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PREPARATION OF ALKYLBENZENES FROM 1-ALKYLCYCLOHEX-2-ENOLS VIA TRICARBONYLIRON COMPLEXES

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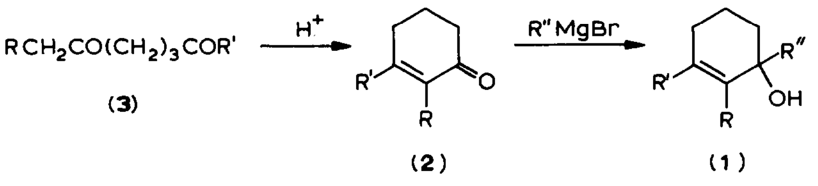
Summary

Tertiary cyclohex-2-enols are converted directly to the related tricarbonyl-1,3-cyclohexadieneiron complexes, in good yield. Tricarbonylcyclohexadienyliron salts are conveniently oxidized to the corresponding alkylbenzenes, by cerium(IV) salts. These reactions were incorporated in a procedure of converting the cyclohexenols to aromatics, suitable for the preparation of materials specifically labelled with carbon isotopes.

In the course of our studies on acid chemistry of aromatics [1], we needed a synthetic method for alkylbenzenes specifically labelled with carbon-13 in the ring or in the side chain. After several alternatives were examined, it appeared that 1-alkylcyclohex-2-enols (1) would be best suited as precursors. For labelled side-chains, the appropriate cyclohex-2-enone (2) can be treated with a labelled Grignard reagent [2]. Ring-labelled ketones 2 can be prepared by the cyclization of a 2,5-dione (3) [3,4].



(a: R = H, R′ = R″ = Me ; b: R = R′ = H, R″ = n-Bu)

The reaction sequence: dehydration-aromatization, was not satisfactory for 1, however. First, dehydration gives comparable amounts of 1,3-cyclohexadiene and 3-methylenecyclohexene derivatives [2]. The latter are more difficult to aromatize than the former. Second, in dehydrogenation by quinones [5], or by catalytic

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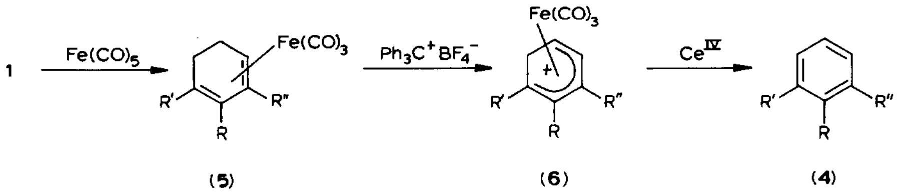
hydrogen transfer [6], Diels–Alder reaction with the hydrogen acceptor interfered. Acceptors that are not dienophiles [7], were difficult to separate from the aromatic hydrocarbon. The gas-phase dehydrogenation [8], on the other hand, requires special installations, and positional isomerization of the alkylbenzene is occasionally observed [8b,9]. Finally, we found that entrainment by the volatile solvents employed for extraction is a major source of losses of the relatively volatile alkylbenzenes. Since the diene intermediates are as volatile as the aromatics, the overall yield drops significantly.

We developed a sequence which avoids volatile intermediates between **1** and the alkylbenzene (**4**); instead, it involves tricarbonylcyclohexadieneiron complexes (**5**), and the corresponding arenium complexes (**6**):



(a: R = H, R′ = R″ = Me ; b: R = R′ = H, R″ = n-Bu ; c: R = n-Bu, R′ = R″ = H)

Tricarbonyliron complexes of 1,3-dienes are easily prepared from dienes and carbonylirons [10,11]. To our knowledge there has been only one report on the direct conversion of allylic alcohols to diene complexes in one step, employing copper sulfate as dehydrating agent in benzene solution, but the yields were disappointing (10–18%) [12]. We found that cyclohexenols **1a** [13], and **1b** [14], react with pentacarbonyliron in boiling dibutyl ether solution [15]. The water formed distills azeotropically with the solvent and can be removed with a Dean–Stark trap. We preferred to reflux the solvent through a bed of molecular sieves. Actually, the yield is not changed significantly if water is not removed [16]. As shown in Table 1, the reaction is slow. Its progress can be followed by monitoring the gas evolution from the mixture.

In several experiments, run for 41–47 h, the isolated yield of complex **5a** varied from 62 to 74%; we could not determine the reason for this variation, but it seemed that freshly prepared **1a** tended to give higher yields.

An attempt at treating **1a** with nonacarbonyldiiron in boiling tetrahydrofuran for 39 h, gave a much lower yield of **5a** (34%).

The investigation of **1b** demonstrated that monoalkylcyclohex-2-enols also react with pentacarbonyliron in dibutyl ether (see Experimental).

