapter 4.
(3) G. L. Closs, *Advan. Alicycl. Chem.*, **1**, 53 (1966).
(4) M. J. Goldstein and B. G. Odell, *J. Amer. Chem. Soc.*, **89**, 6356 (1967).
(5) O. L. Chapman and J. D. Lassila, *ibid.*, **90**, 2449 (1968).
(6) O. L. Chapman, M. Kane, J. D. Lassila, R. L. Loeschen, and H. E. Wright, *ibid.*, **91**, 6857 (1969).
(7) A. S. Kende, Z. Goldschmidt, and P. T. Izzo, *ibid.*, **91**, 6858 (1969).
(8) W. C. Agosta, A. B. Smith, III, A. S. Kende, R. G. Eilerman, and J. Benham, *Tetrahedron Lett.*, 4517 (1969).
(9) G. E. Cartier and S. C. Bunce, *J. Amer. Chem. Soc.*, **85**, 932 (1963).
(10) G. E. Cartier and S. C. Bunce, *Diss. Abstr.*, **25**, 826 (1964).
(11) J. W. Wilt, L. L. Maravetz, and J. F. Zawadski, *J. Org. Chem.*, **31**, 3018 (1966).
(12) There has been considerable interest, however, in the subject of homoconjugative participation of cyclopropyl systems in developing carbonium ion centers which does not usually result in ring expansion. See, *e.g.*, M. Hanack and H. M. Ensslin, *Tetrahedron Lett.*, 4445 (1965); M. J. S. Dewar and J. M. Harris, *J. Amer. Chem. Soc.*, **92**, 6557 (1970), and references cited therein.
(13) Preliminary report: W. F. Berkowitz and A. A. Ozorio, Abstracts, 159th National Meeting of the American Chemical Society, Houston, Texas, Feb 22, 1970, ORGN 142.

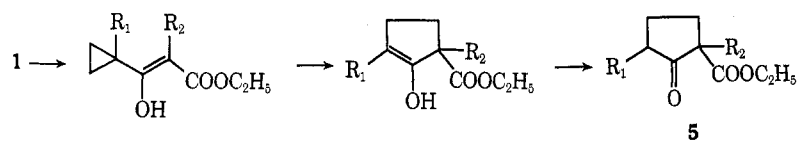
leads us to believe that the reaction affording **2** is catalyzed by glass surfaces[14] while that leading to **3** is not, and thus **2** and **3** are produced by competitive routes (see eq 4).

The substitution pattern of the cyclopentenones **2a–d** produced apparently requires the loss of the oxo group rather than the carbonyl of the carboxyl group. In the latter case the methyl groups of **1d** would appear in the 1 and 5 positions of the product (*e.g.*, **4a,b**) rather than in adjacent positions 2 and 3 as in **2d**.

This result precludes mechanisms involving the direct conversion of **3** to **2** (eq 2) or ones involving prior con-



(2)



(3)

version of **1** to a cyclopentanone carboxylate (**5**), decarbethoxylation[15] to **6**, and subsequent formation of **4a,b**[16] (eq 3).

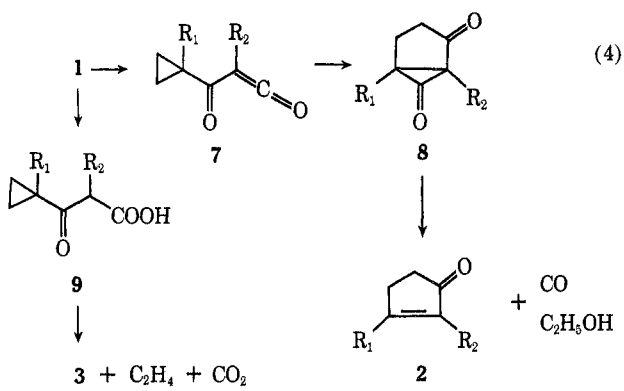
Furthermore, using conditions which would have converted **1** to **2**,[17] we found that cyclopropyl methyl ketone (**3a**) and cyclopentanone were recovered unchanged by pyrolysis (99 and 96% recovery, respectively) and α-carbethoxycyclopentanone (**5**, $R_1 = R_2 = H$) was converted to cyclopentanone (**6**, $R_1 = R_2 = H$) in 48% yield. In none of these reactions was 2-cyclopentenone detectable in the pyrolysate.[18]

We suggest the shown in eq 4 mechanism for the conversion of **1** to **2** and **3**).

Formation of **3** from **1** (*via* **9**) is expected pyrolytic behavior of a β-keto ester.[15b,c] The mechanism is believed to consist of formation of a β-keto acid with subsequent decarboxylation, both steps proceeding by way of cyclic six-centered transition states.[19–21]

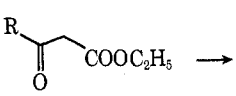
Formation of acylketenes (*e.g.*, **7**) from β-keto esters has never been observed; on the other hand, ketenes[25] have been obtained by pyrolysis of esters in competition with olefin formation.[26] It appears reasonable that the increased acidity of the α hydrogens of β-keto esters might enhance the rate of ketene formation. In addition, pyrolysis of acetoacetic ester has given dehydroacetic acid[27,28] (**10a**), which, it may be noted, can be considered as a Diels–Alder dimer of acylketene **11**[29] (eq 5).

