

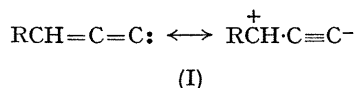
Novel Insertion Reactions of Vinylidene-carbenes into Carbon-Hydrogen and Silicon-Hydrogen Bonds

By J. CYMERMAN CRAIG* and CHARLES D. BEARD

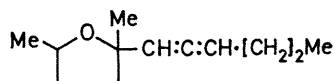
(Department of Pharmaceutical Chemistry, University of California, San Francisco, California 94122)

Summary n-Alkylvinylidene-carbenes generated from 1-bromo-1,2-dienes and KOBU^\dagger insert into the Si-H bond of triethylsilane, into the C-H bond α to oxygen in 2,5-dimethyltetrahydrofuran, and into the C-H bond α to hydroxy in primary alcohols.

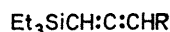
INSERTION of a variety of carbenes into carbon-hydrogen¹ and silicon-hydrogen² bonds, usually regarded as proceeding by a three-centred mechanism,¹ is well established; yet to our knowledge an unequivocal example of this phenomenon has not previously been reported for the zwitterion-carbene (I).[†]



Generation of (I) by reaction of 1-bromohexa-1,2-diene and KOBU^\ddagger in the presence of an excess of 2,5-dimethyltetrahydrofuran (DMTHF) in refluxing benzene gave a 3% yield of (II):[‡] i.r. (neat) ν_{max} 1960 cm^{-1} ; n.m.r. (CDCl_3) δ 5.18 (m, 2H, $\text{CH}=\text{C}=\text{CH}$), 4.07 (m, 1H, H-C-O), and 2.4–0.8 p.p.m. (broad m, 17H, C-H); mass spectrum, M^+ 180. Similarly the allenyl silanes (IIIa) and (IIIb) were obtained in 33 and 29% yield from triethylsilane, KOBU^\ddagger , and the appropriate 1-bromo-1,2-diene in benzene. Spectral properties for (IIIb) are as follows: i.r. (neat) ν_{max} 1950 cm^{-1} ; n.m.r. (CDCl_3) δ 4.86 (m, 2H, $\text{CH}=\text{C}=\text{CH}$), 1.60 (m,



(II)

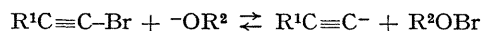


(III) a; R = $[\text{CH}_2]_2\text{Me}$
b; R = Me

3H, $=\text{C}-\text{CH}_3$), and 1.4–0.4 p.p.m. (m, 15H, C-H); mass spectrum, M^+ 168. Both reactions can reasonably be interpreted as insertions of (I) into these particularly reactive single bonds.^{1,2}

Evidence was presented in the preceding communication⁶ that 1-bromo-alk-1-yne are also precursors of (I), perhaps by rearrangement to the isomeric 1-bromo-1,2-diene. A comparison of the reactions of 1-bromohex-1-yne and 1-bromohexa-1,2-diene with the sodium salts of 2-methoxyethanol, 3-methoxypropan-1-ol, and n-butanol in refluxing benzene showed similar product distributions as expected for a common intermediate. Yields were generally lower with bromoalkynes probably because of competing nucleophilic attack on bromine (Table).⁸ Four products were obtained, three of which have been attributed to the reaction of the ambident electrophile (I) with alcohol (alkoxide) and to prototropic shifts, *i.e.*, $\text{R}^1\text{OCH}=\text{C}=\text{CHR}^2$ (V), $\text{R}^1\text{OCH}_2\text{C}\equiv\text{CR}^2$ (VI), and $\text{R}^1\text{OCH}(\text{C}\equiv\text{CH})\text{R}^2$ (VII).⁶ The major product in all these reactions, however, was the allenic alcohol (IV).

