Catalytic Dimerization of Monoalkyl Acetylenes

By Nobue HAGIHARA, Masuhiko TAMURA,
Hiroshi YAMAZAKI and Magosaburo FUJIWARA

(Received May 4, 1961)

It has been described by some investigators[1] that acetylene and substituted acetylenes were polymerized with Ziegler type catalysts forming linear high molecular weight polymer or benzene derivatives.

We observed that with a catalyst obtained in the reaction of chromium tetra-*tert*-butoxide[2] with diethylzinc, monoalkyl acetylenes could be dimerized to the compound I in a good yield.

$$RC\equiv C-CR=CH_2 \qquad (1)$$

---

[1] G. Natta, P. Pino and G. Mazzanti, Belg. Pat. 546151 (1956); W. R. Smith, Brit. Pat. 820510 (1958); B. Franzus, P. J. Canterino and R. A. Wickliffe, *J. Am. Chem. Soc.*, **81**, 1514 (1959).

[2] N. Hagihara and H. Yamazaki, ibid., **81**, 3160 (1959); *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **81**, 821 (1960).

On the other hand, the reaction of monoalkyl acetylenes resulted only in the polymerization to trialkyl benzenes with a catalyst obtained from the reaction of chromium tetra-*tert*-butoxide with triethylaluminum.

n-Propylacetylene dimerizes to 2,4-di-*n*-propyl-1-buten-3-yne (II) in almost quantitative yield at 30°C for 10 hr. at $Et_2Zn/(tert\text{-}BuO)_4Cr$ ratio of 3. II is colorless liquid and boils at 88~89°C (40 mmHg) ($n_D^{20}=1.455$, Found: C, 87.80; H, 11.76. Calcd. for $C_{10}H_{16}$: C, 88.16; H, 11.84%). Fifteen moles of dimer per mole chromium compound were obtained.

The structure of the dimer was estimated as I by molecular weight determination and the presence of infrared absorption corresponding $-C\equiv C-$ and $>C=CH_2$ at 2230 and 890 cm^{-1}. Identity was established by comparison of the infrared spectrum with that of authentic sample (b. p. 87~88°C (40 mmHg), $n_D^{20}=1.457$, Found: C, 87.77; H, 11.97. Calcd. for $C_{10}H_{16}$: C, 88.16; H, 11.84%) which was prepared from 4-nonyen-6-one ($C_3H_7C\equiv C\text{-}COC_3H_7$) and methylene triphenyl phosphorane ($Ph_3P=CH_2$) according to the Wittig reaction.

Optimum ratio of diethylzinc to chromium tetra-*tert*-butoxide was 3 to 1. Although rate of the reaction is fast at high temperature, the formation of tri-*n*-propyl-benzene and high polymer is often considerable in this case.

This type of dimerization is not limited to *n*-propyl-acetylene. *n*-Butylacetylene was dimerized to 2,4-di-*n*-butyl-1-buten-3-yne (b. p. 64.5~65.0°C (5 mmHg), $n_D^{20}=1.459$, Found: C, 87.38; H, 12.31. Calcd. for $C_{12}H_{20}$: C, 87.73; H, 12.27%) and *tert*-butylacetylene to 2,4-di-*tert*-butyl-1-buten-3-yne (b. p. 92~93°C (90 mmHg), $n_D^{20}=1.438$, Found: C, 87.45; H, 11.90. Calcd. for $C_{12}H_{20}$: C, 87.73; H, 12.27%).

It is interesting that the catalytic dimerization of monoalkyl acetylenes with the catalyst in the present work gives exclusively I without the formation of 1,4-dialkylbutenyne ($RC\equiv C\text{-}CH=CHR$).

Osaka University
The Institute of Scientific
and Industrial Research
Sakai, Osaka