Similarly, pyrolysis of β-keto ester **1a** at 760 mm (run 13) gave a white solid which we believe to be the

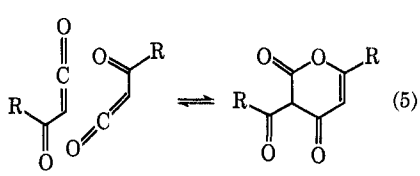


(4)

a, $R_1 = R_2 = H$
b, $R_1 = CH_3$; $R_2 = H$
c, $R_1 = H$; $R_2 = CH_3$
d, $R_1 = R_2 = CH_3$



a, $R = CH_3$
b, $R = c\text{-}C_3H_5$



(5)

analogous pyrandione **10b** (see Experimental Section). Thus, at low pressure (1–3 mm) formation of acylketene

(14) Acid or base washing, followed by thorough washing with distilled water, apparently had little effect on either the per cent conversion or the ratio of **2a** to **3a**.

(15) (a) Thermal decarbethoxylation, while not observed heretofore with α-carbethoxycyclopentanone, is a common reaction of β-keto esters,[15b,c] malonates,[15d] and α-cyano esters.[15e] (b) W. J. Bailey and J. J. Daly, Jr., *J. Org. Chem.*, **22**, 1189 (1957); (c) H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, New York, N. Y., 1965, p 171; (d) W. J. Bailey and J. J. Daly, Jr., *J. Org. Chem.*, **29**, 1249 (1964); (e) W. J. Bailey and J. J. Daly, Jr., *J. Amer. Chem. Soc.*, **81**, 5397 (1959).

(16) Pyrolytic dehydrogenation of cyclopentanone to cyclopentenone was noted at 488–543° (99–314 mm) by E. R. Johnson and W. D. Walters, *ibid.*, **76**, 6266 (1954), and at 532–581° (11–30 mm) by F. M. Delles, *et al.*, *ibid.*, **91**, 7645 (1969). A static system was used in these investigations with much longer contact times than in our flow system.

(17) See Experimental Section.

(18) Glpc conditions used enabled easy detection of less than 1% of **2a** in a mixture of **2a**, **3a**, **4a**, and **5**.

(19) A. Maccoll and P. J. Thomas, *Progr. React. Kinet.*, **4**, 119 (1967).

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(21) (a) D. B. Bigley and J. C. Thurman, *Tetrahedron Lett.*, 2377 (1967); (b) D. B. Bigley and J. C. Thurman, *J. Chem. Soc. B*, 941 (1967); (c) D. B. Bigley and J. C. Thurman, *ibid.*, 436 (1968). Whereas catalytic effects of glass surfaces have not been reported, it is reasonable to assume that they should be minimal since normal ester pyrolysis has been shown to be insensitive to changes in the (clean) surface area of silicaceous packing materials.[22–24]

(22) E. U. Emovon, *J. Chem. Soc.*, 1246 (1963).

(23) D. H. R. Barton, A. J. Head, and R. J. Williams, *ibid.*, 1715 (1953).

(24) M. Szwarc and J. Murawski, *Trans. Faraday Soc.*, **47**, 269 (1951).

(25) (a) H. M. Mackinnon and P. D. Ritchie, *J. Chem. Soc.*, 2564 (1957); (b) R. N. Bennett, A. A. Deans, J. G. H. Harris, P. D. Ritchie, and J. S. Shim, *ibid.*, 4508 (1958); (c) A. L. Brown and P. D. Ritchie, *J. Chem. Soc. C*, 2007, 2013 (1968).

(26) C. H. DePuy and R. W. King, *Chem. Rev.*, **60**, 431 (1960).

(27) (a) S. Nakamura, S. Ishidoya, and U. Okubo, Japanese Patent 2375 (1955); *Chem. Abstr.*, **51**, 14826b (1957). (b) S. Nakamura and S. Ishidoya, Japanese Patent 1884 (1955). *Chem. Abstr.*, **51**, 4442d (1957).

(28) F. Arndt, *Org. Syn.*, **20**, 26 (1940).

(29) (a) H. Stetter and K. Kiehs, *Tetrahedron Lett.*, 3531 (1964); (b) H. Stetter and K. Kiehs, *Chem. Ber.*, **98**, 1181, 2099 (1965).

TABLE II

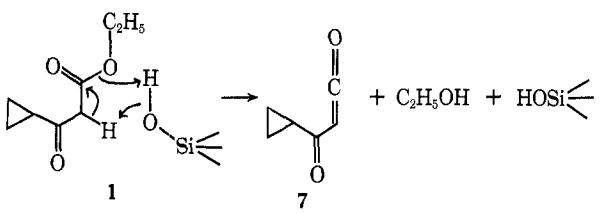
PYROLYSIS OF KETO ESTER 1a UNDER VARIOUS CONDITIONS[a]

Run	Packing material[b]	Product % yields[d] T, °C[c]	2a	3a	C_2H_5OH	% unchanged 1a	Pyrolysate total wt, %[e]
1	A	470	14	36	56	48	68
2	A	575	5	18	37	80	88
3	A	625	8	30	58	78	84
4	B	600	20	16	42	19	69
5	C	460	27	31	65	21	70
6[f]	C	525	54	0	76	17	66
7[f]	C	540	52	0	85	8	79
8	C	565	51	7	74	0	73
9	C	625	46	5	75	0	63
10[g]	C	525	35	1	53 (CH_3OH)	0	78
11[g]	C	575	45	1	73 (CH_3OH)	0	70
12[h]	C	450	14	19	57	0	37[i]
13[j]	A	410	1	9	50	1	48[i]
14[k]	D	400				30	69

[a] Material entered the pyrolysis tube in the vapor state at 1–3 mm unless otherwise noted. [b] A, 6 × 6 mm Pyrex Rasching rings; B, 6-mm Pyrex helices; C, Pyrex glass wool; D, pumice stone. [c] Maximum temperature, ±10°, at the center of the tube oven prior to pyrolysis. [d] Glpc yields based on unrecovered 1a. For glpc conditions, see Experimental Section. [e] Weights of gases formed are not included. Quantitative conversion of 1a to 2a thus would afford only 83% by weight of pyrolysate. [f] Yields of isolated products based on unrecovered 1a. [g] The methyl ester of 1a was pyrolyzed. [h] Pyrolysis at 100 mm. [i] Low recoveries due to cooler tube ends which condensed and charred products. [j] Pyrolysis at 760 mm. A pyrandione (10b) was obtained in 20% yield. See Experimental Section. [k] Pyrolysis at 760 mm over pumice.[27] Pyrandione 10b was obtained in 79% yield (based on unrecovered 1a). See Experimental Section.

