Demethoxycarbonylation on Thermolysis of Dimethyl Halogenomalonates

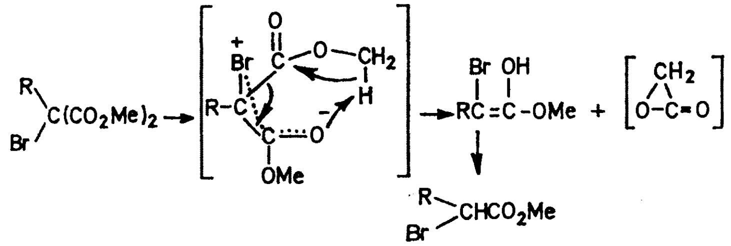
By WATARU ANDO,* HARUO MATUYAMA, SETUKO NAKAIDO, and TOSHIHIKO MIGITA

(*Department of Chemistry, Gunma University, Kiryu, Gunma, Japan*)

Summary Thermal decomposition of dimethyl halogenomalonates leads to halogenoacetates, by demethoxycarbonylation.

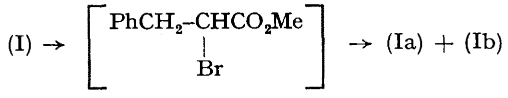
IN a previous report, we have suggested that the formation of acetate from mercaptomalonate may be due to the participation of the neighbouring sulphur, *i.e.*, the carbonyl carbon atom may interact strongly with the sulphur atom attached to the adjacent carbon atom which results in the carbonyl site becoming tetrahedral and in charge dispersal to the bridged sulphur atom.[1] We describe here some results which strongly support participation by vicinal halogeno-substituents, leading to enhanced hydrogen abstraction following the cleavage of the C–CO bond.

$$RSCH(CO_2Me)_2 \xrightarrow{\Delta} RSCH_2CO_2Me$$



The thermolysis of dimethyl benzylbromomalonate (I) at 210° for 1 h gave methyl 3-phenylpropionate (Ia), methyl cinnamate (Ib), and methyl benzalmalonate (Ic). All the thermolyses were carried out in sealed Pyrex tubes without degassing. The ratio of these products varies with reaction temperature and time. The above products suggest that (Ia) and (Ib) may be formed through the benzylbromoacetate (Ii), which was produced by demethoxycarbonylation of the malonate (I) The conversion of (I) into (Ii) may involve elimination through the 7-membered cyclic transition state, as we have similarly suggested in the demethoxycarbonylation of the mercaptomalonate, though in neither case do we have supporting evidence Compound (Ia) may be formed from (Ii) by bromine exchange with hydrogen by easy breaking of the carbon–bromine bond, followed by hydrogen abstraction. The formation of (Ib) and (Ic) may be explained, though less easily, as the result of hydrogen bromide elimination from (Ii) and (I). The mechanism of hydrogen elimination may involve one-step four-membered cyclic process as in the usual *Ei* mechanism.[2,3]

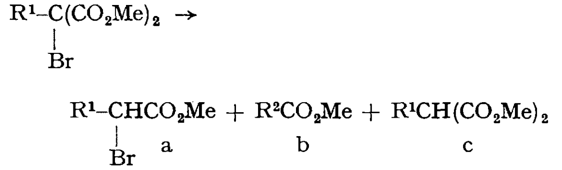
$$(I) \xrightarrow[1\ h.]{210^\circ} \underset{(Ia)\ 22\%}{PhCH_2CH_2CO_2Me} + \underset{(Ib)\ 39\%}{PhCH{=}CHCO_2Me} + \underset{(Ic)\ 39\%}{PhCH{=}C(CO_2Me)_2}$$



$$(I) \rightarrow \left[\begin{array}{c} PhCH_2\text{–}CHCO_2Me \\ \quad\quad | \\ \quad\quad Br \end{array}\right] \rightarrow (Ia) + (Ib)$$

(Ii)

Thermal decomposition of dimethyl methylbromomalonate (II) was also investigated. After heating at 265° for 1 h, three products were separated by g.l.c. in a yield of 67% based on the reacted malonate; these products were (IIa), (IIb), and (IIc) by comparison with authentic samples. There are no olefinic products such as were obtained from benzylmalonate. Their production may depend on the presence of active hydrogen on the β-carbon. The formation of these products may be explained by demethoxycarbonylation (IIa), and bromine and hydrogen exchange (IIb), (IIc), as in the previous case. In the thermolysis of dimethyl bromomalonate (III), dimethyl malonate was mainly obtained together with dibromoacetate, The formation of dimethyl malonate may be due to the exchange of bromine and hydrogen, and the dibromomalonate formed may lose a methoxycarbonyl group by thermolysis, forming dibromoacetate.



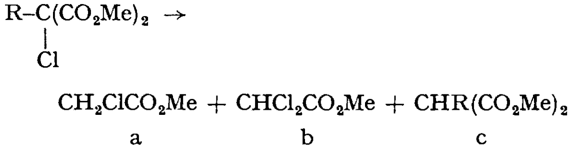
$$\underset{Br}{\overset{}{R^1\text{–}C(CO_2Me)_2}} \rightarrow$$

$$\underset{a}{\underset{Br}{R^1\text{–}CHCO_2Me}} + \underset{b}{R^2CO_2Me} + \underset{c}{R^1CH(CO_2Me)_2}$$

	Conv.	a	b	c
(II) R¹ = Me, 265°, 1 h	67%	30%	8%	62%
			(R² = CHBrMe)	
(III) R¹ = H, 230°, 3 h	57%	13%	37%	50%
			(R² = CHBr₂)	

Since many alkyl- and alkoxy-malonates are stable under the conditions described, an attractive mechanism for the formation of acetate from malonate may involve neighbouring bromine participation followed by hydrogen abstraction by carbonyl oxygen and the cleavage of the C–CO bond as suggested in our previous paper.[1]

Similar demethoxycarbonylations occur in the case of chloromalonates. Dimethyl malonate was the main product in the thermolysis of dimethyl chloromalonate. On the other hand, in the thermolysis of dichloromalonate, dichloroacetate was the principal product.



$$\begin{array}{l}\mathrm{R{-}\underset{\displaystyle Cl}{\underset{|}{C}}(CO_2Me)_2} \rightarrow \\ \underset{\mathrm{a}}{\mathrm{CH_2ClCO_2Me}} + \underset{\mathrm{b}}{\mathrm{CHCl_2CO_2Me}} + \underset{\mathrm{c}}{\mathrm{CHR(CO_2Me)_2}}\end{array}$$

		Conversion	a	b	c
R = H	230°, 10 h	99%	40%	8%	52%
R = Cl	265°, 2·5 h	81	21	60	19

Dimethyl alkylhalogeno- and monohalogeno-malonates, except the compounds containing active β-hydrogen, undergo hydrogen–halogen exchange reaction a little more readily than the demethoxycarbonylation. However, dimethyl dihalogenomalonates do undergo demethoxycarbonylation.

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[3] A. Maccoll, *Adv. Phys. Org. Chem.*, 1965, **3**, 91.