Tetrahedron. Vol. 33, pp. 73 to 75. Pergamon Press 1977. Printed in Great Britain

ALLENES—XXXV[1]

THE ADDITION OF ALLENIC CARBENES TO OXYGEN HETEROCYCLES

S. R. LANDOR*
Exeter University, Exeter EX4 4QD, England

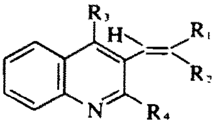
and

V. ROGERS and H. R. SOOD
Thames Polytechnic, London SE 18, England

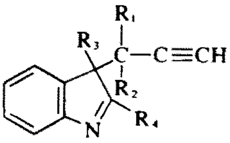
(*Received in the UK* 26 *April* 1976; *Accepted for publication* 21 *July* 1976)

Abstract—Dimethylvinylidene carbene from 1-bromo-3-methylbutadiene and potassium t-butoxide adds to 2,5-dihydrofuran and 2,3-dihydropyran to give the corresponding allenic cyclopropanes. 1,4-Cycloaddition of the allenic carbene to furan followed by hydration during work up yields the bicyclic ketone **11**.

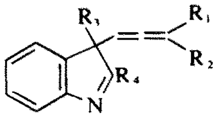
We have recently shown[1] that allenic carbenes[2] add to methylindoles and 2,5-dimethylpyrrole to give the alkenyl quinolines **1** and pyridines **4** through rearrangements and ring expansion of the intermediate adducts. Alkynyl and allenyl 3H-indoles **2** and **3** are formed at the same time by electrophilic attack of the carbene on the 3-position of the indolyl anion.



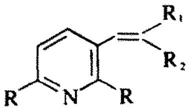
1



2



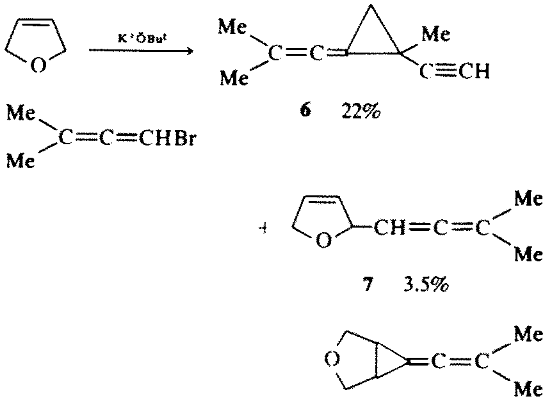
3



4

In contrast the reaction of allenic carbenes with three oxygen heterocycles, which we now report, yields mainly addition products and we have not, so far, detected any products resulting from ring expansion.

Equimolar quantities of 1 - bromo - 3 - methylbuta - 1,2 - diene, 2,5-dihydrofuran **5** and potassium t-butoxide in dry hexane gave a crude product consisting of three components identified as the three allenic compounds **6**, **7** and **8**, (yields estimated from GLC on crude product).

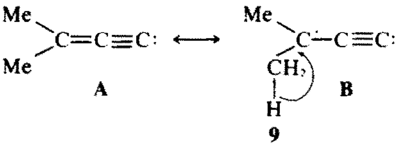


6 22%

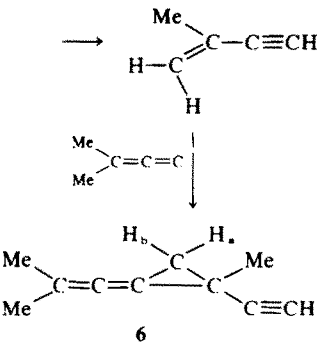
7 3.5%

8 33.5%

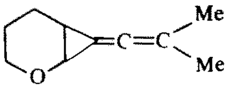
Formation of the allenic cyclopropane **6** may be rationalised by postulation of a prototropic rearrangement of the allenic carbene **9** to give 2-methylbut-1-en-3-yne. A second molecule of allenic carbene then adds exclusively to the double bond of the enyne. Under identical conditions, but in the absence of 2,5-dihydrofuran, the allenic cyclopropane **6** is obtained in 50% yield.[8]