11b (= 7a) from 1a led to 2a, as in eq 4, while at high pressure (760 mm) the higher concentration of 11b permitted dimerization leading to 10b. Furthermore, pyrolysis of the dimer itself (10b) at low pressure gave 2-cyclopentenone-1 in 48% yield (run 22), presumably by way of a retro-Diels–Alder reaction leading to 11b, with subsequent rearrangement to 8 and extrusion of carbon monoxide as in eq 4.

We suggest that the loss of ethanol from 1 to give 7 is catalyzed by silanol groups of the glass surface (eq 6), mainly because we are unable otherwise to construct

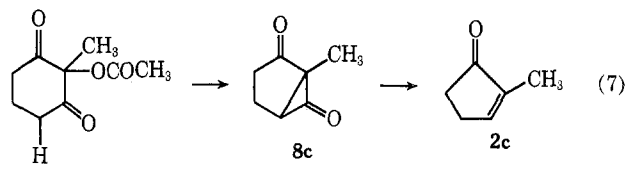


1 7 (6)

a reasonable six-centered cyclic transition state[25c] for dealcoholation.[30] We also think it less likely that the unimolecular rearrangement 7–8 or the decarbonylation 8–2 would be affected by a catalyst.

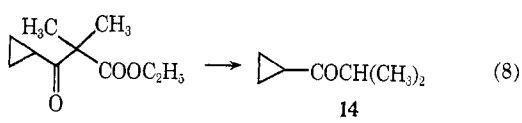
The rearrangement of 7 to 8 has, of course, no precedent as neither acylketenes nor cyclopropanones similar to 8 have ever been isolated. We can only indicate that it may be a thermally allowed[31] $\sigma_{2s} + \pi_{2a}$ electrocyclic reaction with subsequent (or, perhaps, simultaneous) nonlinear chelotropic elimination of carbon monoxide.

Intermediate 8c ($R_2 = CH_3$; $R_1 = H$) has been proposed[32] as the preliminary product of the pyrolytic loss of acetic acid from 12, giving, ultimately, 2c (eq 7). The formation of alkenes by the pyrolytic extrusion of a carbonyl adjacent to an acetoxy group has been noted in other instances, and preliminary formation of cyclopropanones was also proposed.[33]



12 8c 2c (7)

Finally, β-keto ester 13, with no α hydrogens, afforded only ketone 14 in 77% yield upon pyrolysis (run 21). No cyclopentenones or ethanol were observed in the pyrolysate (eq 8).

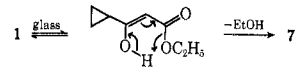


13 14 (8)

Experimental Section

All melting points were obtained on a Mel-Temp apparatus, and neither melting points nor boiling points are corrected. Microanalyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich. Gas–liquid phase chromatography (glpc) was done with a Varian-Aerograph Model A-700, thermal conductivity apparatus. Areas of glpc records were integrated with a planimeter and adjusted for differing response factors by inclusion of an internal standard. Infrared spectra were determined with a Perkin-Elmer Model 237B or a Beckman Model IR-20 grating spectrophotometer. Ultraviolet spectra were determined with a Cary Model 14 or Bausch and Lomb Spectronic 505 recording spectrophotometer. Proton magnetic resonance spectra were obtained with a Varian Model A60-A spectrometer. Pyrolyses were done with a Hevi-Duty Electric Co. Type 77-T (600-W "Multi-Unit") tube oven.

(30) A reviewer suggested the highly plausible alternative of glass surface catalysis of the keto-enol shift with subsequent loss of ethanol, *e.g.*



(31) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970.

(32) T. A. Spencer, A. L. Hall, and C. F. von Reyn, *J. Org. Chem.*, **33**, 3369 (1968).

(33) (a) R. G. Carlson and J. H. Bateman, *ibid.*, **32**, 1608 (1967), and references cited therein; (b) see also A. S. Kende, *Chem. Ind. (London)*, 1053 (1956).

Materials.—Cyclopropyl methyl ketone, 3-methyl-2-cyclopentenone-1, dialkyl carbonates, methyl iodide, benzaldehyde, and 2-acetylbutyrolactone were obtained from Aldrich Chemical Co., Cedar Knolls, N. J., and were distilled prior to use. 2-Cyclopentenone was obtained from K and K Laboratories, Plainview, N. Y., and was distilled and then further purified by preparative glpc.[34] Ethyl 2-cyclopentanone-1-carboxylate (α-carbethoxycyclopentanone) was obtained from K and K and distilled prior to use.

