Rearrangements of 2-Pyrones and Pyran-2-thiones Involving 1,5-Sigmatropic Hydrogen Shifts

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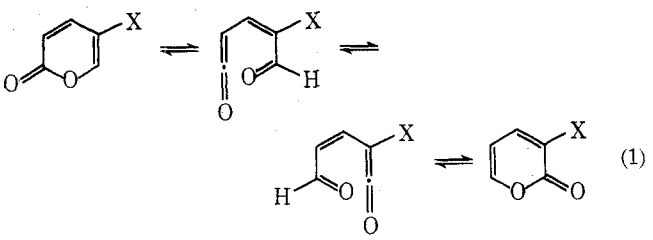
At elevated temperatures, 2-pyrones bearing hydrogen in the 6 position reversibly exchange substituents between the 3 and 5 positions. Evidence is presented from oxygen-18 labeling experiments that the "migrations" actually occur via reversible electrocyclic ring opening to ketene aldehydes which undergo reversible [1,5] sigmatropic shifts of the aldehydic hydrogen. Pyran-2-thiones undergo similar rearrangements and quantitatively afford thiapyran-2-ones. These rearrangements are blocked by the presence of a methyl group in the 6 position.

In a preliminary report,[1] the migration of substituents between the 3 and 5 positions of 2-pyrones during gas-phase pyrolysis was rationalized by invoking reversible electrocyclic ring opening to ketene aldehydes which undergo reversible [1,5] sigmatropic shifts of the aldehydic hydrogen (eq 1). In view of the obvious synthetic utility of



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the reaction and the possible relevence of the postulated mechanistic sequence to a prior mass spectrometric study of isotopically labeled pyrones,[2,3] the results of an investigation of the synthetic scope and mechanism of the rearrangement are presently reported.

The reaction sequence of eq 1 is a priori reasonable since ketene aldehydes related to the hypothesized intermediates have been shown to arise photochemically from 2-pyrone,[4-7] and thermally to reclose very rapidly ($t_{1/2}$ 0.92 μsec at 45.7°). Moreover, thermal sigmatropic shifts of order [1,5] are well-established reactions.[8]

However, one need not rely upon these analogies, satisfying though they may be, since the postulated reaction sequence lends itself to experimental verification in several ways. For example, the carbonyl oxygen of a 5-substituted isomer should become the pyran ring oxygen on rearrangement to the 3-substituted isomer. Similarly, if the sulfur analogs of 2-pyrone also undergo the rearrangement, a pyran-2-thione should, on rearrangement, give a thiapyran-2-one, with an accompanying exchange of the 3 and 5 substituents. Finally, one expects that when a substituent having a lower migratory aptitude than hydrogen occupies the 6 position, it will impede the rearrangement.

Table I lists a number of substituted 2-pyrones which were pyrolyzed to determine the scope of the rearrangement. Previously unreported ^{1}H NMR data for the compounds prepared in this study are shown in Table II.

Pyrones bearing hydrogen in the 6 position and having bromine, methyl, methoxy, or acetoxy substituents in the 3 or 5 positions rearrange readily to give an equilibrium mixture of the 3- and 5-substituted isomers. Coumalyl chloride (2-pyrone-5-carbonyl chloride) does not appear to rearrange, presumably because the equilibrium for carbonyl-substituted 2-pyrones greatly favors the 5-substituted isomer. Note that 3-carbethoxy-2-pyrone rearranges completely (>99% by GLC) to ethyl coumalate, the 5-substituted isomer.[9]

