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SOME REACTIONS OF GRIGNARD REAGENTS WITH CHLOROFORM AND CARBON TETRACHLORIDE IN THE PRESENCE OF CYCLOHEXENE

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Abstract—The reactions of phenylmagnesium bromide and ethylmagnesium iodide with carbon tetrachloride in the presence of cyclohexane are reported. The identified products include 3,3′-bicyclohexenyl, dichloromethylcyclohexane, 7,7-dichloronorcarane, 7,7-dibromonorcarane and 7-bromo-7-chloronorcarane. The phenyl Grignard reagent reacts primarily by an ionic pathway, whilst a radical mechanism also occurs with the ethyl Grignard reagent.

The preparation of dihalocarbenes from polyhalomethanes has been widely studied.[1] Though lithium alkyls have been successfully employed, Grignard reagents do not appear to have been studied as potential initiators of such a reaction. The composition of Grignard reagents is complex[2] but it is a well known simplification to consider that in many reactions they behave as sources of the appropriate carbanions. From this point of view then, Grignard reagents ought to be able to produce dichlorocarbene from, say, chloroform and this could be trapped in the usual way with cyclohexene.

Here we report on such a study in which both chloroform and carbon tetrachloride were reacted with ethyl and phenyl Grignard reagents, in the presence of cyclohexene. Under certain conditions, products arising from dichlorocarbene formation were detected in the complex product mixtures.

RESULTS

The preformed Grignard reagent (0·3 mole) was added to chloroform or carbon tetrachloride (0·4 mole) and excess cyclohexene in ether solution under dry, oxygen free conditions. In all reactions the yield of moderately volatile products arising from reaction with cyclohexene was low (*ca* 10% based on the initial weight of magnesium, assuming an average product molecular weight of 160) and polymeric residues were common. The major reaction presumably occurred between the halomethane and the Grignard reagent. These reactions have been reported and the products are summarised[3] in equations 1–4.

$$\mathrm{CHCl_3 + PhMgBr \longrightarrow Ph_3CH\ (76\%) + some\ Ph_2 + PhBr} \quad (1)$$

$$\mathrm{CHCl_3 + EtMgBr \longrightarrow CH_4 + C_2H_4 + trace\ Et_3CH} \quad (2)$$

$$\mathrm{CCl_4 + PhMgBr \longrightarrow (Ph_3CO)_2\,(30\%) + Ph_3COH\,(6\%) + some\,(Ph_3C)_2} \quad (3)$$

$$\mathrm{CCl_4 + EtMgBr \longrightarrow 1CH_4 + 4C_2H_4} \quad (4)$$

With ethylmagnesium bromide, the products are gaseous and were not collected in the present work but substantial quantities of triphenylmethane and biphenyl were observed in the residue from the reaction of chloroform and phenylmagnesium bromide.

Combined GLC-MS was the main tool used to separate and identify products and some minor components were not successfully identified. The products arising from reactions involving cyclohexene are listed in the Table. These are expressed as approximate percentages of the total products in the distilled fraction.

The 3,3′-bicyclohexenyl produced in reaction I (Table 1) was separated by prep. GLC, as was an 80% pure sample of dichloromethylcyclohexane. None of the other products listed in the Table were isolated but were identified from GLC retention times and/or mass spectra.

The structure of dichloromethylcyclohexane was assigned on the basis of its mass spectrum. A parent ion occurred at *m/e* 166 with the correct relative isotope intensities for two chlorines. The base peak occurred at *m/e* 83. This fragment contained no chlorine and was consistent with a cyclohexanyl ring. The three dihalonorcaranes had very similar mass spectra. The identification of dibromo- and dichloronorcarane was confirmed by comparison of mass spectra with those of authentic samples and the identity of the bromochloro compound was assigned on the basis of its similar breakdown pattern.

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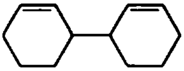
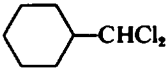
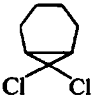
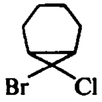
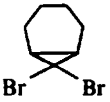
Table 1. Yields[a] of products incorporating cyclohexene obtained in Grignard Reactions.

					
I EtMgBr + $CHCl_3$	70	25	5		
II PhMgBr + $CHCl_3$[b]	trace	7	22	13	2
III EtMgBr + CCl_4[c]	trace	—	25	present	3
IV PhMgBr + CCl_4[d]	trace	—	15	10	3

[a] Expressed as approximate percentages of the total distilled material.

