BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 2618—2623 (1969)

Structure Proof of Diarylmethanes Formed in the Jacobsen Reaction of Monochlorotetramethylbenzenes1)

Hitomi SUZUKI

Department of Chemistry, Faculty of Science, Kyoto University, Sakyo-ku, Kyoto

(Received February 7, 1969)

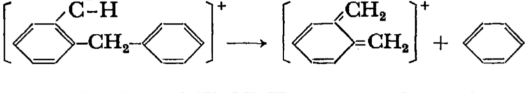
The Jacobsen reaction of monochlorotetramethylbenzenes was found to yield dichloroheptamethyldiphenylmethanes as by-product. Their indefinite structure proof was made on spectroscopy and synthesis. ^{1}H NMR spectra for a variety of polymethyldiphenylmethanes and their chlorine derivatives were determined.

In contact with concentrated sulphuric acid, monochlorotetramethylbenzenes (CTB) undergo disproportionation to give chloropentamethylbenzene (I) and 3-chloropseudocumene-5-sulphonic acid (II).2,3) This is another phase of the Jacobsen reaction, which has long been recognized for its unique feature to orient the ring alkyl groups to vicinal positions.4) Under suitable conditions, however, the reaction was found to yield as by-product an appreciable amount of dichloroheptamethyldiphenylmethanes.5) When considered in connection with the recent proposal of diphenylalkane intermediate for the disproportionation of primary alkyl groups in the Friedel-Crafts reaction,6) this result seems to provide a clue to elucidate the mode of intermolecular methyl transfer in the Jacobsen reaction. In the present work, the structures of these by-products have been definitely established.

New by-product from the Jacobsen reaction of CTB was high-melting, colourless prisms, poorly soluble in ordinary solvents. The analysis fitted the formula $C_{20}H_{24}Cl_2$ and the molecular weight determined from mass spectrum corresponded to 334 (Calcd 335). ^{1}H NMR spectrum showed the presence of one aromatic proton, two methylene protons, and twenty-one methyl protons. This composition was compatible only with dichloroheptamethyldiphenylmethane (DHD), and ruled out the other possibilities of dichloro-octamethyldiphenyl or dichlorohexamethyldiphenylethane.

Chlorodurene (IV) and chloroprehnitene (VI) mainly gave a single DHD (mp 213—215°C and mp 226—227°C, respectively), and the presence of other isomeric impurities was not so important. However, chloroisodurene (V) yielded an intimate mixture of two isomeric DHD (mp 215—216°C)7) in the approximate ratio of 3 : 1, and several attempts for fractional crystallization proved to be fruitless, presumably due to the slight difference in their solubility in organic solvents used.

The mass spectra of these DHD showed intense fragment ion peaks at 166 ($C_{10}H_{11}Cl^+$) or 180 ($C_{11}H_{13}Cl^+$), characteristic for *o*-methyldiphenylmethanes, which arose from the ionic unimolecular rearrangement-dissociation reactions represented as below:8)



Examination of ^{1}H NMR spectra of a variety of polymethyldiphenylmethanes and their chloro derivatives (Table 2) has revealed the following correlations useful for structural assignment: 1) Aromatic protons ortho to the methylene group absorb fairly high field (3.5—4.0 τ) from meta or para protons (3.1—3.3 τ). 2) The replacement of meta or para methyl group by chlorine atom usually gives little effect to the methylene protons. However, an ortho chlorine atom deshields these protons by

---

1) The Reaction of Polysubstituted Aromatics. Part XIII; Part XII: This Bulletin, **42**, 851 (1969).

2) A. Töhl, *Ber.*, **25**, 1527 (1892).

3) L. I. Smith and C. L. Moyle, *J. Am. Chem. Soc.*, **58**, 1 (1936).

4) For recent reviews, *cf.* H. J. Shine, "Aromatic Rearrangements," Elsevier Publishing Company (1967), p. 23.

5) Similar formation of diarylmethanes has recently been reported in the nitration (H. Zollinger, unpublished observations) and the positive hydroxylation of certain polyalkylbenzenes (C. A. Buehler and H. Hart, *J. Am. Chem. Soc.*, **85**, 2177 (1963); H. Hart and C. A. Buehler, *J. Org. Chem.*, **29**, 2393 (1964)).

