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ALLYLATION OF AROMATIC NUCLEUS WITH ALLYL DIPHENYL PHOSPHATE IN THE PRESENCE OF BORON TRIFLUORIDE ETHERATE

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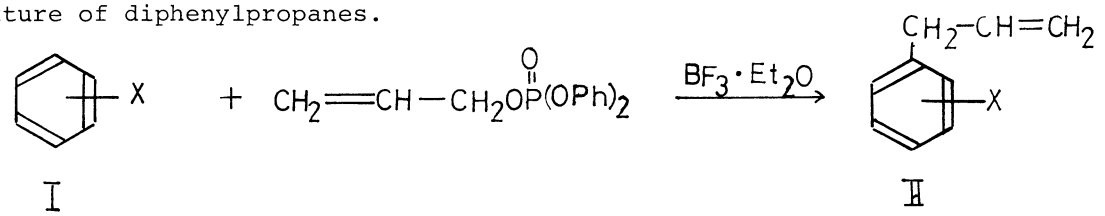
Allyl diphenyl phosphate[ADP] reacted with a large excess of aromatic compounds possessing electrondonating group in the presence of boron trifluoride etherate under mild experimental conditions to give selectively the corresponding monoallylated compounds in the yield of 40-60%.

Allylation of aromatic compounds has been reported by many workers.[1] However, there have been no reports using allyl diphenyl phosphate as an allylating agent except the reaction with aromatic Grignard reagent[2] and the thermolysis with phenolic compounds.[3] In the latter case, the yields are low and many by-products are produced.

We wish to report direct allylation of aromatic compounds at relatively low temperature giving selectively monoallylated products in 40-60% yield. Thus ADP was added into a mixture of aromatic compounds and boron trifluoride etherate at room temperature and the mixture was stirred for 5 hrs. After decomposition of the mixture with ice water, the products were extracted with ether and distilled under reduced pressure. The results are shown in Table.

Electron deficient or hindered aromatic compounds such as acetophenone, nitrobenzene and 1,3,5-tri-t-butylbenzene were unsusceptible to allylation under the conditions. It should be noted that reaction of benzene with ADP in the presence of aluminium trichloride in place of boron trifluoride at room temperature did not give allylbenzene but a 2:3 mixture of 1,1- and 1,2-diphenylpropanes (11.2%).[4,5] These products might be formed through allylbenzene, because treatment of allylbenzene with aluminium trichloride in benzene gave a similar mixture of diphenylpropanes.



I II

Table Reaction of ADP with aromatic compounds in the presence of boron trifluoride etherate

X in I	The ratio of ADP/I/$BF_3 \cdot Et_2O$	Temperature (°C)	Products[a], X in II (% yield[b])
H	1/5/1	r.t.	H(17)
H	1/13.5/1	50	H(57)
Me	1/5/1	r.t.	o-Me(32) + p-Me(10)[6]
Me	"	50	o- + p-(13)
Br	"	r.t.	o-Br(3.3) + p-Br(2.2)[7]
1,2-Me_2	"	"	2,3-Me_2 + 3,4-Me_2(49)[8]
1,3-Me_2	"	"	2,4-Me_2(44) + 2,6-Me_2(10)[8]
1,4-Me_2	"	"	2,5-Me_2(53)[8]
1,3,5-Me_3	"	"	2,4,6-Me_3(54)[9]
OH	"	"	o-OH(16.4) + p-OH(16.4)[10] + CH=CH-CH_2-O-C_6H_5(5.2)[11]
OMe	"	"	o-OMe(14) + p-OMe(28)[12]
OMe	"	50	o-OMe(1.2) + p-OMe(11.8)
1,2-$(OMe)_2$	"	r.t.	3,4-$(OMe)_2$(57)[13]
1-OH,2-OMe	"	"	3-OMe,4-OH(37)[14] + a mixture of x-OMe,y-OH(20)
1-OH,4-Me	"	"	3-Me,4-OH or 3-OH,4-Me(39)

a In most cases, the products were isolated by preparative g.l.c. and their structures were determined by NMR, IR and elementary analyses.

b Based on ADP used.

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