SIMPLE SYNTHESIS OF CONJUGATED BROMOALLENES

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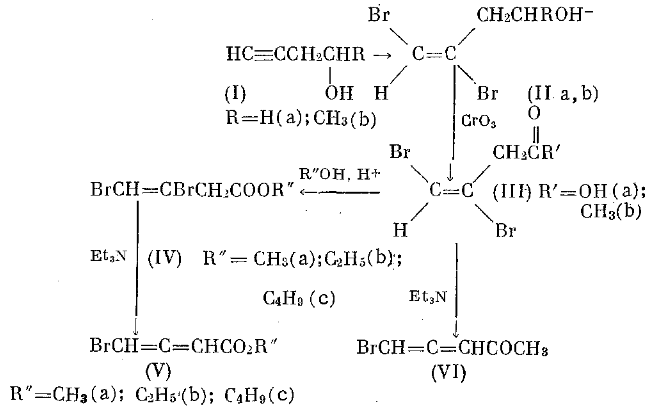
UDC 542.91:547.315'141

Dehydrobromination of the appropriate vinyl halides is one of the possible routes to the synthesis of allenes [1]. However, in a number of aliphatic allenes, this method, which requires the application of strong bases and high temperatures, often leads to rearrangements and isomerizations. These side transformations can be avoided by increasing the rate of dehydrobromination either by using dimethyl sulfoxide as the solvent [2, 3] or by using unsaturated systems activated by electron-accepting groups in this reaction.

In this paper it is shown that the second route can be successfully used for the synthesis of conjugated α-bromoallenes starting from the readily accessible β,γ-acetylenic alcohols.

The bromination of acetylenic alcohols Ia,b in acetic acid results in the formation of vicinal trans-dibromoalkenes (IIa,b) [4], which can be converted in satisfactory yields to acid IIIa or trans-ketone IIIb, respectively, by oxidation with the Jones reagent [5]:



The latter, on treatment with triethylamine in a suitable solvent, is readily dehydrobrominated further at 0-10°C to 1-bromo-1,2-pentadien-4-one (VI), which decomposes at room temperature.

Acid esterification of IIIa by alcohols leads to quantitative yields of the corresponding esters. It was shown by means of gas–liquid chromatography and PMR spectroscopy that all of these esters are mixtures of cis and trans isomers of dibromovinylacetic esters (IVa-c). The NMR spectra of the cis isomers have a weak-field signal which corresponds to the =CHBr group, for which a large spin–spin interaction constant is usually observed [6] (Table 1).

The corresponding α-bromoallenic esters (Va-c) were obtained in 40-60% yields by treatment of the isomeric mixture of dibromo esters (IVa-c) with excess triethylamine at 40-60° for 20-40 min. It was observed that the cis isomers (IV) are converted to allenes at a lower rate. This is in agreement with data regarding the fact that allenes are formed directly by splitting out of HBr at the expense of the allyl hydrogen and not by isomerization of the triple bond, which should have more preferably been formed from the cis isomers by trans-dehydrobromination [2, 3].

Bromoallenic esters V are readily brominated under the usual conditions (Br_2 in chloroform) to form tribromovinylacetic esters (VII), which, from their PMR spectra, probably consist of only the cis isomer:

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 6, pp. 1442-1444, June, 1972. Original article submitted July 29, 1971.

TABLE 1. Spectral Data for Dibromovinylacetic Esters and Bromoallenes

Compound	PMR spectrum (CCl_4), ppm				IR spectrum, ν, cm^{-1}	
	δ_α	δ_γ	δ_{OCH_2}	$J_{\alpha,\gamma}$, Hz	C = O	C = C
IIIb	3,68	6,45	2,14 (CH_3)	0	1722	1600
trans- IVa	3,68	6,65	3,74 (CH_5O)	0	1745	1630
cis- IVa	3,54	6,86	3,70 (CH_3O)	1,1	1745	1632
trans- IVb	3,58	6,6	4,08	0,6	1742	1612
cis-IVb	3,48	6,84	4,08	1,1		
trans- IVc	3,57	6,50	4,0	0	1746	1612
cis- IVc	3,45	6,82	4,0	1,1		
Va	5,62	6,35	3,48 (CH_3O)	6,0	1720	1959 (C=C=C)
Vb.	5,6	6,4	4,12	6,0	1718	1958 (C=C=C)
Vc.	5,53	6,33	4,06	6,0	1718	1958 (C=C=C)
VI	5,5	6,45	2,18 (CH_3)	6,0	1692	1948 (C=C=C)

$$\underset{(V)}{BrCH{=}C{=}CHCO_2R''} \rightarrow \underset{(VII)}{BrCH{=}CBrCHBrCO_2R''} \rightarrow \underset{(VIII)}{[BrCH{=}C{=}CBrCO_2R'']}$$

Compounds VII also undergo dehydrobromination on treatment with triethylamine, but the dibromoallenic esters (VIII) formed are extremely labile and decompose.

EXPERIMENTAL SECTION

The products were analyzed and identified by gas–liquid chromatography with a chromatograph with a glass vaporizer and a flame-ionization detector on a column filled with 10% SE-30 silicone on silanized Chromosorb-W. The IR spectra were obtained with a UR-10 spectrometer, and the PMR spectra were obtained with an HA-60-1L spectrometer.