6) A. Streitwieser, Jr., and L. Reif, *J. Am. Chem. Soc.*, **86**, 1988 (1964); R. M. Roberts, A. A. Khalaf and R. N. Green, *ibid.*, **86**, 1609 (1964).

7) Smith and Molye reported the isolation of an unidentified substance, mp 209.5°C, from V.3)

8) S. Meyerson, H. Drews and E. K. Fields, *J. Am. Chem. Soc.*, **86**, 4964 (1964).

TABLE 1. ¹H NMR AND IR SPECTRA OF DHD FORMED IN THE JACOBSEN REACTION OF CTB

DHD	Mp (°C)	¹H NMR spectra (in $CDCl_3$, τ)		
		ArH	CH_2	CH_3
3′4-Dichloro-2,2′,3,4′,5,5′,6-heptamethyl-diphenylmethane (XVI)	213—215	3.77	6.08	7.91 (3)* 7.71 (1) 7.61 (2) 7.52 (1)
2′,5-Dichloro-2,3,3′,4,4′,5′,6-heptamethyl-diphenylmethane (XVII)	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 (XVIII)		3.76	6.08	7.79** 7.67
2′,6-Dichloro-2,3,3′,4,4′,5,5′-heptamethyl-diphenylmethane (XIX)	226—227	3.74	5.74	7.92 (2) 7.84 (1) 7.78 (1) 7.72 (1) 7.60 (2)

	IR (KBr disc, cm⁻¹)		Analysis		
			C	H	Cl
XVI	767, 805, 826, 867, 941, 1003, 1081, 1155, 1178, 1209, 1229, 1387, 1445, 1460	Found Calcd	71.39 71.64	7.49 7.21	21.42 21.15
XVII	665, 714, 735, 763, 790, 834, 864, 920, 980, 1002, 1175, 1159, 1206, 1303, 1393, 1447, 1460	Found Calcd	71.80 71.64	7.27 7.21	21.45 21.15
XVIII	—	—	—	—	—
XIX	741, 757, 791, 829, 866, 939, 949, 977, 1012, 1069, 1082, 1163, 1186, 1218, 1288, 1313, 1384, 1397, 1436, 1447, 1465	Found Calcd	71.41 71.64	7.30 7.21	

* Relative intensities in parentheses.

** Others are obscured by strong peaks of XVII.

TABLE 2. ¹H NMR SPECTRA OF POLYMETHYLDIPHENYLMETHANES AND THEIR CHLORINE DERIVATIVES

Diphenylmethane	Mp (°C)	¹H NMR spectra (in CCl_4, τ)		
		ArH	CH_2	CH_3
2,2′,3,3′,4,4′-Hexamethyl-	113—114	3.21 (*m*)* 3.49 (*o*)	6.20	7.78 (2)** 7.83 (2) 7.89 (2)
2,2′,4,4′,5,5′-Hexamethyl-	94—95	3.12 (*m*) 3.42 (*o*)	6.27	7.81 (2) 7.85 (4)
2,2′,4,4′,6,6′-Hexamethyl-	134—135	3.34 (*m*)	6.09	7.81 (2) 7.97 (4)
2,2′,3,4,4′,5,6′-Heptamethyl-	123—125	3.22 (*m*) 4.00 (*o*)	6.23	7.72 (2) 7.79 (1) 7.88 (3) 7.95 (1)
2,2′,3,4,4′,6,6′-Heptamethyl-	103—104	3.34 (*m*)	6.05	7.79 (2) 7.89 (2) 7.98 (2) 8.02 (1)
2,2′,3,4′,5,6,6′-Heptamethyl-	104—105	3.28 (*p*) 3.34 (*m*)	6.00	7.91 (3) 8.00 (4)

TABLE 2. (Continued)

