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ADDITION OF CHLOROBROMOMALONIC ESTER TO METHYL ACRYLATE

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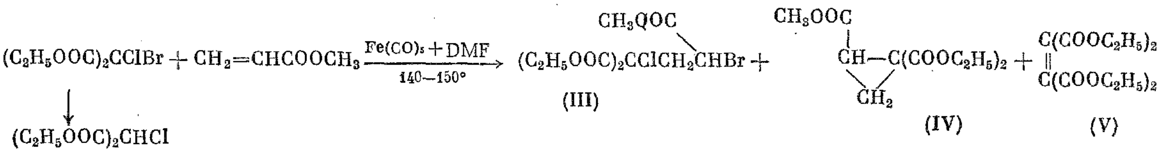
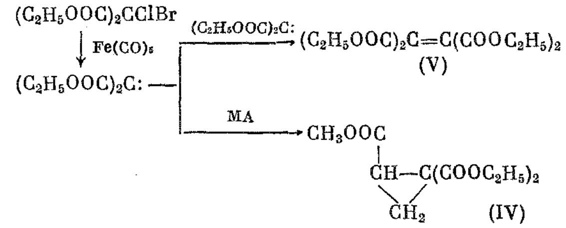
Chlorobromomalonic ester (CBM) [1] permits comparing the reactivity of geminal chlorine and bromine atoms under radical addition conditions. Its closest analogs, the dichloro-(DCM) and dibromomalonic (DBM) esters, when initiated by the coordination initiating system (CI) $Fe(CO)_5$ + DMF, react with methyl acrylate (MA) to give the adducts $(C_2H_5OOC)_2CXCH_2CHXCOOCH_3$, X = Cl (I), Br (II) [2, 3]. Here DBM is a more active addendum than DCM. It seemed expedient to study CBM in the reaction with MA using the same initiation method.

It proved that CBM, when initiated using this system, reacts with MA with cleavage of the C–Br bond and gives adduct (III). Together with this, both of the halogen atoms are cleaved from CBM to give 1,1-dicarbethoxy-2-carbomethoxycyclopropane (IV) and tetraethyl ethylene tetracarboxylate (V). The CBM is also reduced slightly to monochloromalonic ester (MCM).



The formation of (IV) and (V) indicates the possible carbenoid cleavage of the halogen atoms from $(C_2H_5OOC)_2CX_2$(X = Cl, Br) by the $Fe(CO)_5$.



The intermediate formation of carbenoid particles in the reactions of gem-dihalides with $Fe(CO)_5$ was postulated in [4]. It is known [5] that $C_6H_5COCHBr_2$ reacts with $Fe(CO)_5$ to give trans-1,2,3-tribenzoylcyclopropane. The generation of the carbene $(C_2H_5OOC)_2C$: from diazomalonic ester gives (V) [6, 7]. However, by analogy with [8], another possibility exists for the formation of (IV).

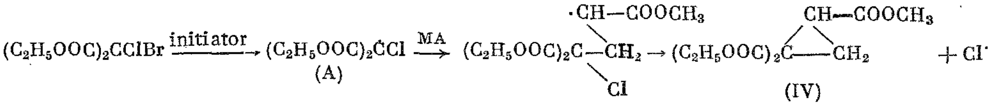


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TABLE 1. Addition of Chlorobromomalonic Ester (CBM) and Dichloromalonic Ester (DCM) to Methyl Acrylate (MA), Initiated by $Fe(CO)_5$ + DMF System (2 h, 145 ± 3°C, Ar atmosphere)

Reagent, mmoles		Initiator, mmoles		Conversion, %		Yield, % of theory			
addendum	MA	$Fe(CO)_5$	DMF	adduct	MA	adduct	(IV)	(V)	MCM
18 (CBM)	18	1,8	5,4	91	56	38(III)	13	27	9
160 (DCM)	160	16	48	72	98	39(I)	6	20	4
160 (DCM)	80	12	36	47	100	14(I)	4	23	5

Here the formation of (V) can also be depicted by the dimerization of the (A) radicals and the subsequent dechlorination of $(C_2H_5OOC)_2CCl_2$ (VI) by $Fe(CO)_5$, but in our case we were unable to find (VI) in the reaction mass. The formation of (V) was observed in the reactions of DCM and DBM with MA [2, 3]. In the present paper the reaction of DCM with MA was studied in more detail; together with (V) we also found (IV) among the reaction products (Table 1). We also studied the behavior of CBM in the absence of MA when exposed to the CI. Diethyl chlorobromomalonate when heated in the presence of the $Fe(CO)_5$ + DMF system undergoes three types of transformations: dehalodimerization to give (V), reduction to MCM, and disproportionation* with a redistribution of the halogen atoms (the yield in % of theory is indicated in parentheses).

