Monatshefte für Chemie 117, 883–886 (1986)

Monatshefte für Chemie
Chemical Monthly

[Bis(2,4-dimethyl-6-*tert.*butyl-phenyl)ketone]chromium tricarbonyl—Stable Torsional Isomers**

Short Communication

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(Received 14 February 1986. Accepted 4 March 1986)

Complexation of bis(2,4-dimethyl-6-*tert.*butyl)ketone with chromium hexacarbonyl yields a mixture of two diastereomeric mono complexes in a ratio of 5 : 1. They can be separated by chromatography on silica gel at room temperature thus representing stable torsional isomers (isolable residual diastereomers).

(Keywords: Residual diastereomers; Torsional barrier; Complexation with hexacarbonylchromium)

[Bis(2,4-dimethyl-6-tert.butyl-phenyl)keton]tricarbonylchrom.
Stabile Torsionsisomere (*Kurze Mitteilung*)

Komplexierung von Bis(2,4-dimethyl-6-*tert.*butyl)keton mit Hexacarbonylchrom liefert eine Mischung von zwei diastereomeren Monokomplexen im Verhältnis von 5 : 1. Sie können durch Chromatographie an Kieselgel getrennt werden und stellen somit stabile Torsionsisomere (= isolierbare Restdiastereomere) dar.

Tricarbonyl chromium complexes of arenes are efficient tools in solving stereochemical problems, since complexation usually decreases the ligand symmetry and (or) increases steric repulsion [1].

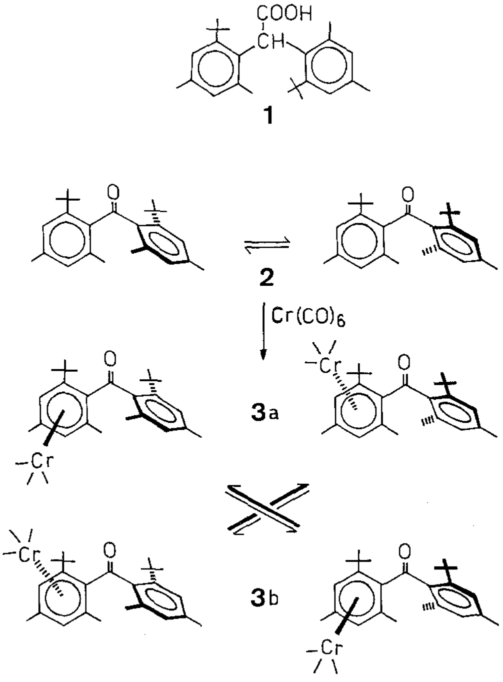
We have applied these techniques extensively to torsional isomeric biphenyls [1, 2] and now have studied complexes of diaryl-methane derivatives. This class of compounds has attracted much interest, because the aryl rings may undergo correlated rotation [3].

** Dedicated to Prof. Dr. *A. Neckel* with cordial wishes on the occasion of the 60th anniversary of his birthday.

Akkerman and *Coops,* for example, investigated diaryl-acetic acids such as **1**, and concluded that in these chiral molecules the internal rotation of both aryl rings is correlated (a counterclockwise rotation of one ring causes a clockwise rotation of the second ring). Racemization, however, can occur only if both aryl rings rotate either clockwise or counterclockwise. The activation parameters for the racemization process could be determined both by optical rotation- and NMR-kinetics [4, 6]. A $\Delta G^{\ddagger}_{298}$ value of 95 ± 1 kJ mol^{-1} was found for **1**.

By analogy the ketone **2** (Scheme 1) is also chiral, if the aryl ring rotation is correlated. However, the racemization barrier is expected to be lower than that of **1**, since a lower barrier was found for bis(2-ethyl-6-methylphenyl)ketone as compared to bis(2-ethyl-6-methylphenyl)methane [7]. Thus, reaction of **2** with chromium hexacarbonyl should result in two diastereomeric monocomplexes **3a**, **3b** (Scheme 1), which interconvert rapidly in the laboratory time scale by a clockwise (or counterclockwise) rotation of both aryl rings to give a pair of residual stereoisomers [8, 9].

