Organometallic Compounds of Group II. Part VI.[1] 1,2-Acenaphthenylenecalcium

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Mercury-activated calcium readily forms an adduct with acenaphthylene in tetrahydrofuran at −35°. Rapid carboxylation gives acenaphthene-*trans*-1,2-dicarboxylic acid as the only acidic product, whereas slow carboxylation produces two further isomeric diacenaphthyl dicarboxylic acids. One of these isomers has been obtained in dimorphic forms, the dimethyl esters of which are thermally interconvertible. An adduct of sodium with acenaphthylene has also been prepared and carboxylated to give acenaphthene-*trans*-1,2-dicarboxylic acid.

Excess of methanolic sodium methoxide converts acenaphthene-*trans*-1,2-dicarboxylic acid into a salt of the *cis*-isomer, whereas the same reagent catalyses the *cis* $\longrightarrow$ *trans* epimerisation of the corresponding dimethyl esters.

THE addition of alkali metals to aromatic hydrocarbons and arylethylenes is well known,[2] but relatively little is known of similar reactions involving metals of Group II. Gilman and Bailie [3] observed both " normal " and " dimerising " additions of calcium, strontium, and barium to 1,1-diphenylethylene in liquid ammonia, and Ivanov and Markov have recently reported the formation of naphthalenemagnesium in the same solvent.[4] Although Mathias and Warhurst were unable to obtain adducts of some Group II metals with naphthalene, anthracene, stilbene, and tri- and tetra-phenylethylene,[5] Utke and Sanderson have since reported the formation of coloured products from reactions between calcium and certain aromatic hydrocarbons (not including acenaphthylene) in liquid ammonia: these products were reasonably assumed to be adducts, but their natures were not established.[6]

Calcium (as the hexammine) can be used instead of sodium in the Birch reduction.[7]

In a previous Paper [8] we reported that the reactivity of calcium towards alkyl and aryl halides was considerably enhanced by superficial amalgamation with a few atoms percent of mercury, particularly if sodium is absent as an impurity. This " activated " calcium has now been found to react with certain aromatic hydrocarbons in tetrahydrofuran, although the scope of the reaction appears to be limited. Thus anthracene, phenanthrene, and stilbene reacted very slowly, but no organocalcium products could be detected. The product of an experiment with diphenylacetylene gave a positive test with the Michler's ketone reagent, but carboxylation gave too small an amount of a crystalline acid for identification, although the melting point (330° decomp.) showed that it was not diphenylfurmaric acid or diphenylmaleic anhydride (the free acid dehydrates spontaneously). Smith and Hoehn treated an ethereal solution of diphenylacetylene with an excess of lithium and obtained, after hydrolysis, 1,2,3,4-tetraphenylbuta-1,3-diene, or 1,2,3-triphenylnaphthalene, depending upon the reaction period.[9]

In contrast with the above hydrocarbons, acenaphthylene readily formed an adduct with activated calcium in tetrahydrofuran at −35°. Carboxylation by an ethereal slurry of solid carbon dioxide gave acenaphthene-*trans*-1,2-dicarboxylic acid (I), m. p. 234° (decomp.). The same acid was obtained by carboxylation of a sodium–acenaphthylene adduct prepared similarly.

The *trans* configuration of acid (I) is the same as that of the dihydrodicarboxylic acids obtained by carboxylation of sodium adducts of naphthalene,[10] phenanthrene,[11] and chrysene.[12] The disodio derivative of 9,10-dimethylanthracene is reported to give a mixture of *cis*- and *trans*-9,10-dihydro-9,10-dimethylanthracene on methanolysis.[13] Assignment of a *trans* configuration to acid (I) is based upon its behaviour towards acetic anhydride and methanolic sodium methoxide. The former reagent, even under mild conditions, invariably produced much gross decomposition of the acid, the products of which sometimes contained small amounts of an intramolecular anhydride (m. p. 184°). Reaction of the acid with an excess of methanolic sodium methoxide, followed by acidification, produced a second acid (m. p. 179° decomp.) treatment of which with acetic anhydride readily gave an almost quantitative yield of the same anhydride. This second acid is clearly acenaphthene-*cis*-1,2-dicarboxylic acid. Its dimethyl ester was readily epimerised to the dimethyl ester of the *trans*-acid by the action of a catalytic proportion of methanolic sodium methoxide. The degree of generality of this procedure for *trans* $\longrightarrow$ *cis* conversion of the acid is currently being examined.

