SYNTHESIS OF TRIMETHOXYMETHYLALLENE

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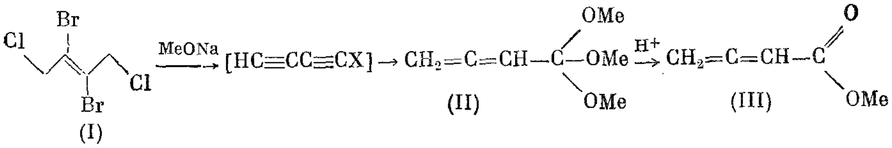
In contrast to the propargyl orthoesters [1], the corresponding allene derivatives are unknown. We developed a simple method for obtaining trimethoxymethylallene (II) by heating E-1,4-dichloro-2,3-dibromo-2-butene (I) with 4 g·equiv of MeONa in methanol.



$$\xrightarrow{MeONa} [HC{\equiv}CC{\equiv}CX] \rightarrow CH_2{=}C{=}CH{-}C(OMe)_3 \xrightarrow{H^+} CH_2{=}C{=}CH{-}C({=}O)OMe$$

The process probably proceeds via the intermediate halodiacetylene, which by subsequent nucleophilic substitution and addition of methoxy anion is converted to (II) in 40-45% yield. Together with (II), we identified the methyl esters of 2,3-butadienoic acid (II) (2-4%) and the β-methoxycrotonic ester (4-7%). The structure of the obtained compounds was confirmed by the IR and PMR spectral data.

The hydrolysis of (II) with dilute HCl solution at 20°C leads to ester (III) in 85% yield. Allene derivatives (II) and (III) can find use in deprotonation reactions [2].

EXPERIMENTAL

The GLC analysis was run on a Chrom-3 chromatograph using a glass column packed with 5% of OV-17. The IR spectra were obtained on a UR-20 spectrometer, and the PMR spectra were obtained on a Varian DA-60-IL instrument in CCl_4 solution and using HMDS as the internal standard. E-1,4-Dichloro-2,3-dibromo-2-butene (I), mp 57-58°, was obtained as described in [3]; PMR spectrum (δ, ppm): 4.46s.

Trimethoxymethylallene (II). With vigorous stirring, to a suspension of 79.0 g (0.28 mole) of (I) in 50 ml of MeOH and 50 ml of DMSO was added in an N_2 atmosphere 300 ml of a solution of MeONa (from 27.6 g) in MeOH (either abs. or technical) in 18-20 min, in such manner that the reaction mixture refluxed moderately. The mixture was refluxed for 1 h, cooled, diluted with 1 liter of water, extracted with ether (3 × 300 ml), and washed in succession with 2% aqueous-ammoniacal $AgNO_3$ solution and saturated NH_4Cl solution. The extracts were dried over $MgSO_4$, the ether was distilled off, and the residue (22-24 g) was distilled through a rotor column (6-8 theoretical plates) to give 14.2 g (47%) of (II), bp 69-70° (27 mm), n_D^{20} 1.4518. Found: C 58.64; H 8.04%. $C_7H_{12}O_3$. Calculated: C 58.31; H 8.32%. Infrared spectrum (film, ν, cm^{-1}): 1958, 840 (CH_2=C=CH). PMR spectrum (δ, ppm): 4.72-4.90 m (3H, CH_2=C=CH), 3.13 br. s (9H, $3CH_3O$), mol. wt. 144 (mass spectrometry). Based on the IR spectrum and GLC analysis, (II) is contaminated with 4-5% of the β-methoxycrotonic ester.

Methyl ester of 2,3-butadienoic acid (III). As in the synthesis of (II), the reaction mass from 79 g of (I) was cooled, hydrolyzed with 0.2 N HCl solution, and then worked up the same as before. Distillation gave 9.5 g (34%) of (III), bp 59-60° (52 mm), n_D^{20} 1.4628, which was identified via the IR and PMR spectral data [4].

CONCLUSIONS

Trimethoxymethylallene is formed by the reaction of MeONa with E-1,4-dichloro-2,3-dibromo-2-butene.

