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ORGANOMETALLIC INTERMEDIATES

V*. FURTHER REACTIONS OF CYCLOPROPENONES WITH NICKEL CARBONYL

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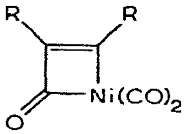
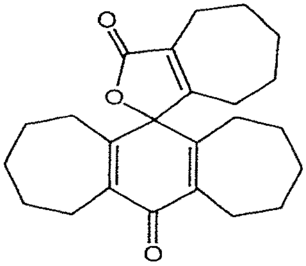
Summary

The reactions of cycloheptacyclopropenone and diphenylcyclopropenone with nickel carbonyl under anhydrous conditions have been investigated and structures deduced for the resulting products.

Our earlier studies [1, 2] on the mechanism of the hydrocarboxylation of acetylenes to acrylic acids indicated that probable intermediates in these reactions are nickelacyclobutenone complexes (I), which can also be generated from cyclopropenones. Subsequently the preparation and characterisation of analogous platinacyclobutenone complexes have been reported [3]. In order to examine the behaviour of nickelacyclobutenone complexes in the absence of hydroxylic substrates the reactions of cyclopropenones with nickel carbonyl under anhydrous conditions have been investigated and the results are now reported.



(I): (a) RR = $-(CH_2)_5-$;
(b) R = Ph



(II)

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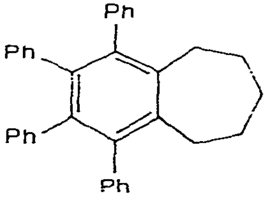
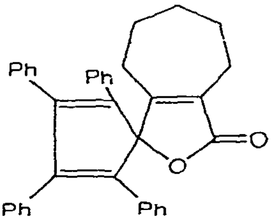
* For Part IV, see ref. 2.

The reaction of cycloheptacyclopropenone with nickel carbonyl in refluxing benzene provides only a trimer whose spectral properties are consistent with the structure (II). Thus the infrared spectrum shows carbonyl absorptions at 1760 and 1640 cm^{-1} and a double bond stretching absorption at 1670 cm^{-1}. The ultraviolet spectrum in ethanol, λ_{max} 244 nm(ϵ 24500) is characteristic of the cyclohexadienone chromophore, and the complex PMR spectrum showed absorption only between δ 1.3 and 2.9 ppm. The same compound has been shown to be formed by bis(1,5-cyclooctadiene)nickel(0) catalysis through addition of a further cycloheptacyclopropenone unit to the first formed 2,3 : 4,5-bis(pentamethylene)benzoquinone. No products attributable to cycloheptyne could be isolated from the nickel carbonyl reaction. Treatment of cycloheptacyclopropenone with nickel carbonyl in the presence of tetracyclone did not form the cycloheptyne derived product (III) but instead the spirolactone (IV). The latter compound has previously been encountered [5] as one of the products of the co-pyrolysis of cycloheptacyclopropenone and tetracyclone. The failure to detect any decarbonylation of cycloheptacyclopropenone to the highly strained cycloheptyne attests to the stability of the derived dicarbonylnickelacyclobutenone (Ia) vis a vis the cycloheptynenickel tricarbonyl complex. Analogous behaviour is observed in the reaction of this cyclopropenone with iron carbonyls [6].

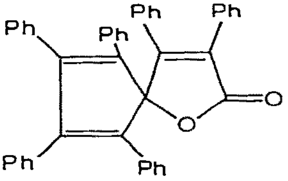


(III)

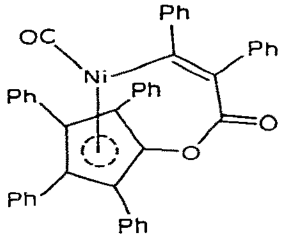


(IV)

In contrast extensive decarbonylation is encountered in the reaction of diphenylcyclopropenone with nickel carbonyl. The products isolated are diphenylacetylene, tetracyclone, bis(tetracyclone)nickel(0) and a complex originally regarded [7] as tris(diphenylcyclopropenone)nickel(0) carbonyl. Improved yields of this compound are obtained if a mixture of diphenylcyclopropenone and diphenylacetylene are treated with nickel carbonyl. This has facilitated further study of the pale green diamagnetic complex, whose correct composition is $C_{45}H_{30}NiO_3$. The infrared spectrum shows a sharp unresolved peak at 2060 cm^{-1}, characteristic of a carbon monoxide ligand and a weak, but sharp, peak at 2010 cm^{-1} assignable to the ^{13}CO vibration. A band at 1720 cm^{-1} due to an organic carbonyl group is also observed. Treatment of the complex with iodine in pyridine results in carbon monoxide evolution and the formation of a nickel-free compound to which structure (V) is assigned. The γ-lactone grouping is evidenced by a carbonyl band at 1750 cm^{-1} and a strong peak at *m/e* 546 in the mass spectrum corresponding to loss of carbon dioxide from the parent ion. The ultraviolet spectrum of (V) is closely similar to that of (IV). In the light of the evidence thus far available the most likely structure for this complex is (VI). Although the mass spectrum does not show a parent ion for (VI) a very weak one corresponding to $(P\text{—CO})^+$ can be observed, in addition to ones corresponding to (V) and tetracyclone.