The anhydride of the *cis* acid was also obtained when the *cis* and the *trans* acids were heated to *ca.* 170°/20 mm.

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[1] Part V, D. Bryce-Smith and B. J. Wakefield, *J. Chem. Soc.*, 1964, 2483.

[2] See, *e.g.*, G. E. Coates, " Organometallic Compounds," Methuen, London, 1960, p. 32.

[3] H. Gilman and J. C. Bailie, *J. Amer. Chem. Soc.*, 1943, **65**, 267.

[4] C. Ivanov and P. Markov, *Naturwiss.*, 1963, **50**, 688.

[5] A. Mathias and E. Warhurst, *Trans. Faraday Soc.*, 1962, **58**, 948.

[6] A. R. Utke and R. T. Sanderson, *J. Org. Chem.*, 1964, **29**, 1261.

[7] H. Boer and P. M. Duinker, *Rec. Trav. chim.*, 1958, **77**, 346, and references therein.

[8] D. Bryce-Smith and A. C. Skinner, *J. Chem. Soc.*, 1963, 577; cf. *Chem. and Ind.*, 1960, 1106.

[9] L. I. Smith and H. H. Hoehn, *J. Amer. Chem. Soc.*, 1941, **63**, 1184.

[10] J. F. Walker and N. D. Scott, *J. Amer. Chem. Soc.*, 1938, **60**, 951.

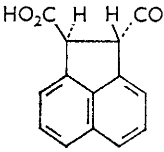
[11] A. Jeanes and R. Adams, *J. Amer. Chem. Soc.*, 1937, **59**, 2608.

[12] S. E. Hunt and A. S. Lindsey, *J. Chem. Soc.*, 1958, 2227.

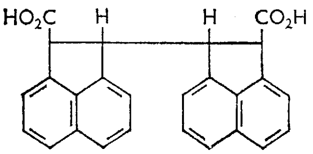
[13] G. M. Badger, M. L. Jones, and R. S. Pearce, *J. Chem. Soc.*, 1950, 1700.

and >250°/20 mm., respectively. Hydrolysis of this anhydride by hot water or cold dilute alkali yielded the *trans* acid; but a sample of the anhydride which had been stored in air for three years was found to have been largely converted into the *cis*-acid. The anhydride was converted by methanol and a trace of concentrated sulphuric acid into a dimethyl ester (m. p. 121°) which was identical with that obtained directly (diazomethane or methanol) from the *cis* acid, and which yielded the *cis* acid upon saponification. Esterification of the *trans* acid gave a dimethyl ester (m. p. 84°) saponification of which led to a mixture of the *cis* and *trans* acids.

Slow carboxylation of 1,2-acenapthenylenecalcium at *ca.* −70° by a stream of carbon dioxide gave acid (I) together with two other acids (A and B) having m. p.s 304° (decomp.) and 301° (decomp.), respectively. Both of these further acids can be assigned the general structure (II) from the evidence of elemental analyses, equivalent weight determinations, ultraviolet spectra, and the molecular weights of their dimethyl esters. Acids A and B were separated from each other on the basis of the insolubility of the sodium salt of B in 30% sodium hydroxide solution. Acid B, when heated with aqueous acetic acid or aqueous acetone gave a further acid C, m. p. 300° (decomp.). The infrared spectra of acids A, B, and C in Nujol mulls were broadly similar to each other, but showed marked differences in detail.



