RADICAL REACTIONS OF BUTYL MERCAPTAN WITH VINYL AND ALLYL ACETATES

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The course of the radical telomerization of acrylic monomers by butyl mercaptan depends significantly on the type of initiation. Telomerization with the formation of significant amounts of higher telomer homologs occurs in the presence of peroxides. On the other hand, only the adduct is formed upon initiation with transition metal carbonyls, in particular, $Mn_2(CO)_{10}$ [1].

In the present work, we studied the reactions of butyl mercaptan with vinyl acetate (VAC) and allyl acetate (AAC) upon peroxide and metal complex initiation.

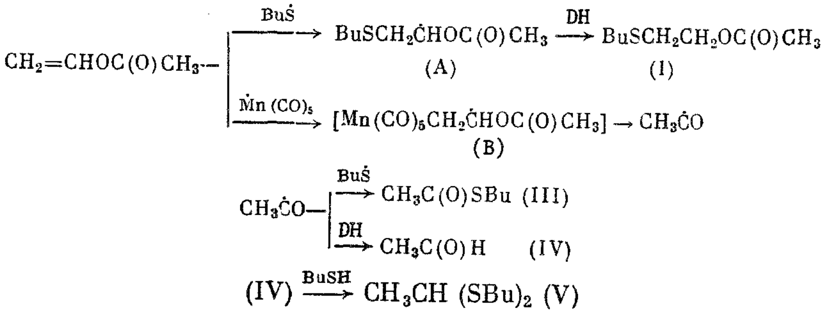
In the absence of initiator, BuSH reacts with VAC at 140°C to give adduct (I) in only ~10% yield. Under the same conditions, in the presence of tert-butyl peroxide (TBP), the adduct yield becomes quantitative (see Table 1). Telomerization of VAC by butyl mercaptan occurs when the M/BuSH ratio is ~3 (M is vinyl or allyl acetate).

$$BuSH \xrightarrow{RO} BuS$$

$$Bu\dot{S} + nCH_2{=}CHOC(O)CH_3 \xrightarrow{BuSH} \underset{(I),\ (II)}{BuS(CH_2CHOC(O)CH_3)_nH}$$

$n = 1$ (I), 2 (II).

The reaction of BuSH with VAC in the presence of $Mn_2(CO)_{10}$ proceeds differently. Products (III)-(V) are formed in this case in addition to (I). The formation of (I) and (III)-(V) may be attributed to competing reactions, namely, the reactions of VAC with thiyl radicals to give type-A radicals and with $Mn(CO_5)$ radicals with the formation of type-B radicals [2]. Radicals (A) react with BuSH to give adduct (I), while radicals (B) apparently largely decompose with the formation of acyl radicals, which are stabilized either by recombination with $BuS^{\cdot}$ radicals or by hydrogen atom abstraction from BuSH to give (III) and (IV), respectively.



$$CH_2{=}CHOC(O)CH_3 \xrightarrow{Bu\dot{S}} \underset{(A)}{BuSCH_2\dot{C}HOC(O)CH_3} \xrightarrow{DH} \underset{(I)}{BuSCH_2CH_2OC(O)CH_3}$$

$$CH_2{=}CHOC(O)CH_3 \xrightarrow{\dot{M}n(CO)_5} \underset{(B)}{[Mn(CO)_5CH_2\dot{C}HOC(O)CH_3]} \rightarrow CH_3\dot{C}O$$

$$CH_3\dot{C}O \xrightarrow{Bu\dot{S}} CH_3C(O)SBu\ (III)$$

$$CH_3\dot{C}O \xrightarrow{DH} CH_3C(O)H\ (IV)$$

$$(IV) \xrightarrow{BuSH} CH_3CH(SBu)_2\ (V)$$

The formation of (V) by the proposed scheme was supported by a special experiment. In the presence of $Mn_2(CO)_{10}$, significant amounts of acetaldehyde are formed in the reaction of VAC with 2-propanol, which cannot enter further reactions with acetaldehyde. Mercaptal (V) is probably formed from (IV) and BuSH. The reaction of (IV) and BuSH at 140°C gives (V) even in the absence of any catalysts.