Diphenylmethane	Mp (°C)	^{1}H NMR spectra (in CCl_4, τ)		
		ArH	CH_2	CH_3
2,2′,3,3′,4,4′,5,5′-Octamethyl-	152—153	3.53 (*o*)	6.19	7.76 (2) 7.80 (4) 7.82 (2)
2,2′,3,3′,4,4′,5,6′-Octamethyl-	165—166	3.22 (*m*) 3.99 (*o*)	6.20	7.71 (1) 7.73 (1) 7.78 (1) 7.82 (1) 7.90 (2) 7.94 (1) 7.97 (1)
2,2′,3,3′,4,5,5′,6′-Octamethyl-	201—203	3.20 (*p*) 4.01 (*o*)	6.16	7.67 (1) 7.74 (3) 7.85 (1) 7.92 (1) 7.97 (2)
2,2′,3,3′,4,4′,6,6′-Octamethyl-	116—117	3.35 (*m*)	6.01	7.80 (2) 7.92 (4) 8.04 (2)
2,2′,3,3′,5,5′,6,6′-Octamethyl-	155—157	3.30 (*p*)	5.95	7.85 (4) 8.04 (4)
2,2′,3,3′,4,4′,5,5′,6-Nonamethyl-	186—187	3.94 (*o*)	6.16	7.67 (1) 7.75 (4) 7.86 (1) 7.93 (3)
2,2′,3,3′,4,4′,5,6,6′-Nonamethyl-	139—141	3.34 (*m*)	5.93	7.77 (2) 7·79 (2) 7.83 (1) 7.92 (3) 8.01 (1)
2,2′,3,3′,4,4′,5,5′,6,6′-Decamethyl-	221—222		5.89	7.78 (2) 7.81 (4) 7.97 (4)
6-Chloro-2,2′,3,3′,4,4′,5,5′-octamethyl-	187—188	3.95 (*o*)	5.96	7.60 (1) 7.72 (2) 7.78 (2) 7.94 (3)
5-Chloro-2,2′,3,3′,4,4′,5′,6-octamethyl-	203—204	3.96 (*o*)	6.15	7.59 (1) 7.71 (1) 7.75 (1) 7.78 (2) 7.88 (1) 7.92 (1) 7.95 (1)
4-Chloro-2,2′,3,3′,4′,5,5′,6-octamethyl-	215—216	4.00 (*o*)	6.20	7.62 (2) 7.71 (1) 7.78 (1) 7.88 (1) 7.93 (3)
4-Chloro-2,2′,3,4′,5,5′,6-heptamethyl-	204—206	3.12 (*m*) 3.85 (*o*)	6.19	7.59 (2) 7.65 (1) 7.82 (1) 7.87 (2) 7.92 (1)

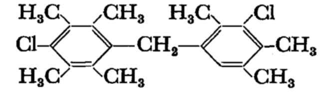
Table 2. (Continued)

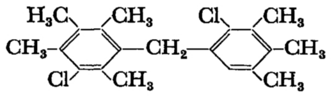
Diphenylmethane	Mp (°C)	^{1}H NMR spectra (in CCl_4, τ)		
		ArH	CH_2	CH_3
3′,5-Dichloro-2,2′,3,4,4′,5′,6-heptamethyl-	205—206	3.77 (*o*)	6.08	7.53 (2) 7.65 (1) 7.76 (1) 7.83 (1) 7.95 (2)
2′,4-Dichloro-2,3,3′,4′,5,5′,6-heptamethyl-	220—221	3.86 (*o*)	6.02	7.60 (3) 7.86 (1) 7.89 (3)
5′,6-Dichloro-2,2′,3,3′,4,4′,5,6′-octamethyl-	224—225		5.70	7.62 (1) 7.65 (1) 7.77 (2) 7.82 (1) 7.91 (1) 8.00 (1) 8.23 (1)
6,6′-Dichloro-2,2′,3,3′,4,4′,5,5′-octamethyl-	221—223		5.39	7.61 (2) 7.76 (2) 7.89 (2) 8.17 (2)
5,5′-Dichloro-2,2′,3,3′,4,4′,6,6′-octamethyl-	225—226		5.86	7.62 (2) 7.78 (4) 8.01 (2)
4,4′-Dichloro-2,2′,3,3′,5,5′,6,6′-octamethyl-	232—233		5.92	7.78 (4) 7.96 (4)
3,3′,5,5′-Tetrachloro-2,2′,4,4′,6,6′-hexamethyl-	274—275		5.76	7.46 (2) 7.79 (4)

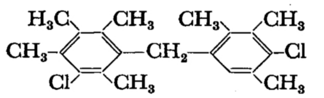
* Positions relative to methylene group.
** Relative intensities.

