with benzene. 0.10 g of a mixture of **3** and bis(triphenylphosphine)gold tetrafluoroborate (**4**) was isolated from the benzene extract. After repeated reprecipitation (benzene—hexane), 0.03 g of **3** was obtained from the mixture, however, we failed to completely separate **3** from **4**, which is indicated by the results of elemental analysis and by the overestimated value of the integrated intensity of the aromatic protons in the ^{1}H NMR spectrum. Found (%): C, 50.13; H, 3.72. $C_{22}H_{24}AuPRu$. Calculated (%): C, 48.77; H, 3.50. ^{1}H NMR ($CDCl_3$, δ): 7.50—7.20 (m); 4.80 (t); 4.56 (s); 4.36 (t).

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Homolytic addition of benzylidene bromide to trimethylvinylsilane and 1-hexene

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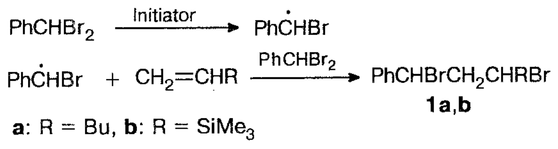
Benzylidene bromide reacts with unsaturated compounds $CH_2{=}CHR$ (R = Bu, $SiMe_3$) in the presence of benzoyl peroxide to give $PhCHBrCH_2CHRBr$ adducts.

Key words: radicals; addition; benzylidene bromide; 1-hexene; trimethylvinylsilane.

An investigation of radical addition and telomerization involving benzyl bromide has shown that it virtually does not react in the presence of peroxides, but selectively reacts at the C—Br bond with metallocomplex systems based on $Fe(CO)_5$ as initiators.[1] In the present work, in a study of radical addition of benzylidene bromide to 1-hexene and trimethylvinylsilane, we unexpectedly obtained the opposite result. When benzoyl peroxide (BP) is used as the initiator, benzylidene bromide selectively reacts at the C—Br bond to give adducts **1a,b** (Scheme 1). These adducts are not formed, however, in the presence of the $Fe(CO)_5$ + DMF system.

Scheme 1



$$\mathrm{PhCHBr_2} \xrightarrow{\text{Initiator}} \mathrm{Ph\dot{C}HBr}$$

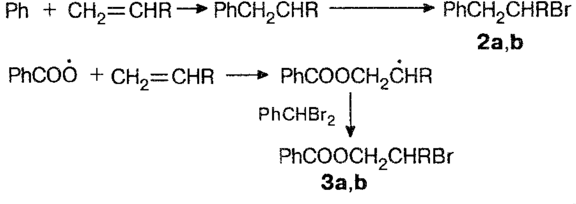
$$\mathrm{Ph\dot{C}HBr} + \mathrm{CH_2{=}CHR} \xrightarrow{\mathrm{PhCHBr_2}} \mathrm{PhCHBrCH_2CHRBr}$$

1a,b

a: R = Bu, **b**: R = $SiMe_3$

Compounds **1a,b** amount to ~80 % of the overall reaction products (Table 1). In addition to these adducts, noticeable amounts of $PhCH_2CHRBr$ (**2a,b**) and $PhCO_2CH_2CHRBr$ (**3a,b**) are formed as a result of the reaction of $CH_2{=}CHR$ with the $Ph^{\cdot}$ and $PhCOO^{\cdot}$ radicals (from BP), according to Scheme 2.

Scheme 2



$$\mathrm{P\dot{h}} + \mathrm{CH_2{=}CHR} \longrightarrow \mathrm{PhCH_2\dot{C}HR} \xrightarrow{\mathrm{PhCHBr_2}} \mathrm{PhCH_2CHRBr}$$

2a,b

$$\mathrm{PhCO\dot{O}} + \mathrm{CH_2{=}CHR} \longrightarrow \mathrm{PhCOOCH_2\dot{C}HR} \xrightarrow{\mathrm{PhCHBr_2}} \mathrm{PhCOOCH_2CHRBr}$$

3a,b

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Table 1. The reactions of $PhCHBr_2$ with alkenes in the presence of BP (10 mol. %), 100 °C, 3 h

Alkene	The $PhCHBr_2$: alkene ratio	The degree of conversion of $PhCHBr_2$ (%)	Yield of **1 a,b** (%)		Reaction products (mol. %)		
			theoretical	based on the consumed $PhCHBr_2$	**1 a,b**	**2 a,b**	**3 a,b**
CH_2=CHBu	4.3	24.6	7.8	31.7	84.6	9.0	6.4
CH_2=$CHSiMe_3$	4.1	39.8	16.0	40.2	79.8	13.7	6.5

Addition of benzoate radicals to monomers has been described earlier.[2] Further interaction of the resulting radical adducts with benzylidene bromide affords compounds **3a,b**.

