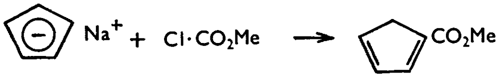
349. *The Cyclopentadienyl Anion. Part I. 1,2-Dimethoxycarbonylcyclopentadienylsodium, a Stabilised Cyclopentadienyl Anion.*

By DAVID PETERS.

The compound mentioned in the title has been synthesised and shown to be stable in neutral or alkaline aqueous solution for several hours and in the atmosphere for many weeks. It is a new example where a cyclopentadienyl anion is stabilised by formally neutral substituents.

IN examining the structure of methyl cyclopenta-1,3-dienecarboxylate (I) (following paper), a new preparative method for this compound was investigated, namely:



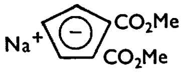
(I)

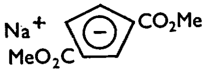
The expected product (I) was obtained, but in low yield (20—30%), and a second product is formed. This paper is concerned with the structure and properties of the latter.

During the addition of the chloroformate, the solution, originally violet, becomes bright green at the half-way stage and brick-red when addition is complete. Acidification and distillation gives ~25% yields each of the expected ester (I) and a high-boiling material. About half of the organic material is lost.

Working up the mixture without hydrolysis gives a brick-red solid (~20% yield) which is shown below to be 1,2-dimethoxycarbonylcyclopentadienylsodium (II).

(II)

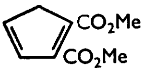


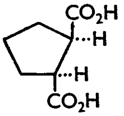


(III)

Elementary analysis and molecular-weight determinations show that the compound is monomeric and contains two carboxyl residues and one atom of sodium per cyclopentadienyl residue. If we assume five-fold symmetry of the unsubstituted anion, there are only two possible structures (II) and (III). In acid solution, the red solid is protonated to give a neutral dimethyl cyclopentadienedicarboxylate, probably (IV). Hydrogenation (Raney nickel) of this material in ethanol–benzene led to the uptake of one mol. of hydrogen

(IV)



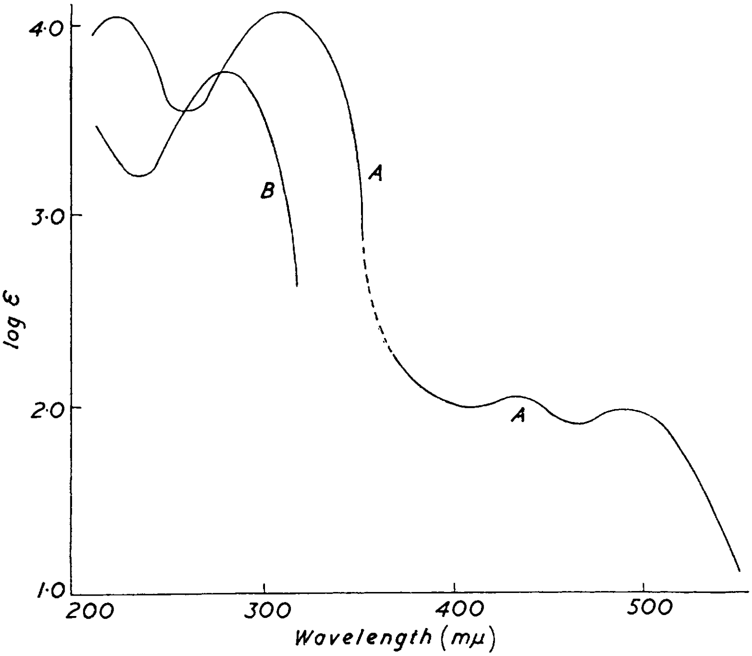


(V)

to give, in 75% yield, a single sharp-boiling oily fraction which was not identified positively but is believed to be a dimethyl cyclopentenedicarboxylate (the structure of this compound was not examined in detail since only three of the six possible cyclopentenedicarboxylic acids are known). Further hydrogenation (Raney nickel) of this fraction in ethanol afforded the oily saturated ester which on acidic hydrolysis gave the known crystalline *cis*-cyclopentane-1,2-dicarboxylic acid (V). The overall yield of this acid was low (~20%) but several stages are involved and there is no indication of the presence of isomers, so it is assumed that the red solid is substantially a single compound.

