Tetrahedron Letters,Vol.24,No.1,pp 71-74,1983 0040-4039/83/010071-04$03.00/0
Printed in Great Britain

REACTION OF TRIPHENYLMETHYL CATION IN TRIFLUOROMETHANESULFONIC ACID. REACTION OF CARBODICATIONS

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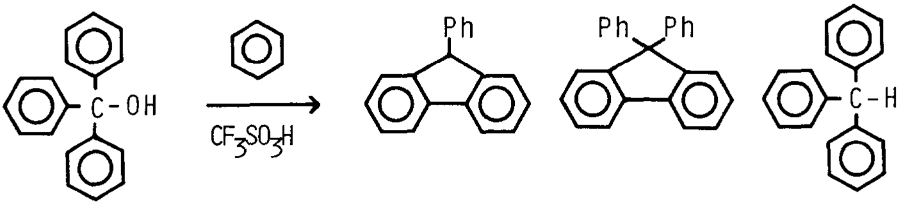
Abstract; *Triphenylmethyl cation reacts in the presence of trifluoromethanesulfonic acid in benzene. Products are 9-phenylfluorene, 9,9-diphenylfluorene, and triphenylmethane. A protonated triphenylmethyl cation and a protonated 9-phenylfluorenyl cation are postulated as intermediates.*

Among the reactions of triphenylmethyl cations, nucleophilic attack of common nucleophiles such as anilines and phenols on the central carbon, and hydride transfer by the cations are well known.[1] In this paper we report on a reaction of triphenylmethanol catalyzed by trifluoromethanesulfonic acid (TFSA) in a benzene solution. Participation of a protonated triphenylmethyl cation in the reaction is proposed.

A mixture of triphenylmethanol (1; 1 mmole) and TFSA (2 mmole) in benzene (60 mmole) was heated at 80°C for 6 hrs to give a reaction mixture composed of 9-phenylfluorene (2; 20%), 9,9-diphenylfluorene (3; 24%), triphenylmethane (4; 21%) and 1 (27%).[2] The reduction of 1 to 4 in refluxing formic acid,[3] and cyclization of 1 to 2 in phosphoric acid at high temperature[4] were described early in this century. The formation of 2 and 4 by heating 1 in sulfuric acid-acetic acid was also reported,[5,6] and more recently 9-(pentafluorophenyl)fluorene and pentafluorophenyldiphenylmethane have been obtained from pentafluorophenyldiphenylmethanol in refluxing formic acid.[7] On a simple consideration, the cyclization of 1 to 2 could be explained



1 2 3 4

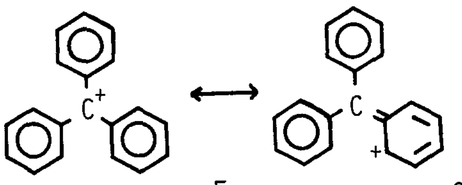
by the intramolecular attack of one phenyl group on another adjacent one of triphenylmethyl cation (5) of which cationic charge delocalizes over the phenyl rings. However, only a trace of 2 and 3 were produced when triphenylmethyl tetrafluoroborate ($5\text{-}BF_4^-$) was heated in a benzene solution in the absence of TFSA (Table; run 5). On addition of TFSA to this reaction mixture, 2 and 3 were obtained in the yields of 19% and 25%, respectively (run 6, and also runs 2 and 4). Trifluoroacetic acid (TFA) worked, but less effectively (runs 3 and 7). Thus we propose a mechanism which involves a protonated triphenylmethyl cation as an intermediate of the cycli-

Table Acid-Catalyzed Reaction of Triphenylmethanol (1) and Triphenylmethyl Tetrafluoroborate (5-BF_4^-) in Benzene

Run[a]	Substrate	Acid[b]	Products (%)[c] 2	3	4	1
1	1	CF_3SO_3H (1 eqt)	5	7	10	71
2	1	CF_3SO_3H (2 eqt)	20	24	21	27
3	1	CF_3CO_2H (2 eqt)	1	1	3	84
4	1	CF_3SO_3H (1 eqt) CF_3CO_2H (1 eqt)	19	27	31	17
5	5-BF_4^-	none	0.5	1	3	52
6	5-BF_4^-	CF_3SO_3H (1 eqt)	19	25	29	19
7	5-BF_4^-	CF_3CO_2H (1 eqt)	7	9	14	43

(a) 80°C for 6 hrs with benzene (60 eqt) and acid. (b) eqt to the substrate is shown in parentheses. (c) Based on VPC.

zation, which explains the requirement of TFSA. The protonation at the relatively electron rich position, 1 (*ipso*) or 3 (*meta*), gives species 6 or 7, probably 6 being the more preferred dication because the cationic centers of 6 are separated by an sp³ carbon. A facile protonation of triphenylmethyl cations by TFSA has been recently reported,[8] which supports the formation of the dication 6 in equilibrium with 5. Intramolecular Friedel-Crafts type reaction of 6 leads to 2. The reaction temperature is moderately high because the cation-cation reaction may require a high activation energy.



