

aldehydes at elevated temperature.⁴ When the tosylhydrazone of 2,3-dimethyl-2-butenal (VIII) was added to a solution of sodium methoxide in diglyme at 150°, 1,3,3-trimethylcyclopropene (V) was obtained in 72% yield. Similarly, the tosylhydrazone of 3-methyl-2-butenal (IX) decomposed under the same conditions to 3,3-dimethylcyclopropene (VI) (b.p. 14°) in 28% yield (based on aldehyde). The structure of VI follows from its hydrogenation to 1,1-dimethylcyclopropane and from the n.m.r. spectrum which exhibits a triplet at 9.07 τ and a septuplet at 3.00 τ ($J = 0.7$ c.p.s.) with the expected intensities for resonance of the *gem*-dimethyl and olefinic protons, respectively.

The fact that the three known methods for the preparation of alkylcarbenes^{2,4,5} lead to the formation of cyclopropenes when extended to the corresponding alkenyl derivatives constitutes a convincing argument for the intermediacy of alkenylcarbenes in these cyclopropene syntheses. Apparently the loss in resonance energy of the carbenes connected with the rotation of the *gem*-dimethyl group is not a prohibitive barrier for ring closure. Non-bonded interactions between adjacent methyl groups in III favor the rotation and probably account for the better yield of cyclopropene formation than from carbene IV in which non-bonded interactions are less serious.

(4) L. Friedman and H. Shechter, *J. Am. Chem. Soc.*, **81**, 5512 (1959); **82**, 1002 (1960).

(5) G. L. Closs, Abstracts of Papers of the 138th Meeting of the American Chemical Society, New York, N. Y., September, 1960, p. 9-P.

DEPARTMENT OF CHEMISTRY
THE UNIVERSITY OF CHICAGO
CHICAGO 37, ILLINOIS

G. L. CLOSS

L. E. CLOSS

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THE REACTION OF 1-ACYLAZIRIDINES WITH LITHIUM ALUMINUM HYDRIDE—A NEW ALDEHYDE SYNTHESIS

Sir:

The reactions of lithium aluminum hydride with *N*-methylanilides,¹ *N*-acylcarbazoles² and 1-acyl-3,5-dimethylpyrazoles³ have been utilized as a synthetic route from carboxylic acids to aldehydes. In the course of investigating the reaction of lithium aluminum hydride with a number of amide derivatives, we observed that the 1-acylaziridines possess highly unusual characteristics. Thus these derivatives exhibit a shift in the carbonyl stretching frequency from 1631–1667 cm^{-1} , characteristic of most tertiary amides, to 1730 cm^{-1} . Such a shift suggests that there is little conjugation within the amide group as contrasted with the usual tertiary amide. The high reactivity suggested by the infrared shift is confirmed by the remarkably high yield of aldehyde, 88%, realized in treating a typical derivative, 1-butyrylaziridine, with lithium aluminum hydride (Table I).

The low reactivity of the diisopropylamide suggests that this may be a useful blocking group in hydride reductions.

(1) F. Weygand, *et al.*, *Angew. Chem.*, **66**, 525 (1953).

(2) F. Wittig and P. Hornberger, *Ann.*, **577**, 11 (1952).

(3) W. Ried and F. J. Königstein, *Angew. Chem.*, **70**, 165 (1958).

The high aldehyde yields from 1-*n*-butyrylaziridine led us to explore the applicability of this reaction for a general aldehyde synthesis. It was established that the 1-acylaziridines need not be isolated, but could be synthesized in ether solution by adding the acid chloride to an equimolar mixture of ethylenimine and triethylamine at 0°. The precipitated triethylammonium hydrochloride is

TABLE I

THE REDUCTION OF *n*-BUTYRYLAMIDES BY LITHIUM ALUMINUM HYDRIDE AT 0°

A solution of lithium aluminum hydride in ether was added to a stirred solution of the tertiary amide ($1\text{LiAlH}_4/4 n\text{-C}_3\text{H}_7\text{CONR}_2$) over 30 minutes at 0°. The mixture was permitted to stir for a further hour, hydrolyzed, and the aldehyde yield determined as the 2,4-dinitrophenylhydrazone.

Amide	Yield of <i>n</i> -butyraldehyde, %
$n\text{-C}_3\text{H}_7\text{CONMe}_2$	25
$n\text{-C}_3\text{H}_7\text{CONEt}_2$	22
$n\text{-C}_3\text{H}_7\text{CON}i\text{-Pr}_2$	No reaction
$n\text{-C}_3\text{H}_7\text{CONMePh}$	58
$n\text{-C}_3\text{H}_7\text{CON}(\text{CH}_2)_3$	33
$n\text{-C}_3\text{H}_7\text{CON}(\text{CH}_2)_4$	16
$n\text{-C}_3\text{H}_7\text{CON}(\text{CH}_2)_2$	88

removed and the lithium aluminum hydride is added. The reaction appears to be quite insensitive to the amount of hydride utilized, since comparable results were realized with the theoretical quantity of lithium aluminum hydride ($\text{LiAlH}_4 + 4\text{RCON}(\text{CH}_2)_2$) or with 100% excess (Table II).

TABLE II

YIELDS OF ALDEHYDE FROM ACID CHLORIDES *via* THE 1-ACYLAZIRIDINES

Acid chloride	Yield of aldehyde, %
<i>n</i> -Butyryl	75, 74 ^a
<i>n</i> -Caproyl	81
2-Ethylhexanoyl	77
Pivaloyl	79, 88 ^a
Cyclopropanecarbonyl	67

^a Lithium aluminum hydride was added in 100% excess over the acid chloride utilized.

