removed, the solvent was evaporated, and the solid was weighed directly.

Infrared Measurements.—Spectra in the 4000–650 cm.$^{-1}$ region were obtained with a Beckman IR-7 instrument. Spectra in the 850–300 cm.$^{-1}$ region were obtained with a Beckman IR-5A instrument with cesium bromide optics.

X-Ray Diffraction Measurements.—All patterns were obtained with a Hayes unit using nickel-filtered Cu Kα radiation and a 7.0-cm. radius camera.

Dipole Moment Measurements.—Dielectric constants were measured with a heterodyne beat apparatus of conventional design. Specific volumes were obtained with a 4.5-ml. Lippincott pycnometer with calibrated side arms. Refractive indices were determined with a differential refractometer at the 436 mμ line of mercury according to the procedure of Brice and Halver.[11] The quantity $\nu = \partial n^2/\partial w^2$ was obtained graphically, and the molar refractivity was calculated as described by Halverstadt and Kumler.[6] Weight fractions were in the range 0.002 to 0.018. Dipole moments were then calculated by the Halverstadt–Kumler procedure.[6]

Acknowledgment.—The generous support provided by Picatinny Arsenal under Contract Ord. 2956 and by the Army Research Office under Contract DA-31-124-ARO(D)-35 is gratefully acknowledged.

(11) B. A. Brice and M. Halver, *J. Opt. Soc. Am.*, **41**, 1033 (1951).

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Organometallic Studies. VII. The Resolution of an Arenechromium Tricarbonyl Racemic Mixture[1,2]

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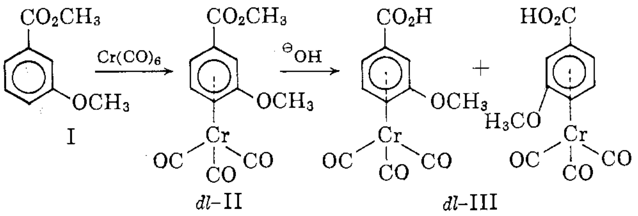
(*m*-Methoxybenzoic acid)-chromium tricarbonyl has been prepared and the resulting racemic mixture has been resolved to yield the pure enantiomers.

An inspection of the formulas of suitably disubstituted arenechromium tricarbonyl derivatives will show that the absence of any elements of symmetry in these compounds should allow them to exist as racemic mixtures and such mixtures should be resolvable into the respective enantiomeric pairs. The compound chosen to test this assumption was the chromium tricarbonyl derivative of *m*-methoxybenzoic acid.[3] Since the –COOH group is known[4] to promote decomposition of hexacarbonylchromium in the reaction with an arene, the methyl ester of *m*-methoxybenzoic acid was treated with hexacarbonylchromium and the resulting compound was hydrolyzed to give the required racemic mixture of III (see Reaction Scheme 1).

Reaction Scheme 1



The procedure for the separation of the enantiomers and the optical rotation data are given in the Experimental section. The optical rotation of the strongly colored solutions of III could not be measured in the polarimeter at the sodium D-line, owing to the limitations of the instrument and the light source. Consequently all rotations of III were measured in sodium hydroxide solutions, since the latter were colored a light yellow.

The optical rotations of the enantiomeric acids themselves were obtained by the use of an optical rotatory dispersion apparatus.[5]

As may be noted from Fig. 1, the optical rotation values for the acids at the sodium D-line exhibit the same sense (+) or (−) as the respective sodium salts of the enantiomeric acids.[6]

This appears to be the first optical resolution of a racemate of an arenechromium tricarbonyl derivative[7] and work is currently in progress to extend this procedure to metal carbonyl derivatives of naphthalene and similar systems in order to attempt studies of the kinetics of racemization of the resolved enantiomers. Such racemization could involve an intermolecular mechanism[8] in the case of benzene derivatives and/or an

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(1) Part VI: R. T. Lundquist and M. Cais, *J. Org. Chem.*, **27**, 1167 (1962).

(2) (a) Communicated in part at the 30th Meeting of the Israel Chemical Society, Jerusalem, April, 1962; see A. Mandelbaum and M. Cais, *Bull. Res. Council Israel*, **11A**, 9 (1962); (b) Communicated at the Symposium on "The Theory and Structure of Complex Compounds," Wroclaw, Poland, June 15–19, 1962.

(3) For a recent review on arenemetal carbonyl complexes see H. Zeiss, "Organometallic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1960, pp. 380–425.