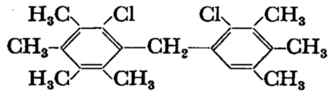
0.20—0.25 τ and the effect is additive. 3) A large downfield shift (0.25—0.30 τ) of the methylene protons is seen when the fourth ortho substituent group is introduced into the ring. Since the third ortho substituent gives little effect, such extra downfield shift is probably to be attributed to a combination of the steric and electronic influence enhanced by the restricted rotation of the benzene rings.

All the DHD showed a peak for ortho hydrogen atom at 3.73—3.77 τ. No chlorine atom is adjacent to the aromatic proton, otherwise the absorption will occur further downfield. The methylene protons of DHD derived from IV, V and VI absorbed at 6.08, 5.93, and 5.74 τ, respectively, indicating the presence of zero, one, and two ortho chlorine atoms. The minor component of the DHD mixture from V and the DHD from IV are supposed to possess a similar constitution in the vicinity of the methylene bridge, since both products showed the same τ-values for the aromatic and methylene protons. With these in mind and assuming no crucial rearrangement of the original hydrocarbon skeleton during the reaction, the tentative structures can readily be formulated as XVI—XIX:

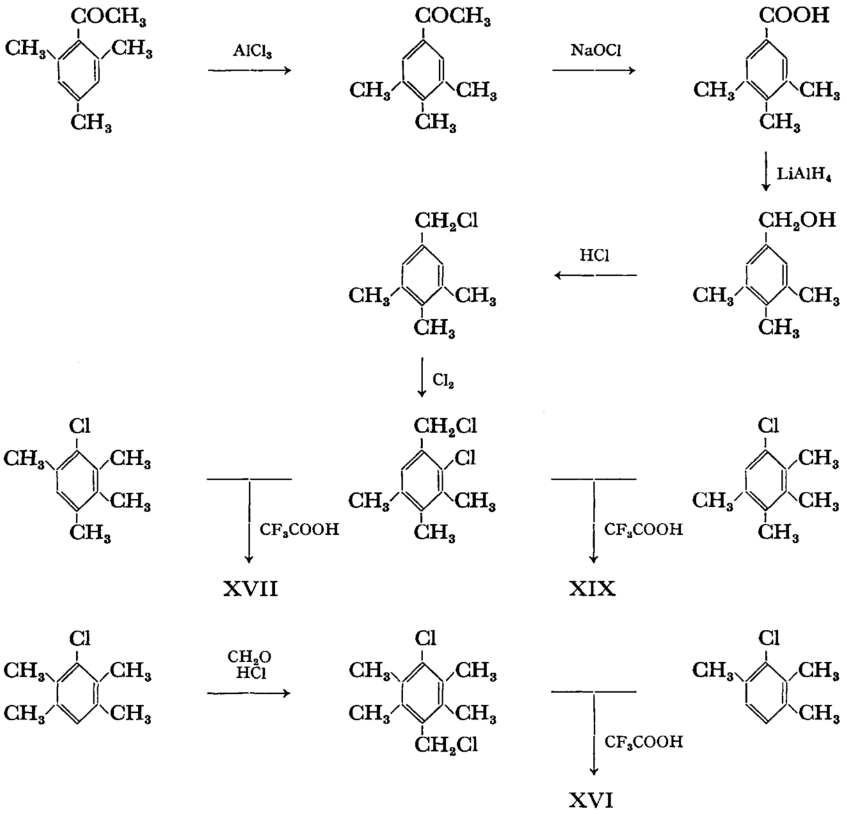

(XVI from IV)


(XVII from V, major product)


(XVIII from V, minor product)


(XIX from VI)

The structural formulae proposed above were finally confirmed through unequivocal synthesis. Authentic specimens were prepared, with the exception of XVIII, according to the sequence outlined in Scheme 1 and their identity with the products was confirmed by the complete coincidence of the infrared spectra. XVIII was not accessible by the reaction of 3-chloropseudocumene with 5-chloro-2,3,4,6-tetramethylbenzyl chloride, instead 3′,5-dichloro-2,2′,3,4,4′,5′,6-heptamethyldi-