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NUCLEOPHILIC ADDITION OF THIOLS TO ACETYLENES IN LIQUID AMMONIA

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The nucleophilic addition of thiols to acetylenes has been well studied [1]. Basically, it obeys the trans-addition rule [2]. The stereospecific trans-nucleophilic addition of thiols to diacetylene was observed only in protic solvents, while mixtures of the cis- and trans-alkylthiobutenynes are formed in aprotic media [3]. In a series of papers by us [4-7] it was shown that diacetylene and its derivatives are easily thiylated in ammonia medium, in which connection the diyne adds only one equivalent of the thiol. In order to develop a new synthesis method for vinyl sulfides we studied in the present paper the behavior of acetylene and some of its derivatives with thiols in ammonia medium.

It was established that acetylene does not react with thiols in liquid NH_3 in the presence of alkalis, whereas monosubstituted acetylenes with acceptor substituents, depending on the nature of the activating group, add either one or two molecules of the thiol without a catalyst.

$$\underset{(Ia-g)}{R^1C\equiv CR^2} + HSR^3 \xrightarrow[\text{liq. }NH_3]{} \underset{(II),\,(III),\,(VII),\,(VIII)}{R^1CH{=}CR^2{-}SR^3} \rightarrow \underset{(IV),\,(V),\,(VI),\,(IX)}{R^1CH_2CR^2(SR^3)_2}$$

$$R^1 = Ph,\ R^2 = H(Ia);\ R^1 = MeOCO,\ R^2 = H\ (Ib);$$
$$R^1 = PhCO,\ R^2 = H\ (Ic);$$
$$R^1 = CN,\ R^2 = H\ (Id);\ R^1 = CN,\ R^2 = Ph(Ie);\ R^1 = CN,\ R^2 = (Me)_2COH(If);$$
$$R^1 = R^2 = NH_2CO(Ig);\ R^1 = Ph,\ R^2 = H,\ R^3 = Bu(II);\ R^1 = MeOCO,$$
$$R^2 = H,\ R^3 = Et\ (III),\ (IV);\ R^1 = PhCO,\ R^2 = H,\ R^3 = Et(V);$$
$$R^1 = CN,\ R^2 = H,\ R^3 = Et(VI);\ R^1 = CN,\ R^2 = Ph,\ R^3 = Pr\ (VII);$$
$$R^1 = CN,\ R^2 = (Me)_2COH,\ R^3 = Pr\ (VIII);\ R^1 = R^2 = NH_2CO,$$
$$R^3 = Et(IX).$$

Phenylacetylene (Ia) reacts with thiols in liquid NH_3 to give vinyl sulfide (II), which has 85% of the cis configuration (based on the PMR data). The conversion of (Ia) reaches 70%, and the yield of sulfide (II) reaches 82% (Table 1). The insertion of a carboxyl group raises the activity of acetylene (Ib). In this case both vinyl sulfide (III) and mercaptal (IV) were isolated from the reaction mass. By varying the ratio of the components the reaction can be directed to give mainly either of the indicated compounds. Sulfide (III) is the cis isomer (SSCC of ethylene protons ∿10 Hz). The stronger electron acceptors (CO, CN) in compounds (Ic, d) enhance the electrophilicity of the acetylene and facilitate the addition of two molecules of the thiol, which leads to the synthesis of mercaptals (V) and (VI), i.e. the reaction does not stop at the step of forming the vinyl sulfides. Disubstituted acetylenes, containing an electron-acceptor substituent, are also easily thiylated in liquid NH_3 without a catalyst. Phenylcyanoacetylene (Ie) stereoselectively adds one equivalent of the thiol in the β-position of the triple bond with respect to the activating CN group. The PMR spectrum of vinyl sulfide (VII) has only one signal of an olefinic proton, which indicates the formation of one of the isomers. The thiolate ion attacks cyanoacetylenic alcohol (If) in a similar manner, and here only vinyl sulfide (VIII) was isolated in 81% yield. Since the starting alcohol (If) easily reacts with NH_3, being converted to the hydroxyl-containing β-aminoacrylonitrile [8], then, in order to suppress the competing reaction, alcohol (If),

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