[CONTRIBUTION NO. 5 FROM THE EXPLORATORY RESEARCH LABORATORY, DOW CHEMICAL OF CANADA, LTD.]

Aromatic Substitution. V.[1a] The Synthesis of a Protonated Toluene Tetrafluoroborate Complex[1b]

BY G. A. OLAH, A. E. PAVLATH[3c] AND J. A. OLAH

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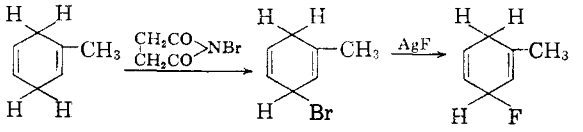
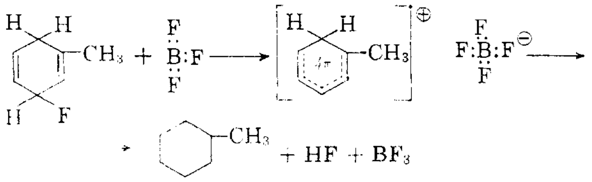
As a further proof of the onium ion salt (or σ-complex) structure of the previously isolated protonated alkylbenzene tetrafluoroborate σ-complexes, a protonated toluene tetrafluoroborate complex was synthesized. 1-Methylcyclohexadiene-1,4 monofluoride or the corresponding monobromide treated with boron trifluoride and silver tetrafluoroborate yields a protonated toluene tetrafluoroborate, which by thermal proton elimination aromatizes to toluene.

The isolation of protonated and deuterated alkylbenzene complexes had been reported previously[2] in the form of stable tetrafluoroborates. To gain further preparative proof for the structure of these intermediate complexes we have now found a synthetic way for preparing one of these complexes, a protonated toluene tetrafluoroborate complex starting from 1-methylcyclohexadiene-1,4.

1-Methylcyclohexadiene-1,4 was prepared after Haak and Wibaut[3] by the Wooster reduction of toluene and purification of the product through the methyltetrabromocyclohexane. 1-Methylcyclohexadiene-1,4 then was brominated following the analogy of the succinimide–bromine bromination of cyclohexadiene-1,4 by Wibaut and Haak.[4] In this way we prepared the 1-methylcyclohexadiene-1,4 monobromide (because of the subsequent use of the compound we were not interested in separating the two possible isomers). The monobromide then was converted with silver fluoride to the corresponding 1-methylcyclohexadiene-1,4 monofluoride

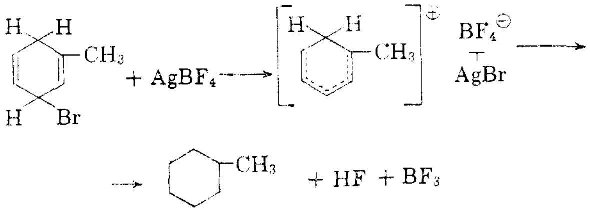


The 1-methyl cyclohexadiene-1,4-monofluoride was used in the complex formation reaction with boron trifluoride in the hope that the electron deficiency sextet of the boron atom may be strong enough also in this case to effect the cleavage of the C–F bond and to bond the fluoride ion together with its unshared electron pair. In this case four remaining π-electrons may be present on five available orbitals and may immediately overlap to form the pentadienate cation structure of a protonated toluene tetrafluoroborate complex, which by loss of a proton can form toluene.



This reaction proceeded only with difficulty. 1-Methylcyclohexadiene-1,4 monofluoride can be prepared only with a very small yield, because during the halogen exchange reaction some rearomatization occurs. However, it was possible to purify the 1-methylcyclohexadiene-1,4 monofluoride in a sufficient amount and to prove the structure by analytical and spectroscopic methods. In the complex formation reaction boron trifluoride causes a large scale polymerization of the cyclohexadiene.

To overcome the above difficulties, we have found a simple and more effective solution—that we can use the 1-methylcyclohexadiene-1,4 monobromide itself as the starting material in the complex formation reaction by using anhydrous silver tetrafluoroborate instead of boron trifluoride. In this way it is possible to eliminate both the halogen exchange reaction and the polymerizing effect of boron trifluoride.



The intermediate protonated toluene tetrafluoroborate complex is a mixture of the ortho and meta protonated isomers (due to the fact that the used 1-methylcyclohexadiene-1,4 monobromide was also a mixture of the corresponding two isomers) and necessarily not identical with that obtained by the direct protonation reaction of toluene with HF + BF_3,[2] where the proton—as proved by the reaction with DF—enters mainly at the *p*-position and only to a lesser extent of the *o*-position to the methyl group. However, since it is a pure protonated toluene tetrafluoroborate, obtained by an independent structure-proving chemical synthesis, it lends further support to the σ-complex intermediate theory of Brown.

