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1-BROMOBICYCLO[1.1.0]BUTANES AND STRONG BASES: PRODUCTS AND MECHANISM †

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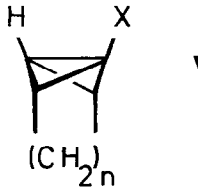
Summary: Treatment of the bromobicyclo[1.1.0]butanes 4a - c with LDA led to the formation of the 1,2,3-butatrienes 6 which were isomerized by excess base to the alkynes 8. Reaction of [1-^{12}C]4c with LDA afforded [3-^{12}C]8d, indicating that bicyclo[1.1.0]but-1(3)-ene 5 was not an intermediate.

1-Halobicyclo[1.1.0]butanes of type 1 with a bridge between C-2 and C-4 eliminate hydrogen halide when treated with a strong base, affording the bicyclo[1.1.0]but-1(3)-ene derivatives 2 as short-lived intermediates. At low temperature (< 0°C), 2 could be trapped by nucleophiles (thiolates, amides, organolithium compounds) or by reactive 1,3-dienes [1]. Above 20°C, tricyclo-[4.1.0.0^{2,7}]hept-1(7)-ene (2, n = 3) has been shown to isomerize to 1,2,3-cycloheptatriene (3, n = 3) [2] in a formally orbital symmetry "forbidden" process [3]. 1-Halobicyclo[1.1.0]butanes 4 without the bridge between C-2 and C-4 might behave differently when exposed to a strong base. Although the formation of 5 seems reasonable, the rearrangement of 5 to 6 is not hampered by orbital symmetry restrictions. Therefore, 5 could evade all trapping efforts by a fast isomerization to 6.

To test this point experimentally, the 1-bromobicyclo[1.1.0]butanes 4a-c were synthesized by the elegant method of Skattebøl and Baird [4] from the dibromocyclopropanes 7a-c and methyllithium. The NMR data of 4a-c are collected in Table 1. When the bromides 4a-c were mixed with 3-5 equiv. of lithium diisopropylamide (LDA) in ether at -20°C, aqueous workup after 2-5 hours afforded in yields of 30-50% 8a, a 1:6 mixture of 8b and c, and, respectively, 8d. The structures of 8a-d are based on their ^{1}H and ^{13}C NMR spectra, which had been recorded previously [5]. It was easy to



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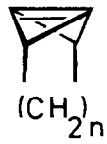

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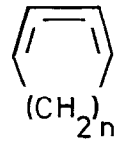

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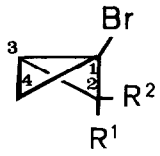
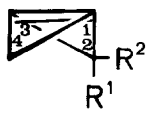


4

4-6:	a	b	c
R^1	H	H	Me
R^2	H	Me	Me



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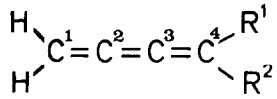

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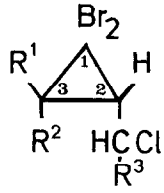
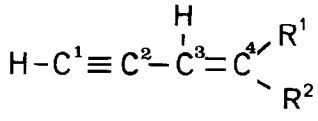