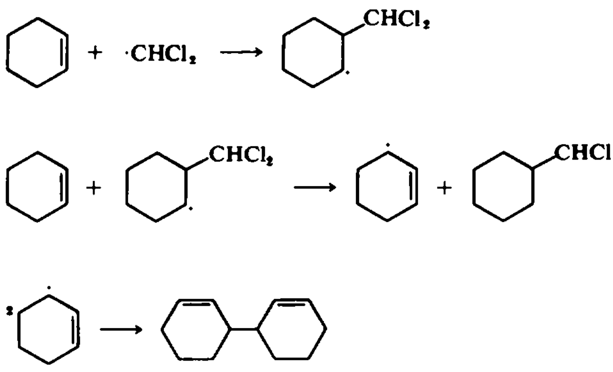
[b] Major components were bromobenzene and biphenyl.

[c] A major component by GLC was indicated by MS to be a complex mixture of cyclohexanyl and cyclohexenyl ring containing compounds. Bromochloronorcarane was present in this mixture.

[d] Major component was chlorobenzene.

DISCUSSION

Analysis of the Table indicates that both radical and ionic reaction paths probably occur in these complex reactions. Relatively high yields of bicyclohexenyl and dichloromethylcyclohexane occur together and with low yields of the norcaranes. It is likely that both the bicyclohexenyl and dichloromethylcyclohexane are formed in radical reactions involving the dichloromethyl radical (eqn. 5).



(5)

Allyl hydrogen abstraction from cyclohexane is a facile reaction.[4,5] However, very little bicyclohexenyl was formed when ethylmagnesium bromide was treated with cyclohexene alone under the same conditions and chloroform is therefore necessary for the formation of the bicyclohexenyl in reaction I (Table 1). The initiation of the radical pathway is no doubt provided by the Grignard reagent. Magnesium (or better, magnesium and iodine) has been shown[6] to catalyse the radical addition of bromotrichloromethane to alkenes and a Grignard reagent could conceivably react similarly, possibly by way of molecule induced homolysis. Recent work[7] has indicated that radical mechanisms in Grignard reactions may not be uncommon.

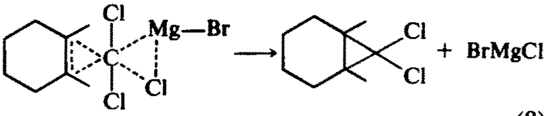
It is of some interest that while the dichloromethyl radical is implicated in these reactions, no evidence was found in any reaction for products arising from formation of the trichloromethyl radical (though it could not be rigorously excluded). In radical formation from chloroform, the C—H bond normally cleaves in preference to the C—Cl bond, due to resonance stabilization of the trichloromethyl radical.[8] The balance is rather close, however, and a significant amount of C—Cl cleavage occurs in deuterochloroform. It is possible to avoid postulating preferential chlorine abstraction if the dichloromethyl radical arises from reaction between dichlorocarbene and chloroform (eqn. 6). However, as the relative amounts of dichloromethylcyclohexane

$$:CCl_2 + CHCl_3 \longrightarrow \cdot CCl_3 + \cdot CHCl_2 \tag{6}$$

and dichloronorcarane produced in reactions I and II (Table 1) are so different, this requires the carbene species generated in each reaction to have rather different characteristics.

Non-radical pathways seem to be implicated in the formation of the dihalonorcaranes, since these were always minor products in those reactions giving relatively high yields of radical initiated products. Kobrich concluded[9] that, in the reaction of lithium alkyls with alkenes to give cyclopropane adducts, trichloromethyl lithium reacts directly with the alkenes without first decomposing to a free carbene. The formation of dichloronorcarane in the present work indicates that a similar process is operating. Thus, reaction of chloroform or carbon tetrachloride with the Grignard reagent to give a carbenoid (Eq. 7) which subsequently reacts with the cyclohexene (Eq. 8) is plausible.

$$PhMgBr + CCl_4 \longrightarrow PhCl + Cl_3CMgBr \qquad (7)$$



(8)

Support for the initial exchange reaction comes from the detection of a substantial amount of chlorobenzene in the reaction of phenylmagnesium bromide and carbon tetrachloride. While trichloromethylmagnesium bromide has not been reported, the trifluoro analogue is known,[10] trichloromethylphenylmercury has been shown[11] to readily react with cyclohexene to give dichloronorcarane, and the carbenoid $Fe(CCl_3)^{2+}$ has been postulated[12] as an intermediate in the reaction of ferrous salts with carbon tetrachloride in the presence of cyclohexene.

The formation of bromochloro- and dibromonorcarane was unexpected and remains unexplained. The obvious explanation of a Grignard reaction with the first formed dichloro compound is untenable as treatment of dichloronorcarane with Grignard reagents gave some evidence of dehalogenation (to chloronorcarane), but no trace of products incorporating bromine. Some halogen rearrangement in the suggested carbenoid prior to reaction with the cyclohexene remains a possibility.