Scheme 1



Contrary to these expectations, complexation of **2** with chromium hexacarbonyl yielded a mixture of two diastereomeric mono complexes **3 a** and **3 b** in a ratio of 5 : 1, which could be easily separated by medium pressure chromatography on silica gel. Both diastereomers are stable in solution ($CDCl_3$) for 24 hours at 20 °C and do not interconvert as shown by NMR. This indicates a lower limit of 100 kJ mol^{-1} for the isomerization barrier. Since such a high barrier is very unlikely for **2**, we conclude that the tricarbonyl chromium unit causes a significant increase in the isomerization barrier. This is also supported by the fact that a higher automerization barrier was found for the mono tricarbonyl-chromium complex of dimesityl-ketone as compared to the mono complex of dimesityl-methane [10].

The isomers **3 a** and **3 b** are stable torsional isomers and represent an example of isolable residual diastereoisomers [8]. Although both diastereomers have to be equimolar mixtures of enantiomers (Scheme 1), preliminary attempts to resolve these racemates by chromatography on triacetyl-cellulose (which has been successful in many other cases [1, 2, 11]) have failed thus far. Nevertheless, optical resolution of **3 a** or **3 b** and subsequent decomplexation would give optically active **2**. The tentative configurational assignment (**a** and **b**, as shown in Scheme 1) is based on the isomeric ratio and on their NMR spectra.

Irradiation of a cooled solution (—40 °C) of either **3 a** or **3 b** in $CDCl_3$ with a photolamp did result in decomplexation giving the starting ketone **2**.

Further detailed investigations, especially X-ray and NMR studies are now in progress in will be reported elsewhere.

Experimental Part

Stereoisomeric [Bis(2,4-dimethyl-6-tert.butyl-phenyl)ketone]tricarbonyl-chromium complexes (**3 a** *and* **3 b**)

A solution of 500 mg (1.43 mmol) of the ketone **2** (m.p. 134–135 °C, prepared according to Ref. [12]) in a mixture of di-*n*-butylether (60 ml) and *n*-heptane (30 ml) was refluxed with 500 mg (2.27 mmol) of $Cr(CO)_6$ for 24 h under Ar in the dark. Chromatography of the residue (after evaporation of the solvents *in vacuo*) on a silicagel-column (50 × 5 cm; Merck—particle size 0.063–0.20 mm) with ethylacetate-ligroin (15 : 85) at 1.5 bar afforded the two stereoisomeric monocomplexes: First band 25 mg (3.6%) of **3 b** (m.p. 164–167 °C); second band 130 mg (18.7%) of **3 a** (m.p. 136–139 °C). $C_{28}H_{34}CrO_4$ (486.5). MS (*m*/e): molecular peak 486.

Decomplexation of both stereoisomers was accomplished by irradiation with a 2000 W photolamp (in $CDCl_3$ at —40 °C) and was complete for **3 b** after 20 and for **3 a** after 30 min. After filtration over silicagel the ^{1}H-NMR spectrum of each solution was identical with that of the ligand **2**.

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Verleger: Springer-Verlag KG, Mölkerbastei 5, A-1010 Wien. — Herausgeber: Österreichische Akademie der Wissenschaften, Dr.-Ignaz-Seipel-Platz 2, A-1010 Wien, und Gesellschaft Österreichischer Chemiker, Eschenbachgasse 9, A-1010 Wien. — Redaktion: Währinger Straße 38, A-1090 Wien. — Hersteller: Adolf Holzhausens Nachfolger, Kandlgasse 19-21, A-1070 Wien. — Verlagsort: Wien. — Herstellungsort: Wien. — Printed in Austria.