Scheme 1

phenylmethane was formed. An attempt to prepare 5,4′-dichloro-6′-iodo-2,2′,3,3′,4,5′,6-heptamethyldiphenylmethane by blocking the reactive 5-position of VII with iodine atom, and to convert this into XVIII by reductive removal of the blocking group was unsuccessful because of the failure to obtain the expected condensation. The reaction proceeded very slowly with the replacement of iodine atom by the benzyl group.

The formation of XIX from VI is rather unusual since the original prehnitene skeleton has been partly modified in the product. This anomaly may be explained by the rearrangement of the initially formed 5′,6-dichloro-2,2′,3,3′,4,4′,5-heptamethyldiphenylmethane through the 1,2-shift of the benzyl group, and may also be responsible for the partial isomerization of VI to V observed during the disproportionation.

Experimental

IR spectra were determined for KBr disc on a Jasco DS-402G spectrophotometer. ^{1}H NMR spectra were measured in carbon tetrachloride unless otherwise stated, using TMS as internal standard, on a JNM-3H spectrometer. Mass spectra were measured on an AEI MS-9 mass spectrometer at source temperature of 200°C. All mp's were determined on a hot-stage and are uncorrected.

Materials. Chlorohemimellithene (III, bp 116—117°C/33 mmHg), chlorodurene (IV, mp 47—48°C, bp 119—121°C/20 mmHg), chloroisodurene (V, bp 113—115°C/20 mmHg) and chloroprehnitene (VI, bp 126—127°C/20 mmHg) were prepared from the corresponding hydrocarbons by chlorination in chloroform.[3] 3-Chloropseudocumene (VII, bp 108—110°C/30 mmHg) was prepared from a mixture of monochloropseudocumenes as described in literature.[9]

3,4,5-Trimethylbenzoic Acid (VIII). 3,4,5-Trimethylacetophenone (58 g)[10] was added dropwise to the 10% sodium hypochlorite solution (600 m*l*) so as to maintain the reaction temperature at 55—60°C. The solution was then treated with a little decolourizing carbon and made acidic with dilute hydrochloric acid. White precipitate was filtered off, washed with cold water, and crystallized from 95% ethanol. Large colourless prisms, mp 220—222°C (lit.[10] 220.5—221.5°C). Yield, 39.3 g (68%).

3,4,5-Trimethylbenzyl Alcohol (IX). To a solution of lithium aluminium hydride (5 g) in dry THF (100 m*l*), a warm, saturated THF solution of VIII (20 g) was added with stirring. The mixture was gently refluxed for 1 hr and then concentrated to one third of the total volume. Upon pouring into excess water, the mixture separated an oil, which soon solidified to

---

9) "Organic Reactions," Vol. 1, John Wiley & Sons, New York (1942), p. 370.

10) D. E. Pearson and J. D. Bruton, *J. Org. Chem.*, **19**, 957 (1954).

crystalline mass and was recrystallized from light petroleum as silky fine, long needles, mp 72—74°C (lit.[11] mp 78°C). Yield, 15.5 g (85%).

3,4,5-Trimethylbenzyl Chloride (X). A solution of IX in ligroin was stirred with concentrated hydrochloric acid, and hydrogen chloride was passed to saturation. Removal of the solvent under reduced pressure, followed by several recrystallization of the residue from light petroleum gave colourless needles, mp 36—37°C. Readily soluble in ordinary solvents.

Found: C, 71.28; H, 7.91%. Calcd for $C_{10}H_{13}Cl$: C, 71.21; H, 7.77%.

2-Chloro-3,4,5-trimethylbenzyl Chloride (XI). A crystal of iodine was added to a solution of X in carbon tetrachloride, and gaseous chlorine was passed at 0°C, controlling the extent of chlorination with gas chromatograph. The solvent was removed under reduced pressure, and the residue was crystallized from light petroleum in the form of colourless needles, mp 57—58°C.

Found: C, 59.20; H, 5.85%. Calcd for $C_{10}H_{12}Cl_2$: C, 59.13; H, 5.96%.