Bromination. An equivalent amount of bromine was added with stirring to a solution of alcohols Ia, b in 70% acetic acid [4] at ≤ 30-35°. The mixture was diluted with ether, washed with water and sodium bicarbonate solution, dried, and distilled to give 70-80% of dibromoalkenes. Trans-1,2-dibromo-1-buten-4-ol (IIa) had bp 86-89° (3 mm) and n_D^{22} 1.5560. According to gas–liquid chromatography and the PMR spectra, IIa contained a trace of trans-1,2,4-tribromo-1-butene; PMR spectrum (CCl_4), δ, ppm: 2.9 (triplet, J = 6 Hz, CH_2), 4.16 (triplet, J = 6 Hz, CH_2Br), 6.57 (=CHBr).

Trans-1,2-dibromo-1-penten-4-ol (IIb) had bp 87-89° (2.5 mm) and n_D^{23} 1.5436. PMR spectrum (CCl_4), δ, ppm: 1.18 (doublet, J = 6 Hz, CH_3), 2.64 and 2.72 (AB spectrum of the CH_2 group, J = 6 Hz), ~ 3.12 (OH), 4.09 (quartet, J = 6 Hz, OCH), 6.47 (=CHBr).

Oxidation of Dibromo Alcohols IIa,b. The oxidation was carried out by the method in [5] at 12-14°. Acid IIIa was separated from the neutral fraction by treatment with saturated sodium bicarbonate solution, dried, and, without additional purification, subjected to esterification with alcohols (at ~20° for 3-4 days in the presence of sulfuric acid). Methyl 3,4-dibromo-3-butynoate (IVa) (a 1:1 mixture of cis and trans isomers) had bp 90-94° (3.5 mm) and n_D^{20} 1.5258.

Ethyl 3,4-dibromo-3-butynoate (a 62:38 mixture of the cis and trans isomers) had bp 60° (0.4 mm) and $n_D^{21.5}$ 1.5124. Found %: C 24.3; H 2.42; Br 60.4. $C_6H_8Br_2O_2$. Calculated %: C 24.6; H 2.74; Br 61.6.

n-Butyl 3,4-dibromo-3-butynoate (IVc) (a 35:65 mixture of cis and trans isomers) had bp 80-84° (0.2 mm) and n_D^{22} 1.5038. Found %: C 30.2; H 3.6; Br 55.8. $C_8H_{12}Br_2O_2$. Calculated %: C 30.0; H 3.7; Br 56.3.

1,2-Dibromo-1-penten-4-one (IIIb) had bp 73-75° (3 mm) and n_D^{21} 1.5412-1.5436 and contained a small amount of starting alcohol (IIb) and bromoallene ketone VI. The 2,4-dinitrophenylhydrazone melted at 156° (from acetonitrile). Found %: C 31.17; H 2.36; N 13.84; Br 36.86. $C_{13}H_{10}Br_2O_4N_4$. Calculated %: C 31.2; H 2.40; N 13.24; Br 37.5.

Dehydrobromination. The dibromo derivatives (0.05 mole) were gradually added under nitrogen with stirring to a solution of 0.1-0.12 mole of triethylamine in 50 ml of ether (or another solvent) and the mixture was held at 40-60° for 30-60 min (the mixture was monitored by gas–liquid chromatography). The mixture was then washed with three 20-ml portions of water and dried with calcium chloride. Distillation yielded 45-60% of the α-bromoallenic esters (90-92% purity). Methyl ester Va was described previously in [7].

Ethyl 4-bromo-2,3-butadienoate (Vb) had bp 47° (0.8 mm) and $n_D^{21.5}$ 1.5158. Found %: Br 41.1. $C_6H_7BrO_2$. Calculated %: Br 41.8.

n-Butyl 4-bromo-2,3-butadienoate (Vc) had bp 63-65° (0.4 mm) and $n_D^{20.5}$ 1.5052. Found %: Br 35.00 $C_8H_{11}BrO_2$. Calculated %: Br 36.8.

Ethyl 2,3,4-tribromo-3-butenoate (VII, R = C_2H_5) was obtained in 86% yield and had bp 80-85° (0.08 mm) and n_D^{22} 1.5396. IR spectrum, ν, cm^{-1}: 1746 (COOR), 3084, and 1626 (BrCH=C). PMR spectrum (CCl_4), δ, ppm: 4.17 (OCH_2–), 5.76 (CHBr), and 6.7 (=CHBr).

n-Butyl 2,3,4-tribromo-3-butenoate (VII, R = N-C_4H_9) was obtained in 80% yield and had bp 150° (bath temperature) (0.2 mm) and n_D^{23} 1.5340. IR spectrum, ν, cm^{-1}: 1744 (COOR), 3090 and 1612 (BrCH=C). PMR spectrum (CCl_4), δ, ppm: 4.18 (OCH_2), 5.82 (CHBr), 6.76 (=CHBr).

CONCLUSIONS

A convenient method has been developed for the synthesis of conjugated bromoallenes starting from β-acetylenic alcohols.

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