(V)



(VI)

The peak corresponding to tetracyclone is of much greater intensity in the mass spectrum of (VI) where it is the base peak, than in that of (V). Unfortunately the complex has been found unsuitable for an X-ray structural determination [8]. The formation of the complex can readily be envisioned as entailing addition of the nickelacyclobutenone (Ib) to tetracyclone, which would explain the higher yield obtained from the diphenylcyclopropenone—diphenylacetylene reaction, as tetracyclone is a major product of the diphenylacetylene nickel carbonyl reaction [9].

Experimental

Infrared spectra were determined on Nujol mulls and ultraviolet spectra recorded for ethanol solutions. Known compounds were identified by comparison (mixed melting point and infrared spectra) with authentic samples.

Reaction of cycloheptacyclopropenone with $Ni(CO)_4$

(*a*) Nickel carbonyl (15 ml) was introduced in a stream of nitrogen into a refluxing solution of cycloheptacyclopropenone [5] (2 g) in dry benzene (80 ml) over a period of 2 h. The filtered solution was evaporated and chromatographed on silica gel in petroleum ether—benzene (1/1). Elution with benzene gave the trimer (II) (0.75 g) m.p. 171.5 - 173° from ethanol. (Found: C, 78.6; H, 8.2; O, 13.0%; Mol. wt. 366 by mass spectrometry. $C_{24}H_{30}O_3$ calcd.: C, 78.6; H, 8.2; O, 13.1%; Mol. wt. 366.)

(*b*) The cyclopropenone (1.4 g) and tetracyclone (1.4 g) in refluxing benzene (120 ml) were reacted with nickel carbonyl (15 ml) as above. Chromatography on silica gel in benzene gave successively a trace of tetracyclone, the 1/1 adduct (IV) (1 g) m.p. 212 - 213° from ethanol (lit. [5] m.p. 214—216°) whose spectroscopic properties were identical with those reported, and finally the trimer (II) (0.7 g).

Reaction of diphenylcyclopropenone with $Ni(CO)_4$

(*a*) Diphenylcyclopropenone [10] (2 g) in benzene (80 ml) was heated under reflux and nickel carbonyl (15 ml) was introduced in a stream of nitrogen over 2 h. The filtered solution was diluted with an equal volume of petroleum ether and chromatographed on silica gel. Benzene—petroleum ether (1/1) eluted successively diphenylacetylene (70 mg) and tetracyclone (0.1 g). Benzene eluted the green diamagnetic complex (VI) (30 mg) m.p. 188 - 189° from benzene—petroleum ether. (Found: C, 80.0; H, 4.5; Ni, 8.4; O, 7.6%; Mol. wt. 685 by osmometry in benzene. $C_{45}H_{30}NiO_3$ calcd.: C, 79.8; H, 4.4, Ni, 8.7; O, 7.1%, Mol. wt. 687.)

(*b*) Diphenylcyclopropenone (5 g) and diphenylacetylene (5 g) in benzene (200 ml) were treated with nickel carbonyl (25 ml) as above. Chromatography on silica gel gave with petroleum ether—benzene (4/1) diphenylacetylene (0.45 g), and a (2/3) mixture yielded tetracyclone (1.3 g). Benzene eluted the complex (VI) (2.25 g) and benzene—ethyl acetate (19/1) provided bis(tetracyclone)nickel(0) (1.5 g) as a brown powder from benzene—petroleum ether, m.p. ca. 245° (dec.) determined using a differential scanning calorimeter. ν_{max} 1595, 1605 cm^{-1}; *m/e* (based on ^{58}Ni) 826(P^+), 442 ($NiPh_4C_5O$), 414 ($NiPh_4C_4$), 384(Ph_4C_5O). The preparation of this compound has been referred to in the literature [11] without any details.

Degradation of (VI)

The complex (VI) (0.65 g) was added to a solution of iodine (0.25 g) in pyridine (5 ml). A rapid evolution of carbon monoxide ensued and the solution was subsequently warmed on the steam bath for a few minutes. Water was added and the green solution extracted with chloroform. The extract was washed successively with dil. H_2SO_4, water and aqueous sodium thiosulphate. Evaporation and crystallisation from ethyl acetate gave the spirolactone (V) (0.4 g) m.p. 201 - 203°. (Found: C,89.6; H, 5.0; O, 5.3%; Mol. wt. 590 by mass spectrometry. $C_{44}H_{30}O_2$ calcd.: C, 89.4; H, 5.1; O, 5.4%; Mol. wt. 590.) λ_{max}^{EtOH} ca. 345 nm (6850), 265 nm (sh) (23200) and 244 nm (29700).

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