This compound was also obtained by stirring a mixture of III (15.5 g), 36% formalin (10%) and concentrated hydrochloric acid (40 m*l*) at 80—90°C for 24 hr under the gentle introduction of hydrogen chloride. Ordinary working-up, followed by fractional distillation gave the starting material (bp 112—113°C/27 mmHg, 7.5 g) and the chloromethylated product (bp 167—168°C/27 mmHg, 8.0 g). Recrystallization of the latter from light petroleum gave white needles, mp 47—49°C, which were identified as XI by comparison with infrared spectra. Some isomeric impurities accompanying the product were difficult to remove.

5-Chloro-2,3,4,6-tetramethylbenzyl Chloride (XII). A mixture of V (13.2 g), 37% formalin (60 m*l*) and hydrochloric acid (60 m*l*) was heated at 80—90°C, and hydrogen chloride was passed with stirring for 8 hr. After cooling, the solid product was filtered off, washed with water, and pressed to remove some oily part. Repeated recrystallization from ethyl acetate gave XII as white needles, mp 111—112°C. Yield of pure product, 8.7 g (48%).

Found: C, 61.09; H, 6.52%. Calcd for $C_{11}H_{14}Cl_2$: C, 60.84; H, 6.50%.

IV and VI similarly gave *4-chloro-2,3,5,6-tetramethylbenzyl chloride (XIII)* as large plates, mp 92—93°C, and *6-chloro-2,3,4,5-tetramethylbenzyl chloride (XIV)* as needles, mp 100—101°C, respectively.

XIII: Found: C, 60.94; H, 6.67%.
XIV: Found: C, 61.00; H, 6.66%.
Calcd for $C_{11}H_{14}Cl_2$: C, 60.83; H, 6.50%.

3-Chloro-5-iodo-1,2,4-trimethylbenzene (XV). VII (15.5 g) was iodinated at 70°C by stirring with iodine (10.2 g), periodic acid dihydrate (4.56 g), and 83% acetic acid (120 m*l*) containing small amounts of sulphuric acid as catalyst.[12] The heavy oily product was distilled under 22 mmHg. The main fraction came over at 167—168°C and weighed 20.7 g (74%).

Found: C, 38.63; H, 3.45%. Calcd for $C_9H_{10}ClI$: C, 38.53; H, 3.59%.

Disproportionation of Monochlorotetramethylbenzene (CTB). A mixture of CTB (16.9 g) and sulphuric acid (98 g) was stirred vigorously in an Erlenmeyer flask fitted with a side-arm for gas exit. The content soon turned dark brown, and sulphur dioxide, accompanied by some hydrogen chloride, was slowly liberated. After 50—55 hr, the reaction was quenched by pouring the mixture onto crushed ice, and any solid products formed were filtered off, washed thoroughly with water and chromatographed on alumina using light petroleum as eluant. Some unchanged CTB and I (5.4—6.3 g) came first, and diarylmethanes (0.8—1.4 g) followed over a wide range of eluates. These diarylmethanes were best crystallized from hot ligroin. Their physical properties are given in Table 1.

Preparation of Chlorinated Polymethyldiphenylmethanes. Chlorinated polymethyldiphenylmethanes were prepared by the following three procedures: 1) Condensation of chloro-hydrocarbons with formaldehyde in hot formic acid. 2) Reaction of a benzyl chloride with hydrocarbons in trifluoroacetic acid. 3) Chlorination of polymethyldiphenylmethanes. The last method had only limited use, because the products usually contained several diarylmethanes as well as some unidentified substances, and their separation was very difficult. In some cases, extensive transbenzylation occurred during the condensation; *e. g.* an attempt to prepare 6′-chloro-2,2′,3,3′,4,4′,5,5′,6-nonamethyldiphenylmethane by condensing VI with 2,3,4,5,6-pentamethylbenzyl chloride in trifluoroacetic acid gave a mixture of three diarylmethanes.

---

[11] H. Krömer, *Ber.*, **24**, 2413 (1891).

[12] H. Suzuki, K. Nakamura and R. Goto, This Bulletin, **39**, 128 (1966).