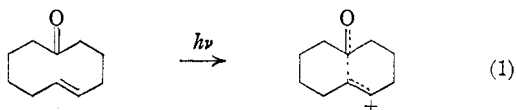


the shift should be to longer wave lengths, it seems likely that the repulsion between the filled π -orbital of the double bond and the π^* -electron of the $n \rightarrow \pi^*$ -excited state is greater than the lowering (of E_3 , cf. ref. 3) achieved by interaction of the π^* -electron with the π^* -orbital of the double bond. A shift which may be similar has been observed for bicyclohepten-7-one.¹³

It may be noted in the figure that a shoulder on the high intensity absorption in isoöctane shifts to longer wave lengths in the more polar solvent, TFP, and, in fact, appears as a maximum.¹⁴ The solvent effect on the maximum demonstrates that the excited state is considerably more polar than the ground state since the absorption band present at ca. 2050 Å. in isoöctane shifts to 2145 Å. in TFP. This absorption region is thus identifiable as that arising from the photodesmotic transition (eq. 1).



The shorter wave length absorption is due to a combination of an $n \rightarrow \sigma^*$ -transition of the carbonyl¹⁵ and the $\pi \rightarrow \pi^*$ -transition of the double bond.¹⁶ The decrease in intensity in this region for the change in solvent from isoöctane to TFP (at 1880 Å., $\Delta\epsilon$ is 1200) corresponds quite closely to the change in intensity observed for acetone at 1900 Å. with a solvent change from isoöctane to water (Z 94.6).¹¹ It has been reported that cyclohexene has a maximum at 1833 Å. (ϵ 7500) in hexane,¹⁷ while there is relatively little difference between the maximal positions for *cis*- and *trans*-2-butenes.¹⁸

A convincing demonstration of a photodesmotic transition using solvent effects was given recently by Leonard, Milligan, and Brown¹⁹ for 1-thiacyclooctan-5-one. It is worthy of note that the adsorption intensity observed for the PD transition of the thia ketone in cyclohexane (2500) is very close to that for the PD transition of the *trans*-cyclo-decane in isoöctane (2300).

(13) C. J. Norton, Ph.D. Dissertation, Harvard University, quoted in ref. 4.

(14) Acetonitrile and methanol exhibit intermediate behavior (as expected) which will be illustrated in a full paper.

(15) Certain observations by W. Simpson have suggested that this transition might actually be $n_2 \rightarrow \pi^*$; M. Kasha, personal communication.

(16) Both of these transitions would be changed in energy according to the theory of ref. 3; since our experiments cannot evaluate this possibility, we refer to them as transitions in the isolated groups.

(17) D. W. Turner, *J. Chem. Soc.*, 30 (1959).

(18) J. T. Gary and L. W. Pickett, *J. Chem. Phys.*, **22**, 599 (1954).

(19) N. J. Leonard, T. W. Milligan and T. L. Brown, *J. Am. Chem. Soc.*, **82**, 4075 (1960).

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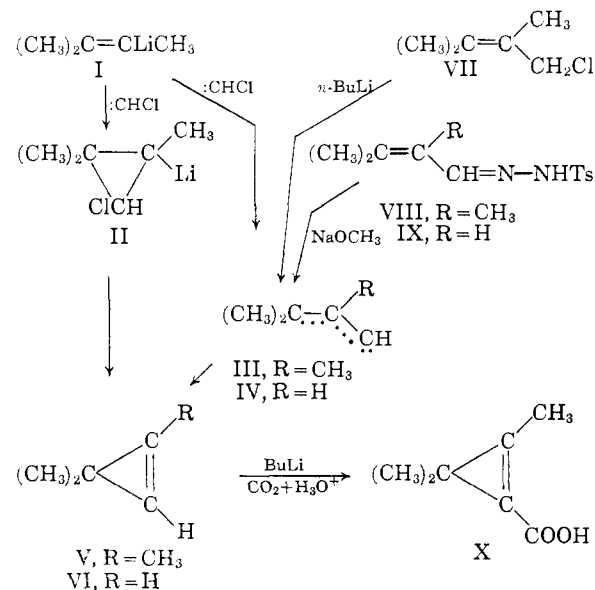
ALKENYL CARBENES AS PRECURSORS OF CYCLOPROPENES

Sir:

Recently we reported a novel synthesis of cyclopropenes based on the reaction of 1,2-dimethyl-

propenyllithium (I) with methylene chloride.¹ Two mechanisms were advanced, both capable of explaining the formation of 1,3,3-trimethylcyclopropene (V) under these conditions: chlorocarbene, generated from methylene chloride and alkenyllithium compound I, was postulated to add to the π -electrons of I to form the hypothetical intermediate II, or to react with the non-bonding electrons of the incipient carbanion of I to yield alkenylcarbene III. Intermediate II could give the observed cyclopropene V by β -elimination of lithium chloride, while alkenylcarbene III can be visualized to cyclize to the same product by rotation of the *gem*-dimethyl group through 90°. The concept that alkenylcarbenes might serve as precursors of cyclopropenes is an intriguing one and led to further investigations.

Attempting the formation of an alkenylcarbene by a more direct route, *n*-butyllithium was added to a solution of 1-chloro-2,3-dimethyl-2-butene (VII) in tetrahydrofuran at -15°. Carbonation and acidification of the reaction mixture yielded 16% of 2,3,3-trimethylcyclopropene-1-carboxylic acid (X), identical in all properties with a previously prepared sample.¹ This result is difficult to explain without invoking the alkenylcarbene intermediate III, generated by α -elimination of hydrogen chloride from VII.² Cyclization of the carbene



leads to V which is converted to 2,3,3-trimethylcyclopropenyllithium on reaction with *n*-butyllithium.³ Carboxylation of the latter gives X.

Another route which appeared to be promising for the preparation of alkenylcarbenes is the base catalyzed decomposition of tosylhydrazones of

(1) G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **83**, 1003 (1961).

(2) For recent examples of α -elimination on alkyl halides under the influence of organo-alkali compounds see: W. Kirmse and W. v. E. Doering, *Tetrahedron*, **11**, 266 (1960); G. L. Closs and L. E. Closs, *Tetrahedron Letters*, **24**, 26 (1960); L. Friedman and J. G. Berger, *J. Am. Chem. Soc.*, **82**, 5758 (1960); **83**, 492 (1961); **83**, 500 (1961).

(3) About the acidity of the olefinic hydrogens in cyclopropenes see: K. B. Wiberg, R. K. Barnes and J. Albin, *ibid.*, **79**, 4994 (1957); and ref. 1.

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.

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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
$n\text{-C}_3\text{H}_7\text{CON}(\text{CH}_2)_5$	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