The reaction mixtures were studied by the GC-MS method. The dimer PhCHBrCHBrPh and stilbene, which originates due to its debromination, were detected among the by-products. In the case of 1-hexene, the products of dehydrobromination of the adduct and $PhCO_2CH_2CH_2Bu$ were also found.

Experimental

GC-MS spectra were recorded on a VG-7070E spectrometer with a 50 cm DV-5 column. The temperature was programmed from 30 to 220 °C (2.5 °C min^{-1}); masses of ions are given for the ^{79}Br isotope. GLC analysis was carried out on a LKhM-80 chromatograph with a 1300×3 mm steel column with 15 % SKTFT-50X on Chromaton N-AW, helium as the carrier gas (60 mL min^{-1}), and a katharometer as the detector. The temperature gradient was 50—250 °C (6 °C min^{-1}).

The experiments on the addition of benzylidene bromide to unsaturated compounds were carried out in 4.5-mL glass tubes according to the previously described procedure.[1] The initiator (BP) was taken in an amount of 10 mol. % of the amount of $PhCHBr_2$. The degree of conversion of $PhCHBr_2$ and yields of the reaction products were calculated from the data of the GLC analysis (see Table 1) using bromobenzene as the reference compound. The structures of the resulting compounds were confirmed by mass spectrometry.

Mass spectra of compounds **1—3**, *m/z* (I_{rel} (%)), the number of Br atoms: **1a** (one of the diastereomers): 332 (0.1), 2 Br, $[M]^{+\cdot}$; 253 (21.4), 1 Br, $[M-Br]^+$; 173 (38.1), $[M-Br-HBr]^+$; 131 (23.8), $[PhCH=CHCH_2CH_2]^+$; 117 (61.9), $[PhCH=CHCH_2]^+$; 105 (14.3), $[PhCH_2CH_2]^+$; 104 (19.0), $[PhCH=CH_2]^{+\cdot}$; 91 (100), $[PhCH_2]^+$. **2a**: 240 (10.7), 1 Br, $[M]^{+\cdot}$; 161 (20.2), $[M-Br]^+$; 117 (14.3), $[PhCH_2CH=CH]^+$; 105 (14.3), $[PhCH_2CH_2]^+$; 104 (14.3), $[PhCH=CH_2]^{+\cdot}$; 92 (16.7), $[PhCH_2]^{+\cdot}$; 91 (100), $[PhCH_2]^+$. **3a**: 284 (0.4), 1 Br, $[M]^{+\cdot}$; 205 (2.6), $[M-Br]^+$; 162 (2.9), 1 Br, $[CH_2=CBrC_4H_9]^{+\cdot}$; 123 (45.2), $[PhCOOH_2]^+$; 105 (100), $[PhCO]^+$; 83 (31.0), $[CH=CHBu]^+$. **1b** (one of the diastereomers): 348 (0.06), 2 Br, $[M]^{+\cdot}$; 333 (0.06), 2 Br, $[M-Me]^+$; 269 (23.8), 1 Br, $[M-Br]^+$; 137 (14.3), 1 Br, $[BrSiMe_2]^+$; 117 (77.4), $[PhCH=CHCH_2]^+$; 91 (13.1), $[PhCH_2]^+$; 73 (100), $[SiMe_3]^+$. **2b**: 256 (8.3), 1 Br, $[M]^{+\cdot}$; 241 (7.1), 1 Br, $[M-CH_3]^+$; 177 (19.0), $[M-Br]^+$; 137 (44.0), 1 Br, $[BrSiMe_2]^+$; 104 (90.5), $[PhCH=CH_2]^{+\cdot}$; 91 (7.1), $[PhCH_2]^+$; 73 (100), $[SiMe_3]^+$. **3b**: 300 (0.1), 1 Br, $[M]^{+\cdot}$; 285 (2.0), 1 Br, $[M-Me]^+$; 221 (2.5), $[M-Br]^+$; 179 (85.7), $[PhCOOSiMe_2]^+$; 163 (2.3), 1 Br, $[M-Me-PhCOOH]^+$; 137 (4.8), 1 Br, $[BrSiMe_2]^+$; 135 (16.7), $[PhCOOCH_2]^+$; 105 (100), $[PhCO]^+$; 73 (34.5), $[SiMe_3]^+$.

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