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ORGANOCOBALT COMPOUNDS

VI*. SOME OXIDATIVE AND THERMAL DEGRADATIONS OF METHINYLNONACARBONYLTRICOBALTS AND (PHENYLACETYLENE)HEXACARBONYLDICOBALT

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Summary

Oxidative and thermal degradation of methinylnonacarbonyltricobalts, $RCCo_3(CO)_9$, yield inter alia, the acetylenes $RC{\equiv}CR$ derived from coupling of two RC groups. Ceric oxidation of (phenylacetylene)hexacarbonyldicobalt is accompanied by carbonyl insertion yielding 2-phenylpropionate.

Recent interest in the chemistry of methinylnonacarbonyltricobalt derivatives prompts us to record some experiments with two complexes of this type and with (phenylacetylene)hexacarbonyldicobalt. As part of a general programme designed to study the reactivity of cobalt complexes derivable from acetylenes [2], we wished to ascertain whether the organic fragments contained in these complexes could be made available as reactive intermediates during degradations. As a first step towards this some simple degradations of phenyl- (Ia) and (benzylmethinyl)-nonacarbonyltricobalts (Ib) were examined.

The phenyl-substituted complex (Ia) was prepared by the standard method [3, 4] from α,α,α-trichlorotoluene and octacarbonyldicobalt in ethanol. This reaction has been represented as either [3] involving nucleophilic substitution of halide by the tetracarbonylcobalt anion present in solutions of octacarbonyldicobalt in polar solvents, or [5] as a radical reaction. The moderate yields and the observation [3] that carbonylation leading to the methoxycarbonyl derivative (I, $R = CO_2Me$) along with the chloro complex (I, R = Cl) occurs when carbon tetrachloride is used in methanol, as well as the reductive loss [6] of hydroxy groups during reaction of e.g. tribromoethanol, Br_3CCH_2OH, which yields the methyl

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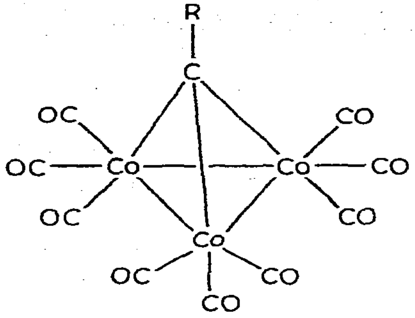
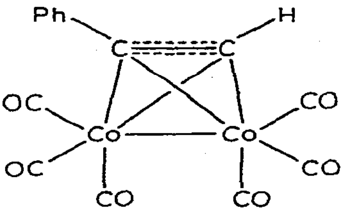
[*] For part V see ref. 1.

complex (I, R = Me), all demonstrate the complexity of the reaction. Seyferth and Millar [5] who examined the reductive coupling of *gem*-dihalides by octacarbonyldicobalt specifically refer to, but apparently did not look for the possible similar behaviour of trihalides as a side reaction in the formation of the methinyl complexes (I). We have identified two products of such coupling among the metal-free products from α,α,α-trichlorotoluene: *cis*-1,2-dichloro-1,2-diphenylethylene and tetrachloro-1,2-diphenylethane. We have also found ethyl phenylacetate, a further example of carbonylation, accompanying the reaction in alcohol.



(I)



(II)

(a) R = Ph ; (b) R = $PhCH_2$

The benzyl-substituted complex (Ib) was prepared by the protonation [7, 8] of (phenylacetylene)hexacarbonyldicobalt (II), a reaction which we find to be equally efficiently effected by such weak acids as acetic or other carboxylic acids as by hydrogen chloride. Among the degradative experiments employed to elucidate the structure (Ib) of this complex, hydrogen peroxide oxidation was shown [8] to yield phenylacetic acid. We find that oxidation with ceric salts in ethanol similarly yields ethyl phenylacetate, but in addition produces 1,4-diphenyl-2-butyne (dibenzylacetylene) in appreciable yield; the proportion of the acetylene product increases as the amount of oxidant is restricted to the minimum necessary to destroy the complex (I) although acetylenes are not oxidised by cerium salt under these conditions and cannot be intermediates. The phenylmethinyl complex (Ia) similarly yields both ethyl benzoate and tolane. Moreover the same acetylenes result in lower yield on simple thermal decomposition of the complexes (Ia, Ib) and some dibenzylacetylene was also obtained on attempted carbonylation of complex (Ib). The formation of acetylenes may be visualised as arising from coupling of two methinyl fragments, RC≡ although it need not be assumed that these become free. In the benzyl case, the overall process represents a simple synthesis of the acetylene, $PhCH_2C{\equiv}C\text{-}CH_2Ph$ from two molecules of phenylacetylene, $PhC{\equiv}CH$.