Ionic pathways are apparently favoured for the phenyl relative to the ethyl Grignard reagent. This is reasonable in that the greater stability of the phenyl carbanion should favour heterolytic reactions in phenylmagnesium bromide compared to the situation with the ethyl Grignard reagent. The results also indicate that chloroform is more likely to react *via* radical pathways than is carbon tetrachloride but the total factors determining this reactivity are not obvious.

EXPERIMENTAL

Ether was dried over sodium and distilled under N_2 as required. Cyclohexane was washed before use with $KHSO_3$ aq, dried, and distilled under N_2. Spectroscopic grade CCl_4 and $CHCl_3$ were passed down an alumina column before use. The Grignard reagents were prepared, under N_2, in the normal way and were blown (N_2) into the reaction vessel.

Reactions were carried out under dry, oxygen free conditions and the following experiment is typical.

EtMgBr *added to cyclohexene and* $CHCl_3$. A solution of EtMgBr [from Mg (7·5 g) and EtBr (50 g)] in ether (120 ml) was added dropwise, with vigorous stirring, to a mixture of cyclohexene (290 g), $CHCl_3$ (72 g) and ether (120 ml). There was an induction period, followed by vigorous reaction. When this subsided the mixture was refluxed for 2 h, cooled, acidified with dilute H_2SO_4, the organic layer separated, and the aqueous material ether extracted (×3). The combined organic extracts were water washed, dried ($MgSO_4$) and concentrated at 70°/20 mm. The residue (9·5 g) was distilled through a 3″ Vigreux column and the fraction (6·9 g), b.p. 80–120°/16 mm, collected.

GLC analysis (10% GE-SE30 on Chromosorb W.A.W. at 100°) indicated the presence of two main compounds. A sample of the second of these was obtained by prep GLC (same column) and was identified as 3,3′-bicyclohexenyl: IR (neat) 3020, 2920, 2855, 2833, 1454, 720 cm^{-1}; *m/e* (70 eV) (rel. intensity) 162 (1), 82 (6), 81 (100), 80 (66), 79 (12), 77 (5), 53 (5); NMR (CCl_4) δ, 5·4–5·8 (m, 2H), 1·1–2·4 (m, 7H). Reaction with bromine and fractional crystallisation of the product from $CHCl_3$ gave the two stereoisomeric forms of 2,2′,3,3′-tetrabromobicyclohexanyl, m.p. 159–162° (lit.,[4] 159°) and m.p. 188–190° (lit.,[4] 189–190°).

The other major component was isolated (80% pure) during the same prep GLC and was analysed by GLC-MS using a 50′ × 0·02″ UCON LB550X SCOT column (80°; helium flowrate 10 ml/min) in a Pye 104 gas chromatograph coupled to a 12″ radius magnetic sector single focussing mass spectrometer[13] operating at 70 eV and a PDP9 computer. The compound was assigned the structure dichloromethylcyclohexane: *m/e* (rel. intensity) 170 (0·1), 168 (0·6), 166 (0·9), 84 (8), 83 (100), 82 (17), 55 (31), 41 (11); NMR (CCl_4) 5·6 (d, 1H, *J* 3·5 Hz). A minor impurity in this sample was identified as 7,7-dichloronorcarane: *m/e* (rel. intensity) 168 (0·2), 166 (1·2), 164 (1·8), 124 (34), 122 (50), 93 (27), 81 (27), 68 (100), 67 (42), 65 (27), 55 (51), 41 (27), 39 (51). An authentic sample had the same GLC retention time and mass spectrum.

PhMgBr *added to cyclohexene and* $CHCl_3$. In the reaction of PhMgBr [Mg (9·5 g), PhBr (47 g), ether (120 ml)] with $CHCl_3$ (48 g) and cyclohexene (290 g), 25 g of product was obtained after concentration. Distillation gave a fraction (6·5 g) b.p. 60–120°/16 mm which was analysed by GLC-MS using a 12′ × ⅛″ glass column packed with 3% Apiezon L on Chromosorb G [150° (5 min) then 6°/min to 220°; helium flowrate 10 ml/min]. Additional compounds identified in this fraction were 7,7-dibromonorcarane: *m/e* (rel. intensity) 256 (2), 254 (4), 252 (2), 214 (19), 212 (37), 210 (19), 93 (57), 77 (26), 68 (100), 67 (33), 65 (20), 55 (28), 41 (19), 39 (43) (identical GLC retention time and MS as an authentic sample[14]). 7-Bromo-7-chloronorcarene: *m/e* (rel. intensity) 212 (1), 210 (4), 208 (3), 170 (13), 168 (50), 166 (40), 129 (30), 93 (64), 77 (29), 68 (100), 67 (49), 65 (28), 55 (47), 41 (23).

The residue from the distillation was composed predominantly of biphenyl (from GLC retention time) and triphenylmethane, m.p. 92° (lit.,[15] 94°).

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