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NOVEL ENE AND INSERTION REACTIONS OF BENZYNE WITH ALKYLBENZENES[1]

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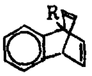
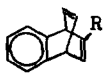
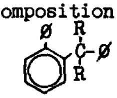
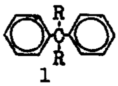
It has been shown that tetrafluorobenzyne reacts with benzene and alkylbenzenes to give only 2 + 4 - cycloadducts (tetrafluorobenzobicyclo[2.2.2]octatrienes) in high yield.[2] In contrast to these results, we have found that (the parent) Benzyne is much less selective and reacts with toluene to give o-benzylbiphenyl (1) and diphenylmethane (2) in addition to the 2 + 4 - cycloadducts. Ethylbenzene, cumene, and mesitylene reacted with benzyne in a similar manner while t-butylbenzene gave only the two cycloaddition isomers.[3] The yields and product compositions from reaction of benzyne with alkylbenzenes are presented in the table.[4]

Products from Reaction of Benzyne with Alkylbenzenes

R-C_6H_5 a)	% Yield b)	Product Composition			
					
CH_3-	13	16	38	45	1
CH_3CH_2-	25c)	14	34	20	32
$(CH_3)_2CH$-	18c)	22	50	14	14
$(CH_3)_3C$-	5	30	70	-	-
1,3,5-$(CH_3)_3$	11	50		50	-

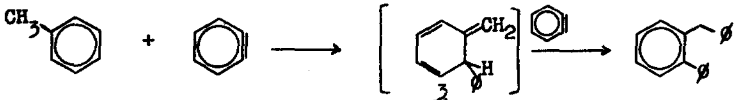
a) **Reaction conducted in neat toluene**, t-butylbenzene, and mesitylene (200 ml) at 45°. Reactions with ethylbenzene and cumene were carried out in 25:75 arene:ethylene chloride solutions (200 ml, 45°) in order to minimize formation of side products (see footnote c).

b) Yield based on benzyne generated from benzenediazonium-2-carboxylate (1.0 g., 6.7 mmole).

c) Benzyne reaction products from styrene and α-methylstyrene are also obtained (11 and 18% yield, respectively). These olefins were found to arise via hydrogen abstraction by o-carboxyphenyl cations.

The isomeric cycloadducts were formed in an essentially statistical ratio of 70:30, very nearly the ratio obtained with tetrafluorobenzyne.[2] Therefore, in this respect benzyne and its perfluoro derivative are similar. At this point the similarity ends, however. The unexpected formation of 1 and 2 and the corresponding derivatives from ethylbenzene, cumene, and mesitylene clearly shows that benzyne is capable of much more extensive chemistry.

The formation of o-benzylbiphenyl can best be explained as the result of two successive "ene" reactions, the first examples ever reported involving benzyne and an aromatic substrate. This pathway has precedence in the extensive number of ene reactions attributed to benzyne in the literature[5] and is consistent with the fact that the ortho isomer is formed exclusively. The more remote possibility that 1 arises from intermediate formation of diphenylmethane or o-methylbiphenyl followed by insertion of benzyne was ruled out by control experiments. All attempts to isolate 3 or o-methylbiphenyl (the product of a 1,3-hydrogen shift on 3) were unsuccessful. Apparently, 3 is so reactive that it cannot survive in the presence of excess benzyne.



Diphenylmethane and the corresponding ethylbenzene and cumene derived products (1,1-diphenylethane and 2,2-diphenylpropane) apparently arise from insertion of benzyne into the benzylic C-H bond. The formation of these products is especially significant in view of the fact that very few insertion reactions of benzyne have ever been reported.[5] Although no definite conclusions regarding the mechanism can be made, no bicumyl or biphenyl was detected, thereby providing evidence against the existence of discrete free radical intermediates. The large increase in yield of insertion products from ethylbenzene and cumene indicates that benzyne acts as an electrophile.

These preliminary results show that substitution of fluorine for hydrogen dramatically alters the reactivity of the aryne bond. Further investigations concerning the aryne-alkylarene ene and insertion reactions and the effect of substituents on aryne reactivity will be published at a later date.

1. Taken in part from the Ph.D. thesis of John M. Brinkley, C.W.R.U.
2. J. P. N. Brewer, I. F. Eckhard, H. Heaney, and B. A. Marples, J. Chem. Soc., (C) 664 (1964).
3. All products were isolated and identified by I.R., nmr, and mass spectral analysis. Compounds 1 and 2 were further identified by comparison with authentic samples.
4. Benzyne generated from o-fluorophenyl-lithium gave identical product ratios from ethylbenzene and toluene thus providing evidence the phenomenon is precursor-independent.
5. R. W. Hoffman, "Dehydrobenzene and Cycloalkynes" Academic Press, New York (1967).