Tetrahedron Letters,Vol.24,No.5,pp 445-446,1983 0040-4039/83/050445-02$03.00/0
Printed in Great Britain

A SIMPLE PREPARATION OF SEVERAL NEW 2,3- AND 1,2,3-SUBSTITUTED BUTA-1,3-DIENES FROM 1,4-DICHLOROBUTYNE[1]

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Summary. Addition of (pseudo) halogens across the triple bond of 1,4-dichlorobut-2-yne, followed by a 1,4-elimination, provides a very simple preparation of ten novel butadienes.

In recent years there has been a great deal of interest in asymmetrically substituted butadienes, both for theoretical reasons and for their synthetic utility.[2-5] In this communication we report the preparation of ten such dienes in two steps from 1,4-dichlorobut-2-yne. This alkyne is an excellent precursor for butadienes since it already contains the requisite skeleton, two π bonds and two substituents. Either two S_N2' reactions[6] or, as in the present report, a 2,3-addition followed by a 1,4-elimination[7] should convert it to a di- or trisubstituted butadiene.

Phenylsulfenyl chloride and bromide, and phenylselenyl chloride and bromide all added to 1,4-dichlorobutyne to form the trihalobutenes 1(a-d) in 80-100% yield (see Table). Since both of the electrophilic bromides were generated in situ[8] the solvent used was CH_2Cl_2, although CH_3CN was found to be markedly superior for the chloride additions. Bromine added quantitatively to the alkyne to give tetrahalide (1e) but iodine added rather slowly (and reversibly) to form (1f) only in refluxing 1,2-dichloroethane.

When the trihalides 1(a-d) underwent reductive elimination, with Al/Hg[9] in buffered methanol, dienes 2(a-d) were formed in 33-76% yields (see Table). All four dienes are very susceptible to polymerization, especially (2a and b), and the neat materials became glasses within 15 minutes; however, they could be characterized by nmr spectroscopy[10] and by subsequent Diels-Alder reactions.[11]

All six adducts 1(a-f) smoothly dehydrohalogenated, on treatment with 1,8-diazabicyclo-[5.4.0]undec-7-ene in benzene at 20°, to form only the 1,2,3-trisubstituted dienes 3(a-f) in 57-91% yield (see Table). The 1-chloro- derivatives (3a-d) were rather more stable than the corresponding 2,3-disubstituted dienes (2a-d) and the two trihalodienes (3e and f) were especially stable. The dienes 3(a-f) were also characterized by their nmr spectra[10] (the 1H proton in all cases appearing as a singlet in the 7.1-7.3δ range) and their Diels-Alder reactions, which also demonstrated the regioisomerism and stereoisomerism shown in Table 1.[11]

Acknowledgment is made to the Donors of the Petroleum Research Fund, administered by the ACS, and to Research Corporation for partial support of this research.

References

1. Preliminary results were presented at the 16th Annual Meeting of the Great Lakes ACS Region at Normal, Illinois, on June 7th, 1982.
2. B.M. Trost, W.C. Vladuchick and A.J. Bridges, J. Am. Chem. Soc. 102, (1980) 3548, 3554.

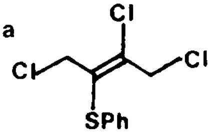
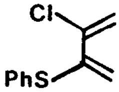
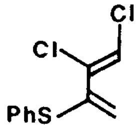
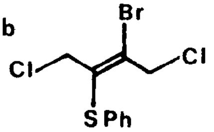
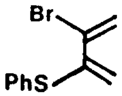
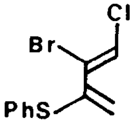
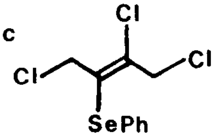
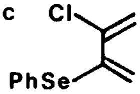
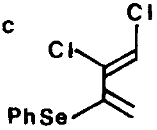
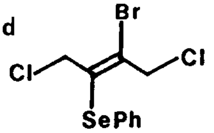
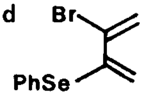
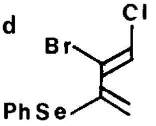
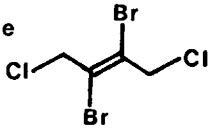
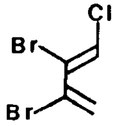
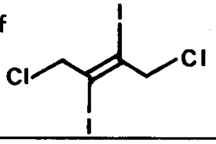
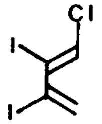
Electro phile	Solvent Temp °C Time	Adduct (1)	% Yield	Diene (2)	% Yield	Diene (3)	% Yield
PhSCl	CH$_3$CN 25 1h	a 	98	a 	68*	a 	69
PhSBr	CH$_2$Cl$_2$ 25 96h	b 	88	b 	33*	b 	57
PhSeCl	CH$_3$CN 25 20h	c 	100	c 	75	c 	86
PhSeBr	CH$_2$Cl$_2$ 40 120h	d 	93	d 	76	d 	68
Br$_2$	CCl$_4$ 25 4h	e 	94	—	—	e 	91
I$_2$	CH$_2$ClCH$_2$Cl 83 120h	f 	86	—	—	f 	71

Table 1. Dichlorobutyne Adducts and Dienes derived from them.

*Yields are based on overall yields of cycloadducts from (1a) and (1b).

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4. S.F. Danishefsky and T. Kitahara, J. Am. Chem. Soc. 96, (1974) 7807.
5. L.E. Overman, L.A. Clizbe, R.L. Freerks and C.K. Marlowe, J. Amer. Chem. Soc. 103, (1981) 2807.
6. Y. Ishino, I. Nishiguchi, F. Takihira and T. Hirashima, Tetrahedron Lett. 21, (1980) 1527.
7. D.C. Balt and B. Ganem, Tetrahedron Lett. 3323 (1978).
8. PhSBr; Thiophenol and N-bromosuccinimide in CH$_2$Cl$_2$. PhSeBr; Diphenyldiselenide and molecular bromine in CH$_2$Cl$_2$.
9. A sample experimental is included in the following paper.
10. For example; Diene 2a, 7.15-7.3 (5H, m), 6.20 (1H, s), 6.0 (1H, d, J=2Hz), 5.64 (1H, d, J=2Hz), 5.50 (1H, s). Diene 2c, 7.22-7.47 (5H, m), 6.36, 5.95, 5.68, 5.51 (all 1H, all slightly broadened singlets). Diene 3a, 7.22 (5H, s), 7.10, 6.12, 5.65 (all 1H, s), ^{13}C 136.85, 133.79, 133.0, 130.05, 129.48, 127.47, 125.01, 121.89. Diene 3b, 7.28 (5H, s), 7.22, 6.12, 5.68 (all 1H, s). Diene 3e, 7.29 (1H, s), 6.40 (1H, d, J=2.5Hz), 5.85 (1H, d, J=2.5Hz).
11. See following paper.

(Received in USA 27 September 1982)