Pyrex Raschig rings and helices were obtained from The Ace Glass Co., Vineland, N. J.; Pyrex glass wool (Corning No. 3950) was obtained from The Scientific Glass Apparatus Co., Bloomfield, N. J. Pumice stone (4–8 mesh) was obtained from Matheson Coleman and Bell. Catalytic activity of the glass surfaces appeared unaltered by either acid or base washing (followed by thorough rinsing with distilled water) and were only water washed and oven dried prior to use. The Vycor pyrolysis tubes (37 × 2.5 cm, 24/40 joints) were manufactured by Mr. Karl Schumann, Columbia University, New York, N. Y. The tubes were packed with fresh packing material for each run.

Thiouracil derivatives were prepared by the appropriate modification of the procedure of Spitzmiller;[35] 2,4-dinitrophenylhydrazone derivatives were prepared by the procedure of Shriner, Fuson, and Curtin.[36]

Ethyl 3-Cyclopropyl-3-oxopropanoate (1a).—Keto ester **1a** was prepared by modification of the procedure of Johnson[37] using 25.0 g (0.30 mol) of cyclopropyl methyl ketone (**3a**) in 70 ml of anhydrous ether and 1 ml of absolute ethanol with a mixture of 55.2 g (1.15 mol) of sodium hydride (50% dispersion in mineral oil) and 260 g (2.2 mol) of diethyl carbonate in 300 ml of anhydrous ether. After the mixture was stirred at room temperature for 36 hr, work-up gave 35 g (75%) of keto ester **1a**, bp 70° (2.8 mm) [lit.[38] bp 99–101° (11 mm)], which was 99.5% pure[34] after one distillation. A repeat of this procedure gave ester **1a** in 82% yield after one distillation.

Methyl 3-Cyclopropyl-3-oxopropanoate (1a Methyl Ester).—Replacement of the diethyl carbonate by 200 g (2.2 mol) of dimethyl carbonate in the procedure used for **1a**, gave, after 72 hr of stirring at room temperature and work-up, 32 g (75%) of 99.5% pure[34] **1a** methyl ester after one distillation, bp 58° (1.5 mm). Stirring for 24 hr reduced the yield to 56%.

Anal. Calcd for $C_7H_{10}O_3$: C, 59.14; H, 7.09. Found: C 59.17; H, 7.03.

Ethyl ester **1a** has ir (CCl_4) 5.75 (ester C=O), 5.88 (ketone C=O), and 3.24 μ (cyclopropyl CH). The methyl ester of **1** has ir (CCl_4) 5.72 (ester C=O), 5.87 (ketone C=O), and 3.24 μ (cyclopropyl CH). The nmr spectrum of **1a** (ethyl ester) shows δ^{CCl_4} 0.74–1.09 (m, 4, cyclopropyl CH_2), 1.22 (t, 3, J = 7 Hz, CH_2CH_3), 1.78–2.24 (m, 1, cyclopropyl methine), 3.41 (s, 2, $COCH_2COO$), and 4.06 (q, 2, J = 7 Hz, CH_2CH_3). The nmr of **1a** methyl ester shows δ^{CCl_4} 0.77–1.10 (m, 4, cyclopropyl CH_2), 1.84–2.32 (m, 1, cyclopropyl methine), 3.54 (s, 2, $COCH_2COO$), and 3.70 (s, 3, $COOCH_3$).

Both esters gave a positive ferric chloride test. Both esters were converted to 2-thio-6-cyclopropyluracil.[35,38] The identity of the derivatives was established by comparison of ir spectra and mixture melting point, mmp 239–41° (lit. mp 234–235°,[38] 239–240°[35]).

Ethyl 3-(1′-Methylcyclopropyl)-3-oxopropanoate (1b).—Keto ester **1b** was prepared by Johnson's procedure[37] using 25.0 g (0.255 mol) of 1-methylcyclopropyl methyl ketone,[39] 260 g (2.2 mol) of diethyl carbonate, and 26.0 g (1.08 mol) of sodium hydride (50% dispersion in mineral oil) in 300 ml of absolute ether. Stirring for 24 hr at room temperature and work-up gave 31.2 g (73%) of keto ester **1b**, bp 73–74° (0.25 mm). A second distillation through a spinning band column gave 29.68 g (70%) of **1b**, bp 51.5–52° (0.025 mm).

Keto ester **1b** gave a positive ferric chloride test: ir (CCl_4) 3.25 (cyclopropyl CH), 5.76 (ester C=O), 5.92 (ketone C=O), and 6.2 μ (enol C=C); nmr δ^{CCl_4} 0.53–0.93 (m, 4, cyclopropyl CH_2), 1.30 (t, 3, J = 7 Hz, $CO_2CH_2CH_3$), 1.4 (s, 3, $CH_3C<$), 3.46 (s, 1.6, $COCH_2COO$), 4.31 (q, 2, J = 7 Hz, $CO_2CH_2CH_3$), 5.21 (s, 0.16, HC=COH), and 12.8 (s, 0.24, HC=COH) (enol content = 20%).

2-Thio-6-(1′-methylcyclopropyl)uracil.—The thiouracil derivative was obtained in 18% yield: mp 212–213°; ir (KBr) 6.11 (C=O), 6.46 (C=S), 8.45 (CS), 13.25 μ (CS); nmr $\delta^{DMSO\text{-}d_6}$ 0.52–1.15 (m, 4, cyclopropyl CH_2), 1.31 (s, 3, CH_3C), 3.32 (s, 2, NH, disappears with addition of D_2O), 5.7 (s, 1, vinyl); uv $\lambda_{max}^{CH_3OH}$ 276 nm (ε 20,350), 219 (20,860); $\lambda_{max}^{CH_3OH,\ pH\ 12}$ 258 nm (ε 17,320), 316 (16,020).

