A Possible Role of Diarylmethanes as the Intermediate for the Disproportionation of Methyl Groups in the Jacobsen Reaction[1]

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(Received January 9, 1969)

Pentamethylbenzene (I)[2] and chlorotetramethylbenzenes (CTB)[3] are known to undergo disproportionation, in contact with concentrated sulfuric acid, to yield hexamethylbenzene (II) and chloropentamethylbenzene (III), respectively. Under suitable conditions, however, an appreciable amount of diarylmethanes (DAM) has been isolated from these reaction mixtures. Thus, CTB (16.9 g) stirred with sulfuric acid (98 g) for 55 hr at room temperature gave III (5.4—6.3 g) and a higher-melting crystalline product (0.8—1.4 g). The latter was defined as dichloroheptamethyldiphenylmethane (DHD) by analysis ($C_{20}H_{24}Cl_2$), mass spectra (*m*/*e*: 334(M^+), 319 (M^+–CH_3), 299(M^+–Cl); very strong rearrangement-dissociation peaks characteristic for *o*-methylated DAM at 180 ($C_{11}H_{13}Cl^+$) and 166 ($C_{10}H_{11}Cl^+$)),[4] infrared spectra and PMR spectra (Table 1). Chlorodurene and chloroprehnitene mainly gave a single DAM (IV and VII, respectively), but chloroisodurene yielded an intimate mixture of two isomers (V and VI), where V was the major component. Their structures have been established by the independent syntheses, with the exception of VI, to which the orientation has been allocated on spectral evidences. These DAM were slightly soluble in sulfuric acid, and, when dissolved in methylcyclohexane and stirred with sulfuric acid for a prolonged period, they could slowly be converted into CTB, chlorotrimethylbenzenesulfonic acids and some unidentified, high-melting substances. Besides these products, however, isomeric DHD with substituent groups at 2,2′,6,6′-positions have been found to yield some III under the same conditions, in accord with the findings that DAM are cleft by acid catalyst to give a benzyl cation,[5] which abstracts the hydride ion to be reduced to the corresponding hydrocarbon.[6]

Although an attempt to isolate a definite DAM from the reaction mixture of I has failed due to a complicated character of the by-product, both 2,2′,3,3′,4,4′,5,5′,6- and 2,2′,3,3′,4,4′,5,6,6′-nonamethyldiphenylmethanes have been found to behave similarly toward sulfuric acid, giving I, a little II and tetramethylbenzenesulfonic acids accompanied by amorphous substances. These results may be taken to suggest a possibility of the arylalkyl cation-alkylation mechanism[7] to play some role in the intermolecular migration of methyl groups in the Jacobsen reaction.

Table 1. PMR spectra of DAM formed in the Jacobsen reaction of monochlorotetramethylbenzenes

DAM	Mp (C°)	PMR spectra (in $CDCl_3$, τ)			
		Ar H	CH_2	CH_3	
3′,4-Dichloro-2,2′,3,4′,5,5′,6-heptamethyl-diphenylmethane (IV)	213—215	3.77	6.08	7.91 (3)* 7.71 (1)	7.61 (2) 7.52 (1)
2′,5-Dichloro-2,3,4′,4,4′,5′,6-heptamethyl-diphenylmethane (V)	219—220	3.76	5.93	7.93 (2) 7.83 (1)	7.76 (2) 7.58 (2)
4′,5-Dichloro-2,2′,3,3′,4,5′,6-heptamethyl-diphenylmethane (VI)		3.76	6.08	7.79** 7.67	
2′,6-Dichloro-2,3,3′,4,4′,5,5′-heptamethyl-diphenylmethane (VII)	226—227	3.74	5.74	7.92 (2) 7.84 (1) 7.78 (1)	7.72 (1) 7.60 (2)

* Relative intensities in parentheses. ** Others are obscured by strong peaks of V.

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