

1. Hordvik, A., Sletten, E. and Sletten, J. *Acta Chem. Scand.* **20** (1966) 2001; **23** (1969) 1852.
2. Hordvik, A., Sletten, E. and Sletten, J. *Acta Chem. Scand.* **23** (1969) 1377.
3. Hordvik, A. and Sæthre, L. J. *Acta Chem. Scand.* **24** (1970) 2261, and to be published.
4. Klingsberg, E. *J. Am. Chem. Soc.* **85** (1963) 3244.
5. Long, R. E. *Ph. D. Dissertation*, University of California at Los Angeles 1965.

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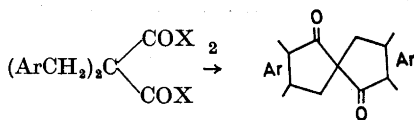
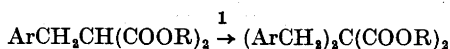
A Modified Synthesis of (±)-2,2'-Spirobi[indan]-1,1'- dione

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Aromatic spiro compounds of high symmetry and low overlap between the aromatic chromophores are of spectroscopic and theoretical interest.

One type of such compounds is derived from the spiro[4.4]nonane system. These compounds are usually synthesized according to the following route



The title spiro compound was previously synthesized by this method,¹ but the yield in step 2 was low.²

It has, however, been demonstrated that the unsymmetric spirodiketone 3',4'-dihydrospiro[indan-2,2'(1'H)-naphthalene]-1,1'-dione could be prepared by cyclization of *o*-carboxy- α -phenethylhydrocinnamic acid.³

In the present communication it is demonstrated that this method can be successfully applied to the synthesis of the

title spiro compound as outlined in Scheme 1.

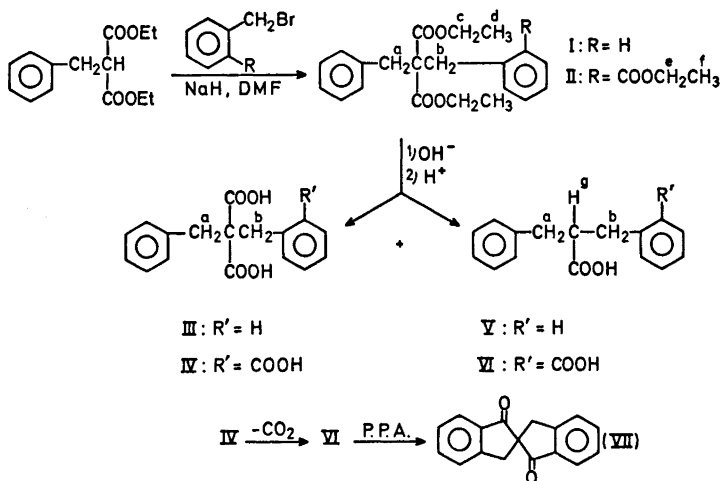
The structures of the compounds II, IV, and VI were established by comparison of their NMR spectra with those for the corresponding known compounds I, III, and V.

Physical data for the spiroketone VII (m.p. and CH-analysis) agreed with those previously reported.¹ Conclusive proof for the structure of VII, however, was afforded by means of the NMR spectrum, the aliphatic part of which displays an AB quartet, owing to the magnetic nonequivalence of the two hydrogens in the methylene groups of VII.

As expected the UV spectrum of VII shows a close resemblance to that of 1-indanone. The UV spectrum of 1-indanone in ethanol displays two absorption bands at 2460 and 2940 Å, respectively. The corresponding absorption bands for VII are positioned at 2520 and 2970 Å, but the extinction coefficients for VII at these two wavelengths are more than 2 times the values for 1-indanone indicating some electronic interaction between the two chromophores in VII.

Experimental. NMR spectra were recorded at 60 Mc/s on a Varian A-60 spectrometer. TMS was used as internal reference standard and the chemical shifts are expressed in τ -values. The coupling constants are expressed numerically in c/s. In the NMR data the notations for the hydrogen atoms according to Scheme 1 are used. The following abbreviations are used: s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). The UV-spectra were recorded on a Bausch and Lomb Spectronic 505 spectrometer.