(4) B. Nicholls and M. C. Whiting, *J. Chem. Soc.*, 551 (1959).

(5) We are greatly indebted to Prof. C. Djerassi, Stanford University, for carrying out the optical rotatory dispersion measurements for our compounds.

(6) Prof. Djerassi has commented in a private communication that whereas the over-all shape of the curves is significant, one cannot put too much value on the precise quantitative data because the measurements were carried out in very dilute solutions.

(7) While this work was in progress, R. Riemschneider and W. Hermann, *Ann.*, **648**, 68 (1961), reported the separation of enantiomers of (α-methyl-γ-carboxy)-cyclopentadienylmanganese tricarbonyl without proof of the respective structure, and more recently L. Westman and K. L. Rinehart, Jr., *Acta Chem. Scand.*, **16**, 1199 (1962), have reported a similar resolution of a trisubstituted ferrocene carboxylic acid derivative.

(8) W. Strohmeier and H. Mittnacht, *Z. Physik. Chem.*, **29**, 22 (1961).

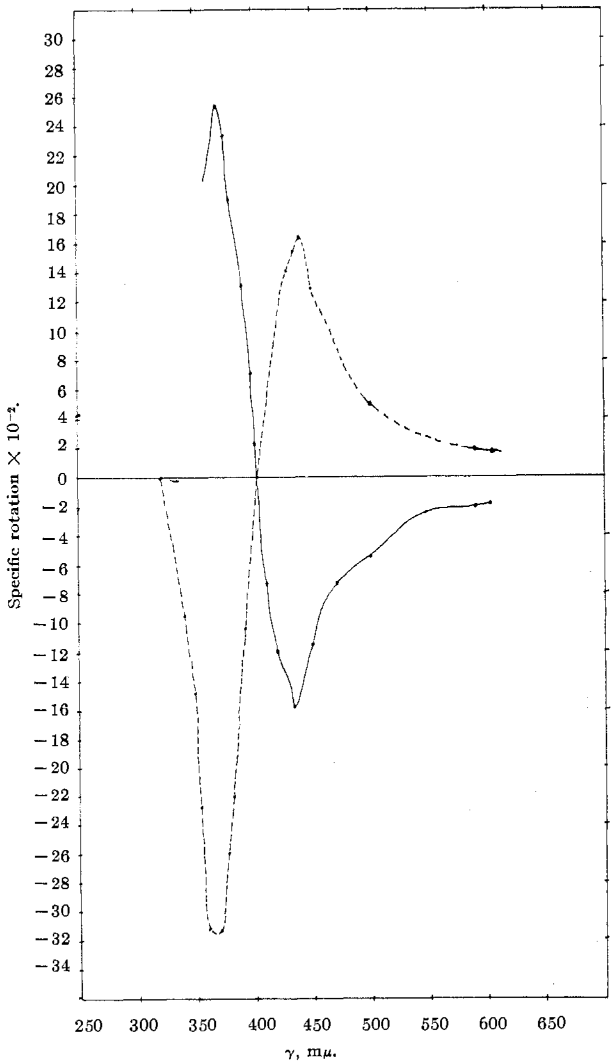

Fig. 1.—Optical rotatory dispersion curves of the resolved enantiomeric acids III: ——— (−)-acid; - - - - - (+)-acid (solvent methanol).

intramolecular mechanism for the naphthalene derivatives.

Experimental

The melting points were determined on a Kofler block. The optical rotation measurements were carried out with a Hilger standard polarimeter. The ultraviolet spectra were measured with a Bausch and Lomb recording spectrophotometer (Spectronic 505).

Preparation of (Methyl *m*-methoxybenzoate)-chromium Tricarbonyl.—Methyl *m*-methoxybenzoate (14.3 g., 0.086 mole) and hexacarbonylchromium (19 g., 0.086 mole) in di-*n*-butyl ether (peroxide-free) (300 ml.) were refluxed for 50 hr. in a nitrogen atmosphere. The mixture was filtered to remove some decomposition material and the filtrate was evaporated to dryness (water-pump vacuum). Upon trituration with petroleum ether, the residue yielded red crystals (10.9 g.), m.p. 52–57°. One recrystallization from hexane–chloroform produced the analytical sample, m.p. 57–58°.

Anal. Calcd. for $C_{12}H_{10}O_6Cr$: C, 47.68; H, 3.33; Cr, 17.21. Found: C, 47.38; H, 3.13; Cr, 17.01.

