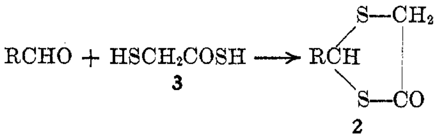
TABLE I

1,3-DITHIOLAN-4-ONE DERIVATIVES


3

2

R	Yield, %	Bp, °C (mm)	Nmr (CCl_4), δ	Element	Calcd, %	Found, %
CH_3	27	85–86 (6)	4.95 (q, 1 H)	C	35.83	35.92
			3.71 (s, 2 H)	H	4.51	4.55
			1.76 (d, 3 H)	S	47.73	47.72
C_2H_5	29	86 (2)	4.74 (t, 1 H)	C	40.54	40.59
			3.63 (s, 2 H)	H	5.44	5.40
			2.28–1.80 (m, 2 H)	S	43.21	43.04
			1.10 (t, 3 H)			
n-C_3H_7	42	96–99 (2)	4.82 (t, 1 H)	C	44.44	44.56
			3.64 (s, 2 H)	H	6.22	6.09
			2.20–1.23 (m, 4 H)	S	39.47	39.54
			0.98 (t, 3 H)			
C_6H_5	31	141–143 (2)	7.60–7.17 (m, 5 H)	C	55.10	55.29
		(mp 50–51)	5.93 (s, 1 H)	H	4.11	4.05
			3.74 (s, 2 H)	S	32.62	32.71

diate, but attempts to isolate **5** resulted in failure. The structures of the products **2** were confirmed with the elemental analyses and nmr spectra presented in Table I. Identification of the products **4** was made by comparison of their physical properties with reported values.[3]

Experimental Section

1,3-Dithiolan-2-one (1).—To a solution of 1,2-ethanedithiol (9.4 g, 0.1 mol) and pyridine (15.8 g, 0.2 mol) in toluene (150 ml), phosgene (9.9 g, 0.1 mol) dissolved in 35 ml of toluene was added at 0°. The mixture was stirred for 3 hr at the same temperature, and precipitated pyridine hydrochloride was filtered off. The filtrate was washed (10% aqueous Na_2CO_3), dried (Na_2SO_4), and distilled. A fraction, bp 78–82° (4 mm), was collected, cooled, and recrystallized from n-hexane to give **1**: mp 34–35° (lit. mp 34°);[1,2] yield 8.1 g (67.5%); nmr (CCl_4) δ 3.69 (s).

Anal. Calcd for $C_3H_4OS_2$: C, 30.01; H, 3.36; S, 53.30. Found: C, 30.03; H, 3.32; S, 53.23.

Mercaptothioacetic Acid (3).—Hydrogen sulfide was passed into a mixture of chloroacetyl chloride (79 g, 0.7 mol) and anhydrous aluminum chloride (2.0 g) at 0° for 30 hr. The reaction mixture was filtered and the filtrate was distilled to obtain chlorothioacetic acid (56.2 g, 72.7%), bp 34–36° (5 mm).

A solution of KOH (90 g) in ethanol (90%, 270 ml) was saturated with H_2S at 0°, and chlorothioacetic acid (30 g, 0.27 mol) was added slowly at about −5°. After KCl was removed by precipitation, the filtrate was concentrated to about 100 ml, acidified with cold 3 N HCl, and extracted with ether. Distillation gave **3**: bp 61–62° (8 mm); yield 24.6 g (84.5%); nmr (CCl_4) δ 5.18 (s, 1 H), 3.60 (d, 2 H), 2.37 (t, 1 H); ir bands at 2550, 1680 cm^{-1}.

Anal. Calcd for $C_2H_4OS_2$: C, 22.23; H, 3.73; S, 59.23. Found: C, 22.45; H, 3.77; S, 58.97.

1,3-Dithiolan-4-one (2).—To a solution of **3** (0.25 mol) and p-toluenesulfonic acid (0.5 g) in benzene (250 ml), aldehyde (0.5 mol) was added slowly at room temperature and stirred for 5 hr. The mixture was then refluxed for 10 hr, the water formed in the reaction being removed continuously by azeotropic distillation, washed (10% aqueous Na_2CO_3), dried (Na_2SO_4), and fractionally distilled to give two fractions and residual tar. The first fraction was the compound **4** (yield 5–15%); the second was redistilled to give **2** (Table I). The ir spectra of **2** showed strong absorption of C=O in the range of 1690–1685 cm^{-1}.