Table I
Pyrolyses of 2-Pyrones

Registry no.	Compd pyrolyzed	Product	Temp, °C	% rearrangement
19978-33-7	5-Bromo-2-pyrone[b]	3-Bromo-2-pyrone[b]	490	53–54[a]
51270-32-7	5-Methyl-2-pyrone	3-Methyl-2-pyrone	650	76[c]
	3-Methoxy-2-pyrone[d]	5-Methoxy-2-pyrone	550	14[e]
51270-29-2	3-Acetoxy-2-pyrone	5-Acetoxy-2-pyrone[f]	550	33[e]
54657-80-6	3-Trifluoroacetoxy-2-pyrone	5-Trifluoroacetoxy-2-pyrone[g]	550	30[e]
	3-Carbethoxy-2-pyrone[i,j]	Ethyl coumalate[h]	540	>99
	Coumalyl chloride[k]		575	0
54657-81-7	5-Carbethoxy-6-methyl-2-pyrone	*l*	650	0
3385-34-0	4,6-Dimethyl-5-carbethoxy-2-pyrone		550	0
		m	650	0
	Pyran-2-thione[n]	Thiapyran-2-one	370	30[e]
			620	100
51270-31-6	4-Methylpyran-2-thione	4-Methylthiapyran-2-one	500	100
54657-82-8	5-Bromopyran-2-thione	3-Bromothiapyran-2-one	480	100
	4,6-Dimethylpyran-2-thione[n]		700	0

[a] Equilibrium value. [b] Reference 18. [c] After two passes through the pyrolysis tube; the first gave 72% rearrangement. [d] R. H. Wiley and C. H. Jarboe, *J. Am. Chem. Soc.*, 78, 2398 (1956). [e] Not an equilibrium value. [f] Some 3-hydroxy-2-pyrone also resulted. [g] Not isolated. Identified by ^{1}H NMR spectrum. [h] Some decarbethoxylation to 2-pyrone occurred. [i] T. B. Windholz, L. H. Peterson, and G. J. Kent, *J. Org. Chem.*, 28, 1443 (1963). [j] Reference 9. [k] J. Fried and R. C. Elderfield, *J. Org. Chem.*, 6, 566 (1941). [l] 6-Methyl-2-pyrone and 6-methylcoumalic acid were produced. [m] Complete decarbethoxylation to 4,6-dimethyl-2-pyrone occurred. [n] R. Mayer and P. Fischer, *Chem. Ber.*, 95, 1307 (1962).

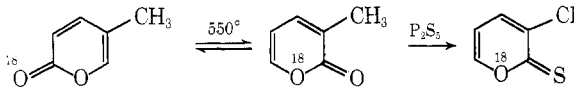
Table II
^{1}H NMR Spectra of 2-Pyrones Prepared in This Study

