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REACTION OF BROMOFORM AND IODOFORM WITH ACRYLIC MONOMERS INITIATED BY $Fe(CO)_5$ + DMF

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Polybromomethanes and polyiodomethanes are rather efficient addends in radical reactions with unsaturated compounds. The use of the $Fe(CO)_5$ + DMF initiating system permits the homolytic addition to acrylic monomers selectively at the carbon–halogen bond without significant polymerization [1-4].

In the present work, the first study was carried out on the reaction of $CHBr_3$ with acrylic monomers as a pathway to the synthesis of α,γ,γ-tribromobutyric acid. The reactions of $CHBr_3$ with acylonitrile (AN), methyl acrylate (MA), and methyl methacrylate (MMA) were carried out at 95-100°C in the presence of the $Fe(CO)_5$ + DMF system. The reaction results depend strongly on the monomer/telogen (M/S) ratio. In the case of M/S = 1, the acrylic monomer predominantly polymerizes and adducts could not be isolated. For M/S = 0.5, the addition of $CHBr_3$ proceeds mainly with the cleavage of the C–Br bond and formation of adducts (I)-(III). The greatest adduct yield was obtained with MA (Table 1).

$$CHBr_3 + CH_2{=}CRX \xrightarrow{Fe(CO)_5 + DMF} CHBr_2CH_2CRBrX$$

$R = H, X = CN$(I), $R = H, X = COOCH_3$(II); $R = CH_3, X = COOCH_3$ (III).

The structure of (I)-(III) were supported by ^{13}C NMR spectroscopy (Table 1). The reaction of $CHBr_3$ with AN gave 1,1,3-tribromopropane (TBP) in addition to (I). The mechanism for the formation of TBP is unclear but a special experiment showed that this product cannot be obtained by heating (I) with $CHBr_3$ in the presence of $Fe(CO)_5$ + DMF.

The exclusive polymerization of the monomer was found in attempts to initiate the reaction of $CHBr_3$ with acrylic monomers by benzoyl peroxide. The ionic addition of $CHBr_3$ to acrylic monomers proceeds with cleavage of the C–H bond in the addend and leads to different adducts [5]. Comparison of the results obtained with our previous data [1-3] indicates that $CHBr_3$ is less effective in this reaction as an addend relative to CBr_4, CCl_2Br_2 and CCl_3Br.

In the case of CHI_3, heating of CHI_3 to the melting point is used due to its low solubility in the reaction medium. This leads to tar formation and reduces the adduct yield [4]. CHI_3 has limited solubility in organic solvents suitable for carrying out homolytic reactions but has good solubility in $CHBr_3$. Carrying out the addition of CHI_3 to AN and MA in $CHBr_3$ initiated by the $Fe(CO)_5$ + DMF system (the $CHBr_3$:CHI_3:monomer mole ratio is 3.9-4.4:1:3) leads exclusively to adducts of CHI_3. This indicates the significantly greater activity of CHI_3 as an addend in these reactions. Under the same conditions (95-100°C), CHI_3 without solvent does not form adducts with AN and MA. In comparison with the use of CHI_3 with AN without sol-

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TABLE 1. Addition of $CHBr_3$ to Acrylic Monomers*

Adduct	$CHBr_3$ conversion, %	Adduct yield, % rel. to $CHBr_3$ consumed	Bp, °C (p, mm Hg)	n_D^{20}	d_4^{20}	^{13}C, ppm on TMS, $^1J_{CH}$, Hz				
						C^1	C^2	C^3	C^4	C^5
$\overset{1}{C}HBr_2\overset{2}{C}H_2\overset{3}{C}HBr\overset{4}{C}N$	93	25	94(1–2)	1,5710	2,2772	36,6 (181)	48,6 (138)	24,5 (162)	115,3	–
$\overset{1}{C}HBr_2\overset{2}{C}H_2\overset{3}{C}HBr\overset{4}{C}OO\overset{5}{C}H_3$	43	78	101(3)	1,5440	2,1015	41,1 (182)	48,1 (136)	42,2 (148)	167,9	53,1
$\overset{1}{C}HBr_2\overset{2}{C}H_2\underset{\substack{\mid\\CH_3}}{\overset{3}{C}}Br-\overset{4}{C}OO\overset{5}{C}H_3$	53	15	113(1–2)	1,5368	1,9789	38,5	55,0	57.6 27,4	169,7	53,0