(I)

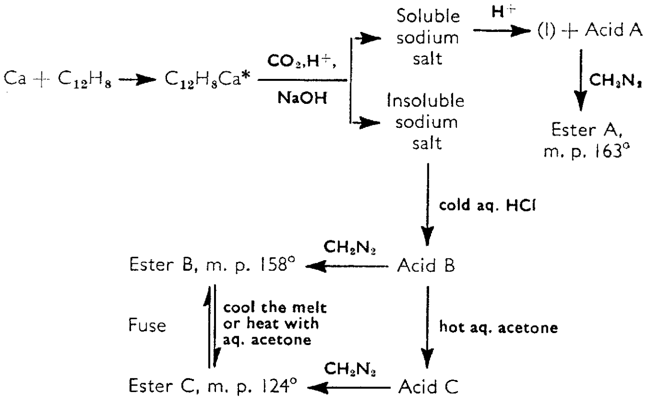


(II)

Reaction of the acids A, B, and C with an excess of diazomethane gave their dimethyl esters, m. p.s 163, 158, and 124°, respectively. These had differing infrared spectra in Nujol mulls. Ester C rapidly resolidified when heated just above its m. p. and finally remelted at 158°. The infrared spectrum of its melt at 160° was identical with that of a melt of ester B. Cooling of ester B or C from 160° to room temperature gave ester C. These transformations are summarised in the Scheme. The infrared spectra of solutions of esters B and C in carbon disulphide were identical, yet different from that of ester A. Evidently, esters B and C are an unusually easily interconvertible pair of dimorphs having a transition temperature near to 124°. One could surmise that these different crystalline forms correspond to two different orientations of the rings about the internuclear bond in structure (II).

It is interesting that methylation of the metastable acid B at room temperature produced ester B which was also metastable under those conditions. This was the only way in which ester B could be obtained at room temperature, for cooling its melt or attempted recrystallisation invariably gave ester C.

Six structural forms (four of which possess enantiomorphs) corresponding to formula (II) are theoretically possible. Examination of models shows that of the six, the *cis-cis-cis* and the *cis-trans-cis* isomers could form virtually unstrained intramolecular anhydrides, the *trans-cis-trans* and the *trans-trans-trans* isomers would be unable to form intramolecular anhydrides, whilst the *trans-cis-cis* and the *trans-trans-cis* isomers might form rather strained anhydrides. Neither acid A, nor acids B and C, formed an anhydride when heated to their decomposition temperatures (>300°) or when treated with acetic anhydride. The mass spectra of the acids were closely similar and showed no peak corresponding to M − 18. Hence, acids A and [B, C] are probably the pair of *trans-cis-trans* and *trans-trans-trans* isomers of structure (II); but which is which has yet to be decided. Likewise, the mechanism of their formation is at present obscure, although speculative possibilities are easily imagined.



* The empirical formula is inferred, and has not been established by analysis. Numerous structural types are possible in principle.

Walker and Scott carboxylated the naphthalene–sodium adduct and obtained equivalent proportions of naphthalene and 1,2-dihydronaphthalene-1,2-dicarboxylic acid.[10] From this result, Paul *et al.* concluded that the formation of a dicarboxylic acid does not necessarily imply the formation of a 2 : 1 sodium–naphthalene adduct.[14] In contrast, in preparations of acenaphthene-*trans*-1,2-dicarboxylic acid by rapid carboxylation of the present calcium or sodium adducts, little or no acenaphthylene was obtained after hydrolysis. This fact suggests that solutions of these adducts contain predominant species formed by transfer of two electrons to each hydrocarbon molecule. The sodium adduct differed from the calcium adduct in failing to give any trace of the acids (II) on slow carboxylation, a fact which is clearly relevant to the mechanistic problem mentioned above.

EXPERIMENTAL

Calcium containing <0·5% of magnesium and <0·2% of sodium was activated as described in Part IV.[8] Reactions with calcium and sodium were conducted under dry

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[14] D. E. Paul, D. Lipkin, and S. I. Weissman, *J. Amer. Chem. Soc.*, 1956, **78**, 116.

argon or nitrogen. Tetrahydrofuran was freshly distilled from powdered calcium hydride.

