CHEMISTRY LETTERS, pp. 507-510, 1980.

ADDITION OF 5-MEMBERED AROMATIC HETEROCYCLIC COMPOUNDS TO ACETYLENES CATALYZED BY TETRARHODIUM DODECACARBONYL: SYNTHESES OF VINYL SUBSTITUTED AROMATIC HETEROCYCLIC COMPOUNDS

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In the presence of a catalytic amount of $Rh_4(CO)_{12}$ furan adds to diphenylacetylene (1a) to give 1-(2-furyl)-1,2-diphenylethylene in a 80% yield. Similarly, from 2-substituted furans are obtained the adducts (3e-3h), in which the furyls attach to the olefin at the 5-position of the rings, in good yields. Thiophene and N-methylpyrrole also react with 1a to afford the corresponding ethylenes.

We have recently reported that under pressure of carbon monoxide tetrarhodium dodecacarbonyl, $Rh_4(CO)_{12}$, activates catalytically an aromatic carbon-hydrogen bond to allow the interaction with unsaturated bonds of heterocummulene,[1)] acetylene,[2)] and olefin.[3)] For example, when diphenylacetylene is treated with benzene, triphenylethylene is obtained in a good yield.[2)] In this communication we wish to report that a carbon-hydrogen bond of a 5-membered aromatic heterocyclic compound such as furan, thiophene, or pyrrole is also activated by the rhodium carbonyl catalyst to add to the triple bonds of acetylenes, giving the corresponding vinyl substituted aromatic heterocyclic compounds.

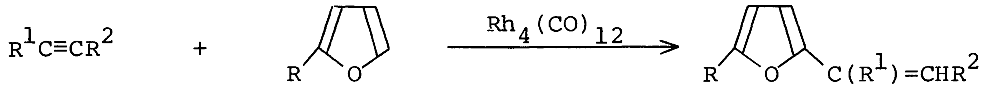
When a mixture of diphenylacetylene (1a, 10mmol), furan (2a, 30ml), and $Rh_4(CO)_{12}$ (0.05mmol) was heated at 220°C for 7hr under pressure of carbon monoxide ($25Kg/cm^2$ at room temperature), 1-(2-furyl)-1,2-diphenylethylene (3a, colorless oil) was obtained in a 80% yield based on the amount of 1a used (4000%/ Rh atom). The product was identified by its elementary analysis, IR, NMR, and mass spectra. In the ^1H NMR spectrum of 3a two sets of resonances due to the furyl ring protons (H^3, H^4, and H^5) were obserbed, indicating it to be a mixture of the (Z)- and (E)-isomers

(78:22).

As we have already mentioned in the reaction of 1a with benzene,$^{2)}$ the present reaction also needs the presence of moderately pressured carbon monoxide (>10Kg/cm^2). When the pressure of carbon monoxide is lower than 10Kg/cm^2, cyclotrimerization of 1a becomes predominant.

Furan reacted also with bis(p-tolyl)acetylene (1b) to give 1-(2-furyl)-1,2-bis(p-tolyl)ethylene (3b, 70%). In the reaction with an unsymmetrical acetylene, 1-phenylpropyne (1c) being possible to give two adducts, 2-(2-furyl)-1-phenylpropene (3c) and 1-(2-furyl)-1-phenylpropene (3d), 3c was obtained as a main product (64%) and 3d as a by-product (6%),$^{4)}$ indicating the reaction to be regioselective.

Similarly, 2-substituted furans such as 2-methylfuran (2b), 2-(methoxycarbonyl)furan (2c), 2-acetylfuran (2d), and furfural (2e) reacted with 1a to give the products (3e-3h) which were formed by the addition of a carbon-hydrogen bond at the 5-position of the furans to 1a. In each case a mixture of the geometrical isomers was obtained. These results are summarized in Table 1.



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1a; $R^1=R^2=C_6H_5$

1b; $R^1=R^2=p\text{-}CH_3C_6H_4$

1c; $R^1=CH_3$, $R^2=C_6H_5$

R=H, CH_3, CH_3CO_2, CH_3CO, and CHO

The addition of furan or a 2-substituted furan to acetylenes occurs regioselectively at an α-position of the ring, indicating the α-C-H bond to be more reactive than the β-C-H one. If the α-positions are occupied by substituents, the reaction at the β-position can take place. For example, 2,5-dimethylfuran reacted with 1a to give 1-[3-(2,5-dimethyl)furyl]-1,2-diphenylethylene (3i)$^{5)}$ in a 40% yield.

To compare the reactivities of furan and benzene to the acetylene is of interest. In an experiment using a mixture of furan and benzene in a molar ratio of 1:1 (each of 0.2mol), the furan adduct 3a was obtained in a 80% yield, but the benzene adduct, triphenylethylene, was detected only in a trace amount. Even using five times of the amount of benzene to that of furan (0.05mol), 3a was a main product (74%), and the amount of triphenylethylene was small (2%). In addition

Table 1. The Adducts of Furans and Diphenylacetylene[a]

				^{1}H NMR[c] δ			Isomer
Adduct (R)	Yield[b]		b.p (m.p)	H^3	H^4	H^5[R]	Ratio (Z/E)
3a (H)	80%	(Z)	116°/1mmHg	5.85(d)	6.26(dd)	7.34(d)	78/22
		(E)		6.14(d)	6.32(dd)	d)	
3e (CH_3)	86%	(Z)	118-20°/1mmHg	5.72(d)	5.91(dd)	[2.33(s)]	79/21
		(E)		6.04(d)	5.95(dd)	[2.18(s)]	
3f (CO_2CH_3)	68%	(Z)	(78-80°)	5.90(d)	d)	[3.89(s)]	83/17
		(E)	-	6.22(d)	d)	[3.81(s)]	
3g ($COCH_3$)	51%	(Z)	(80-82°)	5.97(d)	d)	[2.49(s)]	79/21
		(E)	(65-67°)	6.29(d)	d)	[2.14(s)]	
3h (CHO)	41%	(Z)	152-4°/1mmHg	6.02(d)	d)	[9.57(s)]	59/41
		(E)		6.34(d)	d)	[9.50(s)]	

a) The reaction of the furan (30ml) with 1a (10mmol) in the presence of $Rh_4(CO)_{12}$ (0.05mmol) was carried out at 220°C for 7hr under pressure of carbon monoxide (25Kg/cm^2 at room temperature).

