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NOTE

CROSS-CONJUGATED CYCLOHEXADIENONE-IRON TRICARBONYL COMPLEXES

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Iron tricarbonyl complexes of conjugated cyclic dienones are known[1], but the only complex having a cross-conjugated ligand so far reported is duroquinoneiron tricarbonyl, obtained by the photochemical reaction of 2-butyne and iron pentacarbonyl[2]. We have obtained iron tricarbonyl complexes of 4,4-dimethylcyclohexa-2,5-dienone, cholesta-1,4-dien-3-one, androsta-1,4-dien-3,11,17-trione, and santonin, by reaction of these cross-conjugated cyclohexadienones with iron pentacarbonyl; santonin oxime also gave a complex. Reaction of cholesta-1,4-dien-3-one with diiron nonacarbonyl gave the iron tricarbonyl complex more rapidly but in lower yield.

The infrared spectra of the dienone complexes showed dienone carbonyl stretching peaks at 1660–1675 cm^{-1} and terminal metal–carbonyl stretching peaks at 1940–2080 cm^{-1}. The ultraviolet spectra showed peaks at 6–23 mμ shorter wavelength than the parent dienones, as well as broad absorption at longer wavelengths. The nuclear magnetic resonance peaks of the olefinic protons (reported as τ in the *Experimental*) were very slightly shifted downfield from those of the parent compounds.

4-Methyl-4-(trichloromethyl)cyclohexa-2,5-dienone reacted with iron pentacarbonyl to give a brown solid of unknown structure; the infrared spectrum showed no peaks at 1660–1675 cm^{-1} and 1900–2100 cm^{-1}. The oxime reacted with iron pentacarbonyl in isooctane or butyl ether to regenerate the ketone. This appears to be the first case of deoximation by iron pentacarbonyl alone (*cf.* ref. 3).

EXPERIMENTAL

General

Melting points are corrected. Iron pentacarbonyl and diiron nonacarbonyl (Alfa Inorganics, Inc.) were used as received; distillation of iron pentacarbonyl did not improve results. Solvents were dried and purified by standard methods.

4,4-Dimethylcyclohexa-2,5-dienone

The following preparation of 4,4-dimethylcyclohexa-2,5-dienone is more convenient than those reported[4]. A mixture of 4,4-dimethylcyclohex-2-enone[4] (19.2 g) and selenium dioxide (17.3 g) in dry tert-butanol (2890 ml) and glacial acetic acid

(29 ml) was refluxed while being stirred under nitrogen for 24 h. Additional selenium dioxide (17.3 g) was added, and refluxing continued for one day. The solution was cooled and filtered, and the filtrate distilled at reduced pressure to remove tert-butanol. The residue, taken up in methylene chloride, was washed with 0.1 *N* sodium hydroxide and then treated with ammonium sulfide overnight. The organic layer was separated, washed with water, dried, and distilled at 88–92° at 15 mm (lit.[4] b.p. 86–92° at 15 mm) to give 4,4-dimethylcyclohexa-2,5-dienone (5.6 g).

Preparation of dienone- and (dienone oxime)iron tricarbonyl complexes

A mixture of the dienone or dienone oxime (1 mole) and an excess of iron pentacarbonyl (1.5–3.4 moles), diluted by ten volumes of inert solvent, was refluxed with stirring under nitrogen for 20–80 h; individual reaction conditions are given below. The mixture was cooled and filtered, and the filtrate concentrated to remove solvent and excess iron pentacarbonyl. The residue was then taken up in an organic solvent and chromatographed. The complex descended as a coloured band down the column and was obtained on concentration of the eluate as crystals or as an oil which was distilled.

4,4-Dimethylcyclohexa-2,5-dienone and iron pentacarbonyl (3.34 moles) for 49 h in isooctane: after chromatography in CCl_4 on Florosil, a 36% yield of complex as a yellow oil, b.p. 42–46° at 0.1 mm, ν_{max} in CCl_4 2075 w, 2040 s, 2004 w, 1967 s cm^{-1}, λ_{max} 219 mμ (log ε 4.29) in isooctane, τ 5.96, 6.58 in CCl_4. (Found: C, 50.1; H, 3.9. $C_{11}H_{10}FeO_4$ calcd.: C, 50.4; H, 3.8%.)

Cholesta-1,4-dien-3-one and iron pentacarbonyl (1.51 moles) for 66 h in isooctane: after chromatography in chloroform on alumina, a 51% yield of complex as brownish-green crystals, m.p. 80–81°, ν_{max} in KBr 2030 s, 1952 s cm^{-1}, λ_{max} 219 mμ (log ε 4.27) in isooctane, τ 5.94, 6.82 in $CDCl_3$.

Androsta-1,4-dien-3,11,17-trione and iron pentacarbonyl (3.40 moles) for 82 h in dioxane: after chromatography in chloroform on alumina, a 22% yield of complex as brown crystals, m.p. 167–171°, ν_{max} in $CHCl_3$ 2034 s, 1961 s, 1943 s cm^{-1}, λ_{max} 215 mμ (log ε 4.26) in ethanol. (Found: C, 60.3; H, 5.0. $C_{22}H_{22}FeO_6$ calcd.: C, 60.3; H, 5.1%.)

Santonin and iron pentacarbonyl (3.33 moles) for 40 h in dioxane: after chromatography in methylene chloride on alumina, a 42% yield of complex as brown crystals, m.p. 190–192°, ν_{max} in CH_2Cl_2 2044 s, 1970 s cm^{-1}, λ_{max} 231 mμ (log ε 4.16) in methylene chloride, τ 6.20, 6.70 in $CDCl_3$. (Found: C, 55.9; H, 4.7. $C_{18}H_{18}FeO_6$ calcd.: C, 56.0; H, 4.7%.)

Santonin oxime and iron pentacarbonyl (3.25 moles) for 20 h in dioxane: after chromatography in methylene chloride on Florosil, a 7.7% yield of complex as orange crystals, m.p. 53–55°. (Found: C, 54.2; H, 4.7. $C_{18}H_{19}FeNO_6$ calcd.: C, 53.9; H, 4.8%.)

Reaction of santoniniron tricarbonyl with hydroxylamine

A solution of santoniniron tricarbonyl and hydroxylamine hydrochloride in pyridine/ethanol was heated according to Shriner *et al.*[5]. The oxime complex was obtained as orange crystals, m.p. 53–55°, identical with material prepared by the reaction of santonin oxime with iron pentacarbonyl.

Reaction of cholesta-1,4-dien-3-one with diiron nonacarbonyl

A mixture of cholesta-1,4-dien-3-one (1.01 g) and diiron nonacarbonyl (0.96 g) in dry benzene (30 ml) at 40–50° was stirred under nitrogen for 4 h. The mixture was filtered and the filtrate evaporated at *ca.* 30 mm. The residue was crystallized from hexane to give brownish-green crystals of cholesta-1,4-dien-3-oneiron tricarbonyl, m.p. 79–81° (0.60 g, 44%). The same complex was obtained in 48% yield when the ratio of metal carbonyl to dienone was raised to 2/1.

Recovery of dienones from dienoneiron tricarbonyls

The complexes were decomposed by ferric chloride according to established procedures[6], and the dienones recovered in 86–94% yield, except in the case of santonin-iron tricarbonyl, which gave a black tar. Santonin oxime was regenerated from its complex in 72% yield.

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