The Carbonylation of Cumulenes

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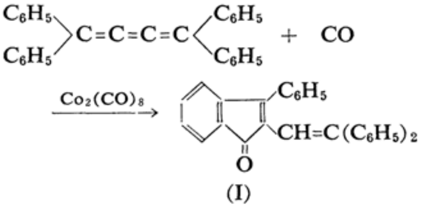
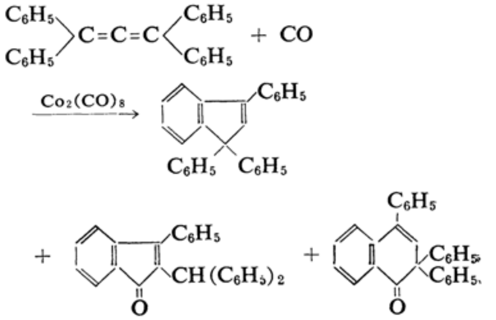
It has previously been shown that cumulenes interact with transition metal carbonyls to yield some new π-complexes.[1] In this paper we wish to describe the carbonylation of tetraphenyl-butatriene and -allene in the presence of dicobalt octacarbonyl.

Tetraphenylbutatriene (2.0 g.) in benzene (50 ml.) was treated with carbon monoxide (150 kg./cm^2) in the presence of dicobalt octacarbonyl (0.2 g.) at 230—250°C. Upon cooling after 6 hr., a red solution was obtained. The reaction mixture was separated by chromatography on alumina with benzene to give 1-diphenylmethylene-3-phenylindene[2] in a 0.04% yield and red prisms (I) (m. p. 147—148°C) in a 70% yield. The elemental analysis and molecular weight determination indicated that I has this composition: (tetraphenylbutatriene)·(CO), I (Found: C, 90.02; H, 5.55; mol. wt. (Rast), 365.5. Calcd. for $C_{29}H_{20}O$: C, 90.59; H, 5.24%; mol. wt., 384.5). The infrared spectrum of I showed the presence of a ketonic carbonyl group (1714 cm^{-1}). The NMR spectrum of I showed a singlet at 3.57τ and a multiplet at 2.67—3.08τ, with a relative intensity of 1 : 19. I absorbed 2 mol. of hydrogen over a Raney-nickel catalyst and was oxidized with chromium trioxide in acetic acid to give *o*-benzoylbenzoic acid and benzophenone. On the basis of this evidence and the melting point described in the literature, I was shown to be 2-(β, β-diphenylvinyl)-3-phenyl-indone (lit.[3] m. p. 147—148°C) as is shown below:



(I)

Analogously, tetraphenylallene in benzene was heated with carbon monoxide (150 kg./cm^2) in the presence of dicobalt octacarbonyl at 230—250°C for 6 hr. After the reaction, a yellow solution was obtained on cooling. The reaction mixture was separated by chromatography on alumina to give 1, 1, 3-triphenylindene (m. p. 133—134°C)[2] in a 41.5% yield, yellow plates (II) (m. p. 155.5—156.5°C) in a 23% yield, and yellow prisms (III) m. p. 172—174°C) in a 17% yield. These compounds were recrystallized from benzene and petroleum-ether. The elemental analyses and molecular weight determinations indicated that both II and III have this composition: (tetraphenylallene)·(CO), II (Found: C, 89.96; H, 5.33; mol. wt. (Rast), 367.0. Calcd. for $C_{28}H_{20}O$: C, 90.29; H, 54.1%; mol. wt., 372.4), III (Found: C, 89.80; H, 5.34%; mol. wt. (Rast), 367.4). The infrared spectra of II and III showed the presence of ketonic carbonyl groups (1714 and 1690 cm^{-1} respectively in Nujol). The NMR spectrum of II showed a singlet at 4.81τ and a multiplet at 2.58—3.09τ, with a relative intensity of 1 : 19. On the basis of this evidence and the melting point described in the literature, II was shown to be 2-diphenylmethyl-3-phenylindone (lit.[4] m. p. 154°C), while III, an isomer of II, seemed to be 2, 2, 4-triphenylnaphthalenone from its infrared spectrum, as is shown below:



(II) (III)

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[1] a) A. Nakamura, P.-J. Kim and N. Hagihara, This Bulletin, 37, 292 (1964); b) A. Nakamura, P.-J. Kim and N. Hagihara, *J. Organometal. Chem.*, 3, 7 (1965).

[2] Identified with an authentic sample by comparing the infrared spectra.

[3] C. F. Koelsch and H. J. Richter, *J. Org. Chem.*, 3, 471 (1938).

[4] W. Baker, J. F. W. McOmie and T. L. V. Ulbricht, *J. Chem. Soc.*, 1957, 4031.