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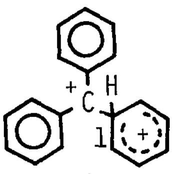

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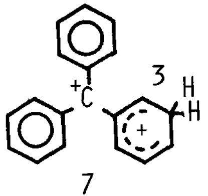

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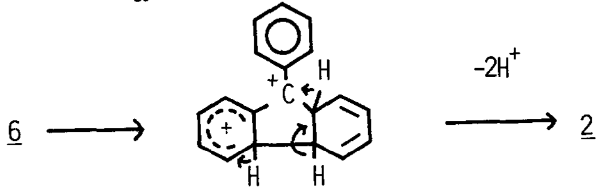
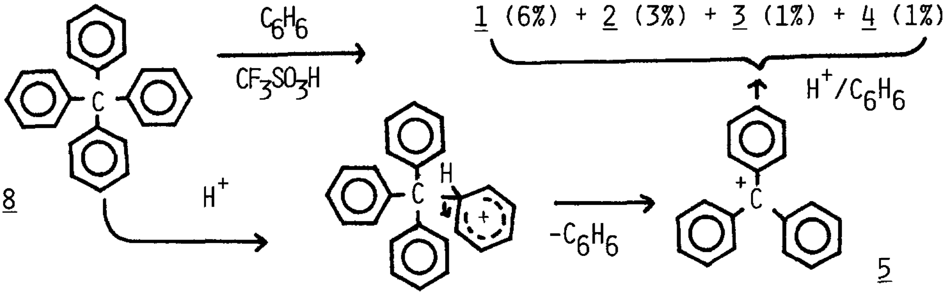
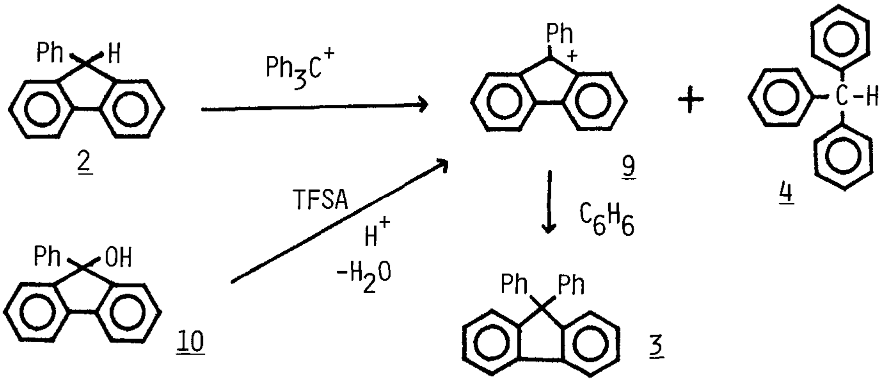
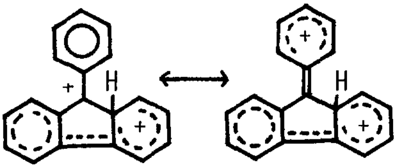


The formation of 9,9-diphenylfluorene (3) was first thought to be the consequence of a Scholl type reaction of tetraphenylmethane (8) which was a possible product formed from 1 (or 5) and benzene. However, 8 was rather stable under similar reaction conditions (benzene-TFSA at 80°C for 6 hrs): more than 80% of 8 was recovered and small amounts of 1 (6%), 2 (3%), 3 (1%) and 4 (1%) were obtained.



The formation of 1-4 are reasonably explained by considering 5 as an intermediate which was formed by elimination of a benzene ring from a protonated tetraphenylmethane.[9] On the other hand the formation of the reduction product, triphenylmethane (4) in the reaction of 1 suggests that the initial product 2 can be oxidized to 9-phenylfluorenyl cation (9) by 5 (5 is reduced to 4).[5] The cation 9 then reacts with benzene to give 3. This hypothesis seems to be supported by; (a) when an equivalent mixture of 1 and 2 in the presence of TFSA and benzene was heated at 80°C for 1 hr, 3 and 4 were obtained in the yields of 47% and 56%, respectively, (b) 9-phenyl-9-hydroxyfluorene (10) in benzene in the presence of TFSA (2 eqt) gave 3 in 92% yield, and (c) 2 alone in benzene-TFSA gave a complex mixture (more than 65% recovery of 2).[10] However, we prefer a mechanism which involves a protonated 9-phenylfluorenyl cation (11), because the reaction of 1 was only slightly catalyzed by TFA, and moreover, 3 was not detected as a product in the TFA-catalyzed reaction of 10 in benzene.[5] Protonated fluorenyl cations have been recently discussed by Olah.[11] TFSA can protonate 9 at the position, 1 or 3 to give the protonated

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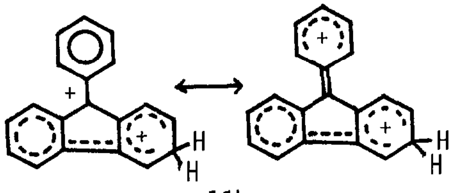
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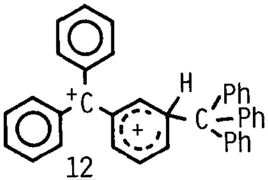
species (11a, b), which reacts with benzene to give 3. The formal central cationic charge is less delocalized than the cation 9, because the positive charge delocalizes more on one benzene ring, and therefore 11 is so reactive that Friedel-Crafts type reaction with benzene is possible.

Though the role of the strong acid is very evident as shown in runs 2, 4 and 6 in the Table, 5 itself also seems to give the products in low yields (runs 3, 5 and 7). The formation of these products in less acidic or aprotic conditions can be explained by; (a) the cation (5) itself can cyclize under the conditions,[12] or (b) 5 can act just as a proton does: the triphenylmethylated cation, such as 12, is a reaction intermediate. Triphenyl cation leaves after cyclization.



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The present results provide a novel chemistry of triphenylmethyl cation, and a participation of a dication in the reaction was demonstrated. Example of reactions involving dicationic species have been illustrated.[13] Dications which have been thought to be unusual chemical species are now becoming common and important intermediates in the chemistry.

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(Received in Japan 16 September 1982)