Registry no.	Compd	Chemical shift, δ[a]					Coupling constants, Hz						
		H-3	H-4	H-5	H-6	Others	$J_{3,4}$	$J_{3,5}$	$J_{3,6}$	$J_{4,5}$	$J_{4,6}$	$J_{5,6}$	Others
31678-73-6	3-Methyl-2-pyrone		7.13	6.15	7.36	2.00 (CH_3)				6.6	2.2	5.4	~1.5 ($J_{3',4}$)
	5-Methyl-2-pyrone	6.31	7.34		7.36	2.00 (CH_3)	9.5		1.3		2.5		1.2 ($J_{5',6}$)
4394-76-7	6-Methyl-2-pyrone	~6	6.40	~6		2.3 (CH_3)	9			6.5			
22682-15-1	4-Methyl-6-chloro-2-pyrone	6.02		6.18		2.19 (CH_3)		1.2					1.3 ($J_{3,4'}$)
51270-28-1	3-Methoxy-2-pyrone		6.6	6.25	7.12	3.8 (CH_3)				7	1.6	5	
54657-83-9	5-Methoxy-2-pyrone[b]		7.33			3.68 (CH_3)	10				3		
496-64-0	3-Hydroxy-2-pyrone		6.7	6.2	7.15	6.0 (OH)				7.2	1.7	5.2	
	3-Acetoxy-2-pyrone		7.2	6.27	6.45	2.3				6.9	1.9	5.1	
54657-84-0	5-Acetoxy-2-pyrone	6.31	7.22		7.58	2.3 (CH_3)	10		1		3		
	3-Trifluoroacetoxy-2-pyrone		7.5	6.5	7.5					7.2	1.8	5.2	
54657-85-1	5-Trifluoroacetoxy-2-pyrone[c]	6.50	~7.5		7.95		10		1		3		
1008-44-2	3-Carbethoxy-2-pyrone		8.20	6.45	7.78	1.31 (CH_3)				6.8	2.3	4.9	
						4.25 (CH_2)	9.5						
25683-10-7	5-Carboxy-6-methyl-2-pyrone[d]	6.45	8.06			2.76 (CH_3)	9.5						
	5-Carbethoxy-6-methyl-2-pyrone	6.12	7.79			2.63 (6-CH_3)	9.5						
						1.36 (CH_3)							
						4.28 (CH_2)							
23639-33-0	Pyran-2-thione	7.20	7.13	6.55	7.86		9.2	1.7	1.3	6.2	1.7	5.2	
54657-86-2	3-Methylpyran-2-thione		7.10	6.44	7.75	2.30 (CH_3)				6.9	1.8	5.0	1.1 ($J_{3,4'}$), 0.8 ($J_{3',6}$) 0.3 ($J_{3',5}$)
	4-Methylpyran-2-thione	7.05		6.38	7.72	2.06 (CH_3)		1.7	1.0			5.1	1.0 ($J_{3,4'}$)
54657-87-3	4,6-Dimethylpyran-2-thione	6.97		6.20		2.07 (4-CH_3)							1.2 ($J_{3,4'}$),
						2.32 (6-CH_3)							~0.5 ($J_{5,6'}$)
	5-Bromopyran-2-thione[e]	6.65	6.00		6.78		8.7		1.0		2.2		
6788-51-8	Thiapyran-2-one	6.48	7.53	6.95	7.78		10.4	0.6	1.0	7.0	2.0	9.2	
51270-30-5	4-Methylthiapyran-2-one	6.32		6.77	7.55	2.24 (CH_3)		0.9	~1			9.5	1.2 ($J_{3,4'}$)
54657-88-4	3-Bromothiapyran-2-one		7.48	6.65	7.85					7.4	1.9	9.0	
54657-89-5	5-Bromothiapyran-2-thione	7.14	6.98		7.45		10.5		1.0		2.2		

[a] Typically, spectra were obtained at 60 MHz in $CDCl_3$. When spectral complexity necessitated, solvent variation and/or use of a 220-MHz spectrometer enabled complete spectral assignments to be made. [b] This compound was not isolated, and the remaining protons were obscured by other components in the mixture. [c] Not isolated. [d] Run in $CDCl_3$-CF_3COOH (2:1). [e] Run in C_6D_6.

At elevated temperatures, several of the substituted 2-pyrones undergo fragmentation reactions. Thus, those bearing carbethoxy groups undergo partial decarbethoxylation or loss of ethylene. Similarly, a small fraction of 3-acetoxy-2-pyrone cracks to 3-hydroxy-2-pyrone.[10] However, most of the pyrones investigated can be recovered in high yield. Typically, the 3 and 5 isomers are readily separated by liquid or gas chromatography.

Further evidence for the rearrangement pathway of eq 1 was obtained by following an oxygen-18 label through the rearrangement. Oxygen-18-labeled 5-methyl-2-pyrone was prepared by hydrolysis of 2-ethoxy-5-methylpyrylium fluoroborate with 30% oxygen-18-enriched water. The label is expected to be exclusively in the carbonyl, since in the case of 2-pyrone labeled in the same manner, all label is lost on conversion of the enriched pyrone to pyran-2-thione.[3] The mixed 3-methyl- and 5-methyl-2-pyrones resulting from pyrolysis of the labeled sample at 550° were separated by liquid chromatography and examined by mass spectrometry. Before pyrolysis, the 5-methyl-2-pyrone contained 27.0 ± 0.5% oxygen-18; after pyrolysis, 27.4 ± 0.8%. The 3-methyl-2-pyrone resulting from the pyrolysis retains the label (26.4 ± 1.0%), as does the 3-methylpyran-2-thione prepared from it (27.1 ± 0.9%). This result is consistent with initial labeling occuring exclusively in the carbonyl, followed by a rearrangement which entails the shift of the oxygen label (eq 2).