Registry No.—1, 2080-58-2; 2 (R = CH_3), 41755-28-6; 2 (R = C_2H_5), 41755-29-7; 2 (R = n-C_3H_7), 41701-10-4; 2 (R = Ph), 41701-11-5; **3**, 30298-36-3; acetaldehyde, 75-07-0; propionaldehyde, 123-38-6; butyraldehyde, 123-72-8; benzaldehyde, 100-52-7.

Raney Nickel Catalyzed Decarbonylation of Formate Esters

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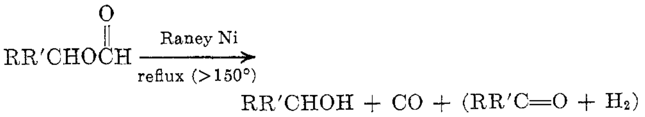
During investigation of a series of formate esters, we had occasion to study the effect of high-temperature treatment in the presence of Raney nickel (activity W2).[1] At reflux the esters were observed to undergo smooth decarbonylation to the corresponding alcohols. Subsequent dehydrogenation to the corresponding aldehydes or ketones also occurred under reaction conditions.[2–5] Typical product distributions for a variety of formate esters are shown in Table I.


$$RR'CHO\overset{O}{\overset{\|}{C}}H \xrightarrow[\text{reflux } (>150°)]{\text{Raney Ni}} RR'CHOH + CO + (RR'C{=}O + H_2)$$

Little reaction was observed below 150°, with rates increasing as the boiling points of the higher formates were approached. As indicated in Table I, conversion of low-boiling esters ($e.g.$, n-hexyl and cyclohexyl for-

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TABLE I

NICKEL-CATALYZED DECARBONYLATION OF FORMATE ESTERS

Registry no.	Compd (solvent)	Wt of ester/ wt of Raney Ni	Reaction temp, °C	Reaction time, hr	Products	Distribution[a]
629-33-4	*n*-Hexyl formate (neat)	25	150–155	30	*n*-Hexyl formate	61
					1-Hexanol	30
					n-Hexaldehyde	9
	n-Hexyl formate (diethoxytetraglycol)	30	230–250	12[b]	*n*-Hexyl formate	42
					1-Hexanol	16
					n-Hexaldehyde	37
					Hexenes	5
4351-54-6	Cyclohexyl formate (neat)	50	155–160	27	Cyclohexyl formate	75
					Cyclohexanol	9
					Cyclohexanone	16
	Cyclohexyl formate (diethoxytetraglycol)	35	230–250	11[b]	Cyclohexyl formate	12
					Cyclohexanol	22
					Cyclohexanone	62
					Phenol	4
41498-71-9	2-*exo*-Norbornyl formate (neat)	50	170–175	19	2-*exo*-Norbornyl formate	41
					2-*exo*-Norbornanol	18
					2-Norbornanone	41
41498-15-1	8-*exo*-Tricyclo$[5.2.1.0^{2,6}]$decyl formate (neat)	37.5	220–230	2	8-*exo*-Tricyclo$[5.2.1.0^{2,6}]$decyl formate	0
					8-*exo*-Tricyclo$[5.2.1.0^{2,6}]$decanol	20
					8-*exo*-Tricyclo$[5.2.1.0^{2,6}]$decanone	75
					Others	5
5331-67-9 (4) 41498-17-3 (5)	8-*exo*-Tricyclo$[5.2.1.0^{2,6}]$dec-4- (or 5-) enyl formate (neat)	50	230–235	3.2	8-*exo*-Tricyclo$[5.2.1.0^{2,6}]$dec-4(5)-enyl formate	9.5
					8-*exo*-Tricyclo$[5.2.1.0^{2,6}]$dec-4(5)-enol	25
					8-*exo*-Tricyclo$[5.2.1.0^{2,6}]$dec-4(5)-anone	62
					Others	13.5
104-57-4	Benzyl formate, 80[c] Benzyl acetate, 8 Benzyl alcohol, 12 (neat)	24	180–190	9	Benzyl formate	18
					Benzyl acetate	11
					Benzyl alcohol	29
					Benzaldehyde	21
					Toluene	19
					Benzene	2
100-51-6	Benzyl alcohol (neat)	20	170–190[d]	15	Benzyl alcohol	15
					Benzaldehyde	14
					Toluene	35
					Benzene	34
					Others	2

