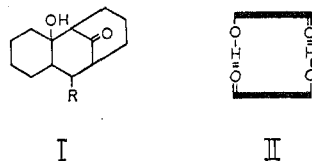


Figure 1.—Concentration dependence of the apparent molar extinction coefficients of compound I, R = CH₃. Carbon tetrachloride solutions at 30°: values observed at 3604 cm⁻¹, ●; at 3395 cm⁻¹, ○. Lines A and B represent the corresponding calculated values for monomer-dimer equilibrium [$K_{\text{dimer}} = 58 \text{ l. mol}^{-1}$ ($\epsilon_{\text{monomer}} 112$ at 3604 cm⁻¹; $\epsilon_{\text{dimer}} 316$ at 3395 cm⁻¹ and 25 at 3604 cm⁻¹)].

tion for the monomer species with data of Joris and Schleyer¹ gives additional support for the axial position of the hydroxy group. Last, but not least, the stereochemistry of the system I was studied independently by different methods with the same results (*cf.* ref 11 and references therein; also ref 7, p 189).

The dimerization constant of I (58 l. mol⁻¹) is an order of magnitude higher than that of *t*-butyl alcohol¹⁰ (0.8 l. mol⁻¹) or the association constant of *t*-butyl alcohol-acetone¹² (1.0 l. mol⁻¹); nevertheless, it is lower



than the dimerization constant of *n*-nonanoic acid¹³ (1500 l. mol⁻¹, all data at 30° and in CCl₄ solutions). In the case of I no special forces can be invoked to assist dimerization, such as resonance effects in carboxylic acids or diols¹⁴ or π - π interaction in hydroxyacetophenones.⁵ The only possible factor is the steric arrangement which allows the simultaneous formation of two hydrogen bonds in the dimer II. In line with that interpretation all six known derivatives of type I give the same pattern.^{2,3} It may be pointed out that in all these compounds the cyclohexane rings probably have a slightly distorted chair conformation.^{15,16} Further, relatively strong and broad bands around 3400 cm⁻¹ were observed for dilute solutions (around $5 \times 10^{-3} \text{ M}$; *cf.* ref 15) of the following compounds:

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(15) G. Eglinton, J. Martin, and W. Parker, *J. Chem. Soc.*, 1243 (1965).

(16) W. A. C. Brown, G. Eglinton, J. Martin, W. Parker, and G. A. Sim, *Proc. Chem. Soc. London*, 57 (1964).

hydroxy-2-butanone¹⁷ (also alleged to be¹ a carbonyl overtone), and decalone and cholestane derivatives containing a cyclohexanone moiety with an axial β -hydroxy group.¹⁸ These substances may constitute a new class of strongly self-associating compounds.⁵

Registry No.—I (R = Me), 1614-94-4.

Acknowledgment.—The author wishes to thank Drs. G. L. Eichhorn, J. J. Butzow, and C. H. Robinson for helpful comments.

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Synthesis of Allenic Acetals from Unsaturated Carbenes¹

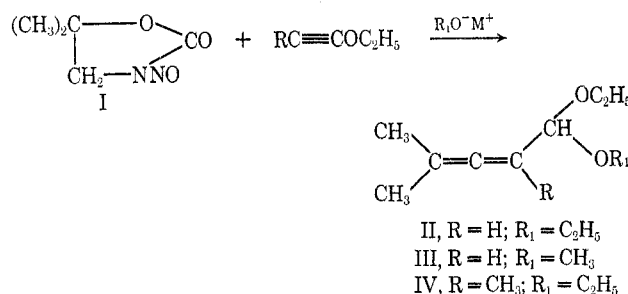
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Dihalocarbenes² and carbethoxycarbene³ react less easily with acetylenes than with olefins. We undertook this study to see if unsaturated carbenes^{4,5} could add to acetylenes, since substituted methylenecyclopropenes might thus be synthesized.

On treatment of a solution of ethoxyacetylene and 5,5-dimethyl-N-nitrosooxazolidone (I)⁵ in 1,2-dimethoxyethane (glyme) with solid lithium ethoxideacetate,⁶ the theoretical amount of nitrogen was rapidly evolved. By suitable procedures 4-methyl-2,3-pentadienyl diethyl acetal (II) was isolated in 35% yield.



When sodium methoxide was used instead of lithium ethoxide, the mixed ethyl methyl acetal III was formed in 33% yield. In addition to the allenic acetals II and III, there was formed a mixture of higher boiling products which on alkaline hydrolysis yielded quantities of

(1) This research was supported by Special Fund (178107) of The Ohio State University and Grant 5552 of The National Science Foundation.