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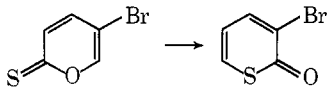
Pyran-2-thione and 4-methylpyran-2-thione rearrange completely to the isomers having sulfur in the ring. Pyran-2-thione isomerizes more readily than any other compound studied, being 30% converted in a single pass through a 370° tube. Indeed, this isomerization is so facile that it occurs extensively during attempted gas chromatography at 160° (150° injector). Rearrangement of 4-methylpyran-2-thione to 4-methylthiapyran-2-one is complete (by ^{1}H NMR) in one pass at 500°. The quantitative rearrangement of the preceding pyran-2-thiones to thiapyran-2-one is readily understandable in view of the destabilization of a

thiocarbonyl group relative to its carbonyl isomer.[11] The rearrangement of pyran-2-thiones to thiapyran-2-ones is accompanied by exchange of the substituents in the 3 and 5 positions. 5-Bromopyran-2-thione rearranges completely to 3-bromothiapyran-2-one (eq 3).



(3)

In contrast to the facile rearrangement of pyran-2-thione, 4-methylpyran-2-thione, and 5-bromopyran-2-thione, 4,6-dimethylpyran-2-thione is unreactive even at 700°. Apparently, the methyl group in the 6 position impedes the rearrangement, a view consistent with the paucity of reports of [1,5] sigmatropic shifts of methyl groups.[12]

The ability to interchange substituents between the 3 and 5 positions of the 2-pyrone ring is of obvious synthetic application. Since most 2-pyrones are available only by multistep reaction sequences, this rearrangement can, in many cases, provide a second isomeric pyrone with little additional effort and offers additional flexibility in the initial synthetic approach, since in a number of instances, either of the isomers may be utilized. The reaction also makes thiapyran-2-ones readily available, since pyran-2-thiones are generally obtainable by the action of P_2S_5 on 2-pyrones. The usual method of obtaining thiapyran-2-ones starts from the dithiopyrones, which are generally prepared from enamines and carbon disulfide.[13,14] This earlier method gives limited control over substituents, two of which, arising from two molecules of enamine, must be the same. In the context of these rearrangements, it should be recalled that it has recently been shown possible to exchange substituents between the 4 and 6 positions of 2-pyrone by photolysis in sulfuric acid.[15]

Experimental Section

Pyrolyses of 2-pyrones were carried out by sublimation or distillation (0.1–1 Torr) through a hot Vycor tube (370–700°) packed with Pyrex helices (Table I). Isomeric composition of the product mixtures was determined by ^{1}H NMR spectroscopy and/or GLC. The 5- and 3-substituted isomers are readily distinguished by ^{1}H NMR, since there are two large vicinal coupling constants (ca. 7 and 5 Hz) in the 3-substituted isomers and only one (ca. 10 Hz) in the 5-substituted isomers.[16] The isomeric sulfur analogs are also readily distinguishable; the pyran-2-thiones are brilliant orange whereas the thiapyran-2-ones are almost colorless. Consistencies in the ^{1}H NMR spectra of the sulfur analogs were also observed. Substitution of a sulfur for the carbonyl oxygen results in a downfield shift of H-3 of about 0.8–1.0 ppm,[17] but in no significant changes in the proton coupling constants. Replacing the ring oxygen with sulfur, however, shifts H-5 downfield by 0.4–0.5 ppm and also increases $J_{5,6}$ to 9.0–9.5 Hz. As in the 2-pyrones, the substitution pattern in the sulfur analogs is revealed by the number of large vicinal coupling constants. In addition, most of the new pyrones isolated were examined by mass spectrometry. All gave appropriate molecular ions.

5-Bromopyran-2-thione. A solution of 5-bromo-2-pyrone[18] (2.0 g) in 30 ml of benzene was heated under reflux with 2.54 g of P_2S_5. At 24-hr intervals, the solution was decanted from the P_2S_5 residue onto similar amounts of fresh P_2S_5. After 4 days the solution was chromatographed on 100 g of silica gel with benzene.