$$(C_2H_5OOC)_2CClBr \xrightarrow{Fe(CO)_5} \underset{(V)}{(C_2H_5OOC)_2C}\underset{(37)}{=C(COOC_2H_5)_2} + \underset{(16)}{(C_2H_5OOC)_2CHCl} + \underset{(16)}{(C_2H_5OOC)_2CCl_2} + \underset{(6)}{(C_2H_5OOC)_2CBr_2}$$

The absence of adducts (I) and (II) (from DCM and DBM) in the reaction mass when CBM adds to MA, initiated by the $Fe(CO)_5$ + DMF system, indicates that the disproportionation of CBM is slight under the addition conditions selected by us.

All of the mentioned reaction products were isolated in the pure state by preparative GLC, and their structure was confirmed by the PMR and ^{13}C NMR spectra, and also by the fact that the found and calculated molecular refractions coincided.

EXPERIMENTAL

GLC analysis: LKhM-8MD-M5 chromatograph (katharometer); stainless steel columns: 1) 1000 × 3 mm, packed with 5% SE-30 deposited on Chromaton N-AW-HMDS (0.16-0.20 mm), and 2) 2000 × 3 mm, packed with SKTP-50X deposited on Chromaton N-AW-HMDS (0.16-0.20 mm); carrier gas = helium (1.5-2 liter/h). The internal standard method was used for the quantitative analysis ($CH_3COCCl_2COOC_2H_5$ for the starting products, and $CH_3COCHCl(COOC_2H_5)CH_2CHClCOOCH_3$ for the reaction products). Preparative GLC: Tswett-1 chromatograph equipped with a preparative attachment, and 500 × 5 mm stainless steel column packed with 5% XE-60 deposited on Chromaton N-AW-DMCS (0.20-0.25 mm). The PMR spectra were taken on a Perkin-Elmer R-12 instrument (60 MHz) using 50% CCl_4 solutions of the compounds. The ^{13}C NMR spectra were obtained on a Bruker HX-90 instrument using $CHCl_3$ as the internal standard (77.17 ppm from TMS). The chemical shifts are given from TMS.

Chlorobromomalonic ester (CBM) was obtained by the bromination [1] of $ClCH(COOC_2H_5)_2$, n_D^{20} 1,4630, d_4^{20} 1.4964. PMR spectrum: 1.35 (6H, CH_3), 4.40 (4H, CH_2). ^{13}C NMR spectrum: 13.3 (CH_2), 63.5 (CH_2), 64.2 (CClBr), 162.4 (CO). Found: C 30.71; H 3.5; Hal 42.40%. $C_7H_{10}BrClO_4$. Calculated: C 30.74; H 3.69; Hal 42.18%.

The disproportionation of CBM was run in a 2-ml glass ampul in an argon atmosphere (2 h, 140°). The weight of CMB was 0.3856 g. Analysis of the reaction mixture by GLC gave 0.1415 g of CBM, 0.0451 g of $ClCH(COOC_2H_5)_2$, 0.0513 g of $CCl_2(COOC_2H_5)_2$, 0.0285 g of $CBr_2(COOC_2H_5)_2$, 0.0827 g of (V), and 0.0365 g of unidentified products.

The addition of CBM to methyl acrylate (MA) was run in 15-ml sealed glass ampuls in an argon atmosphere (2 h, 145 ± 3°). The reaction mass from three identical experiments was diluted in half with $CHCl_3$, washed in succession with 10% HCl solution and water, dried over $MgSO_4$, and fractionally distilled at 1 mm. The preparative GLC of the 113-120° fraction gave cyclopropane (IV), n_D^{20} 1.4465, d_4^{20} 1.1580. Found: C 53.29; H 6.84%. $C_{11}H_{16}O_6$. Calculated: C 54.09; H 6.60%. PMR spectrum: 1.28 t and 1.31 t (6H, CH_3CH_2O), 1.67 m (2H, CH_2 ring), 2.39 and 2.57 d.d (1H, CH), 3.62 s (3H, $COOCH_3$), 4.09 and 4.14 q (4H, CH_2O). ^{13}C NMR spectrum (in CCl_4, δ 95,99 from TMS): 13.8 ($^{13}CH_3CH_2O$), 19.1 (CH_2 ring), 27.1 (CH ring), 36.4 (C ring), 51.5 (CH_3O),

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*This reaction under homolytic conditions was observed previously for other types of CClBr groupings [9].