TABLE 1

FORMATION OF TRICARBONYL-1,3-DIMETHYL-1,3-CYCLOHEXADIENEIRON (**5a**) FROM 1,3-DIMETHYLCYCLOHEX-2-ENOL (**1a**) [a]

Reaction time (h)	Isolated yield (%)
16	30
33	72
42	74

[a] Molar ratio Fe(CO)$_5$ to **1a**, 4/1.

The product from the first step was converted without purification to the solid (salt) complex **6** [17]; purification of **5** by column chromatography is possible [18], but was found not necessary. The hydride transfer from unsubstituted, mono-, or disubstituted tricarbonylcyclohexadieneiron complexes to the triphenylmethyl cation has been amply described [10b,18,19]. We used the literature procedure [18], with only minor modifications (see Experimental) *.

A number of oxidizing agents have been used to regenerate dienes from their tricarbonyliron complexes [18,19c,23]. We found no literature indication, however, of any example of the recovery of aromatic ligands from the tricarbonylcyclohexadienyliron salts (e.g. **6**) [11]. We expected that oxidation of a cationic complex **6** would be more difficult than the oxidation of the neutral complexes **5**. Instead, we found that cerium(IV) ammonium nitrate [23b], or sulfate, react smoothly with **6a** and **6b** at 0°C [24]. At higher temperatures, heavy side-products become important, especially with the nitrate. It is known that alkylbenzenes undergo ring nitration and side-chain oxidation by ceric ammonium nitrate [25]. The yields of alkylbenzene, after purification by bulb to bulb distillation under vacuum, were 58% for *m*-xylene (**4a**) and 73% for n-butylbenzene (**4b**).

In conclusion, we have demonstrated that conversion of tertiary alkylcyclohexenols (**1**) to tricarbonylcyclohexadieneiron complexes (**5**) and regeneration of alkylbenzenes (**4**) from the corresponding tricarbonylcyclohexadienyliron salts (**6**) can be achieved in good yield. Coupled with the well known conversion of **5** to **6**, these reactions provide a convenient procedure for converting the cyclohexenols **1** to the corresponding aromatics **4**.

Experimental

General. Gas-liquid chromatographic analyses were performed on a 4.5 m, 3 mm O.D. column with 5% Carbowax 20M on Gaschrom Q (Supelco, Inc.), using a Perkin–Elmer Sigma-115 instrument. Proton NMR spectra were obtained at 90 MHz, with a Varian EM-390 instrument. IR spectra were recorded on a Perkin–Elmer 283B instrument. Melting points (Fischer model 355 digital instrument) are uncorrected. Silica gel TLC plates were supplied by EM Laboratories, Inc. (Merck). The reagents and solvents employed were commercial materials and were used as purchased unless stated otherwise.

1-Alkylcyclohex-2-enols (1). 1,3-Dimethylcyclohex-2-enol (**1a**) [2a,13], and 1-butylcyclohex-2-enol (**1b**) [14], were obtained from the corresponding ketones, redistilled before use (**2a**, b.p. 56–57°C at 0.75 mmHg [2b,3,26]; **2b**, b.p. 57°C at 10–12 mmHg [27]), and alkyllithium derivatives.

Tricarbonyl-1,3-dimethylcyclohexa-1,3-dieneiron (5a). Alcohol **1a** (4.2 g, 33 mmol) was dissolved in di-n-butyl ether (65 ml, distilled over calcium hydride) in a flask containing a few crystals of hydroquinone, and pentacarbonyliron (20 ml, 29.2 g,

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* The salt complex obtained from **1b** via **5b**, is probably a mixture of **6b** and **6c**. We did not investigate the actual structure, but note that literature reports on the related methyl derivative are contradictory. Thus, it was reported that a mixture of all tricarbonylmethylcyclohexadieneiron isomers gives exclusively **6d** (R = Me, R′ = R″ = H) [19c], while pure **5** (R = R′ = H, R″ = Me) gave a 6/4 mixture of **6d** with **6e** (R = R′ = H, R″ = Me), upon hydride loss [18a,20]. Discrepancies exist as well between chemical shifts [21,22], coupling patterns [21,22], and peak assignments [15b,18a] in the ^{1}H NMR spectra of isomers **6d**, **6e**, and **6f** (R = R″ = H, R′ = Me) in previous papers.

148 mmol) was added. The flask was fitted with an adapter containing a 3 cm thimble filled with Linde 4Å molecular sieves, and with a chilled water condenser. The top of the condenser was connected to a gas bubbler containing silicone oil, the installation was purged with nitrogen, and the reactant mixture was boiled under reflux for 47 h.

