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Solvent Incorporation in Bromination of Acetylenes in Alcohols

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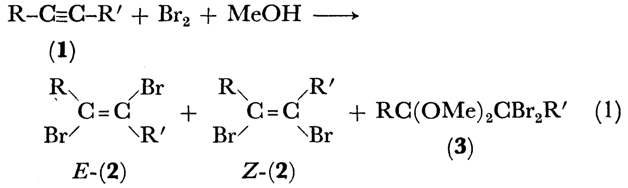
Synopsis. The reactions of acetylenes with bromine in alcohols at 20—25 °C afford dibromodialkoxyalkanes in good yields together with variable amounts of dibromoalkenes. Similar treatment of phenylacetylene with copper(II) bromide gives only bromophenylacetylene and 2-phenyl-1,1,2-tribromoethylene, the latter being formed by dibromination of the former with copper(II) bromide.

Contrary to fluorination[1)] and chlorination[2)] of acetylenes in alcohols where solvent incorporation occurs, it has been reported that bromination of 1-hexyne in methanol gave only 1,2-dibromo-1-hexene and none of solvent incorporated products.[2)] This seems to be strange since bromination of olefin in alcohols usually gives both dibromoalkanes and alkoxybromoalkanes.[3)] During studies on halogenation of acetylenes by molecular halogen and metal halides,[4,5,6)] we found that bromination of acetylenes in methanol actually gives dibromodimethoxyalkanes as well as dibromoalkenes. It should be noted that the reactions of acetylenes with *N*-bromosuccinimide in alcoholic solvents have been known to produce dibromo acetals.[7)]

Results and Discussion

When the reactions of various acetylenes with equimolar amount of bromine were carried out by adding methanolic solution of bromine to that of acetylene (**1**) at 20—25 °C and by stirring the resulting solution for 0.5—3 h, dibromodimethoxyalkanes (**3**) were obtained in good yields together with minor amounts of isomeric dibromoalkenes (**2**) [Scheme (1)], leaving excess **1** unreacted. In the reactions of phenylacetylene the following facts were revealed: (i) The product ratio is not much changed by lowering the reaction temperature or increasing the amount of methanol. (ii) The use of excess of bromine to **1** results in a slight decrease of the amount of **3**. (iii) The reaction proceeds also in ethanol or ethylene glycol to give **2** and **3**-analogue, while almost only **2** is obtained in 2-propanol or *t*-butyl alcohol. In ethylene glycol the attack of second alkoxyl group occurred intramolecularly to give 2-(dibromomethyl)-2-phenyl-1,3-dioxolane. The reaction with 1-hexyne gave (**3**; R=*n*-Bu, R′=H) in 40—60% yield in contrast to the report by Hennion *et al.*,[2)] though the reason for the discrepancy is not yet clear. Typical results are shown in Table 1. The formation of only **3** as the solvent-incorporated product without any appreciable amounts of bromomethoxyalkenes may suggest that enol ethers are more reactive to electrophilic addition than acetylenes in these cases.



When phenylacetylene was treated with copper(II) bromide instead of bromine in methanol, bromophenylacetylene (**4**) and 2-phenyl-1,1,2-tribromoethylene (**5**) were obtained, none of (**3**; R=Ph, R′=H) being formed. Tribromination of terminal acetylenes with copper(II) bromide in refluxing methanol has been reported by Castro *et al.*[8)] The mechanism which involves dibromination followed by tetrabromination and subsequent dehydrobromination has been proposed for this reaction. We would like to suggest another possible pathway for tribromination which consists of the initial formation of **4** followed by its dibromina-

TABLE 1. BROMINATION OF ACETYLENES IN ALCOHOLS

(1)			Br_2 (mmol)	Alcohol		Temp (°C)	Time (h)	Products and yields[a)]		
R	R′	(mmol)			(ml)			E-(2)	Z-(2)	(3)
Ph	H	2.5	2.5	MeOH	25	25	0.5	7	trace	65
Ph	H	2.5	5	MeOH	25	25	0.5	13	2	75[b)]
Ph	H	5	5	MeOH	100	25	0.5	7	trace	79
Ph	H	2.5	2.5	MeOH	25	−60	0.5	7	trace	70
Ph	H	5	5	EtOH	100	20	3	28	0	39[c)]
Ph	H	5	5	$HOCH_2CH_2OH$	100	20	3	trace	0	55[d)]
Ph	Me	5	5	MeOH	100	20	3	37	0	63
n-Hexyl	H	5	5	MeOH	100	20	3	29	0	53
n-Bu	H	5	5	MeOH	100	20	3	29	0	52

a) Determined by NMR using a suitable internal standard; on the basis of a half mole of **1**. b) Yields are based on **1**; other product, a small amount of **4**. c) $PhC(OEt)_2CHBr_2$. d) $PhC(OCH_2CH_2O)CHBr_2$.