On extending the ceric oxidation to the precursor (II) we found that the major product of reaction in methanol was methyl 2-phenylpropionate, PhCHMeCOOMe. This constitutes an unusual carbonylation occurring during oxidative degradation. More commonly ceric salts liberate neutral ligands from metal carbonyl complexes without change. Finally we record the reductive degradation of the benzylmethinyl complex (Ib) with sodium borohydride to give ethylbenzene and dodecacarbonyltetracobalt.

Experimental

All reactions were conducted under nitrogen. Chromatography was carried out on neutralised alumina. Light petroleum refers to the fraction of b.p. 40—60° unless otherwise stated.

Reaction of α,α,α-trichlorotoluene with octacarbonyldicobalt

The carbonyl (34.0 g, 0.1 mol) was stirred in ethanol (50 ml) for 1.5 h, the solution changing from the initial dark brown to a light greenish colour. α,α,α-Trichlorotoluene (19.5 g, 0.1 mol) was then added and the mixture refluxed for 2.5 h during which the colour changed to deep violet. After cooling, the mixture was diluted with water (500 ml), extracted with light petroleum and the extract evaporated under reduced pressure. 1,1,2,2-Tetrachloro-1,2-diphenylethane (1.9 g, m.p. 160—161°)crystallised from the residue; it showed only aromatic protons in its NMR spectrum at τ 2.6 ppm (m). (Found: C, 51.5; H, 3.0. $C_{14}H_{10}Cl_4$ calcd.: C, 51.5; H, 3.1%.) The remaining dark violet oil was taken up in methanol and cooled in ice when the complex (Ia) (11.5 g) separated. The mother liquors were evaporated under reduced pressure and the residue was chromatographed using light petroleum as eluant. From the first dark oily fraction a colourless solid separated which showed only a single proton resonance in its NMR spectrum (τ 2.8 ppm, C_6H_5) and was identified as *cis*-1,2-dichloro-1,2-diphenylethylene (m.p. 63°). (Found: C, 67.0; H, 4.4. $C_{14}H_{10}Cl_2$ calcd.: C, 66.9; H, 4.7%.) Both these chloro compounds had melting points in good agreement with numerous literature values. The second fraction, a brown oil having a fruity smell, distilled at 75° /0.5 mmHg and was shown to be ethyl phenylacetate (1.5 g) by NMR and infrared comparison with an authentic sample.

Preparation of complex (Ib) using acetic acid

A solution of (phenylacetylene)hexacarbonyldicobalt (II) (2.0 g, 5 mmol) in benzene (100 ml) was heated with ten drops of glacial acetic acid for 4—5 h at 70—80°, solvent was then removed under reduced pressure and the residue chromatographed in light petroleum (b.p. 60—80°) which eluted starting material (≈ 50 mg). Benzene/light petroleum (1/9) then eluted the phenylethinyl complex (Ib) (600 mg).

Propynehexacarbonyldicobalt (2 g) was similarly converted to the propinyl complex (I, R = Et) (≈ 450 mg) and other acids (benzoic, cinnamic etc.) were shown to be effective in place of acetic.

Ceric oxidation of complex (Ia)

(a). The complex (0.5 g, 1 mmol) and ceric ammonium nitrate (0.5 g, 1 mmol) were refluxed in ethanol (30 ml) for 5 h. The resulting light orange solution was diluted with water (200 ml) and extracted with ether and with light petroleum. On concentrating the dried extracts in vacuo crystalline diphenylacetylene (40 mg, 25%) separated and was identified by m.p. and IR comparison

with an authentic sample. The mother liquors showed a broad peak at 1755 cm^{-1} (ester; see *b*) in the infrared spectrum.

(b). When excess of the ceric salt (2 g, 4 mmol) was employed the colour of the complex (Ia) had disappeared, leaving an orange solution, after the mixture had stood for 15 min at room temperature. It was therefore not heated, but worked up as above after standing for 2 h. No diphenylacetylene separated and distillation afforded ethyl benzoate, identified by its NMR spectrum and by infrared comparison with an authentic sample.

A separate experiment established that the acetylene is unchanged (90% recovery) by the ceric salt under these conditions.

Ceric oxidation of complex (Ib)

(a). Refluxing the complex (0.5 g, 1 mmol) and ceric ammonium nitrate (1.2 g, 2 mmol) in ethanol for 4—5 h followed by work-up as in the preceding experiments yielded a pale yellow oil. GLC gave only one large and a second very minor peak. The former had the same retention time as an authentic sample of ethyl phenylacetate and IR comparison of a distilled sample of the oil confirmed this identity.