Carbonyliron excess (IR 2010, 1995 cm^{-1}) [28] and solvent were distilled off at 25–30°C and 50–55°C, respectively, under water aspirator vacuum (ca. 30 mmHg). The residue was taken up in pentane, filtered through Celite (Johns–Manville) [19c], dried (potassium carbonate), and the solvent was distilled off. The product (5.9 g, 72% yield) was a bright yellow liquid. IR and NMR spectra agreed with literature [15b].

*Tricarbonyl-2-butylcyclohexa-1,3-dieneiron (**5b**).* **5b** was prepared in the same way as **5a** from the alcohol **1b** (7.6 g, 49 mmol) and $Fe(CO)_5$ (27 ml, 39,3 g, 200 mmol) in dibutyl ether (80 ml). The product (9.5 g, 70%) was a brown liquid. IR 2022, 1975 cm^{-1} (neat) [15b,31].

The structure for this complex was chosen based on the observation that dehydration of alcohol **1b** at temperatures below 150°C should give mostly [29], or only [30] 2-butylcyclohexa-1,3-diene, (with some 3-butylidenecyclohexene), as shown for the methyl analog [29,30]. On the other hand, if the dehydration is assisted by the carbonyliron, a 1-butylcyclohexenylcarbonyliron complex should be formed as an intermediate. As demonstrated for the ethyl analog, such an intermediate should lead exclusively to **5b** [31].

*Tricarbonyl-1,3-dimethylcyclohexa-1,3-dienyliron tetrafluoroborate (**6a**).* Triphenylmethyl fluoroborate from freshly opened bottles was used as such. Older material was purified by treatment with acetic anhydride (0.5 ml per gram of trityl salt) and enough acetic acid to dissolve most of the solid, at room temperature for 30 min under argon, followed by precipitation with dry ether. The supernatant solution was decanted off, and the solid was rinsed with dry ether, then dried in a flow of argon. The dry salt (18.1 g, 54.8 mmol) was dissolved in 150 ml of dry methylene chloride and added all at once to the complex **5a** (5.9 g, 23.8 mmol). The burgundy-colored solution was kept stoppered for 2.5 h at room temperature, then it was poured into a beaker containing 1200 ml of ether saturated with water. The bright yellow solid was filtered off and washed several times with wet ether. Dried in air, the product weighed 6.6 g (83% yield). M.p. 195–197°C (decomp.). IR 2100, 2040 cm^{-1} (Nujol mull). The NMR spectrum (CF_3COOH solution) agreed with literature [18a].

*2- and 3-Butylcyclohexa-1,3-dienyltricarbonyliron tetrafluoroborates (**6b, 6c**).* The crude diene complex **5b** (9.5 g, 34.3 mmol) was converted to the complex salt in the same way as described for **5a**, by reaction with 27.5 g (83 mmol) of Ph_3CBF_4. The crude salt was sticky and grey-yellow; it was purified to a bright yellow solid, by one extra precipitation with ether from methylene chloride solution. Yield: 5.6 g (45%). IR 2105, 2050 cm^{-1} (Nujol mull).

*m-Xylene (**4a**).* The complex salt **6a** (6.5 g, 19.4 mmol) was placed in a 500 ml long-necked flask cooled in an ice-water bath, and a solution of cerium(IV) ammonium nitrate (42.6 g, 77.7 mmol) in distilled water (120 ml) was added at once. The flask was mounted immediately in an installation for steam distillation, the receiving flask of which was cooled at −75°C. Foaming was observed in the reaction flask, which was maintained at 0°C, with magnetic stirring until no further gas evolution was noticed (2 h). The cooling bath was replaced by a heating mantle, and the flask was brought to the boiling point of its contents over a period of 2 h. Steam was then passed through the mixture and the distillate collected at −75°C. When distillation was completed, the distillate was allowed to thaw and extracted three times with isopentane. Drying (K_2CO_3) and evaporation of solvent gave 1.7 g (61%) *m*-xylene still containing some heavier materials (yellow). Bulb to bulb distillation on a vacuum line (ca. 0.1 mmHg) between −40 and +4°C (receiver cooled in liquid nitrogen) gave a pale yellow distillate (1.6 g, 58%), analyzed by GLC (2 min at 90°C, 12°/min to 200°C) as 90.4% **4a**.

Oxidation with cerium(IV) ammonium sulfate gave *m*-xylene of 97.6–99.6% purity by GLC (colorless).

n-Butylbenzene (4b). **4b** was likewise obtained by oxidation of the corresponding complex salt (**6b**, **6c**, 5.6 g, 15.4 mmol) with cerium(IV) ammonium sulfate (38 g, 60 mmol). Work-up as described above (steam distillation for 1.75 h) gave **4b** (1.9 g, 77% crude yield). Bulb to bulb distillation from −2°C to +31°C gave 1.7 g (73% yield) **4b** of 97.1% purity by GLC (2 min at 100°C, 12°/min to 200°C).

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