The first colored band gave 0.03 g of red crystalline material which, after sublimation at 50° (5 Torr), melted at 163° dec. The ^{1}H NMR spectrum (Table II) is appropriate for 5-bromothiapyran-2-thione. The mass spectrum has base peaks at *m/e* 162 and 164 (M − CS) and molecular ions at *m/e* 206 and 208 ($C_5H_3BrS_2$).

The second colored band afforded 0.2 g of orange crystals melting at 122–126° dec after sublimation [50° (5 Torr)]. The ^{1}H NMR spectrum (Table II) is consistent with that expected for 5-bromopyran-2-thione. The mass spectrum has the molecular ions at *m/e* 190 and 192 (C_5H_3BrOS) as the base peaks, with prominent ions at *m/e* 146 and 148 (M − CS) and *m/e* 162 and 164 (M − CO). On standing under nitrogen but exposed to light, this material is partially converted into an insoluble, high-melting, nonvolatile solid. The mass spectrum of 5-bromopyran-2-thione thus stored shows, in addition to the expected peaks, weak "triplets" at *m/e* 380, 382, and 384, indicative that a dimerization has occurred.

A third chromatographic fraction afforded 1.6 g of unreacted 5-bromo-2-pyrone.

3-Acetoxy-2-pyrone.[19] A solution of 3-hydroxy-2-pyrone (0.25 g) in 10 ml of acetyl chloride was heated under reflux, until after 5 hr ^{1}H NMR showed that acetylation was complete. The excess acetyl chloride was removed under vacuum, and the residual oil was subjected to molecular distillation at 0.1 Torr. After recrystallization from cold diethyl ether, the 3-acetoxy-2-pyrone melts at 34–36°.

3-Trifluoroacetoxy-2-pyrone. A solution of 3-hydroxy-2-pyrone (1.0 g) in ca. 5 g of trifluoroacetic anhydride was allowed to stand at 25° for 18 hr, after which time ^{1}H NMR showed that no 3-hydroxy-2-pyrone remained. The solvent was removed under vacuum to leave an oil which contained a trace of trifluoroacetic acid. The 3-trifluoroacetoxy-2-pyrone was pyrolyzed without further work-up to avoid hydrolysis.

2-Ethoxy-5-methylpyrylium Fluoroborate. To a mixture of 5-methyl-2-pyrone (0.33 g) and triethyloxonium fluoroborate[20] (0.65 g) was added 0.65 g of methylene chloride, and the homogeneous mixture was allowed to stand for 18 hr. After removal of the solvent, ^{1}H NMR showed about 85% conversion of the pyrone to the salt. The mixture was redissolved in 2 g of methylene chloride and allowed to stand for 24 hr, by which time alkylation of the pyrone was about 90% complete by ^{1}H NMR. Addition of 20 ml of ether caused separation of the salt as a dark brown oil. Repeated washing with ether afforded noncrystalline 2-ethoxy-5-methylpyrylium fluoroborate which, by ^{1}H NMR, contained only a trace of 5-methyl-2-pyrone and triethyloxonium fluoroborate: ^{1}H NMR (CH_2Cl_2) δ 1.55 (t, J = 7 Hz, 3 H, CH_3), 2.32 (d, J = 1 Hz, 3 H, CH_3), 4.88 (q, J = 7 Hz, 2 H, CH_2), 7.35 (dd, J = 9, 1 Hz, H-3), 8.40 (m, H-6), 8.51 (dd, J = 9, 2 Hz, H-4).

5-Methyl-2-pyrone (C=^{18}O). To the preceding oxonium salt was added 0.18 g of water containing 30.0% oxygen-18. After 2 hr at 25°, the mixture was taken into ether and treated at 0° for 3 hr with 2 g of $NaHCO_3$. It was then filtered; the $NaHCO_3$ was washed with more ether. The ether was removed under vacuum to leave 0.28 g of brown oily 5-methyl-2-pyrone which showed no impurities by ^{1}H NMR and which (by mass spectrometry) contained 27.0 ± 0.5% oxygen-18.