9

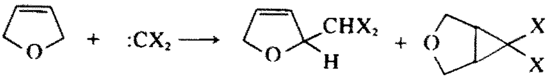


6



10

The allenyl 2,5-dihydrofuran **7** is the product of an insertion reaction analogous to that which has previously been observed[3] for the reaction of dichloro- and dibromo-carbene with 2,5-dihydrofuran:

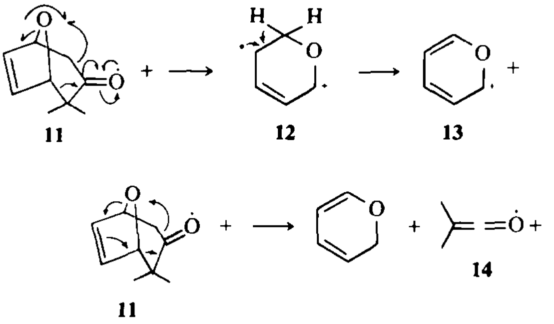


and more recently for the reactions of allenic carbenes with ethers.[4]

The reaction of the allenic carbene **9** with 2,3-dihydropyran gave a single product (70% crude and 49% distilled adduct) identified as the 2-oxanorcarane **10**. The allenic cyclopropanes **6**, **8** and **10** all show the intense band in the IR spectrum at 2010 cm^{-1} noted earlier.[2]

Neither insertion products nor the product from addition of allenic carbene to enyne **6** could be detected and this is readily explained by the strong nucleophilic properties of the double bond in dihydropyran giving rise to a fast reaction with the allenic carbene so that it reacts as soon as it is generated, thus preventing any side reaction.

The reaction of allenic carbene with furan gave a low melting ketone as the main volatile product (10%) together with a little of the carbene dimer **6** (1%). The ketone, which gave a crystalline 2,4-dinitrophenylhydrazone, analysed as $C_9H_{12}O_2$, and was identified as 2,2 - dimethyl - 8 - oxa - bicyclo[3,2,1]oct - 6 - en - 3 - one **11**.[5] It showed two 3H singlets at τ 9.04 and 8.69 in the NMR for the two magnetically different methyl groups on C_2, a 2H AB quartet for the nonequivalent protons on C_4, each being further coupled with the proton at C_5, with τ_A 7.82 (J = 16 and 1 Hz) and τ_B 7.16 (J = 16 and 5 Hz), a 1H doublet for the proton at C_1 and 1H doublet of triplets for the proton at C_5 and a 2H multiplet at τ 3.7 (not resolved) for the olefinic protons at C_6 and C_7. The mass spectrum showed a molecular ion *m/e* 152, a base peak of *m/e* 82 reasonable for the resonance stabilised cation **12**, *m/e* 81 for **13** and *m/e* 70 for the dimethylketene cation **14**.



The formation of the bicyclic ketone is best explained by a concerted ionic [2 + 4] cycloaddition of propargyl cation (9B†) to furan followed by addition of t-butanol to the dipolar adduct and hydrolysis during work up (route A).

Similar cycloadditions with allylic cations are now well established;[7] although the linear carbene renders the concerted cycloaddition sterically less attractive it is symmetry-allowed and in the absence of an alternative reaction pathway with lower free energy of activation (such as polymerisation*) it is not unlikely. An alternative two step mechanism (route B) is sterically even less attractive but cannot be ruled out.

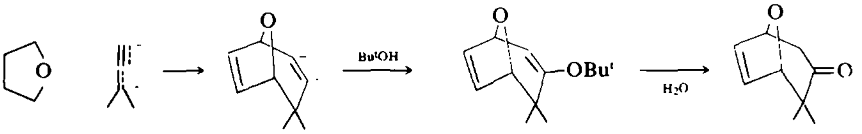
EXPERIMENTAL

GLC was carried out on a Pye 104 chromatograph, PGLC on a Pye 105 instrument, both fitted with flame ionisation detectors, IR spectra were determined on Perkin Elmer 257 and 337 instruments, UV spectra on a Unicam SP 800 and Bausch and Lomb Spectronic 505 spectrophotometers for alcoholic solutions, NMR spectra were measured in $CDCl_3$ with a Varian A60 spectrometer using Me_4Si as internal standard.