(2) W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964, p 177.

(3) I. A. D'yakonov, R. N. Gmyzina, and L. P. Danilkina, *J. Org. Chem. USSR*, **2**, 2038 (1966).

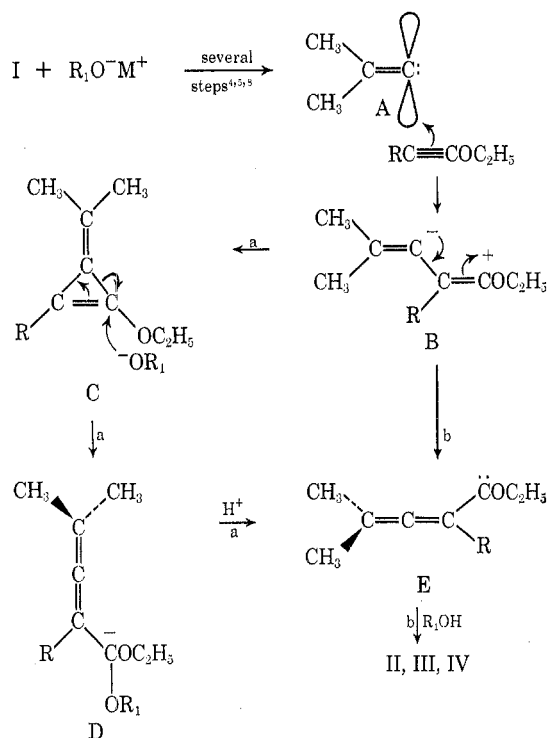
(4) M. S. Newman and A. O. M. Okorodudu, *J. Org. Chem.*, **34**, 1220 (1969).

(5) M. S. Newman and T. B. Patrick, *J. Amer. Chem. Soc.*, **91**, 6461 (1969).

(6) W. M. Jones, M. H. Grasley, and W. S. Brey, Jr., *ibid.*, **85**, 2754 (1963).

2-methyl-1,2-propanediol as previously described.⁵ When 1-ethoxypropyne⁷ was used in place of ethoxyacetylene, a 37% yield of 2,4-dimethyl-2,3-pentadienal diethyl acetal (IV) was obtained. Thus, a new route to allenic acetals is at hand.

In line with a previous suggestion⁵ for the mechanism of reaction of an unsaturated carbene with olefins, the following mechanism for the reaction of unsaturated carbenes with alkoxyacetylenes is proposed.



The vacant orbital on the carbene carbon of A lies in the plane of the paper as represented. We assume that electrophilic attack⁹ by A occurs on the nonoxygenated carbon of the ethoxyacetylene to yield B which then proceeds by paths a or b to the allenic product.⁹ Cyclization (path a) would lead to a methylenecyclopropene C so labile that attack of alkoxide ion as shown¹⁰ would be expected to yield D which on protonation yields the allenic acetals II, III, or IV. Alternately, rehybridization of the dipolar ion B (path b) could yield the carbene E which would react with an alcohol to give the final acetal II, III, or IV. The changes of B to C and B to E involve different geometrical paths. We cannot suggest which change is more favorable but prefer that which leads to E because this path does not require a ring closure followed by re-opening.

Attempts to react I with 3-hexyne under similar conditions were unsuccessful.

(7) D. G. Farnum, M. A. T. Heybey, and B. Webster, *J. Amer. Chem. Soc.*, **86**, 673 (1964).

(8) M. S. Newman and A. O. M. Okorodudu, *ibid.*, **90**, 4189 (1968).

(9) Other mechanisms may be written but, as crucial experiments have not been conceived, only the two paths shown are discussed.

(10) Some cases where bases have been shown to add to cyclopropenes are K. B. Wiberg, R. K. Barnes, and J. Albin, *J. Amer. Chem. Soc.*, **79**, 4994 (1957); T. C. Shields and P. D. Gardner, *ibid.*, **89**, 5425 (1967); G. L. Closs in "Advances in Alicyclic Chemistry," Vol. I, H. Hart, and G. J. Karabatsos, Ed., Academic Press, New York, N. Y., 1966, p 83.

