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REACTIONS OF BENZENES WITH ACETYLENES CATALYZED BY RHODIUM CARBONYL UNDER CARBON MONOXIDE

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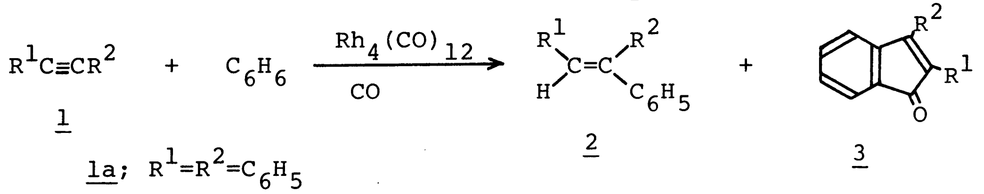
The reaction of benzene with diphenylacetylene catalyzed by $Rh_4(CO)_{12}$ under carbon monoxide gives triphenylethylene and 2,3-diphenylindenone. The reactions of mono-/di-substituted benzenes with the acetylene also give the corresponding olefins and 2,3-diphenylindenones.

We have recently reported that the additions of an aromatic carbon-hydrogen bond to the unsaturated bonds of diphenylketene and aryl isocyanates are catalyzed by $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$ to give 2,2-diphenylacetophenones and N-aryl benzamides, respectively, and that the tendencies of the orientation and the relative rates affected by the substituents, when monosubstituted benzenes are used, indicate the reaction to be nucleophilic in nature.[1)] Since it seemed that the application of such reactions to the other unsaturated compounds is of importance for organic synthesis, we examined the reactions of benzenes with acetylenic compounds. We now wish to report the formation of ethylenes and indenones from benzenes and acetylenes, which are attributable to the cleavages of one and two C-H bonds of benzenes.

When a mixture of diphenylacetylene (1a, 1g), benzene (30ml), and $Rh_4(CO)_{12}$ (0.040g) was heated at 220°C for 7hr under $25Kg/cm^2$ pressure of carbon monoxide, triphenylethylene (2a, 45%) and 2,3-diphenylindenone (3a, 10%) were obtained as the benzene adducts of 1a, together with 1-benzylidene-2,3-diphenylindene, a dimer of 1a (4, 8%),[2)] trans-stilbene (5, 12%),[3)] and 2,3,4,5-tetraphenylcyclopentenone (6, 16%).[3)]

As Fig. 1 shows, the composition of the products varies with the pressure of carbon monoxide. In the low pressure region the trimerization of 1a to hexaphenylbenzene (7) is predominant in accordance with the result reported by Iwashita et al., which was obtained in the experiment without carbon monoxide.[4)] Increasing the pressure, the trimerization is depressed and the addition of benzene to the acetylene becomes remarkable, giving the adducts 2a and 3a. The maximum yield of 2a is attained in the region of 25-30Kg/cm^2 pressure of carbon monoxide, and the use of a higher pressure such as 100Kg/cm^2 results to the formation of the other products whose structures are not determined yet.



1a; $R^1=R^2=C_6H_5$
1b; $R^1=C_6H_5$, $R^2=CH_3$
1c; $R^1=R^2=p\text{-}CH_3C_6H_5$

In a similar condition 1-phenylpropyne (1b) gave (E)-methylstilbene (2b, 13%) and 2-phenyl-3-methylindenone (3b, 10%), and bis(p-tolyl)acetylene (1c) gave 1,2-bis(p-tolyl)-1-phenylethylene (2c, m.p. 88-89°C, 34%), presumably (Z)-form, and 2,3-bis(p-tolyl)indenone (3c, 14%). The formation of only one of the geometrical isomers of olefins (2b and 2c) indicates that the addition of benzene proceeds stereo- and regioselectively, and those of 3b and 3c clearly demonstrate that the phenylene moieties of the indenones are derived from benzene, and thus two carbon-hydrogen bonds of benzene are cleavaged.