Pyrolysis of 5-Methyl-2-pyrone (C=^{18}O). The labeled 5-methyl-2-pyrone (0.28 g) was pyrolyzed at 450° to afford 0.22 g of pyrolysate. The 3-methyl- and 5-methyl-2-pyrone were separated chromatographically (silica gel, methylene chloride), the former being eluted first. ^{1}H NMR verified the completeness of separation. Mass spectrometry indicated isotope enrichments of 26.4 ± 1.0% in the 3-methyl-2-pyrone and 27.4 ± 0.8% in the 5-methyl-2-pyrone.

3-Methylpyran-2-thione. The aforementioned labeled 3-methyl was converted to the thione by the method used to prepare 5-bromopyran-2-thione and was chromatographed on silica with chloroform. The initially eluted yellow material was identified as 3-methylpyran-2-thione by ^{1}H NMR. Further elution gave unreacted 3-methyl-2-pyrone. The thione was examined by mass spectrometry and found to contain 27.1 ± 0.9% oxygen-18 enrichment.

Preparation of 4-Methyl-6-chloro-2-pyrone.[19] Over 15 min, 88 g of PCl_5 was added to a slurry of 50.6 g of 3-methylglutaconic anhydride[21] in 100 ml of $POCl_3$. Hydrogen chloride was evolved, and the anhydride dissolved to give a dark red solution. After 1 hr at 95°, ^{1}H NMR showed ca. 75% conversion. More PCl_5 (20 g) was added, and the heating was continued. After 1 hr, no anhydride could be detected by ^{1}H NMR. The $POCl_3$ was removed under vacuum and the crude material was distilled at 135° (~20 Torr) to give 4-methyl-6-chloro-2-pyrone as an oil which crystallized on cooling.

Preparation of 4-Methyl-2-pyrone.[19] Zinc dust (30 g) was added slowly to a solution of 4-methyl-6-chloro-2-pyrone (15.2 g) in 75 ml of acetic acid, held at 0°. The mixture was stirred at 25° overnight, then filtered under nitrogen. The zinc was washed with ether, and the combined filtrates were concentrated under vacuum. The residual oil was stirred with ice and neutralized with Na_2CO_3. After filtration of the precipitated zinc salts, the aqueous filtrate was extracted three times with several times its own volume of ether to afford, on solvent removal, 10.5 g of 4-methyl-2-pyrone as a yellow oil showing no impurities by ^{1}H NMR. This material was distilled at 115° (6 Torr).

4-Methylpyran-2-thione.[19] Using the previously described

P_2S_5 method, 4-methyl-2-pyrone (2.0 g) afforded 2.4 g of pasty yellow crystals which were chromatographed on silica gel with a mixture of pentane and methylene chloride. The heart cut of the yellow band gave 1.75 g of yellow solid which afforded 1.0 g of 4-methylpyran-2-thione, mp 70–71°, after recrystallization from cyclohexane–benzene.

Preparation of Methyl 4-Formylpentanoate. The enamine from pyrrolidine and propionaldehyde[22] (230 g) was added to freshly distilled, neat methyl acrylate (195 g). A yellow color and an exothermic reaction ensued. The temperature was kept below 40° by cooling, and, after 1 hr, the colorless mixture was heated on a steam bath for several hours.

A portion of the reaction mixture (27 g), while chilled in ice, was treated with 11.5 ml of concentrated hydrochloric acid. After 2 hr, this mixture was extracted twice with ether and the combined extracts were washed with water and saturated sodium chloride solution, dried over Drierite, and concentrated under vacuum to leave methyl 4-formylpentanoate (84%) as a colorless oil: ^{1}H NMR (CCl_4) δ 9.21 (1 H, d, J = 1.5 Hz, CHO), 3.64 (3 H, s, OCH_3), 1.5–2.6 (5 H, m, aliphatic), 1.12 (3 H, d, J = 7 Hz, CH_3); dinitrophenylhydrazine mp 90.5–91.5° (ethanol).