60.7 and 61.4 (OCH_2), 164.3 ($^{13}COOCH_3$), 167.9 and 168.6 ($^{13}COOC_2H_5$). The assignments were based on the multipleticity of the C–H in the spectrum, taken without suppressing the C–H couplings, and also taking into account the data on the esters of 1,2-cyclopropanedicarboxylic acid [10]. The preparative GLC of the 134-137° fraction gave adduct (III), 1-chloro-3-bromo-1,1-dicarbethoxy-3-carbomethoxypropane in 38% yield, n_D^{20} 1.4690, d_4^{20} 1.4066. Found: C 36.98; H 4.56; Hal 31.55%. $C_{11}H_{16}BrClO_6$. Calculated: C 36.74; H 4.48; Hal 32.08%. PMR spectrum: 1.31 t (6H, CH_3CH_2O), 3.01 m (2H, CH_2), 3.73 s ($COOCH_3$), 4.24 q (4H, CH_2O), 4.49 (1H, CHBr). ^{13}C NMR spectrum: 13.3 ($^{13}CH_3-CH_2O$), 38.4 (CH_2), 41.7 (CHBr), 52.5 (CH_3O), 62.9 (CH_2O), 68.0 (CCl), 165.0 and 165.2 ($^{13}COOC_2H_5$), 168.8 ($^{13}COOCH_3$). From the fraction with bp 137-140° we isolated (V) in 27% yield, mp 54-55° (from alcohol), cf. [6, 11-14]. Found: C 53.02; H 6.11%. $C_{14}H_{20}O_8$. Calculated: C 53.16; H 6.37%. Raman spectrum (Ramanor HG 5145 Å, Ar^+ laser): $\nu C=C$ 1659 cm^{-1}, $\nu C=O$ 1737 cm^{-1}. PMR spectrum: 1.34 t (CH_3), 4.26 q (CH_2O). ^{13}C NMR spectrum (in CCl_4): 13.63 (CH_3) 61.6 (OCH_2), 135.1 (C=C,) 161.3 (CO). The obtained (V) was identical with the tetraethyl ethylene tetracarboxylate that was synthesized from CBM by heating in the presence of $Fe(CO)_5$ + DMF [2 h, 140°, sealed ampul. Amounts: $Fe(CO)_5$ 2.5 mmoles, CBM 5 mmoles, DMF 7.5 mmoles. Yield of (V) 48%]. Without the coinitiator we were unable to obtain (V) from CBM due to marked tarring.

Addition of Dichloromalonic Ester (DCM) to MA. With stirring, to 36.65 g (0.16 mole) of DCM, heated to 150°, was added dropwise a mixture of 13.77 g (0.16 mole) of MA, 3.13 g (16 mmoles) of $Fe(CO)_5$, and 3.51 g (48 mmoles) of DMF, and the mixture was heated for another 30 min. The reaction mass of two identical experiments was combined and distilled to give 20.5 g of recovered DCM with bp 115-116° (14 mm). Based on the GLC data, the residue contained 3.37 g of (IV), 29.0 g of (I), and 15.8 g of (V). The preparative GLC of the 113-120° (1 mm) fraction gave 1,1-dicarbethoxy-2-carbomethoxycyclopropane (IV) in 6% yield, n_D^{20} 1.4465, d_4^{20} 1.1580, which, based on the analysis and spectral characteristics, is identical with the (IV) obtained from the reaction of CBM with MA. From the 145-155° (2 mm) fraction we isolated adduct (I), 1,3-dichloro-1,1-dicarbethoxy-3-carbomethoxypropane in 40% yield, n_D^{20} 1.4587, d_4^{20} 1.2692. Found: C 42.01; H 5.12; Cl 21.84%. $C_{11}H_{18}Cl_2O_6$. Calculated: C 41.92; H 5.12; Cl 22.50%. PMR spectrum: 1.35 t (6H, CH_3CH_2O), 3.00 oct (2H, CH_2), 3.85 s (3H, $COOCH_3$), 4.1-4.7 m (OCH_2 + CHCl). The still residue was analyzed by GLC and found to contain (V) in 23% yield, which was identified via an authentic sample.

CONCLUSIONS

1. The addition of chlorobromomalonic ester to methyl acrylate, initiated by the $Fe(CO)_5$ + DMF system, proceeds with the cleavage of the C–Br bond in the addendum and the formation of $(C_2H_5OOC)_2CClCH_2CHBr-COOCH_3$.

2. The chlorobromo- and dichloromalonic esters when treated with $Fe(CO)_5$ are capable of cleaving both halogen atoms and, in the absence of an unsaturated compound, form tetraethyl ethylene tetracarboxylate, while with methyl acrylate they form 1,1-dicarbethoxy-2-carbomethoxycyclopropane.

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