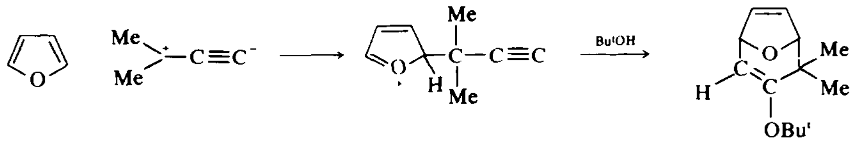
Reaction of 1-*bromo*-3-*methylbuta*-1,2-*diene with* 2,5-*dihydrofuran and potassium t-butoxide.* 1-Bromo-3-methylbuta-1,2-diene (14.7 g, 0.1 mol) was added dropwise to a cold (−10°) mixture of freshly distilled 2,5-dihydrofuran (7 g, 0.1 mol, b.p. 27–28° at 160 mmHg), dry hexane (100 ml) and potassium t-butoxide (12.32 g, 0.11 mol) under dry nitrogen during 45 min. The mixture was allowed to stir for an additional 2 h at 0° and 12 h at room temp. Water (50 ml) was added, the organic layer separated, and the aqueous layer extracted with petroleum ether (40–60°, 2 × 25 ml) and then with ether (3 × 30 ml). The combined extracts were dried ($MgSO_4$) and concentrated on a rotary evaporator at 40° (20 mmHg) to give a residue (8 g) shown by GLC on silicone oil at 90° to consist of three components R_t 5.7 (37%), 9.8 (6%) and 16.0 min (57%) and a trace of unreacted bromoallene, R_t 2.1 min. Fractional distillation gave two fractions. The first fraction (0.7 g) b.p. 29–30° at 2 mmHg was shown by GLC on silicone oil at 90° to consist of 95% of the first component. Purification by P GLC on silicone oil at 80° gave 2 - ethynyl - 2 - methyl - 1 - (2 - methylprop - 1 - enylidene)cyclopropane as a colourless liquid, which slowly became yellow on standing (Found: C, 90.96; H, 8.94, *m/e* 132. $C_{10}H_{12}$ requires: C, 90.90; H, 9.09%; M, 132), ν_{max} 3285 (≡C–H), 2095 (C≡C), 2010 ($\triangleright$=C=C) cm^{-1}; λ_{max} 221 (ϵ 10,590) and 248 nm (ϵ 1.237); τ 8.55 (3H, s, $\triangleright$–$\underline{H}_3$), 8.5 (1H, d, Ha J 6.5 Hz), 8.32 (6H, s $(C\underline{H}_3)_2C=$), 8.14 (1H, d, Hb, J 6.5 Hz), and 8.02 (1H, s, C≡C$\underline{H}$); The second fraction was 2 - (3 - methylbuta - 1,2 - dienyl) - 5 - dihydrofuran ν_{max} 3065, 1965 (C=C=C) and 1600 (C=C) cm^{-1}; τ 8.3 (6H, d, $(=C(C\underline{H}_3)_2)$, 5.36 (2H, m, $-C\underline{H}_2-O$), 4.7–5.1 (2H, m, $-O-C\underline{H}-C\underline{H}=$) and 4.15 (2H, m, $-C\underline{H}=C\underline{H}-$). The third fraction (2.7 g, 20%), b.p. 49–50° at 2 mmHg, R_t 16.0 min, solidified on standing; it crystallised from hexane to give 6 - (2 - methylprop - 1 - enylidene) - 3 - oxabicyclo[3,1,0]hexane as colourless needles, m.p. 46–47°. (Found: C, 79.19; H, 8.81, *m/e* 136. $C_9H_{12}O$ requires C, 79.36; H, 8.88%; M, 136), ν_{max}. 3010 (cyclopropane) 2010. ($\triangleright$=C=C) and 1065 cm^{-1}; λ_{max} 215 (ϵ 3,225) and 250$_{sh}$ nm (ϵ 446); τ 8.25 (6H, s, $=C(C\underline{H}_3)_2$), 7.62 (2H, m, $-C\underline{H}-C\underline{H}-$) and 6.1 (4H, dd, $C\underline{H}_2-O-C\underline{H}_2$, J 8 Hz).