Support for this scheme is found in the results obtained in a study of the addition of BuSH to AAC. In the presence of TBP, BuSH and AAC form the adduct, $BuSCH_2CH_2CH_2OC(O)CH_3$ (VI) in quantitative yield. In the presence of $Mn_2(CO)_{10}$ and without initiator, these reagents give only the adduct but in low yield (Table 1). The lack of reaction by-products in

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TABLE 1. Reaction of Butyl Mercaptan with Vinyl and Allyl Acetates (M)

Initiator (mole % relative to BuSH)	M/BuSH	Conversion, %		Yield of (I) or (VI), %
		M	BuSH	
$M=CH_3C(O)OCH=CH_2$				
–	1.1	17	17	9 (I)
TBP (1)	1.1	100	100	96 (I)
TBP (1)	3.1		100	83* (I)
$Mn_2(CO)_{10}$ (4)	1.1	33	37	8** (I)
$Fe(CO)_5$ (4)	1,1	0	0	–
$M=CH_3C(O)OCH_2CH=CH_2$				
TBP (1)	1,0	100	100	98 (VI)
–	1.0	30	31	27 (VI)
$Mn_2(CO)_{10}$ (4)	1,1	30	32	26 (VI)
$Fe(CO)_5$ (4)	1,0	0	0	

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*The yield of (II) was 11%.

**(III) and (V) were also formed in 11 and 14% yields, respectively, while (IV) was identified in the reaction mixture by gas-liquid chromatography.

this case is apparently related to the inability of the intermediate radical adduct, $[Mn(CO)_5CH_2\dot{C}HCH_2OC(O)CH_3]$, to undergo fragmentation at the O–C bond.

$Fe(CO)_5$, in contrast to $Mn_2(CO)_{10}$, inhibits the addition of BuSH to VAC and AAC as noted for the addition of BuSH to alkenes [3].

EXPERIMENTAL

The ^{13}C NMR spectra were taken on a Bruker WP-200SY spectrometer at 50.31 MHz using the gmodecho mode at room temperature in CCl_4 (95.99 ppm from TMS). The gas-liquid chromatographic analysis of the reaction mixtures was carried out on an LKhM-8MD chromatograph with a katharometer detector and helium as the gas carrier on 1 m × 3 mm and 3 m × 3 mm columns packed with 15% SKTFT on Chromaton N-AV-HMCD 0.15-0.20 mm and a 2 m × 3 mm column packed with 5% Carbowax 20M on Chromaton N-AW-DMCS 0.16-0.20 mm in a stationary mode and with temperature programming. The analytical experiments (Table 1) were carried out in glass ampuls sealed in an argon atmosphere by the freeze–thaw technique. The ampuls were heated at 140°C with stirring. The conversion of the starting compounds and product yields were determined by gas-liquid chromatography relative to an internal standard.

Telomerization of Vinyl Acetate by Butyl Mercaptan. A mixture of 83 mmoles VAC, 27 mmoles BuSH, and 0.5 mole TBP was heated in an argon atmosphere in a sealed ampul for 5 h at 140°C. Distillation gave 22 mmoles 2-butylthioethyl acetate (I), bp 73°C (2 mm), d_4^{20} 0.9902, n_D^{20} 1.4580. Found, %: C 54.61; H 9.03; S 18.01. $C_8H_{16}O_2S$. Calculated, %: C 54.54; H 9.09; S 18.18. ^{13}C NMR spectrum (δ, ppm): 20.5 ($\underline{C}H_3C{=}O$), 170.0 (C=O), 65.5 (OCH_2), 31.7 ($\underline{C}H_2S\underline{C}H_2$), 30.3 ($SCH_2\underline{C}H_2$), 22.0 ($\underline{C}H_2CH_3$), 13.6 ($\underline{C}H_3$). We also obtained 2 mmoles 4-butylthio-3-acetoxybutyl acetate (II), bp 133°C (2 mm), d_4^{20} 1.0580, n_D^{20} 1.4680. Found, %: C 54.83; H 8.62; S 12.53. $C_{12}H_{22}O_4S$. Calculated, %: C 54.96; H 8.40; S 12.21. ^{13}C NMR spectrum (δ, ppm): 20.6, 20.4 ($\underline{C}H_3C{=}O$), 169.1, 166.9 (C=O), 60.1 (OCH_2), 31.9, 31.5 ($OCH_2\underline{C}H_2$), ($S\underline{C}H_2\underline{C}H_2$), 69.5 (CH), 35.5 ($CH\underline{C}H_2$), 21.7 ($\underline{C}H_2CH_3$), 13.6 ($CH_3$).