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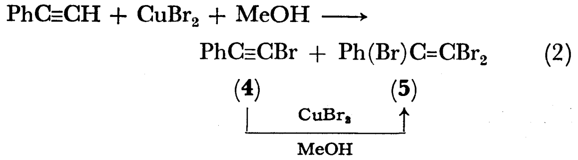

$$\mathrm{PhC{\equiv}CH + CuBr_2 + MeOH \longrightarrow PhC{\equiv}CBr + Ph(Br)C{=}CBr_2} \qquad (2)$$

(**4**) (**5**)

tion, since we confirmed separately that **4** reacted with copper(II) bromide in methanol to give **5** [Scheme (2)]. As to the formation of **4**, the direct exchange of hydrogen by bromine may be conceivable as one of the possible pathways, since *E*- and/or *Z*-**2** did not give any **4** by dehydrobromination under these reaction conditions.

Experimental

Phenylacetylene, 1-phenyl-1-propyne, and 1-phenyl-1-butyne were prepared by the literature method.[4] 1-Hexyne, 1-octyne, alcohols, bromine, and copper(II) bromide were commercial products and used without further purification. The purification of these reagents by distillation or drying *et al.* did not give any effects on the results. The GLC analyses were carried out on Shimadzu 4BMPF and 4CMPF apparatus using EGSS-X (1 and 3 m) columns (N_2 as the carrier gas). The NMR spectra were recorded with a Varian EM-360 and a JEOL JNM-MH-100 apparatus using CCl_4 solvent (TMS as an internal standard). Authentic samples of **2**,[6] **4**,[9] and **5**[8] were prepared by the reported methods.

*Formation of (**3**; R=Ph, R′=H).* To a stirred methanol (25 ml) solution of phenylacetylene (0.51 g, 5 mmol) was added a methanol (25 ml) solution of bromine (0.80 g, 5 mmol) drop by drop (*ca.* 3—5 min) at 20—25 °C and the resulting mixture was stirred for 0.5 h during which period the red color of bromine gradually disappeared. The mixture was then added with aqueous sodium thiosulfate (*ca.* 1%, 150 ml) and extracted with benzene (70 ml×3). The benzene extract was washed with water and dried over $MgSO_4$. This extract was revealed to contain phenylacetylene, *E*- and *Z*-(**2**; R=Ph, R′=H), (**3**; R=Ph, R′=H), and trace amounts of **4**, **5**, and an unidentified compound by GLC analysis. Evaporation of benzene left 0.6 g of a white solid which contained *E*-**2**, *Z*-**2**, and **3** of the ratio of 9: 1: 90 (by NMR). Recrystallization from ethanol afforded 0.4 g of pure (**3**; R=Ph, R′=H): mp 65—67 °C, NMR δ 3.27 (s, 6H), 5.91 (s, 1H), 7.15—7.75 (m, 5H). Found: C, 36.62; H, 3.53%. Calcd for $C_{10}H_{12}O_2Br_2$: C, 37.07; H, 3.73%.

Identification of other **3** which was isolated similarly as above or by column chromatography on alumina (hexane as an eluent) was as follows: (**3**: R=Ph, R=Me), mp 49—51 °C, NMR δ 2.27 (s, 3H), 3.48 (s, 6H), 7.0—7.7 (m, 5H). Found: C, 39.04; H, 4.11%. Calcd for $C_{11}H_{14}O_2Br_2$: C, 39.08; H, 4.17%. $PhC(OEt)_2CHBr_2$, mp 35—36 °C, NMR δ 1.22 (t, 6H), 3.54 (q, 4H), 5.84 (s, 1H), 7.1—7.6 (m, 5H). Found: C, 41.20; H, 4.66%. Calcd for $C_{12}H_{16}O_2Br_2$: C, 40.94; H, 4.58%. $PhC(OCH_2CH_2O)CHBr_2$, mp 69—72 °C, NMR δ 3.73—4.0 (m, 2H), 4.0—4.38 (m, 2H), 5.66 (s, 1H), 6.9—7.7 (m, 5H). Found: C, 37.25; H, 3.06%. Calcd for $C_{10}H_{10}O_2Br_2$: C, 37.30; H, 3.13%. The following two products were identified by NMR without isolation: (**3**; R=*n*-Bu, R′=H), δ 0.8—2.2 (m, 7H), 2.57 (t, 2H), 3.27 (s, 6H), 5.70 (s, 1H); (**3**; R=*n*-Hexyl, R′=H), δ 0.85—2.4 (m, 11H), 2.60 (t, 2H), 3.29 (s, 6H), 5.67 (s, 1H).

*Formation of **4** and **5**.* A heterogeneous mixture of phenylacetylene (0.26 g, 2.5 mmol), copper(II) bromide (2.70 g, 12.5 mmol) and methanol (25 ml) was kept at 25 °C for 24 h with stirring. Water (100 ml) was added to the mixture and the resulting solution was extracted with benzene (70 ml×3). The benzene extract was treated as described above. The GLC analysis of the residue revealed the presence of **4** (0.31 g, 1.7 mmol, 68% yield on the basis of the acetylene charged), a trace amount of *E*-**2**, and **5** (0.12 g, 0.35 mmol, 14% yield).

Treatment of **4** (1 mmol) with $CuBr_2$ (3 mmol) in methanol (10 ml) at reflux temperature for 5 h afforded 69% yield of **5**. Similar reaction at 25 °C gave 11% yield of **5**, leaving 84% of **4** unreacted.

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