Experimental

1-Methylcyclohexadiene-1,4 was prepared after Haak and Wibaut[3]; b.p. 114–115°, n^{20}_{D} 1.4712 (the corresponding values of Haak and Wibaut[3]: b.p. 114.5–115°, n^{20}_{D} 1.4703).

1-Methylcyclohexadiene-1,4 Monobromide.—The reaction was carried out according to the procedure elaborated for the bromination of cyclohexadiene-1,4 by Wibaut and Haak[4]; 19.2 g. (0.2 mole) of 1-methylcyclohexa-1,4-diene was dissolved in 200 ml. of carbon tetrachloride and at 10° 37.4 g. (0.21 mole) of succinimide bromide was added in small portions with stirring. After the addition was completed, which took about an hour, the mixture was stirred

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[1] (a) Part IV, THIS JOURNAL, **80**, 6535 (1958). (b) The work was started in the authors' earlier laboratory, the Chemical Central Research Institut of the Hungarian Academy of Sciences, Budapest, Hungary; partly delivered as a paper at the XVI International Congress of the International Union of Pure and Applied Chemistry in Paris, July 18, 1957; (c) Department of Chemistry, McGill University, Montreal, Canada.

[2] G. A. Olah and S. J. Kuhn, THIS JOURNAL, **80**, 6535 (1958).

[3] F. A. Haak and J. P. Wibaut, *Rec. trav. chim.*, **69**, 1382 (1950).

[4] J. P. Wibaut and F. A. Haak, *ibid.*, **69**, 1387 (1950).

again for 4 hours and was then allowed to stand overnight. The reaction mixture was thereafter filtered and the carbon tetrachloride distilled off at 0.1 mm. pressure. A yellow oily residue remained. This oil could not be distilled by means of a normal vacuum distillation even at 0.001 mm. pressure without decomposition. It could be purified only be sealing it in a flask connected by a wide tube to a receiver flask at 10^{-5} mm. pressure at room temperature, while the receiver flask was cooled to liquid air temperature. In 48 hours about 1.6 g. of 1-methylcyclohexadiene-1,4 monobromide distilled over in this way. It was colorless but rapidly turned yellow on standing; n^{20}D 1.5670. *Anal.* Calcd. for C_7H_9Br (172.9): Br, 46.21; C, 48.58; H, 5.21. Found: Br, 47.7; C, 48.49; H, 4.81. The high bromine and the low hydrogen value indicated contamination with dibromocyclohexadiene derivatives, which was to be expected from the method of separation used.

1-Methylcyclohexa-1,4-diene Monofluoride.—1-Methylcyclohexadiene-1,4 monobromide (17.3 g. 0.1 mole) was dissolved in 35 ml. of acetonitrile and at room temperature with effective stirring a saturated solution of 14 g. (0.11 mole) of silver fluoride in acetonitrile was added. A white precipitate could be instantly observed, which increased in amount as the reaction continued. The reaction mixture was stirred for another 6 hours, during which time the yellow-brown silver fluoride was almost completely dissolved and a white silver bromide precipitate was formed. After standing overnight the mixture was filtered and the acetonitrile distilled over at 0.01 mm. pressure. The remaining product could not be distilled with decomposition even at 10^{-3} mm. pressure. It was purified in a similar way to that described for the 1-methyl-cyclohexadiene-1,4-monobromide at 5×10^{-4} mm. pressure at around 0°. In 48 hours about 1.9 g. of distillate was collected, as a colorless liquid, rapidly turning yellow-brown on standing, n^{20}D 1.4971. *Anal.* Calcd. for C_7H_9F (112): C, 75.00; H, 8.03; F, 16.95. Found: C, 74.83; H, 7.90; F, 17.12.

The acetonitrile distilled over contained toluene, the presence of which was shown by preparing the 2,4-dinitrotoluene, m.p. 71°. (The acetonitrile–toluene azeotrope has a boiling point at atmospheric pressure of 81.1°).