Anal. Calcd for $C_8H_{10}N_2SO$: C, 52.60; H, 5.49; N, 15.36; S, 17.55. Found: C, 52.62; H, 5.45; N, 15.19; S, 17.49.

Ethyl 3-Cyclopropyl-3-oxo-2-methylpropanoate (1c).—Keto ester **1c** was prepared from 20.7 g (0.211 mol) of cyclopropyl ethyl ketone,[40] 26 g (1.08 mol) of sodium hydride (50% dispersion in mineral oil), and 260 g (2.2 mol) of diethyl carbonate in 300 ml of anhydrous ether. The mixture was stirred at room temperature for 48 hr, and work-up gave 26.2 g (73%) of **1b**, bp 72–74° (1.3–1.5 mm), after one distillation through a Teflon annular spinning band column.

Anal. Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.75; H, 8.31.

Keto ester **1c** gave a positive ferric chloride test: ir (CCl_4) 3.25 (cyclopropyl CH), 5.75 (ester C=O), 5.86 μ (ketone C=O); nmr δ^{CCl_4} 0.73–1.10 (m, 4, cyclopropyl CH_2), 1.26 (t, 3, J = 7 Hz, $CO_2CH_2CH_3$), 1.3 (d, 3, J = 7 Hz, $CHCH_3$), 1.80–2.28 (m, 1, cyclopropyl methine), 3.58 (q, 1, J = 7 Hz, $CHCH_3$), 4.2 (q, 2, J = 7 Hz, $CO_2CH_2CH_3$).

2-Thio-5-methyl-6-cyclopropyluracil.—The thiouracil derivative was prepared in 17% yield: mp 238–239°; ir (KBr) 6.16 (C=O), 6.50 (C=S), 8.33 (CS), 12.68 μ (CS); uv $\lambda_{max}^{CH_3OH}$ 280 nm (ε 21,390), 223 (18,230); $\lambda_{max}^{CH_3OH,\ pH\ 12}$ 261 nm (ε 18,570), 318 (17,160); nmr $\delta^{DMSO\text{-}d_6}$ 0.75–1.17 (m, 4, cyclopropyl CH_2), 1.58–2.16 (m, 1, cyclopropyl methine), 1.90 (s, 3, $C=CCH_3$), 3.3 (s, 2, NH, disappears upon addition of D_2O).

Anal. Calcd for $C_8H_{10}N_2OS$: C, 52.72; H, 5.53; N, 15.37; S, 17.59. Found: C, 52.64; H, 5.54; N, 15.40; S, 17.67.

Ethyl 3-(1′-Methylcyclopropyl)-3-oxo-2-methylpropanoate (1d).—Keto ester **1b** (90.28 g, 0.531 mol) was added dropwise to a stirred suspension of 14.0 g (0.584 mol) of sodium hydride (50% dispersion in mineral oil) in 1.5 l. of benzene at room temperature under nitrogen. When hydrogen evolution ceased, 141.9 g (1.00 mol) of methyl iodide was added rapidly and the resulting mixture was refluxed overnight under nitrogen and then poured into 1 l. of dilute aqueous acid. The aqueous layer was extracted twice with 100-ml portions of ether which were combined with the organic layer, dried over magnesium sulfate, and concentrated under reduced pressure to an oil which was distilled, affording 85.60 g (87%) of crude **1d**, bp 69–70° (1 mm). Further distillation on a Teflon annular spinning band column did not separate a small amount of unmethylated **1b**, and the crude keto ester **1d** was therefore purified as follows.

A mixture of 25.17 g (*ca.* 0.137 mol) of crude **1d**, 2.91 g (0.0275 mol) of benzaldehyde, 109 μl (1.1 mmol) of piperidine, and 300 μl (5.2 mmol) of glacial acetic acid in 200 ml of benzene was refluxed for 3 hr with removal of water (0.34 ml). The reaction mixture was washed with 5% hydrochloric acid, saturated aqueous sodium bicarbonate, and water, dried over magnesium sulfate, and concentrated *in vacuo* to an oil which, upon spinning band distillation, gave 20.4 g (81% recovery) of **1d**, bp 67–67.5° (0.9 mm).

Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 65.30; H, 8.77.

Keto ester **1d** gave a *negative* ferric chloride test: ir (CCl_4) 3.24 (cyclopropyl CH), 5.74 (ester C=O), 5.90 μ (ketone C=O); nmr δ^{CCl_4} 0.58–1.00 (m, 4, cyclopropyl CH_2), 1.24 (t, 3, J = 7 Hz, $CO_2CH_2CH_3$), 1.24 (d, 3, J = 7 Hz, $>CHCH_3$), 1.36 (s, 3, $CH_3C<$), 3.67 (q, 1, J = 7 Hz, $>CHCH_3$), 4.13 (q, 2, J = 7 Hz, $CO_2CH_2CH_3$).

2-Thio-5-methyl-6-(1′-methylcyclopropyl)uracil.—The thiouracil derivative was prepared in 20% yield: mp 225–226°; ir (KBr) 6.14 (C=O), 6.45 (C=S), 8.23 (CS), 12.94 μ (CS); uv $\lambda_{max}^{CH_3OH}$ 279 nm (ε 21,010), 219 (19,190); $\lambda_{max}^{CH_3OH,\ pH\ 12}$ 263 nm (ε 16,170), 320 (11,770); nmr $\delta^{DMSO\text{-}d_6}$ 0.65–0.94 (m, 4, cyclo-

(34) A 5 ft × 0.25 in. column packed with 60–80 Chromosorb W coated with 20% by weight of SE-30 silicone gum rubber was used for both analysis and isolation. The internal standard used was 4-methylcyclohexanone.