There is no doubt then that the two methoxycarbonyl groups are intact and in the 1,2-position. It remains to establish whether the sodium atom is firmly bonded to the organic fragment, as in ferrocene and the organolithium compounds, or whether it is free. The following three-fold evidence shows that the ions are free, certainly in water and very probably in the other solvents and in the solid state: (*a*) The solid does not melt; it is soluble in polar solvents and insoluble in non-polar solvents. (*b*) Lead and barium salts are formed by double decomposition in water; they have the same colour as the sodium salt. (*c*) The electrical conductivity of the aqueous solution is that of a 1 : 1 electrolyte. At first sight it may seem that the solubility and conductivity data may be accounted for by supposing that the anion (A^-) reacts rapidly with water: $A^- + H_2O \rightleftharpoons AH + OH^-$. This equilibrium would certainly lie far to the right with the unsubstituted anion, but that this cannot be the case for the substituted one is shown by three further points: (i) the concentrated aqueous solution is neutral or at most slightly alkaline; (ii) extraction of the neutral aqueous solution with organic solvents removes nothing; (iii) the electrical conductivity of the aqueous solution at infinite dilution (Λ_0 81 ohm^{-1} cm.^{2}) is very different from that of sodium hydroxide (Λ_0 250 ohm^{-1} cm.^{2}). Thus the compound is ionic.

Absorption spectra of 1,2-*dimethoxycarbonylcyclopentadienylsodium* (*A*) *in neutral or alkaline aqueous solution, in ethanol, and in tetrahydrofuran, and* (*B*) *in* 0·1N-*hydrochloric and -sulphuric acid.*



The ultraviolet spectrum of the anion in neutral or alkaline aqueous solution (see Figure) shows two intense peaks, at 225 and 310 mμ, and there is weak adsorption in the 435 and 490 mμ regions. Protonation of the anion leads to a marked change in the position of the bands and in the general appearance of the spectrum. Extraction of the acidified aqueous solution removes the protonated species, as shown by the spectrum of the organic phase.

Discussion.—The unsubstituted cyclopentadienyl anion reacts vigorously with hydroxylic solvents, oxygen, and nucleophiles generally. The introduction of two carboxyl groups stabilises the anion to these reagents. This stabilisation may be expressed in valence-bond terminology by saying that the forms (VI) and (VII) contribute substantially to the wave function of the ground state of the substituted anion while forms such as (VIII) contribute little to the wave function of the neutral butadienyl grouping in (IV). This accords well with current ideas of sacrificial and isovalent resonance,[1] compound (VIII) being a high-energy form since one double bond has been lost. In the substituted anion there is isovalent resonance between three structures with the same number of double bonds (II, VI, VII) and, presumably, comparable energies.

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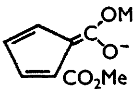
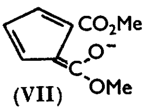
[1] Muller and Mullikan, *J. Amer. Chem. Soc.*, 1958, **80**, 3489.

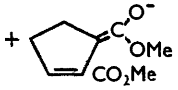
This ion and that isolated by Linn and Sharkey (see below) differ in an important respect from the earlier examples[2] of stabilised cyclopentadienyl anions (IX—XII) where



(VI)

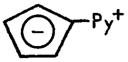


(VII)

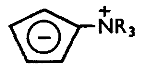


(VIII)

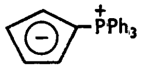
the molecules as a whole are electrically neutral although structures with charge separation may be the most important contributors to the wave functions. The present example, and Linn and Sharkey's, show that stabilisation can be achieved by electrically neutral substituents. It appears that one positively charged substituent is about equal to two



(IX)



(X)

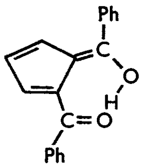


(XI)

(XII)

methoxycarbonyl groups and it is noteworthy that this is the ratio which would be expected if the inductive effects of the groups are the predominant factor.[3] The inductive effect of a nitro-group approaches that of a positively charged substituent, and the mononitro-derivative is indeed stable.[4]

(XIII)



(XIV)

The similar anion was reported by Linn and Sharkey[5] when they obtained compound (XIII), presumably *via* the anion (XIV); they also prepared the sodium and the potassium salt of the di-*p*-chloro-analogue.