Reaction of Vinyl Acetate with Butyl Mercaptan in the Presence of $Mn_2(CO)_{10}$. A mixture of 174 mmoles VAC, 166 mmoles BuSH, and 3 mmoles $Mn_2(CO)_{10}$ was heated in a sealed ampul in an argon atmosphere for 5 h. Distillation gave 12 mmoles butylthiol acetate (III), bp 73°C (25 mm), d_4^{20} 0.9528, n_D^{20} 1.4590. Found, %: C 54.45; H 9.29; S 24.07. $C_6H_{12}OS$. Calculated, %: C 54.54; H 9.09; S 24.24. ^{13}C NMR spectrum (δ, ppm): 29.8 ($\underline{C}H_3C{=}O$), 194.5 (C=O), 31.2 (SCH_2), 28.2 ($SCH_2\underline{C}H_2$), 21.4 ($\underline{C}H_2CH_3$), 13.0 (CH_3). We also obtained 10 mmoles adduct (I) and 9 mmoles of the dibutylmercaptal of acetaldehyde (V), bp 89°C (2 mm), d_4^{20} 0.9270, n_D^{20} 1.4878. Found, %: C 58.10; H 10.26; V 31.09. $C_{10}H_{22}S_2$. Calculated, %: C 58.25; H 10.68; S 31.07. ^{13}C NMR spectrum (δ, ppm): 22.7 ($\underline{C}H_3CH$), 45.6 (CH), 31.2, 31.5 (SCH_2), 29.4 ($SCH_2\underline{C}H_2$), 21.7 ($\underline{C}H_2CH_3$), 13.2 (CH_3).

Reaction of Vinyl Acetate with 2-Propanol in the Presence of $Mn_2(CO)_{10}$. A mixture of 6 mmoles VAC, 6.8 mmoles 2-propanol, and 0.2 mmole $Mn_2(CO)_{10}$ was heated at 140°C for 3 h in a sealed ampul in an argon atmosphere. Product (IV) was found in the reaction mixture in ~10% yield by gas-liquid chromatography.

Reaction of (IV) with BuSH. A mixture of 5.5 mmoles BuSH and 4.5 mmoles acetaldehyde was heated in a sealed ampul in an argon atmosphere for 3 h at 140°C. The yield of (V) was 1.8 mmoles (40%) as indicated by gas-liquid chromatography.

Reaction of Allyl Acetate with BuSH in the Presence of TBP. A mixture of 60 mmoles AAC, 6.6 mmoles BuSH, and 0.8 mmoles TBP was heated in a sealed ampul in an argon atmosphere for 5 h. Distillation gave 5.8 mmoles 3-butylthiopropyl acetate (VI), bp 94°C (1 mm), d_4^{20} 0.9783, n_D^{20} 1.4631. Found, %: C 56.36; H 9.38; S 17.02. $C_9H_{18}O_2S$. Calculated, %: C 56.84; H 9.47; S 16.84. ^{13}C NMR spectrum (δ, ppm): 20.3 ($\underline{C}H_3C{=}O$), 169.7 (C=O), 62.6 (OCH_2), 28.6, 28.1 ($OCH_2\underline{C}H_2$), ($SCH_2\underline{C}H_2$), 31.5, 31.4 ($\underline{C}H_2S\underline{C}H_2$), 21.7 ($\underline{C}H_2CH_3$), 13.4 ($CH_3$).

CONCLUSIONS

The reactions of vinyl acetate and allyl acetate with butyl mercaptan in the presence of tert-butyl peroxide and $Mn_2(CO)_{10}$ lead to an adduct. Acetaldehyde, butyl thioacetate, and the dibutylmercaptal of acetaldehyde are also formed in the case of $Mn_2(CO)_{10}$.

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BEHAVIOR OF 4-HYDROXY-4-METHYL-2-PENTYNONITRILE IN WATER IN THE PRESENCE OF LITHIUM HYDROXIDE

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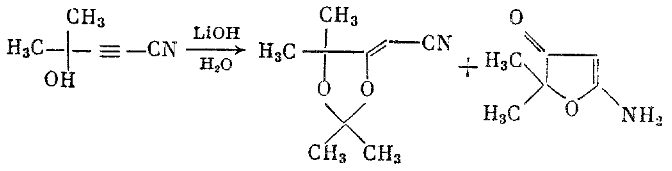
The effect of the nature of the base cation on the reactivity of tertiary cyanoacetylenic alcohols has been noted in our previous work [1]. In particular, the formation of oxetanes is observed in dioxane in the presence of strong bases such as KOH, NaOH, and CsOH. Under analogous conditions, LiOH facilitates the formation of 1,4-dioxane derivatives [2].

A further study of the behavior of tertiary cyanoacetylenic alcohols upon the action of bases has shown that the solvent has a significant effect on the course of the reaction. Thus, we found that 4-hydroxy-4-methyl-2-pentynonitrile (I) in water in the presence of LiOH gives substituted 1,3-dioxolane (II) and 2,3-dihydro-3-furanone (III) instead of the expected 1,4-dioxane [2].



(I) (II) (III)

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