(±)-Triethyl benzyl-*o*-carboxybenzylmalonate (II). To a stirred suspension of 0.12 mol sodium hydride (50% in mineral oil) in 50 ml of dry DMF was added 27.43 g (0.11 mol) of diethyl benzylmalonate in an atmosphere of dry nitrogen. The internal temperature was maintained at 60° during 2 h. After formation of the sodium derivative, 26.7 g (0.11 mol) of ethyl α -bromo-*o*-toluate,⁴ was added during 10 min, in which time the internal temperature rose to 90°. Stirring and heating was continued at 60° for 1.5 h. Most of the solvent was removed by distillation *in vacuo*. To the residue was added water (50 ml) and ether (90 ml). After extraction of the ethereal solution with sodium carbonate (5%) and drying over calcium sulphate, the ether was evaporated *in vacuo*. The residue was distilled at 0.8 mm to give 34.9 g (75%) of II with b.p. 200–210°. NMR



Scheme 1.

spectrum (CCl₄), τ : 2.18–2.85, m, 9 H (arom. protons); 6.78 s, 2 H (H_A); 6.35, s, 2 H (H_B); 6.11, q, 4 H (H_C); 9.02, t, 6 H (H_D), $J_{cd}=7$ c/s; 5.74, q, 2 H (H_E); 8.65, t, 3 H (H_F), $J_{ef}=7$ c/s. NMR spectrum of I (CCl₄), τ : 2.83, m, 10 H (arom. protons); 6.85, s, 4 H (H_A); 5.99, q, 4 H (H_C); 8.93, t, 6 H (H_D), $J_{cd}=7$ c/s.

Benzyl-o-carboxybenzylmalonic acid (IV). 13.45 g (0.033 mol) of triethyl benzyl-*o*-carboxybenzylmalonate was added to a solution of potassium hydroxide, 10.96 g (0.196 mol) in ethanol (50 ml). The mixture was refluxed for 20 min. During this time the potassium salt of IV had separated. After filtration and drying, the potassium salt (7.7 g) was dissolved in water (40 ml) and the solution acidified with conc. hydrochloric acid (7 ml). Next day the precipitate was filtered and dried to give IV (5.01 g, 46.9%) m.p. 172–174.4°. NMR spectrum ((CD₃)₂SO), τ : 2.13–2.78, m, 9 H (arom. protons); 6.82, s, 2 H (H_A); 6.38, s, 2 H (H_B). NMR spectrum of III ((CD₃)₂SO), τ : 2.71, m, 10 H (arom. protons); 6.90, s, 4 H (H_A).

The alcoholic alkaline filtrate, from the isolation of the potassium salt of IV, was evaporated under reduced pressure. The residue was dissolved in water and the solution acidified with hydrochloric acid. The separated oil, 5 g (after work up), was shown by TLC to be a mixture of the acids IV and VI with R_F -values 0.07 and 0.36, respectively. TLC was performed on silica gel with ethanol-water-conc. ammonia (9:0.5:0.5) as eluent.

Acta Chem. Scand. 26 (1972) No. 2

(±)-2,2'-*Spirobi[indan]-1,1'-dione* (VII). *Benzyl-o-carboxybenzylmalonic acid* (IV) was decarboxylated to *benzyl-o-carboxybenzylacetic acid* (VI), m.p. 177.8–180°. (Found: equiv. wt. 143.9. Calc. for C₁₇H₁₆O₄: 142). NMR spectrum ((CD₃)₂SO), τ : 2.03–2.77, m, 9 H (arom. protons); 7.13, m, 2 H (H_A); 6.78, m, 2 H (H_B); 6.98, m, 1 H (H_G). NMR spectrum of V ((CD₃)₂SO), τ : 2.75, m, 10 H (arom. protons); 7.13, m, 5 H (H_{ag}). The decarboxylation was performed by heating the acid IV (9.21 g, 0.028 mol) at 150° for 1.5 h. After cooling 45 ml of polyphosphoric acid was added and the mixture was heated at 150° for 1.25 h, during which time the reaction mixture was intermittently stirred with a spatula. The reaction mixture was poured onto crushed ice and the separated precipitate filtered by suction. The precipitate was treated with warm sodium carbonate solution and the insoluble product filtered off. The dried product, 6.18 g, m.p. 172.5–174.2, was sublimed at 200° and 0.2 mm to give 5.35 g sublimate. Recrystallization of the sublimate from benzene (charcoal) gave 3.79 g VII, m.p. 173.6–176°. From the mother liquid was obtained 0.51 g, m.p. 173–176.2°. The total yield of purified product was 61.8%.

NMR spectrum (CDCl₃), τ : 2.5–3.0, m, 8 H (arom. protons); 6.69, d, 2 H (half of AB); 6.75, d, 2 H (half of AB), $J_{AB}=16.5$ c/s; UV absorption (in 96% ethanol): λ_{max} 2520 Å (ϵ 28 666); 2970 Å (ϵ 5413).

