Cyclizations of Acetylene Derivatives with Tri-β-styrylchromium*[1]

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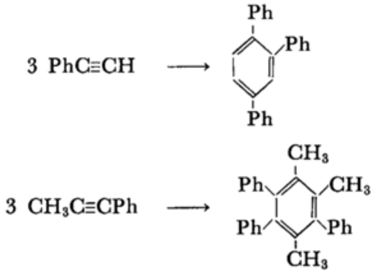
It is known that triorganochromium compounds are decomposed rapidly by either the acidic hydrogen of acetylene or monosubstituted acetylenes to give no cyclization product,[1)] and that those materials cyclize disubstituted acetylenes to give two types of products,[1-3)] hexasubstituted benzene derivatives and condensed products in which two molecules of the acetylene are combined with one of the groups attached to chromium by hydrogen abstraction. In these reactions, an unsym-disubstituted acetylene derivative has not been used as the acetylene derivative.

In cyclizations with tri-β-styrylchromium, 1, 2, 4-triphenylbenzene was obtained from phenylacetylene, *i. e.*, monosubstituted acetylene. Moreover, 1, 2, 4-trimethyl-3, 5, 6-triphenylbenzene was produced, with no 1, 3, 5-trimethyl-2, 4, 6-triphenylbenzene, from methylphenylacetylene, *i. e.*, unsym-disubstituted acetylene. In these reactions no condensed product was obtained.



It seems that the tri-β-styrylchromium compound is stabilized by a great conjugated system of the styryl group to be stabilized against the acidic hydrogen of phenylacetylene.

The reason why 1, 2, 4-triphenylbenzene is produced from phenylacetylene, while 1, 2, 4-trimethyl-3, 5, 6-triphenylbenzene is produced from methylphenylacetylene, is probably as follows: two molecules of the acetylene derivative approach a chromium compound along the direction of less resistance, forming a 1, 4-disubstituted cyclobutadiene complex or a 1, 4-disubstituted butadiene biradical, and then the third acetylene molecule reacts with the complex or the biradical formed above to produce a 1, 2, 4-trisubstituted benzene derivative.

Experimental

Cyclization of Phenylacetylene with Tri-β-styrylchromium. A tetrahydrofuran solution of β-styrylmagnesium bromide (63 m*l*, 40.4 mmol) was added, under nitrogen at −75°C, to 5.0 g (13.3 mmol) of chromium trichloride tristetrahydrofuranate[4)] suspended in 200 m*l* of tetrahydrofuran. This solution changed rapidly from deep purple to brown. After the mixture had been stirred for 1 hr at −75°C, 4.4 m*l* (40.4 mmol) of phenylacetylene were added to the solution obtained above. The reaction mixture was allowed to warm to 20°C over a 2 hr period and then refluxed for 6 hr. After the solvent had been evaporated *in vacuo*, the residue was hydrolyzed with ice water and the organic products were extracted with benzene. The brownish residue obtained from the benzene solution was dissolved in a minimum amount of benzene and chromatographed on 80 g of activated alumina. Elution with 150 m*l* of *n*-hexane gave 2.6 g of a white crystalline material. The recrystallization of this material from *n*-hexane gave 1, 2, 4-triphenylbenzene melting at 120°C (lit.[5)] mp 119—120°C). The present sample was identical in all respects with an authentic sample.

Found: C, 93.65; H, 6.32%. Calcd for $C_{24}H_{18}$: C, 94.12; H, 5.88%. Further elution with 150 m*l* of *n*-hexane gave 2.1 g of 1t, 4t-diphenylbutadiene-(1, 3) melting at 152.5°C (lit.[6)] mp 152°C).

Found: C, 92.84; H, 7.12%. Calcd for $C_{16}H_{14}$: C, 93.15; H, 6.85%. Finally, elution with 300 m*l* of benzene gave intractable tars which were not investigated further.

Cyclization of Methylphenylacetylene with Tri-β-styrylchromium. A tetrahydrofuran solution of β-styrylmagnesium bromide (94 m*l*, 60.4 mmol) was added, under nitrogen at −75°C, to 7.5 g (20 mmol) of chromium trichloride tristetrahydrofuranate suspended in 250 m*l* of tetrahydrofuran. After the mixture had been stirred for 1 hr at −75°C, 22 m*l* (180 mmol) of methylphenylacetylene were added to the solution. This reaction mixture was allowed to warm to 20°C over a 2-hr period and then refluxed for 6 hr. Then, the tetrahydrofuran and the unreacted methylphenylacetylene were evaporated *in vacuo*. The residue was hydrolyzed with ice water, and the organic products

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*[1] The essence of this paper was presented at the 20th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1967.

1) H. Zeiss, Organometallic Chemistry, Am. Chem. Soc. Monograph No. 147, Reinhold, New York, 1960, p. 411.

2) W. Herwig, W. Metlesics and H. Zeiss, *J. Am. Chem. Soc.*, **81**, 6203 (1959).

3) H. P. Throndsen, W. Metlesics and H. Zeiss, *J. Organometal. Chem.*, **5**, 176 (1966).

4) R. P. A. Sneeden and H. Zeiss, *J. Organometal. Chem.*, **4**, 355 (1965).

5) C. G. Overberger and J. M. Whelan, *J. Org. Chem.*, **24**, 1155 (1959).

6) M. Tsutsui and M. N. Levy, *Z. Naturforsch.*, **21b**, 823 (1966).

were extracted with benzene. The brownish residue obtained from the benzene solution gave, by chromatography on activated alumina, 1.8 g of 1t, 4t-diphenylbutadiene-(1, 3) and 7.1 g of white crystalline of 1, 2, 4-trimethyl-3, 5, 6-triphenylbenzene melting at 224°C (lit.[7] mp 225—227°C).

Found: C, 93.10; H, 6.85%. Calcd for $C_{27}H_{24}$: C, 93.06; H, 6.94%. The remainder was intractable tars which were not investigated further.

Cyclization of Diphenylacetylene with Tri-β-styrylchromium. A tetrahydrofuran solution of β-styrylmagnesium bromide (118 m*l*, 60.7 mmol) was added to 7.5 g (20 mmol) of chromium trichloride tristetrahydrofuranate and 3.6 g (20 mmol) of diphenylacetylene in 250 m*l* of tetrahydrofuran under nitrogen at −75°C. After it had been stirred for 1 hr at −75°C, the reaction mixture was allowed to warm to 20°C over a 2 hr period and then refluxed for 15 hr. After the solvent had been evaporated *in vacuo,* the residue was hydrolyzed with ice water and the organic products were extracted with benzene. The brownish residue obtained from the benzene solution gave, by chromatography on activated alumina, 1.77 g of 1t, 4t-diphenylbutadiene-(1, 3) and 3.10 g of white crystalline of hexaphenylbenzene melting at 415°C (lit.[3] mp 408—415°C). The present sample was identical in all respects with an authentic sample.

Found: C, 93.94; H, 5.80%; mol wt, 520 (osmotic pressure in benzene). Calcd for $C_{42}H_{30}$: C, 94.38; H, 5.62%; mol wt, 534.

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[7] W. Huebel and C. Hoogzand, *Chem. Ber.*, **93**, 103 (1960).