Reaction of 1 - *bromo* - 3 - *methylbuta* - 1,2 - *diene with* 2,3-*dihydropyran and potassium t-butoxide.* 1 - Bromo - 3 -

Route A: concerted ionic [2 + 4] cycloaddition



Route B: electrophilic attack followed by ring closure



---

*High concentration or a large excess of furan gives mainly polymeric products.

†The allenic carbene in the singlet state has a pair of electrons in an sp orbital and a linear delocalised carbonium ion type structure $>\overset{+}{C}\text{--}C\equiv C(\uparrow\downarrow)$ similar to that of a propargyl cation.

methylbuta - 1,2 - diene (14.7 g, 0.1 mol) was added dropwise to a slurry of potassium t-butoxide (12.32 g, 0.11 mol) and 2,3-dihydropyran (8.4 g, 0.1 mol) in dry hexane (100 ml) under nitrogen at −10° during the 45 min, the colour of the reaction mixture started changing to yellow immediately and finally became light brown. The mixture was allowed to stir for an additional 2 h at 0° and 15 h at room temperature. Water (100 ml) was added, the organic layer separated and the aqueous layer was extracted with light petroleum ether (3 × 20 ml) and then with ether (3 × 30 ml). The combined extracts were dried ($MgSO_4$), filtered and concentrated on a rotary evaporator to give a light yellow liquid (10.5 g). Distillation gave 2 - oxa - 7 - (2 - methylprop - 1 - enylidene)norcarane (7.35 g, 49%). b.p. 50–51° at 0.5 mmHg, n_D^{20} 1.5253 (Found: C, 79.73; H, 9.37. $C_{10}H_{14}O$ requires C, 80.0; H, 9.33), $\nu_{max.}$ 2010 (▷=C=C) and 1080 cm^{-1}; $\lambda_{max.}$ 214 (ϵ 7,582) and 256 sh nm (ϵ 416); GLC on silicone oil at 110° showed a single peak, R_t 15.0 min; τ 8.23 (6H, 2s, $(C\underline{H}_3)_2C=$), 7.83–8.65 (5H, m, –$C\underline{H}_2$–$C\underline{H}_2$–$C\underline{H}$–) 6.17–6.73 (2H, m, –$C\underline{H}_2$–O–) and 5.91 (1H, d, O–$C\underline{H}$–, J 7 Hz).

Reaction of 1 - *bromo* - 3 - *methylbuta* - 1,2 - *diene with furan and potassium t-butoxide.* (a) 1 - Bromo - 3 - methylbuta - 1,2 - diene (29.5 g, 0.2 mol) was added dropwise to a well stirred slurry of potassium t-butoxide (24.64 g, 0.22 mol) and furan (13.6 g, 0.2 mol) in dry hexane (150 ml) under nitrogen at −10° during 1 h. The mixture was stirred for 2 h at −10° and the left stirring overnight at room temperature (*ca.* 10 h). Water (100 ml) was added, the organic layer was separated, and the aqueous layer extracted twice with ether (100 ml). The combined extracts were washed with water (2 × 50 ml), dried ($MgSO_4$), filtered and the filtrate was concentrated to give a light brown residue (16.3 g). Fractional distillation gave (i) unreacted 1 - bromo - 3 - methylbuta - 1,2 - diene (4 g, 13%), b.p. 50° at 50 mmHg, identified by IR and GLC; (ii) a light yellow liquid (1 g), b.p. 34–40° at 0.5 mmHg shown by GLC on silicone oil at 100° to contain two components, R_t 4.5 (27%) and 11.7 min (73%) which were separated by PGLC on silicone oil at 115° to give 2 - ethynyl - 2 - methyl - 1 - (2 - methylprop - 1 - enylidene)cyclopropane with identical IR GLC with those of a sample of **6** prepared above. The second component was found to be identical to the third fraction described below. Fraction (iii), gave as a light yellow liquid 2,2 - dimethyl - 8 - oxa - bicyclo[3,2,1]oct - 6 - en - 3 - one (2.4 g, 9%) b.p. 46–48° at 0.5 mmHg, solidified on standing, m.p. 41–42° (Found; C, 70.81; H, 7.79; *m/e* 152. $C_9H_{12}O_2$ requires C, 71.05; H, 7.89%; M, 152), ν_{max} 3085 (=CH), 1710 (C=O), 1600 (C=C), 1115 (C–O–C), 960 and 720 cm^{-1}; λ_{max} 209 (ϵ 1520) and 251 nm (ϵ 380); τ 9.04 (3H, s, $C\underline{H}_3$), 8.69 (3H, s, $C\underline{H}_3$), 7.82 (1H, ABqd, J_{AB} 16 Hz; J_{AX} 1 Hz) and 7.16 (1H, ABqt, J_{AB} 16 Hz; J_{AX} 5 Hz), 5.58 (1H, d, J 1 Hz), 5.05 (1H, dt, J 5 Hz; 1 Hz) and 3.7 [2H, m (appeared as broad singlet)], *m/e* (relative intensity) 152 (M^+ 54), 124 (20), 109 (27), 95 (33), 82 (100), 81 (74), 71 (21), 70 (77), 68 (21), 54 (21), 42 (33); its 2,4-dinitrophenylhydrazone crystallised from methanol as light brown needles, m.p. 155–157° (Found: C, 54.04; H, 4.83; N, 16.73. $C_{15}H_{16}N_4O_5$ requires: C, 54.21; H, 4.81; N, 16.86%).

