Me   Me   Me   Me
CO.CH:CH.CH:CH.CO   CO.CH$_2$.CH:CH.CH$_2$.CO
I   II

HOCO.CH:CH.CH:CH.COOH
V   HOCO.CH$_2$.CH:CH.CH$_2$.COOH
III

Me$_2$C(OH).CH$_2$.CH:CH.CH$_2$.C(OH)Me$_2$
IV

tion of (I) with zinc and acetic acid gave (II) in 70–75 per cent yield[2]. In view of these publications, we are prompted to report the methods by which we have synthesized the diketones (I) and (II).

Dihydromuconic acid (III) was readily prepared by reaction of 1 : 4-dibromobut-2-ene with cuprous cyanide in acetonitrile, and hydrolysis of the resulting 1 : 4-dicyanobut-2-ene (30–35 per cent overall yield). Treatment of the diacid chloride of (III) with cadmium dimethyl gave, in 15 per cent yield, the required diketone (II), melting point 35–36° (found : C, 68·4 ; H, 9·0 ; calc. for C$_8$H$_{12}$O$_2$: C, 68·55 ; H, 8·65 per cent) (Karrer et al.[2] give m.p. 30–31°), which was characterized as the bis-2 : 4-dinitrophenyl-hydrazone, melting point 208–209° (found : C, 48·1 ; H, 4·15 ; N, 22·55. C$_{20}$H$_{20}$O$_8$N$_8$ requires C, 48·0 ; H, 4·05 ; N, 22·4 per cent). The optimum conditions for the preparation of (II) by this route have not as yet been elucidated. In this work the cadmium dimethyl solutions used were prepared from methyl-magnesium bromide and cadmium chloride, and were shown by application of the Gilman test to contain none of the Grignard reagent (cf. Cason[3]). However, in some experiments, the diketone (II) was obtained in admixture with a glycol (probably IV), melting point 86° (found : C, 69·4 ; H, 11·4. C$_{10}$H$_{20}$O$_2$ requires C, 69·7 ; H, 11·7 per cent), which on catalytic hydrogenation yielded 2 : 7-dimethyloctane-2 : 7-diol. The latter crystallized from a mixture of ether and light petroleum (b.p. 40–60°) in needles, melting point 92–93°, and from water in plates, melting point 58–59° (Zal'kind and Aizikovich[4] give melting point 88–89° from light petroleum and 57–59° from water).

When the diacid chloride[5] of trans trans muconic acid (V) was treated with cadmium dimethyl, a product was obtained from which the diketone (I) was readily isolated, albeit in very poor yield (c. 2 per cent). The diketone, melting point 126–127°, exhibited light-absorption maxima (in alcohol) at 2720 and 2790 A., ε = 31,000 and 32,000 respectively (Karrer et al.[1] give melting point 126–126·5° ; light absorption maximum in alcohol, 2760 A. ; ε = 33,000).

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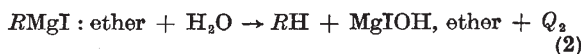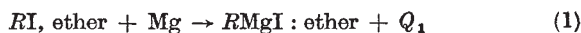[3] Cason, J., Chem. Rev., 40, 15 (1947).
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Heat of Formation of the Grignard Reagent, CH$_3$MgI : Ether

EXPERIMENTAL determinations of carbon-metal and carbon-halogen bond dissociation energies have been investigated in this Department during the past few years[1-4]. The first work undertaken was a calorimetric study of the formation and subsequent decomposition of a Grignard reagent.

$$RI, \text{ether} + Mg \rightarrow RMgI : \text{ether} + Q_1 \quad (1)$$

$$RMgI : \text{ether} + H_2O \rightarrow RH + MgIOH, \text{ether} + Q_2 \quad (2)$$

From (1) and (2), the heat of formation of the RI compound can be obtained :

$$Q_f(RI,l) = Q_f(RH,g) + Q_f(MgIOH, \text{ether}) - Q_f(H_2O,l) - Q_1 - Q_2. \quad (3)$$

From $Q_f(RI,g)$, and the corresponding R—H dissociation energy, the R—I bond dissociation energy can be found. Even if the absolute value of the heat of formation as given by (3) is doubtful (owing to uncertainty in the value assumed for $Q_f(MgIOH)$), the gradations in Q_f values for a series of RI compounds should be reliable.

It soon became clear that the study of this reaction with the required degree of accuracy would be both a difficult and long task ; so it was allowed to take second place to work on the hydrolysis and iodination of the alkyls of zinc, cadmium[1,2] and mercury. But the earlier studies were sufficiently complete to enable us to give a value for Q_f (CH$_3$MgI : ether) which is an important thermochemical datum in view of the great versatility of the Grignard reagent.

The reaction

$$CH_3I, \text{ether} + Mg \rightarrow CH_3MgI : \text{ether} + Q_1$$
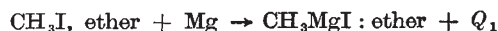
was studied in vacuo in an adiabatic calorimetric system[1]. The percentage reaction and the extent of any side reactions were checked by decomposing the Grignard reagent with water and analysing and measuring the gas produced. Experiments carried out in this way with reagents of high purity went cleanly with negligible side-reactions.

It was found that $Q_1 = 65 \cdot 4^5 \pm 0 \cdot 2$ k.cal./mole, leading to,

$$Q_f(CH_3MgI : \text{ether}) = 65 \cdot 4 + Q_f(CH_3I, \text{ether}).$$

Using the value of $3 \cdot 6^5 \pm 0 \cdot 1$ k.cal./mole for $Q_f(CH_3I,l)^2$ (methyl iodide has a negligible heat of solution in ether), we obtain

$$Q_f(CH_3MgI : \text{ether}) = 69 \cdot 0 \pm 0 \cdot 3 \text{ k.cal./mole.}$$

This value applies to a Grignard solution of 1 mole CH$_3$MgI in c. 22·5 moles diethyl ether.

It is hoped shortly to widen the scope of this work on the lines indicated above.

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