A typical procedure is given. Cyclopropanecarbonyl chloride (42.2 g., 0.40 mole) was added over a period of one hour to a stirred solution of ethylenimine (17.5 g., 0.40 mole) and triethylamine (40.0 g., 0.40 mole) in 200 ml. of ethyl ether under cooling by an ice-salt mixture. The reaction mixture was stirred for an additional 0.5 hour and precipitated triethylamine hydrochloride was filtered off and washed with 100 ml. of ether. The combined ether solution was cooled to 0° and 80 ml. of 1.25 *M* lithium aluminum hydride in ether was added to the stirred solution over 0.5 hour. After an additional hour, cold 5 *N* sulfuric acid was added, the ether layer was separated, and the aqueous layer extracted. The combined ether extracts were washed with water, sodium

bicarbonate, water again, and dried over sodium sulfate. Analysis of an aliquot with 2,4-dinitrophenylhydrazine indicated a yield of 67%. Distillation yielded 16.8 g. of cyclopropanecarboxaldehyde, b.p. 97–100° at 740 mm., n_D^{20} 1.4302, a yield of 60%.

The reduction of acid chlorides by lithium tri-*t*-butoxyaluminumhydride provides a convenient route to aldehydes that is especially valuable for aromatic derivatives.⁴ The present procedure, as well as the reduction of dimethylamides by lithium di-⁵ or triethoxyaluminumhydride,⁶ appears to be particularly valuable for the conversion of aliphatic acid derivatives into the corresponding aldehydes.

Acknowledgment.—We are indebted to the Eli Lilly Company for a research grant which made this investigation possible.

(4) H. C. Brown and R. F. McFarlin, *J. Am. Chem. Soc.*, **80**, 5372 (1958); H. C. Brown and B. C. Subba Rao, *ibid.*, **80**, 5377 (1958).

(5) H. C. Brown and A. Tsukamoto, *ibid.*, **81**, 502 (1959).

(6) A. Tsukamoto, Ph.D. Thesis, Purdue University Libraries, (1959).

RICHARD B. WETHERILL LABORATORY
PURDUE UNIVERSITY
LAFAYETTE, INDIANA

HERBERT C. BROWN
AKIRA TSUKAMOTO

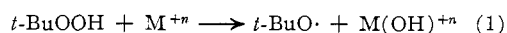
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METAL ION-FREE RADICAL REACTIONS: COUPLING OF FREE RADICALS

Sir:

The use of metal ions and complex metal ions in influencing the course of organic reactions has been of considerable chemical importance; the mechanisms of the role of metal ions in these reactions, however, has been little understood. Initially, we have been exploring the realm of the interaction of metal ions with organic free radical intermediates.¹

We wish to report the application of metal ions in inducing the mutual interaction of free radicals. In particular we have studied the increase in the frequency of coupling of methyl radicals in the presence of certain metal ions in aqueous solution. Methyl radicals were produced at 25° from the reaction of *tert*-butyl hydroperoxide with a reducing metal ion by reactions (1) and (2)



If titanous chloride is the initial reducing agent the relative yields of ethane and methane in the presence of various added metal ions are given in Table I.

This table shows that ions of Co, Mn and particularly Ni are effective in inducing the dimerization of methyl radicals to ethane and in decreasing concomitantly the yield of methane.

In a similar manner if ferrous sulfate is used as reducing agent a relatively high ethane to methane ratio is obtained as shown in Table II. This indi-

(1) J. Kumamoto, H. E. De La Mare and F. F. Rust, *J. Am. Chem. Soc.*, **82**, 1935 (1960); J. Kochi, *ibid.*, **78**, 4815 (1956).

TABLE I

Added ions	M^a	$\text{C}_2\text{H}_6/\text{CH}_4$	Yield of CH_4 , % ^b
None	..	0.33	52
H_2SO_4	0.12	.28	49
MgSO_4	.08	.29	45
LiCl	.16	.22	52
MnSO_4	.08	.95	47
CoCl_2	.08	.95	45
NiCl_2	.08	4.9	53
NiSO_4	.08	4.5	49
PtCl_4	.04	^c	..
CuCl_2	.08	^c	..

^a To approximate constant ionic strength. As methane and ethane. ^c Product is methyl chloride.

cates that iron is as effective as the salts of manganese, cobalt, and nickel in diverting the methyl radicals to ethane formation. The addition of fluoride ion to complex the iron causes a decrease in the yield of ethane relative to methane.

TABLE II

Ammonium fluoride, M	$\text{C}_2\text{H}_6/\text{CH}_4$
None	4.9
0.055	1.7
.166	0.85
.332	.27
.650	.17

These results indicate that certain ions, particularly those of the transition series, namely, Mn, Fe, Co, Ni, are effective in promoting the dimerization of methyl radicals. We also have observed a similar behavior of ethyl radicals derived from *tert*-amyl hydroperoxide, in which both dimerization and disproportionation are increased in the presence of these metal ions. This effect is illustrated in Table III.

TABLE III

Added ion	$n\text{-C}_4\text{H}_{10}/\text{C}_2\text{H}_6$	$\text{C}_2\text{H}_4/\text{C}_2\text{H}_6$
None	0.27	0.071
CoSO_4	1.05	.13
NiSO_4	1.17	.20

There are several possible interpretations for the phenomena observed here. We prefer to postulate the process as proceeding through a *metal ion-free radical complex* of relatively longer life than a simple alkyl radical. The greater stability of the alkyl moiety in such a complex would allow the ethane formation by a second order dimerization process to be more probable than with a simple methyl radical. Similarly its reactivity with respect to hydrogen abstraction to produce methane would be diminished.