UV absorption of 1-indanone (in 96 % ethanol): λ_{\max} 2460 Å (ϵ 11 963); 2940 (ϵ 2634).

1. Leuchs, H. and Radulescu, D. *Ber.* **45** (1912) 189.
2. Ingold, C. K. and Wilson, C. L. *J. Chem. Soc.* **1934** 776.
3. Herz, W. *J. Am. Chem. Soc.* **79** (1957) 5011.
4. Pifferi, G. and Testa, E. *Tetrahedron* **22** (1966) 2107.

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Lanthanide-Induced Shifts in Proton Magnetic Resonance Spectra of Some Simple Di-, Tri-, and Tetracoordinate Sulfur Compounds

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Lanthanide "shift reagents", introduced by Hinckley in 1969,¹ have been rapidly and widely adopted as powerful tools in the analysis of proton magnetic resonance spectra of several classes of organic molecules possessing Lewis base character.^{2,3} Sulfur-containing substrates studied are as yet few, comprising sulfoxides,⁴⁻⁶ thioamides,⁹ and thionocarbamates,¹⁰ besides a number of somewhat more special cases including sulfone,⁸ thioether,^{8,11} *p*-toluenesulfonyl,¹² thioketal,^{13,14} hemithioketal,¹⁴ phosphorothiolate,¹⁵ phosphorodithiolate,¹⁵ and thiolohypophosphite¹⁶ groupings.

In connection with current work in this laboratory, we have measured the paramagnetic shifts induced by tris(7,7-dimethyl-1,1,1,2,2,3,3-heptafluoro-4,6-octanedionato)europium(III), (Eu(fod)₃),¹⁷ in the ¹H-spectra of deuteriochloroform solutions

of a series of di-, tri-, and tetracoordinate dimethyl sulfur compounds. The data are presented in Table 1. All measurements were performed at constant substrate concentration, with increasing amounts (up to 30 mol %) of Eu(fod)₃ added. The induced shifts, believed to be pseudo-contact in nature,² were extrapolated to 100 mol % Eu(fod)₃ by the least-squares method (from observed shifts at 0, 10, 20, and 30 mol %) and are presented as $\Delta_{\text{Eu(fod)}_3}$ -values, as defined by Demarco *et al.*¹⁸

The correlation between the electronegativity of the functional group (expressed as δ_0 -values) and the induced shifts is obvious (compare compounds Nos. 1, 2, 4, 5, and 6). Qualitative application of the simplified third-order distance dependence equation,² $\Delta_{\text{Eu(fod)}_3} \propto r^{-3}$, to the *N-p*-toluenesulfonyl derivatives 3, 7, and 8, reveals the oxygen atoms of the sulfonyl-groups as the predominant coordination sites, competitively affected though by the introduction of an oxygen atom or, even more, an NH-group on the dimethylated sulfur atom. The competitive effect is reflected also in the aromatic moiety.

The present data suggest that rare-earth chemical-shift reagents may prove useful as a diagnostic tool in future studies of tri- and tetra-coordinate sulfur compounds.

1. Hinckley, C. C. *J. Am. Chem. Soc.* **91** (1969) 5160.
2. Sanders, J. K. M. and Williams, D. H. *J. Am. Chem. Soc.* **93** (1971) 641.
3. Armitage, I. and Hall, L. D. *Can. J. Chem.* **49** (1971) 2770.
4. Andersen, K. K. and Uebel, J. J. *Tetrahedron Letters* **1970** 5253.
5. Fraser, R. R. and Wigfield, Y. Y. *Chem. Commun.* **1970** 1471.
6. Fraser, R. R., Petit, M. A. and Saunders, J. K. *Chem. Commun.* **1971** 1450.
7. Greene, J. L., Jr. and Shevlin, P. B. *Chem. Commun.* **1971** 1092.
8. Kishi, M., Tori, K., Komeno, T. and Shingu, T. *Tetrahedron Letters* **1971** 3525.
9. Walter, W., Becker, R. F. and Thiem, J. *Tetrahedron Letters* **1971** 1971.
10. Bauman, R. A. *Tetrahedron Letters* **1971** 419.
11. Hart, H. and Love, G. M. *Tetrahedron Letters* **1971** 625.
12. Girard, P., Kagan, H. and David, S. *Tetrahedron* **27** (1971) 5911.