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TABLE III
PYROLYSIS OF KETO ESTERS 1a–d, 13, AND 10b[a]

Run	Starting material	T, °C[b]	Products, % yield 2a–d	3a–d	EtOH	Other	% recovery starting material	Total pyrolysate wt, %[c]
8	1a	565	51	7	74		0	73
7[d]	1a	540	47	0	78		8	79
15[e]	1b	500	65	9	86		0	67
16[d]	1b	500	60	0	82		0	68
17[e]	1c	585	65	2	87		0	66
18[d]	1c	585	60	0	83		0	70
19[e]	1d	535	81	2	61		9	71
20[d]	1d	570	68	0	75		0	75
21[e]	13	610				77 (14)	8	58
22[e]	10b	600	48	3			0	51

[a] Glass wool packing, 1–3 mm. [b] Maximum temperature, ±10°, at the center of the pyrolysis tube. [c] Weights of gases are not included in the total. Quantitative conversion of **1b** to **2b** would thus afford an 83.5% yield of pyrolysate by weight. [d] Yield based on weights of materials isolated by distillation and weight of keto ester committed to pyrolysis. [e] Glpc yield, based on unrecovered starting material. For individual glpc conditions, see Experimental Section.

propyl CH_2), 1.26 (s, 3, CH_3-c-C_3H_4), 1.90 (s, 3, C=CCH_3), 3.32 (s, 2, NH, disappears upon addition of D_2O).

Anal. Calcd for $C_9H_{12}N_2SO$: C, 55.08; H, 6.16; N, 14.29; S, 16.35. Found: C, 55.03; H, 6.20; N, 14.37; S, 16.41.

Ethyl 3-Cyclopropyl-3-oxo-2,2-dimethylpropanoate (13).—Keto ester **13** was prepared by the methylation procedure used for **1d** with 9.65 g (0.0567 mol) of keto ester **1c**, 2.86 g (0.059 mol) of sodium hydride (50% dispersion in mineral oil), and 24.2 g (0.17 mol) of methyl iodide in 500 ml of benzene, affording 8.38 g (84%) of keto ester **13** after one distillation, bp 55–57° (1.2 mm). Redistillation through a Teflon annular spinning band column using a reflux ratio of 50:1 gave 7.40 g (71%) of keto ester **13**, bp 52–53° (1.0 mm). (No difficulty was encountered in separating **13** from traces of **1c**.)

Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.26; H, 8.76. Found: C, 65.15; H, 8.85.

Keto ester **13** gave a negative ferric chloride test: ir (CCl_4) 3.25 (cyclopropyl CH), 5.76 (ester C=O), 5.87 (ketone C=O), 7.23, 7.27 μ (*gem*-dimethyl); nmr δ^{CCl_4} 0.68–1.12 (m, 4, cyclopropyl CH_2), 1.25 (t, 3, J = 7 Hz, $CO_2CH_2CH_3$), 1.32 (s, 6, $>C(CH_3)_2$), 1.7–2.16 (m, 1, cyclopropyl methine), 4.18 (q, 2, J = 7 Hz, $CO_2CH_2CH_3$).

Pyrolysis Procedure.—The degassed material to be pyrolyzed was distilled at 1–3 g/hr, at 1–3 mm, into the top end of a 37 × 2.5 cm Vycor tube packed tightly with glass wool (16–18 g in 33 cm) or other packing (**1a**, runs 1–4, 14) and heated over 30 cm by a tube oven mounted horizontally at a 10–15° angle. The temperature was measured by a thermocouple at the center of the tube oven prior to insertion of the tube, which was temperature equilibrated for at least 30 min prior to use. Pressures were measured by a McLeod gauge on the line between the cold trap and a mechanical pump.

The hot product vapor was collected in a Dry Ice or liquid nitrogen cooled trap. On small runs (1–2 g) the pyrolysate was analyzed by glpc and yields were calculated using internal standards. On preparative runs (10–38 g) the trapped pyrolysate was distilled on a Teflon annular spinning band column and yields were based on isolated materials. Individual conditions and product yields are summarized in Table III.

Products.—Ketones **2a–d**, **3a–d**, **14**, and cyclopentanone were isolated for identification by preparative glpc of the pyrolysates of the corresponding keto esters (**1a–d**, **13**, **5**). In no case were isomeric ketones (*e.g.*, **2c** or **3c** from **1b**) noted.[41] Ethanol was isolated by preparative glpc and identified by comparison of glpc retention times and ir spectra with a commercial sample.

2-Cyclopentenone-1 (2a)[34,42] and 3-Methyl-2-cyclopentenone-1 (2b).[42]—Ketone **2a** was isolated from the pyrolysates of **1a** and **10b**. Ketone **2b** was isolated from the pyrolysate of **1b**. Both ketones were identified with commercial samples by comparison of glpc retention times, ir, uv, and nmr spectra and by the mixture melting points of the 2,4-dinitrophenylhydrazone derivatives.

2-Methyl-2-cyclopentenone-1 (2c).[42]—The ketone was obtained from the pyrolysates of **1c**, with bp 42–43° (0.25 mm) [lit. bp 46–48° (0.2 mm),[43] 59.1° (18.5 mm)[44]]: ir (CCl_4) 5.86 (C=O), 6.11 μ (C=C) [lit. 1705 (5.86), 1640 cm^{-1} (6.10 μ);[45] 1711 (5.84), 1642 cm^{-1} (6.09 μ)[43]]; uv $\lambda_{max}^{C_2H_5OH}$ 227 nm (ε 14,700) [lit. $\lambda_{max}^{95\%\ C_2H_5OH}$ 227 nm (ε 11,220);[45] 226 (8550)[43]]; nmr δ^{CCl_4} 1.70 (d, 3, J = 2 Hz, small side bands, CH=CCH_3, cis), 2.25–2.78 (m, 4, J = 2 Hz, $CH_2C'H_2$), 7.26–7.48 (m, 1, J = 1.5 Hz, CH=CCH_3, cis) (consistent with literature nmr values[43,45]). The 2,4-dinitrophenylhydrazone derivative had mp 223.5–224° (lit. mp 221–222°,[44] 219–220°[46]).