[a] Product distribution determined by ir-glc area per cent (see Experimental Section). [b] Total recycle time, not actual contact time. [c] Benzyl formate was prepared by the method of Stevens and Van Es;[18] composition was that obtained in a refined fraction.[a] [d] Reaction temperature was controlled by periodic removal of volatiles. Volatiles were recomposited with product mixture for analysis.

mates) was enhanced by continuously feeding these materials to a suspension of Raney nickel in a high-boiling solvent. The volatile components were flashed overhead and recycled to increase conversion.

It is noteworthy that *n*-hexaldehyde, formed by *in situ* dehydrogenation of 1-hexanol, was not further oxidized to hexanoic acid or decarbonylated to *n*-pentane, even at 230–250°. The only olefinic product observed was a mixture of hexenes, presumably formed by formate pyrolysis.[6] Of further significance was the observation that the double bond in 8-*exo*-tricyclo$[5.2.1.0^{2,6}]$dec-4- (or 5-) enyl formate was not hydrogenated under reaction conditions.[7]

Control experiments indicated that the decarbonylation was specific for formate esters. Cyclohexyl acetate and phenyl acetate were unaffected even after prolonged contact with the catalyst.[8]

These results stand in contrast to the work of Matthews, Ketter, and Hall,[9] who observed that alkyl formates were converted to the corresponding alcohols by treatment with palladium on charcoal. Under these conditions benzyl formate was converted primarily to toluene and carbon dioxide with only small amounts of benzene, benzaldehyde, and benzyl alcohol detected. Raney nickel treatment of refluxing benzyl formate, on the other hand, afforded benzyl alcohol, benzaldehyde, and toluene as the principal products (Table I).

The reaction pathway apparently involved formate decarbonylation to benzyl alcohol, which control experiments indicated then underwent dehydrogenation to benzaldehyde. Measurable amounts of benzene were formed from the subsequent nickel-catalyzed decarbonylation of benzaldehyde.[10,11]

Our data suggest that the formate decarbonylation process need not involve discrete free-radical intermediates. The energetics for homolysis of the formyl

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(8) The stability of phenyl acetate in the presence of Raney nickel obviates the possibility of a hydrolytic pathway resulting from traces of residual caustic in the catalyst. All esters investigated were thermally stable under reaction conditions in the absence of catalyst.

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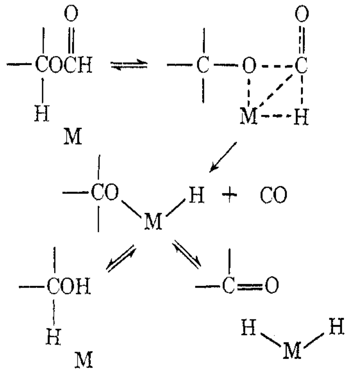
hydrogen bond would be similar to that of aldehydes[12] and would produce the corresponding alkoxycarbonyl radical. Recent investigations indicated that this radical is quite stable at moderate temperatures and undergoes coupling rather than decarboxylation.[13] Loss of CO_2 has been observed[14] in instances where decarboxylation leads to stable alkyl radicals. Products of radical coupling or significant amounts of products derived from loss of CO_2 were not observed under our reaction conditions, even with benzyl formate where substantial driving force for formation of the stable benzyl radical might be expected. As indicated in Table I, toluene was likely formed from hydrogenolysis of benzyl alcohol.

A probable mechanism involves initial cleavage of the ester linkage to yield catalyst-bound alkoxy and carbonyl species. Loss of carbon monoxide would produce an adsorbed alcohol intermediate similar to that proposed for hydrogen–deuterium exchange and oxidation of alcohols over metallic surfaces.[15-17] This intermediate could then partition to either or both alcohol and carbonyl products (Scheme I). The product composition obtained from treatment of formate esters in the presence of Raney nickel is compatible with the intermediacy of highly polar species. The initial ester cleavage likely involves closely bound ionic or radical moieties which are formed *via* electron transfer with the metal surface.