(b) Using the same procedure, 1 - bromo - 3 - methylbuta - 1,2 - diene (14.7 g, 0.1 mol), furan (13.6 g, 0.2 mol) potassium t-butoxide (12.32 g, 0.11 mol) and dry hexane (100 ml) gave a product (8.4 g) shown by GLC on silicone oil at 100° to contain six components, R_t 4.5, 5.0, 7.5, 11.7, 12.5 and 15.0 min, which could not be separated by PGLC.

Reaction of 1 - *bromo* - 3 - *methylbuta* - 1,2 - *diene with potassium t-butoxide.* 1 - Bromo - 3 - methylbuta - 1,2 - diene (7.35 g, 0.05 mol) was added dropwise to a vigorously stirred slurry of potassium t-butoxide (6.16 g, 0.055 mol) in dry hexane (50 ml) under nitrogen at −10° during 30 min. The mixture was stirred under dry nitrogen for 2 h at 0° and 10 h at room temp. Water (50 ml) was added, the product extracted with ether (3 × 25 ml), the combined extracts dried ($MgSO_4$), evaporated and distilled to give 2 - ethynyl - 2 - methyl - 1 - (2 - methylprop - 1 - enylidene)cyclopropane (1.6 g, 50%) b.p. 30–31° at 3 mmHg, ν_{max} 3300 (≡C–H), 2100 (C≡C) and 2020 (▷=C=C); GLC on silicone oil at 80° gave a single peak, R_f 15.3 min; an identical single peak resulted from a 50:50 mixture of the product with an authentic specimen described above.

REFERENCES

[1] S. R. Landor, V. Rogers and H. R. Sood, *J. C. S. Perkin I* (1976), in press.

[2] S. R. Landor and P. F. Whiter, *J. Chem. Soc.* 2625 (1965).

[3] J. C. Anderson and C. B. Reese, *Chem. Ind.* 575 (1963).

[4] J. Cymerman Craig and C. D. Beard, *Chem. Comm.* 692 (1971).

[5] N. J. Turro, S. S. Edelson, J. R. Williams, T. R. Darling and W. B. Hammond, *J. Amer. Chem. Soc.* **91**, 2283 (1969), have previously prepared this compound from 2,2-dimethylcyclopropanone and furan.

[6] The Conversation of Orbital Symmetry (Edited by R. B. Woodward and R. Hoffman), p. 86. Verlag Chemie and Academic Press, New York (1970).

[7] H. M. R. Hoffman, D. R. Joy and A. K. Suter, *J. Chem. Soc. B* 57 (1968).

[8] A. F. Bramwell, L. Crombie and M. H. Knight, *Chem Ind.* 1265 (1965), mention having obtained this adduct without giving details.