EXPERIMENTAL

Tetrahydrofuran was refluxed and distilled over sodium until the sodium remained clean. Ultraviolet spectra were recorded on a Hilger Uvispek. Raney nickel was prepared as described elsewhere.[6]

Preparation of 1,2-*Dimethoxycarbonylcyclopentadienylsodium*.—Methyl chloroformate (94 g., 1·0 mole) was added dropwise to a stirred solution of cyclopentadienylsodium (1·0 mole, from sodium, 24 g., and cyclopentadiene, 70 g.) in dry tetrahydrofuran (600 c.c.) under dry nitrogen at 0°. The solvent was removed at reduced pressure and the residue was shaken repeatedly with dry ether (1 l.). The ether was removed from the filtrate and the residue distilled, to give methyl cyclopenta-1,3-dienecarboxylate (23 g., 0·2 mole), b. p. 110—130°/15 mm., which partly solidified in 30 min. Crystallisation from light petroleum (b. p. 60—80°) gave the dimer, Thiele's ester (8 g.), m. p. and mixed m. p. 82—83°. The red ether-insoluble residue (92 g.) was extracted (Soxhlet) for 16 hr. with ethyl acetate. The buff-coloured residue (45 g., 0·77 mole) was sodium chloride (95% pure by chloride assay). The ethyl acetate extracts were evaporated at reduced pressure until free from solvent, giving a pink solid (44 g.), free from chloride. This material was extracted (Soxhlet) for 2 weeks with chloroform, the extracted material being removed each day. Fourteen fractions of 1,2-*dimethoxycarbonylcyclopentadienylsodium* (34 g.) were obtained. Fractions 3—12 were identical in appearance [Found, for

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[2] Lloyd and Sneezum, *Chem. and Ind.*, 1955, 1221; Ramirez and Levy, *J. Org. Chem.*, 1956, **21**, 488, 1333; *J. Amer. Chem. Soc.*, 1957, **79**, 67, 6167; Spooncer, *Diss. Abs.*, 1956, **16**, 458.

[3] Peters, *J.*, 1957, 2654.

[4] Thiele, *Ber.*, 1900, **33**, 666.

[5] Linn and Sharkey, *J. Amer. Chem. Soc.*, 1957, **79**, 4970.

[6] Paul and Hilly, "Newer Methods of Organic Chemistry," Interscience Publ. Inc., New York, 1948, p. 65.

fraction 3: C, 52·2; H, 4·8; Na, 10·5. For fraction 8: C, 52·1; H, 4·6; Na, 10·5%; *M* (cryoscopic in H_2O), 200. $C_9H_9O_4Na$ requires C, 52·9; H, 4·4; Na, 11·3%; *M*, 204 (van't Hoff *i* factor = 2)].

