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STUDIES ON FRIEDEL-CRAFTS CHEMISTRY. 5. THE $\text{AlCl}_3\text{-CH}_3\text{NO}_2$ -CATALYZED FRIEDEL-CRAFTS REACTIONS OF BIS (BROMOMETHYL) BENZENES WITH BENZENE

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STUDIES ON FRIEDEL-CRAFTS CHEMISTRY. 5.[†]

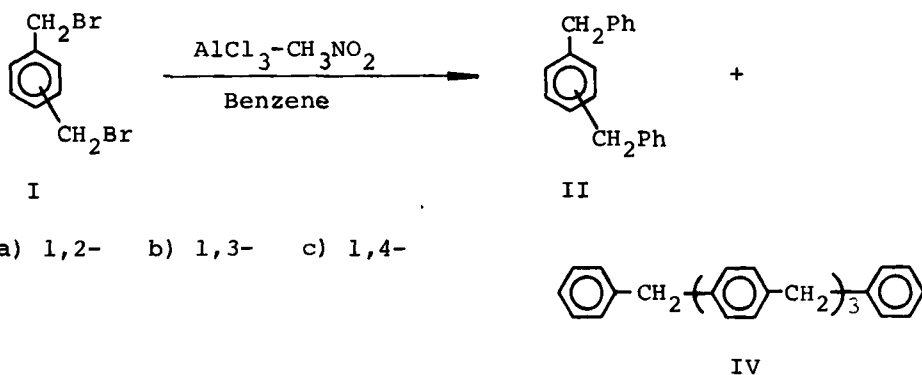
THE AlCl_3 - CH_3NO_2 -CATALYZED FRIEDEL-CRAFTS REACTIONS
OF BIS(BROMOMETHYL)BENZENES WITH BENZENE

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There are few preparatively useful procedures for the synthesis of 1,2-dibenzylbenzene (IIa). The Friedel-Crafts reaction of 1,2-bis(bromomethyl)benzene (Ia) with benzene,¹ catalyzed by AlCl_3 , FeCl_3 , TiCl_4 or SnCl_4 , gives the desired IIa in low yield in each cases. Diphenylmethane is formed as a by-product by the transbenzylation reaction of IIa and anthracene and other unidentified products are also formed. The recently reported preparation² of IIa [and of 1,4-dibenzylbenzene (IIc)]

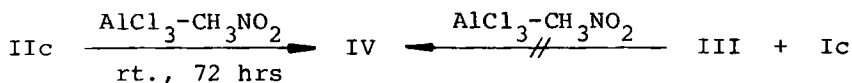


by the AgClO_4 -promoted benzylation of benzene with Ia [and with

1,4-bis(bromomethyl)benzene (Ic) in the synthesis of IIc] is not practical because AgClO_4 is expensive.

In the course of other studies, we needed substantial quantities of IIa. Therefore, we re-investigated the reactions of I with benzene using $\text{AlCl}_3\text{-CH}_3\text{NO}_2$ complex as a catalyst, which is known not to be active in the transbenzylation reaction of some arylmethanes.³ The reaction of Ia-c with benzene was carried out in the presence of this catalyst, and the results are summarized in Table 1. The desired compound IIa was obtained in 75% yield when the reaction was carried out at room temperature, whereas diphenylmethane (III) was detected in the reactions conducted at elevated temperatures. 1,3-(IIb) and 1,4-Dibenzylbenzene (IIc) were obtained in 52 and 62% yields, respectively, and a small amount of α,α' -bis(4-benzylphenyl)-p-xylene (IV) was isolated in the reaction of Ic with benzene.

The reaction of III with Ic in the presence of $\text{AlCl}_3\text{-CH}_3\text{NO}_2$ complex did not give IV; only resinous materials and unreacted III were obtained. However, when IIc was treated with $\text{AlCl}_3\text{-CH}_3\text{NO}_2$ complex in benzene for 72 hrs, IV was formed in 2% yield. We tentatively propose, therefore, that IIc is an intermediate in the formation of IV.



In summary, $\text{AlCl}_3\text{-CH}_3\text{NO}_2$ complex effectively catalyzes the Friedel-Crafts reaction of I with benzene to give II.

FRIEDEL-CRAFTS REACTIONS OF BIS(BROMOMETHYL)BENZENES WITH BENZENE

Table 1. The AlCl_3 - CH_3NO_2 -Catalyzed Friedel-Crafts Reactions of Bis(bromomethyl)benzenes with Benzene.

Run	Benzene ml	I g	AlCl_3 g ^{a)}	CH_3NO_2 g	Time hr	Products,	
						II g (Yield)	IV g (Yield)
1	15	2.00 (Ia)	0.50	1.13	6	1.43 (74)	0
2	500	50.00 (Ia)	12.6	17.3	6	36.8 (75)	0
3	50	5.00 (Ib)	1.26	1.73	5	2.55 (52)	0
4	50	5.00 (Ic)	1.26	1.73	2.5	2.78 (57)	0.06 (1)
5	50	5.00 (Ic)	1.26	1.73	5	3.03 (62)	0.26 (3)

a) Molar ratio of I : AlCl_3 = 1 : 0.5

EXPERIMENTAL

All melting points are uncorrected.

Reaction of I with benzene.- After a mixture of I, AlCl_3 and CH_3NO_2 in benzene was stirred at room temperature for a period shown in Table 1, it was poured into a large excess of 1% hydrochloric acid. The organic layer was separated, and the aqueous layer was extracted with benzene. The combined extract was dried over sodium sulfate and evaporated in vacuo to leave the residue.

Compound IIa [colorless prisms (methanol) of mp. $73-75^\circ$ (lit.,² $77-78^\circ$)] was obtained by extracting the residue with hot methanol and evaporating the methanol extract in vacuo.

Compound IIB [colorless liquid (lit.,⁵ bp. $153-159^\circ/0.25$ mmHg)] was obtained via column chromatography (alumina) of the residue using hexane as eluent and was confirmed to be pure (>99%) by G.C. analysis.

Compound IIc [colorless prisms (methanol) of mp. 85° (lit.,⁷

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86 °)] and IV[*colorless prisms (methanol) of mp. 128-131 ° (lit.,⁴ 127-128.5 °)*] were obtained as a mixture via column chromatography (Wako gel, C-300) of the residue using hexane as eluent. The separation of the two was easily accomplished by recrystallization from methanol, in which IIc is much more soluble than IV.

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