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Carbonylation of Phenylacetylene by Rhodium Carbonyl Chloride

Jitsuo Kiji, Susumu Yoshikawa, and Junji Furukawa

Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606

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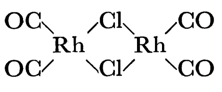
Synopsis. The reaction of phenylacetylene with carbon monoxide catalyzed by rhodium carbonyl chloride ($Rh_2(CO)_4Cl_2$) gives 3,6-diphenyl-1-oxa-[3,3,0]bicycloocta-3,6-diene-2,4-dione.

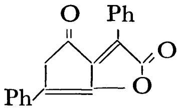
Although acetylenic compounds are known to react with carbon monoxide under the influence of transition-metal catalysts,[1] there have been few studies of the carbonylation of acetylene with rhodium carbonyl chloride ($Rh_2(CO)_4Cl_2$, I); the carbonylation of diphenylacetylene giving a cyclopentadienone and a quinone is catalyzed by I in benzene.[2] This paper will deal with a novel carbonylation of phenylacetylene with I.

Results and Discussion

The reaction was carried out in a benzene solution under the pressure of carbon monoxide. After the reaction, no phenylacetylene was recovered and deep-red needles were separated from the reaction mixture. The elemental analysis and the mass spectrum indicated that the product (II) is composed of two molecules of phenylacetylene and three molecules of carbon monoxide. The infrared spectrum taken with a KBr disk has three carbonyl bands, at 1788 (sh), 1753 and 1740 cm^{-1}, which can be assigned to an unsaturated γ-lactone and a five-membered cyclic ketone. The NMR spectrum in hexa-deuteriodimethyl sulfoxide at 90 °C shows a sharp singlet at 6.2 τ due to methylene protons and complicated peaks at 1.7—2.6 τ due to phenyl protons. The hydrogenation of II over platinum on carbon absorbed two moles of hydrogen to form a saturated compound, $C_{19}H_{16}O_3$ (by mass spectrometry). The reaction of II with 2,4-dinitrophenylhydrazine gave the corresponding hydrazone, in which the γ-lactone ring remained unchanged. From these observations, the product was proved to be 3,6-diphenyl-1-oxa-[3,3,0]bicycloocta-3,6-diene-2,4-dione (II).



I



II

This reaction is characteristic of terminal acetylenes. The formation of II can be explained by the following mechanism; phenylacetylene adds oxidatively to rhodium to form a rhodium hydride,[3] and this is followed by the insertion of phenylacetylene and carbon monoxide. These processes involve two internal cyclizations, which give five-membered cycles. Many examples of a similar internal cyclization to form a lactone have been reported by Chiusoli and Cassar.[4]

The products other than II were oily polymeric materials containing a γ-lactone moiety, but their structure could not be determined. The formation of this polymeric product can presumably be explained on the assumptions that the mode of the insertion of phenylacetylene was not uniform and that the resulting intermediates were not suitable for the cyclization giving II, but gave a linear structure containing the γ-lactone group.

Similarly, from the reaction of *t*-butylacetylene a colorless carbonylated product was obtained.[5] Methylacetylene gave a 1,4-quinone derivative. In this carbonylation of α-acetylene, the substituent on the acetylenic carbon has a great influence on the course of the reaction.

Experimental

Carbonylation. A benzene solution containing 400 mg of $Rh_2Cl_2(CO)_4$ and an excess of phenylacetylene (8 g) was allowed to react with carbon monoxide under a pressure of 50 kg/cm^2 at 120 °C. After 12 hr, II was separated from the reaction mixture, gathered, and washed with benzene to give deep-red needles (yield, 1.07 g); mp 234—235 °C. Found: C, 79.08; H, 4.46; O, 16.42%. Calcd for $C_{19}H_{12}O_3$: C, 79.01; H, 4.19; O, 16.63%.

Hydrogenation of II. Compound II (370 mg) was hydrogenated in ethyl acetate (150 ml) at room temperature under an atmospheric pressure, using Pt on carbon (5%, 500 mg) as the catalyst. Subsequent chromatography on silica gel with ethyl acetate gave 146 mg of colorless product (III); mp 140—141.5 °C. IR (KBr): 1770, 1750 cm^{-1} (ν_{CO}). Found: C, 78.16; H, 5.70; O, 16.27. Calcd for $C_{19}H_{16}O_3$: C, 78.10; H, 5.48; O, 16.42.

References

1) C. W. Bird, "Transition Metal Intermediates in Organic Synthesis," Academic Press, New York (1967), p. 205.

2) S. McVey and P. M. Maitlis, *J. Organometal. Chem.*, **19**, 169 (1969).

3) J. P. Collman and J. W. Kang, *J. Amer. Chem. Soc.*, **89**, 844 (1967).

4) C. P. Chiusoli and L. Cassar, *Angew. Chem.*, **79**, 177 (1967).

5) Chromatography of the reaction mixture on Florisil (Floridin Co., U.S.A.), using benzene as the solvent, gave colorless prisms; mp 175 °C. Mass m/e 330 (M^+); IR (KBr) 1755, 1710 cm^{-1} (ν_{CO}); NMR ($CDCl_3$, TMS) τ 9.00, 8.76, 8.70 (27H of *t*-butyl) and 7.00, 2.40, 2.64 (3H).