Hydrogenation of 1,2-*Dimethoxycarbonylcyclopentadienylsodium.*—The sodium compound (5 g.) in water (200 c.c.) and ethanol (50 c.c.) was shaken with benzene (75 c.c.), sulphuric acid (5 c.c. in 20 c.c. of water) was added to the emulsion, and the mixture extracted immediately. Further extraction with benzene (2 × 25 c.c.) gave a red benzene solution which was dried briefly (Na_2SO_4) and diluted with ethanol (50 c.c.). Hydrogenation over Raney nickel at atmospheric pressure led to the uptake of 600 c.c. of hydrogen (theory 550 c.c.) in 2 hr. Filtration and distillation gave a dimethyl cyclopentenedicarboxylate (3·4 g., 75%), b. p. 134—136°/14 mm. (Found: C, 58·7; H, 6·7. Calc. for $C_9H_{12}O_4$: C, 58·7; H, 6·6%), which decolorised potassium permanganate in acetone immediately. An ethereal solution of this oil was extracted thoroughly with sodium carbonate solution. Extraction of the acidified aqueous solution with chloroform gave only a trace of solid. The ester (2·4 g.) was recovered by drying and distilling the ethereal layer. Hydrolysis of the ester with acid or base gave a mixture of acids, m. p. 160—170°. The ester (1·8 g.) was hydrogenated in ethanol (50 c.c.) over Raney nickel, taking up 240 c.c. of hydrogen (theor. 224 c.c.) in 2 hr. Distillation gave *dimethyl* cis-*cyclopentane*-1,2-*dicarboxylate* (1·2 g.), b. p. 125—126°/15 mm. (Found: C, 57·9; H, 8·0. $C_9H_{14}O_4$ requires C, 58·1; H, 7·6%). Refluxing this ester (1·2 g.) with concentrated hydrochloric acid (2 c.c.) for 30 min. and cooling to 0° gave a white solid (0·8 g.), m. p. 115—125°. Two crystallisations from ethyl acetate gave *cis-cyclo*pentane-1,2-dicarboxylic acid (0·5 g.), m. p. and mixed m. p. 133—135°. Refluxing the acid with aniline and pouring the mixture into cold dilute sulphuric acid gave the anil, m. p. and mixed m. p. 88—89° (from aqueous ethanol). Refluxing the acid with acetic anhydride for 2 hr. and distilling the product gave the anhydride, m. p. 75° (lit.,[7] 73°).

Lead and Barium Salts from 1,2-*Dimethoxycarbonylcyclopentadienylsodium.*—The sodium salt (0·3 g.), dissolved in water (1 c.c.), was treated with 1 c.c. of a M-solution of lead acetate or barium chloride. The red precipitate was centrifuged off, washed several times with water, and filtered, giving the *lead* (Found: C, 37·5; H, 3·4; Pb, 36·1. $C_{18}H_{18}O_8Pb$ requires C, 38·0; H, 3·2; Pb, 36·4%), and the *barium salt* (Found: C, 43·4; H, 4·3; Ba, 26·8. $C_{18}H_{18}O_8Ba$ requires C, 43·3; H, 3·6; Ba, 27·45%). Silver, mercuric, and cupric salts gave intractable oily precipitates and complex colour changes, presumably due to oxidation of the organic anion by the metal ions.

Conductivity of Aqueous Solutions of 1,2-*Dimethoxycarbonylcyclopentadienylsodium.*—The conductivity of 0·1—0·0005M-solutions at 25° gave a straight line plot of Λ against $\sqrt{c}$ from which a Λ_0 of 81 ohm^{-1} cm.^2 was calculated.

pH *of Aqueous Solutions of* 1,2-*Dimethoxycarbonylcyclopentadienylsodium.*—The pH of freshly prepared aqueous solutions (0·1, 0·01, and 0·001M) were measured on a Pye Universal pH meter. All solutions had pH 7·4—7·6.

Preparation of Authentic cis-*Cyclopentane*-1,2-*dicarboxylic Acid.*—*cis*-Cyclopentene-1,2-dicarboxylic acid, prepared by Nandi's method,[8] as modified by Gupta and Saha,[9] had m. p. 178° (Found: C, 53·9; H, 5·3. Calc. for $C_7H_8O_4$: C, 53·85; H, 5·2%). It did not take up hydrogen over Raney nickel but took up the calculated quantity slowly over platinum to give *cis*-cyclopentane-1,2-dicarboxylic acid, m. p. 133—135° (lit.,[7,10] 140°; 131—133°) (Found: C, 53·3; H, 6·5. Calc. for $C_7H_{10}O_4$: C, 53·2; H, 6·4%). The anil, prepared as described above, had m. p. 88—89° (lit.,[10] 88°) (Found: C, 72·3; H, 6·1; N, 6·8. Calc. for $C_{13}H_{13}O_2N$: C, 72·6; H, 6·1; N, 6·5%).

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[7] Perkin, *Ber.*, 1885, **18**, 3250; *J.*, 1887, **51**, 240; 1894, **65**, 572.
[8] Nandi, *J. Indian Chem. Soc.*, 1934, **11**, 213.
[9] Gupta and Saha, *ibid.*, 1952, **29**, 331.
[10] Blomquist and Kwiatek, *J. Amer. Chem. Soc.*, 1951, **73**, 2100.