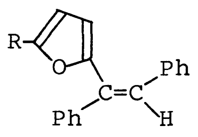
b) Based on the acetylene used.

c) The spectra were measured in $CDCl_3$ ($J_{3,4}$=4Hz, $J_{4,5}$=2Hz).

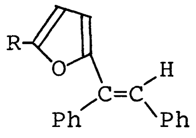
d) The peaks are hidden by phenyl proton peaks.

2,5-bis(1,2-diphenylvinyl)furan (4),[6] which is the addition product of 3a to 1a, was formed in a 4% yield. These results show that the reactivity of furan is much greater than that of benzene, and that benzene can be used as a diluent in the reaction of furan with acetylenes.

All the adducts obtained in these reactions consist of two geometrical isomers (Z and E), of which the ratios are 83:17(3f)-59:41(3h). In the ^{1}H NMR spectra (Table 1) the 3-furyl protons (H^3) of major products are shielded more than those of minor ones. This shielding seems to be due to the phenyl ring at the cis-position, similar to the case of (E)-α-phenyl-β-(2-furyl)acrylic acid.[7] Therefore, we assign the major products to the (Z)-isomers (trans-addition products) and the minor ones to the (E)-isomers (cis-addition products).



(Z)



(E)

In the case of 3g (R=$COCH_3$) the (Z)- and (E)-isomers could be isolated by column chromatography on silica. When an isomer mixture of 3g consisting of a ratio of (Z):(E)=26:74 was heated at 220°C, the isomer ratio changed to (Z):(E)=75:25, which was close to that in the catalytic reaction between 2d and 1a. This fact shows the (Z)-isomer to be thermodynamically more stable than the (E)-isomer. We assume that in the present reaction the (E)-isomer is first formed, and then isomerizes to the (Z)-isomer.

In this catalytic system thiophene and N-methylpyrrole also reacted with 1a to give 1-(2-thienyl)-1,2-diphenylethylene (5, 48%)8) and 1-[2-(N-methyl)pyrrolyl]-1,2-diphenylethylene (6, 31%),9) respectively. The order of the reactivities of these heterocycles and benzene to the acetylene could be estimated from the competitive experiments; furan>thiophene>N-methylpyrrole>benzene.

Further studies on the mechanism and applications of this reaction are in progress.

References and Notes

1) P. Hong, H. Yamazaki, K. Sonogashira, and N. Hagihara, Chem. Lett., 535 (1978).

2) P. Hong, B-R. Cho, and H. Yamazaki, Chem. Lett., 339 (1979).

3) P. Hong and H. Yamazaki, Chem. Lett., 1335 (1979).

4) 3c; Colorless oil (b.p. 105°/1mmHg), NMR(CDCl$_3$) δ2.13(d,2Hz,3H,CH$_3$), 6.34(m,2H, H^3 and H^4) and 7.0-7.4(m,7H,=CH,H^5, and Ph). 3d(not isolated); NMR(CDCl$_3$) δ1.68(d,7Hz,3H,CH$_3$).

5) 3i; Colorless oil (b.p. 145-7°/1mmHg), NMR(CDCl$_3$) (Z) δ5.89(s,1H,H^4), 2.21(s,3H, CH$_3$), and 1.90(s,3H,CH$_3$); (E) δ5.73(s,1H,H^4), 2.25(s,3H,CH$_3$), and 1.77(s,3H,CH$_3$). This compound is easily oxidized to give 3-(1,2-diphenylvinyl)-3-hexene-2,5-dione (colorless crystals, m.p. 120-1°).

6) 4; Colorless crystals (m.p. 167-8°), M$^+$ 424, NMR(CDCl$_3$) δ5.85(s,2H,H^3 and H^4), 7.05(m,10H,2Ph), and 7.30(bs,12H, 2Ph and 2=CH).

7) S. Fisichella, G. Mineri, G. Scarlata, and D. Sciotto, Tetrahedron, 31, 2445 (1975).

8) The compound 5 was obtained as a colorless oil, from which a crystalline product (m.p. 66-7°, M$^+$ 262), presumably one of the geometrical isomers, was isolated by crystallization from hexane.

9) Both the geometrical isomers were isolated by chromatographic separation on silica: 6(Z); colorless crystals (m.p.67-8°), NMR(CDCl$_3$) δ3.14(s,3H,N-CH$_3$), 5.98 (dd,1H,H^3), 6.19(t,1H,H^4), and 6.8-7.4(m,=CH and 2Ph). 6(E); colorless crystals (m.p. 94-5°), NMR(CDCl$_3$) δ3.22(s,3H,N-CH$_3$), 6.12(m,2H,H^3 and H^4), 6.57(t,1H,H^5), 6.73(s,1H,=CH), 7.05(s,5H,Ph), and 7.19(s,5H,Ph).

(Received February 16, 1980)