SCHEME I



Experimental Section

Materials.—The chemicals used in this investigation were obtained from suitable commercial sources and checked for purity prior to use or were synthesized using literature methods. Raney nickel was obtained from W. R. Grace, Davison Chemical Division, as Davison Raney nickel, grade 28. The material possessed approximately the same activity as Raney nickel, W2.[1] The following compounds were prepared by the indicated methods and were used as reactants or for comparison purposes: benzyl formate, prepared by the method of Stevens and Van Es;[18] cyclohexyl formate and *exo*-2-norbornyl formate, prepared by addition of formic acid to the corresponding olefins;[19] cyclohexyl acetate, prepared from cyclohexanol by treatment with acetic anhydride–pyridine and product purity confirmed by ir analysis;[20] 8-*exo*-tricyclo[5.2.1.$0^{2,6}$]dec-4- (or 5-) enyl formate and 8-*exo*-tricyclo[5.2.1.$0^{2,6}$]decyl formate, prepared by the method of Bergman and Japhe;[21] and 8-tricyclo[5.2.1.$0^{2,6}$]dec-4- (or 5-) enone, 8-tricyclo[5.2.1.$0^{2,6}$]decanone, and 8-exo-tricyclo[5.2.1.$0^{2,6}$]decanol, prepared by the method of Bruson and Reiner.[22]

Analyses.—Glc analyses were performed on an F & M 5750 chromatograph using both a 10 ft × 0.25 in. stainless-steel column of 15% FFAP on Chromosorb W (60/80 mesh) and a similar column of 10% W-98 on Chromosorb G (60/80 mesh). Individual peaks were identified by comparison with authentic materials and by infrared spectral comparisons[20] of the product mixtures. Further confirmation was provided by nmr spectral analyses.

Typical Procedure.—In a typical experiment, a 50-ml, three-neck flask was equipped with a distillation head with provision for variable take-off, a thermometer, and a nitrogen inlet tube. Weighed amounts of 2-*exo*-norbornyl formate (15 g) and Raney nickel (0.3 g) were added to the flask. The system was maintained under a positive nitrogen pressure and the contents were stirred magnetically and heated to reflux (170–175°). Reaction progress was followed by glc analysis. When heating was discontinued (19 hr), the reaction vessel was allowed to cool and a small amount of filter aid was introduced. The contents of the flask were then collected by suction filtration and subjected to analysis by ir-glc (Table I). Typical material balances ranged from 85 to 97%.

Registry No.—Nickel, 7440-02-0.

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[20] Infrared spectra for comparative purposes were taken from collections of spectra in "Documentation of Molecular Spectroscopy," Butterworths, London, or "Sadtler Standard Spectra," Sadtler Research Laboratories, Inc., Philadelphia, Pa.

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New Lossen Rearrangement Precursors. The Relative Rates of Rearrangement of Nitrophenylbenzhydroxamates in Aqueous Base

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Data in the literature support the theory that the rate of the Lossen rearrangement is directly proportional to the acidity of the leaving group or its conjugate acid where the leaving group is a basic anion.[2-6] However, all of the examples of hydroxamic acid derivatives which have been studied are acylhydroxamates where the leaving group is a carboxylic acid or its conjugate base. Therefore, the data available to test this theory are limited to a relatively narrow range of acidities ($pK_a = 2–5$) for the leaving group or its conjugate acid. The objective of this study was to prepare Lossen rearrangement precursors where the conjugate acids of the basic anion leaving groups have pK_a values >5 in order to test the classical theory over

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[2] R. D. Bright and C. R. Hauser, *J. Amer. Chem. Soc.*, **61**, 618 (1939).

[3] W. B. Renfrow, Jr., and C. R. Hauser, *J. Amer. Chem. Soc.*, **59**, 2308 (1937).

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[5] C. Walling and A. N. Naglieri, *J. Amer. Chem. Soc.*, **82**, 1820 (1960).

[6] D. C. Berndt and H. Shechter, *J. Org. Chem.*, **29**, 916 (1964).