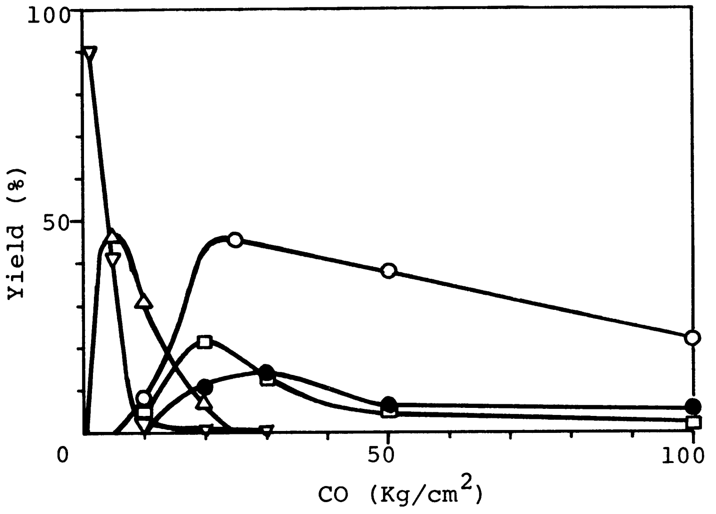


Fig.1. Dependence of the Product Yields on the Pressure of Carbon Monoxide in the Reaction of Diphenylacetylene(1a) with Benzene: 1a(1g), C_6H_6(30ml), $Rh_4(CO)_{12}$ (0.040g), 220°C, 7hr.
△; 1a, ○; triphenylethylene(2a),
●; 2,3-diphenylindenone (3a),
□; 2,3,4,5-tetraphenylcyclopentenone(6),
▽; hexaphenylbenzene(7)

Monosubstituted benzenes such as toluene, anisole, and fluorobenzene also reacted with 1a to yield 1-aryl-1,2-diphenylethylene (2d-2f) and 2,3-diphenylindenones (3d-3f). The distribution of the positional isomers (o-, m-, and p-) of the olefins 2d-2f and the relative rates which were determined from competitive experiments with

Table 1. The Addition of Monosubstituted Benzene to Diphenylacetylene

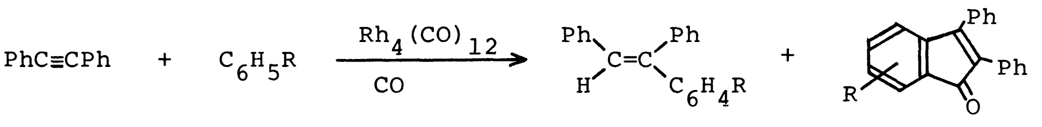
C_6H_5R	Product[a)]	Yield (%)	Isomer ratio (%)[b)] ortho	meta	para	Relative rate[c)]
C_6H_6	$PhCH{=}C(Ph)C_6H_5$ (2a)	45	-	-	-	1
$C_6H_5CH_3$	$PhCH{=}C(Ph)C_6H_4CH_3$ (2d)	24	6	65	29	0.4
$C_6H_5OCH_3$	$PhCH{=}C(Ph)C_6H_4OCH_3$ (2e)	42	64	26	10	2.7
C_6H_5F	$PhCH{=}C(Ph)C_6H_4F$ (2f)	49	70	22	8	2.8

a) The products were identified by comparison of their retention time in G.L.C. and their spectroscopic data with those of authentic samples prepared from dehydration of the corresponding 1-aryl-1,2-diphenylethanol.

b) The isomer ratios of 2d and 2e were estimated by G.L.C. (condition: 1.5% OV-17 on Shimalite W; 200-220°C), and that of 2f by ^{19}F NMR.

c) The relative rates were determined from competitive reactions with benzene: C_6H_6(0.3mol), C_6H_5R(0.3mol), 1a(1g), $Rh_4(CO)_{12}$(0.040g), CO(25Kg/cm^2),220°C, 7hr.