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*M/S = 0.5; 10 mole % $Fe(CO)_5$, 30 mole % DMF relative to the monomer.

vent at 145°C [4], the reaction at 95-100°C in $CHBr_3$ proceeds with less tar formation and somewhat greater conversion (10% on the average), while the T_2:T_1 ratio in the telomer mixture is not significantly altered.

$$CHI_3 + CH_2{=}CHCN \xrightarrow[CHBr_3]{Fe(CO)_5 + DMF} \underset{T_1}{CHI_2CH_2CHICN} + \underset{T_2}{CHI_2(CH_2CHCN)_2I}$$

Thus, the telomerization of AN by iodoform in $CHBr_3$ may be carried out under conditions milder than those reported in our previous work [4].

EXPERIMENTAL

Gas-liquid chromatography of the starting compounds and products was carried out on a 1300 × 3 mm steel column packed with 15% SKTFT-50Kh on Chromaton N-AW (0.16-0.20) and 60 ml/min helium gas carrier flow rate. A katharometer detector was used. Preparative gas-liquid chromatography was carried out on a 1300 × 9 mm steel column packed with 20% SKTFT-50Kh on Chromaton N-AW (0.16-0.20) with 80 ml/min helium gas carrier flow rate at 150°C. The column chromatography of iodine-containing products was carried out on silica gel L100/160. The column diameter was 1.5 cm. The height of the adsorbent column was 40 cm. Elution was carried out consecutively with CCl_4 and 1:1 CCl_4–$CHCl_3$. The ^{13}C NMR spectra were obtained for 50% solutions in CCl_4 relative to TMS on a Bruker WP-200 spectrometer.

The Addition of $CHBr_3$ to Acrylic Monomers. A sample of 50 mmoles $CHBr_3$, 25 mmoles monomer, 2.5 mmoles $Fe(CO)_5$ and 7.5 mmoles DMF was loaded into a glass ampule. The ampule was frozen, evacuated, filled with argon and sealed before heating on an oil bath for 2 h at 95-100°C. The reaction products from three identical experiments were combined. The iron salts were removed by passage through a silica gel layer in CCl_4 and the product was distilled. The yields of (I)-(III), physical indices and ^{13}C NMR spectral data are given in Table 1. In the case of AN, adduct (I) contained 1,1,3-tribromopropane as an impurity, which was isolated by preparative gas-liquid chromatography and identified by its ^{13}C NMR spectrum [6]. Gas-liquid chromatography indicated that the (I)/TBP ratio was 92:8. Significant tar formation was observed in the reactions of AN and MMA. The elemental analysis data for (I)-(III) correspond to the calculated values.

Addition of CHI_3 to Acrylic Monomers. The reactions were carried out in sealed ampules with stirring at 95°C for 2 h both with and without $CHBr_3$. The reaction products were separated by column chromatography according to our previous procedure [4] and identified using authentic samples relative to their ^{13}C NMR spectra. The lack of $CHBr_3$ adducts and telomers was shown by gas-liquid chromatography and ^{13}C NMR spectroscopy. The yields were given relative to CHI_3 consumed.

Reaction of CHI_3 with Acrylonitrile. a) A mixture of 11.8 mmoles CHI_3, 47.6 mmoles $CHBr_3$, 35.5 mmoles AN, 0.6 mmole $Fe(CO)_5$, and 1.8 mmol DMF gave 6.1 mmoles CHI_3, 2.1 mmoles (37%) CHI_2CH_2CHICN, and 1.4 mmole (24%) $CHI_2(CH_2CHCN)_2I$.

b) The same procedure but without $CHBr_3$ did not give the above reaction products.

Reaction of CHI_3 with Methyl Acrylate. A sample of 10.2 mmoles CHI_3, 44.8 mmoles $CHBr_3$, 31.4 mmoles MA, 0.5 mmole $Fe(CO)_5$ and 1.5 mmole DMF gave 3.6 mmole CHI_3 and 2.9 mmoles (44%) $CHI_2CH_2CHICO_2CH_3$.

CONCLUSIONS

The $Fe(CO)_5$ + DMF system, in contrast to peroxide initiation, permits us to carry out the addition of bromoform with selective cleavage of the C–Br bond to readily polymerizing acrylonitrile, methyl acrylate, and methyl methacrylate. Iodoform was shown to be significantly more active than bromoform in these reactions, which permits carrying out the radical addition and telomerization of iodoform in bromoform at lower temperature than without solvent.

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