The petroleum ether triturate was fractionally distilled under vacuum and there was recovered 5 g. of methyl *m*-methoxybenzoate, b.p. 70° (0.2 mm.).

Preparation of (*m*-Methoxybenzoic acid)-chromium Tricarbonyl (III).—(Methyl *m*-methoxybenzoate)-chromium tricarbonyl (3 g., 0.01 mole) dissolved in a solution of potassium hydroxide (1.3 g.) in methanol (80 ml.) and water (2 ml.) was kept at room temperature for 12 hr. The mixture was then diluted with water (250 ml.) and acidified with concentrated hydrochloric acid solution, whereupon red crystals were formed. These were filtered, washed with water, and dried in a vacuum desiccator over phosphorus pentoxide to yield 2.6 g. (93% yield) of III. The acid III appeared to decompose partially when heated in various organic solvents and consequently the analytical sample was prepared by dissolving it in diethyl ether and concentrating the solution under vacuum to yield red crystals, m.p. 147–148° dec.

Anal. Calcd. for $C_{11}H_8O_6Cr$: C, 45.84; H, 2.78; Cr, 18.05. Found: C, 45.64; H, 2.88; Cr, 17.89.

Optical Resolution of (*m*-Methoxybenzoic acid)-chromium Tricarbonyl. A. Preliminary Separation of Diastereoisomeric Salts.—A filtered solution of racemic (*m*-methoxybenzoic acid)-chromium tricarbonyl (4 g., 0.014 mole) in acetone–ethyl acetate (3:1, 60 ml.) was added to a solution of brucine (6.3 g., 0.0135 mole) in acetone–ethyl acetate (3:1, 240 ml.) and the mixture was set aside. The yellow crystals which were formed were filtered, dried to yield crop I (5.9 g., 57% yield), and analyzed without further purification.

Anal. Calcd. for $C_{34}H_{34}O_{10}N_2Cr$: C, 59.81; H, 5.02; Cr, 7.82; N, 4.10. Found: C, 59.67; H, 5.34; Cr, 7.90; N, 4.33; $[\alpha]_D$ −42° (*c* 0.3, CH_3NO_2).

The filtrate obtained after collection of crop I was evaporated to dryness (water-pump vacuum) to yield crop II, an amorphous yellow powder (3.9 g.); $[\alpha]_D$ −25° (*c* 0.5, CH_3NO_2).

B. (−)-(*m*-Methoxybenzoic acid)-chromium Tricarbonyl.—The yellow crystals, crop I (1.0 g.), were heated in nitromethane (200 ml.) and the hot solution was filtered to yield 0.360 g. of yellow crystals, crop III, $[\alpha]_D$ −54° (0.24, CH_3NO_2). The filtrate upon cooling yielded further crops of crystalline salt which had rotations $[\alpha]_D$ −44–46°. The diastereoisomer, crop III (1.0 g.), was shaken with a mixture of 1 *N* hydrochloric acid solution (20 ml.) and diethyl ether (40 ml.). The ether layer was washed with hydrochloric acid solution, then with water, and then extracted with 3% sodium hydroxide solution until the ether layer was colorless. The combined alkaline layers were acidified with concentrated hydrochloric acid solution to yield 0.39 g. of red crystalline material (92.5% yield), whose infrared spectrum was superimposable with that of the racemic acid.

Recrystallization from diethyl ether yielded crystals with an optical rotation $[\alpha]_D$ −47° (*c* 0.5, 3% aqueous NaOH solution).

C. (+)-*m*-(Methoxybenzoic acid)-chromium Tricarbonyl.—The amorphous diastereoisomer, crop II (3.8 g.), was triturated with acetone (40 ml.) and filtered. The filtrate was evaporated under vacuum to yield 3.36 g. of yellow powder with an optical rotation $[\alpha]_D$ −24° (*c* 0.5, CH_3NO_2). Decomposition of the salt with mineral acid and work-up as in B yielded the (+)-acid, $[\alpha]_D$ +46° (*c* 0.51, 3% aqueous NaOH solution). The ultraviolet spectra of both the (+)- and the (−)-acid showed the same absorptions, λ_{max} 318 mμ (log ε 4.02), typical of benzene-chromium tricarbonyl derivatives.

Acknowledgment.—We wish to thank Ethyl Corporation, Detroit, Michigan, for generous supplies of hexacarbonylchromium.