benzene are affected by the substituents, as shown in Table 1, and the tendencies are similar to those in the reactions of diphenylketene and aryl isocyanates.[1)] For the indenones 3d-3f four positional isomers are also expected, and all of them were confirmed by the isolation in the case of anisole.[5)]



2d-2f 3d-3f

R=CH_3, OCH_3, and F

From the isomer ratios of 2d and 2e it is clear that the ortho position in anisole and the meta position in toluene are the most reactive sites. These facts may suggest selective introduction of 1,2-diphenylvinyl group into the 2-position of 4-methylanisole by the reaction with 1a. Then it was found that the reaction gives 2-(1,2-diphenylvinyl)-4-methylanisole (8a) preferentially.[6)]

The formation of the ethylenes 2 can be explained in terms of the following steps; i) the oxidative addition of benzene to the rhodium catalyst, ii) the insertion of an acetylene into the resulting Ph-[Rh]-H intermediate, and iii) the reductive elimination of PhC(R)=C(R)-[Rh]-H. The generation of the indenones 3 in which the phenylene moieties are derived from benzene is very interesting. The isolations of a phenylene-iridium complex[7)] from benzene and η-$C_5H_5Ir(CO)_2$, and a benzotitanacyclopentadiene complex[8)] from $(\eta\text{-}C_5H_5)_2Ti(C_6H_5)_2$ and 1a via a phenylene -titanium intermediate[9)] have been reported. And the benzotitanacyclopentadiene complex reacts with carbon monoxide to give 3a.[8] These facts may suggest the presence of a phenylene-rhodium and a benzorhodiacyclopentadiene intermediates for the formation of 3 in our present study.

References and Notes

1) P. Hong, H. Yamazaki, K. Sonogashira, and N. Hagihara, Chem. Lett., 535 (1978).
2) It has been reported that the dimer 4 is obtained by the reaction of 1a with $RuH(NO)(PPh_3)_3$; R. A. Sauchez-Delgado and G. Wilkinson, J. Chem. Soc. Dalton, 804 (1977).
3) The products 5 and 6 may be formed by the hydrogenation of 1a and 2,3,4,5-tetraphenylcyclopentadienone (9),respectively, with hydrogen molecule which is generated in the formation of 3 or in water gas shift reaction of concomitant water in CO gas or the solvent. In fact, the intermediate 9 (6-9%) was obtained in the lower pressure region of CO (5-10Kg/cm^2).
4) Y. Iwashita and F. Tamura, Bull. Chem. Soc. Jpn., 43, 1517 (1970).
5) Four isomers of 3e ($R=OCH_3$) were obtained in a 6% total yield, and their structure were estimated from ^1H NMR spectra ($CDCl_3$, δ).

Position(OCH_3)	m.p.(lit.)	H^4	H^5	H^6	H^7	OCH_3
4	135-6°	-	6.90(m,2H)		7.48(m)	3.53
5	158-9°	6.64(d)	-	6.60(dd)	7.50(d)	3.78
6	167-8°(168-9°)[10]	6.99(d)	6.75(dd)	-	7.15(d)	3.81
7	182-4°	6.8-7.0(m,2H)			-	3.52

6) The compound 8a and the 3-isomer (8b) were obtained in a ratio of 7.7:1, and their structures were estimated by comparison of the chemical shifts of the OCH_3 and CH_3 groups with those of the positional isomers of 2d and 2e: 8a [m.p. 79-80°C, δ2.26(CH_3) and 3.50(OCH_3)]; 8b [not isolated. δ2.02(CH_3) and 3.74(OCH_3)].
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8) H. Masai, K. Sonogashira, and N. Hagihara, Bull. Chem. Soc. Jpn., 41, 750(1968).
9) J. Dvorak, R. J. O'Brien, and W. Santo, J. Chem. Soc., Chem.Commun., 411(1970).
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