(b). When reaction was conducted by stirring the complex (0.5 g, 1 mmol) with ceric salt (0.6 g, 1 mmol) for 16 h at room temperature, the product gave two GLC peaks in the ratio 4/1. The minor peak corresponded in retention time to ethyl phenylacetate whereas the major peak corresponded with phenylacetaldehyde.

(c). Using a deficiency of ceric salt (0.3 g, 0.5 mmol) and leaving the reaction mixture in the dark at room temperature for 25 h gave an oil, whose GLC analysis gave three peaks, ratio 1/2/3, and corresponding in retention time to phenylacetaldehyde, ethyl phenylacetate, and 1,4-diphenyl-2-butyne respectively.

Thermal decomposition of complex (Ia)

The complex was stable on prolonged refluxing in ethanol, benzene, tetrahydrofuran or dioxane. Complete destruction of the complex (0.2 g) occurred on refluxing in diglyme (25 ml) for 8 h as shown by the deposition of cobalt metal and change in colour of the solution from dark reddish-brown to pale yellow. Removal of solvent left a viscous mass from which diphenylacetylene (12 mg) separated on trituration with light petroleum. Concentration of the mother liquors afforded an unidentified yellow powder. More rapid decomposition with formation of some diphenylacetylene occurred when the triphenylphosphine substituted complex, $PhCCo_3(CO)_8PPh_3$ [9], was similarly decomposed in refluxing diglyme.

Thermal decomposition of complex (Ib)

Like complex (Ia), complex (Ib) was stable in refluxing ethanol, tetrahydrofuran and benzene and also in 1,2-dimethoxyethane and pyridine, but decomposed in refluxing diglyme to cobalt metal and 1,4-diphenyl-2-butyne, identified by its IR spectrum and by conversion to 1,4-diphenyl-2,2,3,3-tetrabromobutane.

The first few ml of solvent distilled from the reaction mixture were found by IR spectroscopy to contain an aromatic substance and on GLC gave a peak of the same retention time as toluene.

Attempted carbonylation of complex (Ib)

A solution of the complex (2 g) in n-hexane (10 ml) was placed under 200 atm pressure of carbon monoxide in a 200 ml autoclave and then heated to 70° for 8 h. After cooling and filtration the product was chromatographed. Light petroleum/ether (1/2) eluted 1,4-diphenyl-2-butyne (30 mg) identical with samples from the above experiments.

Ceric oxidation of complex (II)

The complex (1 g, 2.7 mmol) and ceric ammonium nitrate (1.7 g, 6 mmol) were stirred in methanol causing rapid gas evolution and a colour change from deep red to orange. After 24 h, water (200 ml) was added, the mixture extracted with light petroleum and the extract dried ($CaCl_2$) and evaporated. The infrared spectrum of the residual pale yellow oil showed peaks attributable to phenylacetylene and an ester peak at 1760 cm^{-1}. Distillation gave an oil of b.p. 75°/0.05 mmHg (175 mg, 40%) identified as methyl 2-phenylpropionate by its NMR spectrum [τ 2.85 (5H, Ph); 6.4 (3H, OMe); 6.8 (1H, m, $C\underline{H}Me$) and 8.5 ppm (3H, d, $CH\underline{Me}$)] and by infrared comparison with an authentic sample.

Borohydride reduction of complex (Ib)

The complex (0.2 g) dissolved in 1,2-dimethoxyethane (15 ml) was stirred with a large excess of sodium borohydride for 4 h. The resulting pale yellow solution was diluted with water, extracted with light petroleum, the extract dried (Na_2SO_4) and the solvent removed under reduced pressure leaving ethylbenzene, identified by infrared spectral and GLC comparison with an authentic sample.

When less borohydride (0.5 g) was employed, the solution remained dark and on work-up as above after 2 h reaction time yielded crystalline dodecacarbonyltetracobalt; the mother liquors again contained ethylbenzene, identified by its IR and NMR spectra.

Reaction of complex (Ib) with triphenylphosphine

Like several analogues [9] complex (Ib) reacted readily with triphenylphosphine. When the complex (0.133 g, 0.25 mmol) and the phosphine (0.14 g, 0.5 mmol) were stirred in tetrahydrofuran (20 ml) for 18 h the deep violet colour of the solution changed to brown and after removal of solvent the residue was chromatographed. Petroleum ether/benzene (1/1) eluted the product, $PhCH_2$-$CCo_3(CO)_8PPh_3$, (50 mg) which formed brown crystals. (Found: C, 53.2; H, 3.2. $C_{34}H_{22}Co_3O_8P$ calcd.: C, 53.3; H, 2.9%.) This was followed by bis[(triphenylphosphine)tricarbonylcobalt], m.p. 221°, identified by its infrared spectrum.

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