Experimental Section¹¹

4-Methyl-2,3-pentadienal Diethyl Acetal (II).—To a stirred solution of 10 g (0.07 mol) of I¹ in 100 ml of glyme and 24.5 g of ethoxyacetylene¹² at room temperature was added in four portions 8 g (0.08 mol) of solid lithium ethoxide ethanolate.⁸ The theoretical amount of nitrogen was evolved during 1 hr, cooling being necessary to keep the temperature near 40°. After pouring the reaction mixture onto ice a conventional work-up yielded 3.93 g (35%) of II as a pale yellow liquid, bp 72–77° at 16 mm (94% pure by glpc). The analytical sample was obtained by preparative glpc on a 12 ft \times $\frac{3}{8}$ in. aluminum column packed with 12% Carbowax 20M on 60–80 Chromosorb W at 120° using a helium flow of 100 ml/min. The infrared spectrum had a characteristic allene band at 1992 cm^{-1} (5.0 μ) and acetal bands at 1160 cm^{-1} (8.6, 9.3 μ). The nmr showed a complex multiplet at δ 4.77 (2 H, vinyl H and acetal H, AB pattern ($J \sim 8-10$ cps), the A part being further coupled with the vinyl methyl groups ($J \sim 3$ cps), a complex multiplet at δ 3.48 (4 H, OCH_2CH_3),¹³ singlets at 1.83 and 1.80 (6 H, vinyl CH_3 , $J \cong 3$ cps), and a triplet at 1.17 (6 H, OCH_2CH_3). The parent peak in the mass spectrum (70 eV) was at 170, mol wt 170.

Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.6; H, 10.6. Found: C, 70.5; H, 11.0.

A sample of II was prepared from 1-bromo-3-methyl-1,2-butadiene¹⁴ via the Grignard reagent reaction with ethyl orthoformate.¹⁵ The crude reaction product (28% yield, bp 63–80° at 17 mm) was separated into two components (4:1) by preparative glpc. The major component proved to be identical with II as shown by ir and nmr spectra, and retention time on glpc analysis.

After heating a solution of II in 3:1 water-glyme containing a small amount of sulfuric acid at 90° for 90 min, a small amount of 4-methyl-3-ketovaleraldehyde was isolated by preparative glpc. This compound proved identical with authentic ketoaldehyde prepared by acylation of methyl isopropyl ketone with ethyl formate as described.¹⁶

4-Methyl-2,3-pentadienal Ethyl Methyl Acetal (III).—This compound was prepared in 33% yield as described for II except that dry sodium methoxide was used in place of lithium ethoxide. The crude product, bp 65–70° (15 mm), was purified by preparative glpc to yield the analytical sample: ir band at 5.0 μ ; nmr δ 4.77 (m, 2 H, $=CH$, $CH(OR)_2$), 3.48 (m, 2 H, OCH_2R), 3.22 (s, 3 H, OCH_3), 1.73, 1.66 (two broadened singlets, 6 H, $=C(CH_3)_2$), 1.17 (t, 3 H, OCH_2CH_3).

Anal. Calcd for $C_9H_{16}O_2$: C, 69.2; H, 10.3. Found: C, 68.9; H, 10.6; parent peak (mass spectrum, 70 eV) m/e 156, mol wt 156.

2,4-Dimethyl-2,3-pentadienal Diethyl Acetal (IV).—A solution of I in glyme and excess 1-ethoxypropyne⁷ was treated with lithium ethoxide ethanolate⁸ as described for the synthesis of II. There was obtained in 37% yield a pale yellow oil, bp 79–84° (12 mm), which was about 95% pure by glpc. The analytical sample, obtained by preparative glpc, had an ir band at 5.0 μ and nmr bands at δ 5.73 (s, 1 H, $CH(OR)_2$), 3.42 (m, 4 H, OCH_2CH_3), 1.67 (s, 6 H, $=CCH_3$), 1.52 (s, 3 H, $=CCH_3$), 1.13 (t, 6 H, OCH_2CH_3 , $J = 7$ cps).

Anal. Calcd for $C_{11}H_{20}O_2$: C, 71.6; H, 10.9. Found: C, 71.5; H, 11.1; parent peak (mass spectrum, 70 eV) 184, mol wt 184.

Registry No.—II, 6136-99-8; III, 24472-13-7; IV, 24472-14-8.

(11) All temperature readings are uncorrected; microanalysis are by the Galbraith Laboratories, Knoxville, Tenn. Nmr spectra in CCl_4 relative to $(CH_3)_4Si$ were taken on a Varian A-60 instrument. Analytical glpc were performed on a 6 ft by $\frac{1}{8}$ in. aluminum column packed with 7% Carbowax 20M on 60–80 mesh Chromosorb W.

(12) Obtained from the Farchan Research Laboratories, Willoughby, Ohio.

(13) For explanation of ABC₂ pattern see P. R. Shafer, D. R. Davis, A. Vogel, and J. D. Roberts, *Proc. Nat. Acad. Sci. U. S. A.*, **47**, 49 (1961).

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