Preparation of 4-Formylpentanoic Acid. The preceding methyl ester (257 g) was hydrolyzed by treatment at 25° with a solution of 232 g of K_2CO_3 in 1 l. of water with subsequent addition of 500 ml of methanol. It is necessary to make the ester basic before methanol is added, to avoid formation of the dimethyl acetal. After 12 hr at 25°, the desired acid was isolated by removal of the methanol under vacuum and ether extraction of the acidified hydrolysis mixture. Evaporation of the ether afforded 195 g of crude acid (84%). A portion of this acid was purified by distillation [110° (3 Torr)]: ^{1}H NMR (CCl_4) δ 10.45 [1 H, s, COOH), 8.96 (1 H, s, CHO), 1.4–2.8 (5 H, m, aliphatic), 1.16 (3 H, d, J = 7 Hz, CH_3); dinitrophenylhydrazone mp 167.5–169° (ethanol). Anal. Calcd for $C_6H_{10}O_3$: C, 55.37; H, 7.74. Found: C, 55.12; H, 7.65.

Preparation of 5-Methyl-3,4-dihydro-2-pyrone. The procedure of Pettit et al.[23] was followed, using 15.7 g of 4-formylpentanoic acid. The crude 5-methyl-3,4-dihydro-2-pyrone was obtained as a colorless oil (64%) and was purified by distillation [75° (5 Torr)]: ^{1}H NMR (220 MHz, CCl_4) δ 6.3 (1 H, dt, J = 1.5, 1.5 Hz, vinyl), 2.55 (2 H, br t, J = 7.5 Hz, CH_2CO), 2.30 (2 H, br t, J = 7.5 Hz, allylic CH_2), 1.68 (3 H, dt, J = 1.5, 0.9 Hz, CH_3). Anal. Calcd for $C_6H_8O_2$: C, 64.27; H, 7.19. Found: C, 64.23; H, 7.16.

Preparation of 5-Methyl-2-pyrone.[19] The dihydropyrone (2.25 g) was brominated with *N*-bromosuccinimide as described by Pettit et al.[23] and dehydrobrominated with 1,5-diazabicyclo-[4.3.0]non-5-ene. On distillation, 5-methyl-2-pyrone was obtained in 40% yield.

Registry No.—P_2S_5, 1314-80-3; acetyl chloride, 75-36-5; trifluoroacetic anhydride, 407-25-0; 2-ethoxy-5-methylpyrylium fluoroborate, 54657-91-9; triethyloxonium fluoroborate 368-39-8; 3-methylglutaconic anhydride, 54657-92-0; 4-methyl-2-pyrone, 22682-12-8; methyl 4-formylpentanoate, 40630-06-6; methyl 4-formylpentanoate 2,4-DNP, 54657-93-1; pyrrolidine and propionaldehyde enamine, 13937-88-7; 4-formylpentanoic acid, 3619-43-0; 4-formylpentanoic acid 2,4-DNP, 3770-62-5; 5-methyl-3,4-dihydro-2-pyrone, 54657-94-2.

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Halomethyl Metal Compounds. 75. Organomercury Reagents for Room Temperature Dihalocarbene Generation[1]

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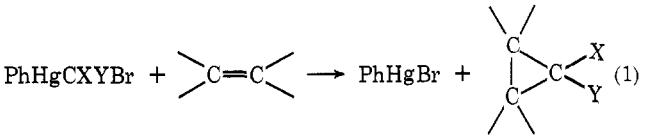
The new organomercury reagents $PhHgCCl_2I$, PhHgCClBrI, and $PhHgCBr_2I$ were prepared and found to be effective divalent carbon transfer agents. They react with carbenophiles within 1–4 days at room temperature and within minutes at 80°. The reasons for their high reactivity are discussed.

Phenyl(bromodichloromethyl)mercury, phenyl(dibromochloromethyl)mercury, and phenyl(tribromomethyl)mercury react with a wide variety of carbenophiles (e.g., eq 1, which shows their reaction with an olefin).[3,4] At 80°, these reactions are rapid and go to completion within 2 hr. At lower temperatures, the rates are correspondingly slower. These reactions proceed even at room temperature, but 16–18 days are required in order to obtain high product yields.[5]



(1)

X, Y
Cl, Cl
Cl, Br
Br, Br