Two plausible pathways other than insertion for the formation of (IV) were considered and rejected as follows: (A) a Wittig⁷ type rearrangement of one of the ethereal products (V), (VI), or (VII); however, treatment of pure samples of each under the reaction conditions, with KOBU^\ddagger in toluene, or n-butyl-lithium in refluxing THF failed to effect a rearrangement; (B) positive bromine in 1-bromo-alk-1-yne is a potential oxidant and treatment with alkoxide could establish an equilibrium condition.⁸



Oxidation of the original alcohol to aldehyde followed by reaction with (I) or acetylide ion (with subsequent rearrangement) is possible as is attack by (I) at the α -methylene of the

[†] Three-centred mechanisms have been suggested as possibilities in reactions with dimethylmalonate³ and 2-methylbut-3-yne-N-methylcarbamate;⁴ however, nucleophilic attack of the corresponding anion on the ambident electrophile (I) seems more likely.

[‡] Satisfactory analytical and spectral data were obtained for the compounds reported herein.

postulated hypobromite (or its anion). Neither of these pathways should be favourable when bromodienes are employed and in fact the ratio of products was unchanged

be found in the reported insertion of methoxycarbonylmethylene into the tertiary C-H bond of propan-2-ol (9%).⁹ Products which could be attributed to insertion at other

TABLE

(IV)	R ¹ CH(OH)-CH=C=CHR ² (IV)		% Yield of (IV) (yield of total products) ^a	
	R ¹	R ²	From R ² C≡CBr	From R ² CH=C=CHBr
(a)	$\overline{\text{CH}\cdot\text{O}\cdot\text{CMe}_2\cdot\text{O}\cdot\text{CH}_2}$	-(CH ₂) ₃ Me	8(14)	—
(b)	-CH ₂ OMe	-(CH ₂) ₂ Me	9(15)	13(26)
(c)	-(CH ₂) ₂ OMe	-(CH ₂) ₂ Me	4(7)	5(12)
(d)	-(CH ₂) ₃ Me	-(CH ₂) ₂ Me	4(8)	6(13)

^a Yield of total products (IV, V, VI, and VII) resulting from reaction of (I) with alcohol or alkoxide.

while the yield doubled. Preliminary interconversion is unlikely, as g.l.p.c. showed the reaction with bromodiene to be complete within 5 min., whereas the bromoacetylene reaction was less than 1% complete in the same time. Adding n-butyraldehyde to several of the reactions produced no crossover product nor did it increase the yield of (IVd) in the case of n-butanol, offering further evidence against an aldehyde intermediate.

The absence of alternative explanations prompts us to suggest insertion of the carbene into the C-H bond of the carbon atom bearing the hydroxy-group. An analogy may

positions were not observed while ethers other than DMTHF were unreactive under these conditions (*e.g.*, 1,2-dimethoxyethane, tetrahydrofuran). The unique zwitterion-carbene electronic structure of (I) may facilitate hydrogen bonding between the alcohol and C-1 of the carbene and perturb the relative rates of C-H or O-H attack. Space-filling molecular models reveal that in the postulated hydrogen-bonded arrangement, the empty orbitals at C-1 of the carbene (assuming *sp*-hybridization) indeed are located in close proximity to the C-H bond in question.

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¹ W. Kirmse, "Carbene Chemistry," Academic Press, New York, 1964, ch. 2; D. Seyferth, J. M. Burlitch, K. Yamamoto, S. S. Washburne, and C. J. Attridge, *J. Org. Chem.*, 1970, **35**, 1989.

² M. S. Newman and C. D. Beard, *J. Amer. Chem. Soc.*, 1969, **91**, 5677; D. Seyferth, R. Damrauer, J. Mui, and T. F. Jula, *ibid.*, 1968, **90**, 2944.

³ V. J. Shiner and J. S. Humphrey, *J. Amer. Chem. Soc.*, 1967, **89**, 622.

⁴ J. D. Remwick, *Chem. and Ind.*, 1966, 1637.

⁵ S. R. Landor and P. F. Whiter, *J. Chem. Soc.*, 1965, 5625.

⁶ J. C. Craig and C. D. Beard, preceding communication.

⁷ D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, 1965.

⁸ G. R. Ziegler, C. A. Welch, C. E. Orzech, S. Kikkawa, and S. I. Miller, *J. Amer. Chem. Soc.*, 1963, **85**, 1648. J. F. Arens, *Rec. Trav. chim.*, 1963, **82**, 183.

⁹ O. P. Strausz, T. Do Minh, and H. E. Gunning, *J. Amer. Chem. Soc.*, 1968, **90**, 1660.