Reaction of 1-Methylcyclohexa-1,4-diene Monofluoride with Boron Trifluoride.—1-Methylcyclohexa-1,4-diene monofluoride (5.6 g. 0.05 mole) was saturated with boron trifluoride, starting at −50° and gradually decreasing the temperature to −65° as the boron trifluoride was introduced. An all-glass apparatus was used to avoid atmospheric moisture. A bright brown color appeared with evolution of heat (possibly through the partial polymerization of the cyclohexadiene by boron trifluoride); 2.9 g. of boron trifluoride was taken off. The specific conductivity of the complex so formed at the melting point (−65°), $\kappa = 1.0 \times 10^{-3}\ \Omega^{-1}$ cm.$^{-1}$. *Anal.* Calcd. for $C_7H_9BF_4$ (179.8): BF_4, 48.3. Found: BF_4, 43.1.

The complex, when warming up, began to decompose at −50° with strong boron trifluoride evolution while it separated into two phases: a lower phase miscible with water and containing hydrogen fluoride and an upper, organic layer, not miscible with water. The organic layer after separation, drying and distillation consisted of 1.1 g. of toluene, b.p. 110°, n^{20}D 1.4967, and some resinous material.

Reaction of 1-Methylcyclohexa-1,4-diene Monobromide with Silver Tetrafluoroborate.—To 3.5 g. (0.002 mole) of 1-methylcyclohexa-1,4-dienemonobromide 3.9 g. (0.02 mole) of anhydrous silver tetrafluoroborate was added in small portions with effective stirring and avoiding atmospheric moisture at −60°. The silver tetrafluoroborate dissolved in the organic layer followed by an immediate quantitative precipitation of silver bromide. The organic complex so formed melted at −65 −64°, $\kappa = 1.10^{-3}\ \Omega^{-1}$ cm.$^{-1}$. On heating the complex, boron trifluoride was evolved and again two phases were formed: the organic upper layer was toluene and the lower layer hydrogen fluoride. One and six-tenth grams of toluene was formed (90%). The filtered silver bromide was 3.72 g. (about 100%).

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Aromatic Substitution. VI. Intermediate Complexes and the Reaction Mechanism of Friedel–Crafts Alkylations and Acylations[1]

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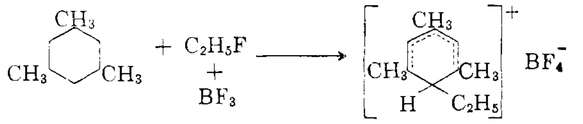
σ-Complex type intermediates of Friedel–Crafts alkylations and acylations with a molar ratio of 1:1:1 were isolated by the low temperature interaction of methylbenzenes, alkyl fluorides and boron trifluoride, and alkylbenzenes, acyl fluorides and boron trifluoride, respectively. On the basis of the intermediate complexes the reaction mechanism is discussed.

From our experience gained during the isolation and investigation of the protonated and deuterated alkylbenzene tetrafluoroborate complexes,[2] we were encouraged to examine the structure of the intermediate complexes of other electrophilic aromatic substitutions of such common interest as the Friedel–Crafts alkylations and acylation.

Alkyl fluorides are quite soluble in methylbenzenes. When, for example, an equimolecular amount of ethyl fluoride is dissolved in toluene at −80° (or in other methylbenzenes at low temperatures which are determined by the freezing points of the hydrocarbons) a homogeneous solution is obtained. When boron trifluoride is introduced into this homogeneous solution at low temperature, a lower, brightly colored phase separates immediately. The amount of this phase is increased by introducing more boron trifluoride. One mole of boron trifluoride is taken resulting in a homogeneous solution. In this way it was possible to isolate the methylbenzene:boron trifluoride complexes with a molar ratio of 1:1:1.



Some of the properties of these complexes are listed in Table I.

TABLE I

$ArHC_2H_5{}^+BF_4{}^-$ COMPLEXES

Ar	M.p. dec., °C.	κ(Ω⁻¹ cm.⁻¹) × 10³	Color	Formula	—BF₄, %— Calcd.	Found
$CH_3C_6H_5$	−80	0.2	Yellow	$C_9H_{14}BF_4$	41.6	40.8
m-$(CH_3)_2C_6H_4$	−75	.1	Red	$C_{10}H_{16}BF_4$	39.0	37.7
sym-$(CH_3)_3C_6H_3$	−15	.2	Orange	$C_{11}H_{18}BF_4$	37.8	36.4

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(1) The work was started in the author's earlier laboratory, the Chemical Central Research Institut of the Hungarian Academy of Sciences, Budapest (Hungary). Preliminary communications appeared in *Nature*, **178**, 1344 (1956); **179**, 146 (1957). Partly delivered as a paper at the XVI International Congress of the International Union of Pure and Applied Chemistry in Paris, July 18, 1957.

(2) G. A. Olah and S. J. Kuhn, THIS JOURNAL, **80**, 6540 (1958).