2,3-Dimethyl-2-cyclopentenone-1 (2d).[47]—The ketone was isolated from pyrolysates of **1d** with bp 50° (0.1 mm) [lit. bp 80° (10 mm);[48] 90–92° (25 mm);[49] 87–89° (20 mm)[50]]: ir (CCl_4) 5.86 (C=O), 6.05 μ (C=C) [lit. 1701 (5.87), 1656 cm^{-1} (6.04 μ)[43]]; uv $\lambda_{max}^{C_2H_5OH}$ 234 nm (ε 14,500) [lit. 235 nm (log ε 3.04);[49] 234 nm (ε 13,660);[48] 235 nm (ε 11,784);[51] 234 nm (ε 13,580)[43]]; nmr δ^{CCl_4} 1.63 (s, 3, CH_3), 2.04 (s, 3, CH_3), 2.10–2.67 (m, 4, $CH_2C'H_2$) (consistent with literature[43] nmr values). The 2,4-dinitrophenylhydrazone derivative had mp 231–232° (lit. mp 233°,[52] 230–231°[51]).

Cyclopropyl Methyl Ketone (3a).[34]—Ketone **3a** isolated from the pyrolysates of **1a** was identified with a commercial sample by comparison of glpc retention times, ir and nmr spectra, and mixture melting point of the 2,4-dinitrophenylhydrazone derivatives. Ketone **3a** was also recovered unchanged (99% recovery) when pyrolyzed at 575° (1–3 mm) with glass wool packing.

1-Methylcyclopropyl Methyl Ketone (3b).[42]—Ketone **3b** isolated from the pyrolysates of **1b** was identified with a sample prepared by the procedure of Goldman[39] by comparison of glpc retention times, ir and nmr spectra, and mixture melting point of the 2,4-dinitrophenylhydrazone derivatives.[53,54]

Cyclopropyl Ethyl Ketone (3c).—Ketone **3c** isolated from pyrolysates of **1c** was similarly identified with a sample prepared by the procedure of Julia[40b] (cadmium method). The 2,4-dinitrophenylhydrazone derivative had mp 167.5–168° (lit.[40b] mp 162–163°).

Anal. Calcd for $C_{12}H_{14}N_4O_4$: C, 51.80; H, 5.07; N, 20.13. Found: C, 51.51; H, 4.98; N, 20.13.

(41) However, a trace of what is probably 4-methyl-2-cyclopentenone-1 was isolated from a pyrolysate of **1b**.

(42) A 10 ft × 0.25 in. column packed with 69–80 Chromosorb W coated with 20% by weight of Apiezon L was used for analysis and collection. The internal standard was 4-methylcyclohexanone.

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(47) A 5 ft × 0.25 in. column packed with 60–80 Chromosorb W coated with 20% by weight of Apiezon L was used for both analysis and collection. The internal standard used was 4-methylcyclohexanone.

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1-Methylcyclopropyl Ethyl Ketone (3d).[47]—Ketone **3d** was isolated from pyrolysates of **1d** and was identified by the following data: ir (CCl_4) 3.24 (cyclopropyl CH), 5.92 μ (C=O); nmr δ^{CCl_4} 0.48–0.73 (m, 2, cyclopropyl CH cis or trans to C=O), 0.81–1.28 (m, 2, cyclopropyl CH trans or cis to C=O), 0.98 (t, 3, J = 7.5 Hz, CH_2CH_3), 1.35 (s, 3, CH_3C), 2.43 (q, 2, J = 7.5 Hz, CH_2CH_3).

Anal. Calcd for $C_7H_{12}O$: C, 74.95; H, 10.78. Found: C, 75.09; H, 10.87.

The 2,4-dinitrophenylhydrazone derivative had mp 120.5–121°.

Anal. Calcd for $C_{13}H_{16}N_4O_4$: C, 53.42; H, 5.52; N, 19.17. Found: C, 53.17; H, 5.47; N, 19.23.

Cyclopropyl Isopropyl Ketone (14).[42]—Ketone **14** was isolated from the pyrolysates of **13** and was identified by the following data: ir (CCl_4) 3.24 (cyclopropyl CH), 5.88 (C=O), 7.20 7.33 μ (>$C(CH_3)_2$); nmr δ^{CCl_4} 0.56–1.02 (m, 4, cyclopropyl CH_2), 1.13 (d, 6, J = 7 Hz, $CH(CH_3)_2$), 1.68–21.6 (m, 1, cyclopropyl methine), 2.45–2.99 (q, 1, J = 7 Hz, degenerate $CH(CH_3)_2$).

Anal. Calcd for $C_7H_{12}O$: C, 74.95; H, 10.78. Found: C, 74.85; H, 10.65.

The 2,4-dinitrophenylhydrazone derivative had mp 183° (sharply);

Anal. Calcd for $C_{13}H_{16}N_4O_4$: C, 53.42; H, 5.52; N, 19.17. Found: C, 53.25; H, 5.51; N, 19.22.