7

7:	a	b	c
R^1	H	H	Me
R^2	H	H	Me
R^3	H	Me	H

8:	a	b	c	d
R^1	H	Me	H	Me
R^2	H	H	Me	Me



8

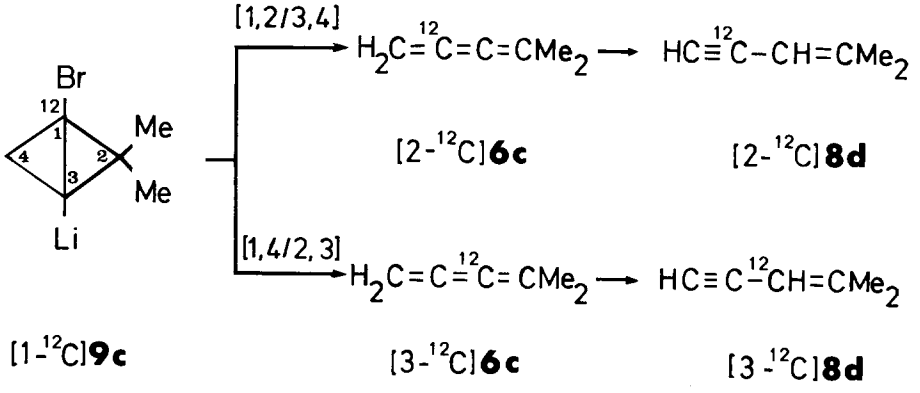
demonstrate that the alkynes 8 were formed by isomerization of the butatrienes 6, caused by the excess of LDA. After dropwise addition of one equiv. of a solution of LDA to a solution of 4a or of 4c in ether at -20°C, the ^{1}H NMR spectra of the solutions showed intense signals of 6a [6] or of 6c [7], which disappeared quickly, when base addition was continued.

To find out, if the assumed intermediates 5a and c could be trapped, mixtures of 4a or 4c and lithium thiophenolate or 2,5-dimethylfuran were treated with an excess of LDA at -20°C. However, no products containing the bicyclo[1.1.0]butane structure were isolated, leaving the question on the intermediacy of 5 unanswered.

To reach a decision on this point, [1-^{12}C]4c was synthesized from [1-^{12}C]7c. For this purpose, commercially available $^{12}CDCl_3$ (^{12}C content ≥ 99.95%) was converted to $^{12}CDBr_3$ by anhydrous $AlBr_3$ in 71% yield [8]. Reaction of $^{12}CDBr_3$ with 1-chloro-3-methylbut-2-ene in CH_2Cl_2 with conc.

NaOH under phase-transfer conditions furnished a 72% yield of [1-^{12}C]7c, from which [1-^{12}C]4c was obtained in 34% yield by reaction with methyllithium in ether. The ^{13}C NMR spectrum of [1-^{12}C]4c indicated that the ^{13}C proportion of C^1 was below ^{13}C NMR detection: the singlet of the ^{13}C NMR spectrum of 4c at δ 28.9 was not observed in the spectrum of [1-^{12}C]4c.

Mixing [1-^{12}C]4c with 4 equiv. of LDA at -20°C followed by aqueous workup produced a sample of the alkyne 8d, the ^{13}C NMR spectrum of which gave a clear answer to the posed question: the signal of the olefinic C^3 (at δ 105.4 in the ^{13}C NMR spectrum of 8d) was completely absent in the spectrum of the sample, showing that [3-^{12}C]8d was the only product. This result immediately eliminated 5c as an intermediate. In this molecule, the bicyclo[1.1.0]butane side-bonds C^1-C^2 and C^2-C^3 are equivalent, as are the bonds C^1-C^4 and C^3-C^4. Neglecting kinetic isotope effects, cleavage of opposite side bonds (C^1-C^2/C^3-C^4 and, respectively, C^2-C^3/C^1-C^4) should occur with equal probability, leading to a 1:1 mixture of [2-^{12}C]6c and [3-^{12}C]6c, and, after base-induced isomerization, finally to a 1:1 mixture of [2-^{12}C]8d and [3-^{12}C]8d.



As 5c is not an intermediate in the hydrogen bromide elimination of 4c, and as 4c, in the absence of electrophilic catalysts, is stable at the reaction temperature, a possible candidate for rearrangement seems to be the lithiated species 9c. Lithium bromide elimination from 9c is then accompanied by cleavage of the bonds C^2-C^3 and C^1-C^4 in a concerted, but not necessarily in a synchronous fashion [9]. The high regioselectivity of bond breaking of the bicyclo[1.1.0]-butane framework of 9c is, however, not fully understood. The mechanistic alternative of single electron transfer (SET) from LDA to 4c followed by ring opening of the radical anion of 4c appears to be less attractive, because no evidence of SET was obtained in previous investigations, when halides of type 1 were treated with LDA [1].

Table 1. NMR data of 4a-c, 6c and 8d

4a	^{1}H NMR (CCl_4) δ 1.10 (broadened s, 2 H), 1.80 (tt, J = 3 Hz and J = 1 Hz, 1 H), 1.99 (d, J = 3 Hz, each line broadened by small coupling, 2 H); ^{13}C NMR ($CDCl_3$) δ 6.6 (d), 15.1 (s), 38.7 (t).
4b	^{1}H NMR (CCl_4) δ 1.05 (broadened s, 1 H), 1.15 (m, 4 H), 1.58 (d, J = 3 Hz, each line broadened by small coupling, 1 H), 1.93 (d, J = 3 Hz, each line broadened by small coupling, 1 H); ^{13}C NMR (C_6D_6) δ 12.3 (d), 14.0 (q), 23.9 (s), 36.2 (t), 43.8 (d).
4c	^{1}H NMR see Lit. [4]; ^{13}C NMR (C_6D_6) δ 14.0 (q), 17.9 (d), 23.0 (q), 28.9 (s), 37.3 (t), 51.8 (s).
6c	^{1}H NMR see Lit. [7]; ^{13}C NMR ($CDCl_3$) δ 24.5 (q), 85.4 (t), 117.8 (s), 156.5 (s), 166.2 (s).
8d	^{1}H NMR see Lit. [5e]; ^{13}C NMR (C_6D_6) δ 20.8 (q), 24.5 (q), 80.0 (d), 81.9 (s), 105.4 (d), 149.6 (s).

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References and Notes

† Dedicated to Professor Rolf Huisgen on his 65th birthday.

1) a. J. Harnisch, H. Legner, U. Szeimies-Seebach, and G. Szeimies, Tetrahedron Lett. 1978, 3683. b. H.-G. Zoch, E. Kinzel and G. Szeimies, Chem. Ber. 114, 968 (1981). c. G. Szeimies, J. Harnisch and O. Baumgärtel, J. Am. Chem. Soc. 99, 5183 (1977). d. R. Römer, J. Harnisch, A. Röder, A. Schöffer, G. Szeimies, G. Germain, and J. M. Arrieta, Chem. Ber. 117, 925 (1984). e. U. Szeimies-Seebach, A. Schöffer, R. Römer, and G. Szeimies, Chem. Ber. 114, 1767 (1981). f. H.-G. Zoch, A.-D. Schlüter and G. Szeimies, Tetrahedron Lett. 1981, 3835.

2) H.-G. Zoch, G. Szeimies, R. Römer, G. Germain, and J.-P. Declercq, Chem. Ber. 116, 2285 (1983).

3) R. B. Woodward and R. Hoffmann, Angew. Chem. 81, 797 (1969); Angew. Chem., Int. Ed. Engl. 8, 781 (1969).

4) N. O. Nilsen, L. Skattebøl, M. S. Baird, S. R. Buxton, and P. Slowey, Tetrahedron Lett. 1984, 2887.

5) ^{1}H NMR of 8a: a. A. P. Ebdon and T. N. Huckerby, J. Mol. Struct. 54, 89 (1979). ^{13}C NMR of 8a: b. J. Kowalewski, M. Granberg, F. Karlsson and R. Vestin, J. Magn. Res. 21, 331 (1976). ^{1}H NMR of 8b and c: c. L. Eisenhuth, H. Siegel and H. Hopf, Chem. Ber. 114, 3772 (1981). ^{13}C NMR of 8b and c: d. M. T. W. Hearn, J. Magn. Res. 22, 521 (1976). ^{1}H NMR of 8d: e. M. Karpf and A. S. Dreiding, Helv. Chim. Acta 60, 3045 (1977).

6) R. W. Kunz, V. Bilinski, W. von Philipsborn and A. S. Dreiding, Org. Magn. Res. 22, 349 (1984).

7) T. L. Jacobs and P. Prempree, J. Am. Chem. Soc. 89, 6177 (1967).

8) I. F. Harlow and O. C. Ross, Chem. Zentralbl. 1933 I, 1682.

9) M. J. S. Dewar, J. Am. Chem. Soc. 106, 209 (1984).

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