Cyclopentanone (6).[54]—Cyclopentanone was recovered in 96% yield from the pyrolysate[55] of cyclopentanone and was produced in 48% yield by pyrolysis[55] of α-carbethoxycyclopentanone (**5**). The compound was identified with a commercial sample by comparison of glpc retention times, ir and nmr spectra, and mixture melting point of the 2,4-dinitrophenylhydrazone derivatives. No cyclopentenone was observed in either pyrolysate.[18]

3-Cyclopropanecarbonyl-6-cyclopropyl-2*H*-pyran-2,4(3*H*)-dione (10b).—This dehydroacetic acid analog was obtained by pyrolysis of **1a** at 760 mm. The keto ester was carried through the hot tube by stream of prepurified nitrogen (25 ml/min). Part of the pyrolysate solidified and, upon filtration and recrystallization (ethanol), afforded a white solid, mp 66–66.5°, in 20% yield. This material gave a positive ferric chloride test: ir (CCl_4) 3.24 (cyclopropyl CH), 5.82, 6.16, 6.52, 10.19 μ; uv $\lambda_{max}^{C_2H_5OH}$ 319 nm (ϵ 14,200), 233.5 (13,500); $\lambda_{max}^{C_2H_5OH,\ pH\ 12}$ 298 nm (ϵ 15,200), 232 (20,200);[56] nmr δ^{CDCl_3} 0.94–1.37 (m, 8, cyclopropyl CH_2), 1.56–2.05 (m, 2, cyclopropyl methine), 3.29–3.80 (dd, 1, J = 2.7 Hz, vinyl H), 5.99 (s, 1, enolic H).

Anal. Calcd for $C_{12}H_{12}O_4$: C, 65.45; H, 5.49. Found: C, 65.39; H, 5.43.

Pyrandione **10b** was also prepared in 80% yield by passing 39.2 g (0.25 mol) of keto ester **1a**, on a stream of prepurified nitrogen at 1 atm, over a 6-in. segment of pumice[27] at 400°. The pyrolysate was distilled under reduced pressure giving 11.7 g (29.8%) of unreacted **1a** and 15.2 g (55.5%) of **10b**, bp 125–126° (0.05 mm), which solidified upon cooling, mp 65–66°. This material was identified with the above sample by comparison of ir spectra.

Gases.—Carbon monoxide, carbon dioxide, and ethylene were identified in the untrapped pyrolysis product stream (1–3 mm) by comparison of glpc retention times with those of commercial samples. A 6 ft × 0.25 in. column packed with Porapak Q at room temperature was used for these analyses in a Gow-Mac, Model 69-100, thermal conductivity instrument. A gas sample volume of 7.5 ml was used.

Registry No.—**1a** methyl ester, 32249-35-7; **1a** ethyl ester, 24922-02-9; **1b**, 32249-37-9; **1b** thiouracil derivative, 32249-38-0; **1c**, 21741-37-7; **1c** thiouracil derivative, 32249-40-4; **1d**, 32249-41-5; **1d** thiouracil derivative, 32249-42-6; **2a**, 930-30-3; **2b**, 2758-18-1; **2c**, 1120-73-6; **2d**, 1121-05-7; **3d**, 25111-31-3; **3d** 2,4-DNPH, 32249-48-2; **10b**, 32249-49-3; **13**, 32249-50-6; **14**, 6704-20-7; **14** 2,4-DNPH, 32304-06-6.

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(55) The pyrolysis was done at 575° (1–3 mm) with glass wool packing.

(56) Dehydroacetic acid: $\lambda_{max}^{95\%\ C_2H_5OH}$ 310 nm (ϵ 11,200); $\lambda_{max}^{C_2H_5OH,\ pH\ 12}$ 294 nm (ϵ 8150) [J. A. Berson, W. M. Jones, and L. F. O'Callaghan, *J. Amer. Chem. Soc.*, **78**, 622 (1956)].

Nuclear Magnetic Resonance Spectroscopy. Proton Spectra of 2-Pyridones[1a]

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The proton magnetic resonance spectra of 2-pyridone, 1-methyl-2-pyridone, and 1-(2′-pyridyl)-2-pyridone in deuteriochloroform solution were recorded at 100 and 220 MHz. A computer-assisted analysis of these spectra yielded the chemical shifts and consistent sets of coupling constants. Some regularities in the effects of structure and concentration on the chemical shifts were observed. The spectra of 2-pyridone in deuterium oxide and benzene-d_6 were briefly explored.

The purpose of this study was to complete and refine the existing pmr data of 2-pyridone (**1**) and 1-methyl-2-pyridone (**2**) and to determine the spectral parameters of 1-(2′-pyridyl)-2-pyridone (**3**).[2] It is now commonly assumed[3] that the 2-pyridone, usually written as **1a**, is the predominant species in a tautomeric equilibrium with 2-hydroxypyridine (**1c**). Compounds **2** and **3** can only exist in the lactam form, represented as the resonance hybrid **1a** and **1b**. The numbering used in all tables and discussions is as shown in these structures.

The spectral analysis of **3** was of interest because it possesses both the 2-pyridone ring (A) and the pyridine ring (B) as an aromatic N substituent.

Assuming fast chemical exchange for the N–H proton, the ring protons of 2-pyridone represent an asymmetric four-spin system whose pmr spectrum is characterized by four chemical shifts and six coupling constants. The 60-MHz spectra of other 2-substituted pyridines have been analyzed rigorously as ABCD and, sometimes to a good approximation, as ABKL and AA′KL systems.[4]

The 100-MHz and 220-MHz spectra discussed in this paper approximate ABKX types but were treated as

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