1,2-*Acenaphthenylenecalcium*.—(a) *Rapid carboxylation*. Half of a solution of acenaphthylene (31 g.) in tetrahydrofuran (100 ml.) was added to activated calcium (from 8 g. calcium) in tetrahydrofuran (50 ml.) at 0°. After stirring for 5 min. the mixture became brown, and the temperature was then reduced to −35° over 20 min. More tetrahydrofuran (50 ml.) was added, and the remainder of the acenaphthylene solution was run in over 3 hr. The mixture was stirred at −35° for a further 3 hr. and then poured on to an ethereal slurry of solid carbon dioxide. Conventional working-up gave *acenaphthene*-trans-1,2-*dicarboxylic acid* (8·4 g.), m. p. 227°. Recrystallisation from a large volume of boiling water containing a little charcoal gave a colourless sample, m. p. 234° (decomp.) [Found: C, 69·25; H, 4·15%; Equiv. 120. Calc. for $C_{12}H_8(CO_2H)_2$: C, 69·4; H, 4·15%; Equiv. 121]. The acid was soluble in acetone and acetic acid, but insoluble in benzene. It had $\lambda_{max.}$ 289 mμ (ethanol). Oxidation by alkaline permanganate in aqueous pyridine gave naphthalic acid (m. p. mixed m. p., equiv., infrared spectrum). Excess of diazomethane converted acenaphthene-*trans*-1,2-dicarboxylic acid to the trans-*dimethyl ester*, m. p. 84° (Found: C, 70·8; H, 5·2. Calc. for $C_{16}H_{14}O_4$: C, 71·1; H, 5·2%). When refluxed for 2 days with an excess of methanolic sodium methoxide solution, and then acidified, the *trans* acid was converted to *acenaphthene*-cis-1,2-*dicarboxylic acid*, recrystallisation of which (from water) to constant m. p. gave a pure sample, m. p. 179° (decomp.) (Found: equiv. 120). When treated with diazomethane, this acid was converted to the cis-*dimethyl ester* which, after several recrystallisations from methanol, had m. p. 121° (Found: C, 72·2; H, 5·20%). This *cis*-ester (0·135 g.) was heated under reflux for 75 min. in methanol (10 ml.) containing 7 equiv. % of sodium methoxide. 6 Ml. of methanol was distilled off, and the residue cooled to give crystals (0·07 g.) of the corresponding *trans*-ester, m. p. and mixed m. p. 84°, having the correct infrared spectrum. Concentration of the filtrate gave 0·02 g. of slightly impure *trans*-ester, m. p. 81—83°.

The action of acetic anhydride at 50° for 70 min., then overnight at room temperature, converted the above *cis* acid to *acenaphthene*-cis-1,2-*dicarboxylic anhydride*, (93% yield), one recrystallisation of which from benzene gave pure needles, m. p. 184° (Found: C, 74·9; H, 3·65. Calc. for $C_{14}H_8O_3$: C, 75·0; H, 3·6%). Identical treatment of acenaphthene-*trans*-1,2-dicarboxylic acid gave mainly tar from which, after extraction with benzene, was obtained the same anhydride in *ca*. 10% yield. Esterification of the anhydride by methanol containing a trace of concentrated sulphuric acid gave the *cis* dimethyl ester (m. p., mixed m. p., infrared spectrum).

Neutral products from the preparation of 1,2-acenaphthenylenecalcium were extracted with Girard's reagent T to remove a small quantity of an unidentified ketone. Distillation gave acenaphthylene (m. p., infrared spectrum) (6 g.), and a brown residue which was dissolved in benzene. Addition of ether to this solution precipitated a flocculent white solid. Repeated dissolution and reprecipitation in this way gave a *hexamer of acenaphthylene*, m. p. *ca*. 345° (decomp.) [Found: C, 94·05; H, 5·60%; *M* (Rast), 932, 922. Calc. for $C_{72}H_{48}$: C, 94·7; H, 5·3%; *M*, 912].

(b) *Slow carboxylation*. 1,2-Acenaphthenylenecalcium prepared as in (a) was carboxylated at −70° by a slow current of carbon dioxide: a test with Michler's ketone reagent was negative after 4 hr. The residue was hydrolysed, and acidic products were extracted into 30% sodium hydroxide solution. This solution slowly deposited crystals when kept for 1 hr. Acidification of an aqueous solution of the crystals gave *acid B* (see text), m. p. 301° (decomp.) (5·5 g.) [Found: Equiv. 201. Calc. for $C_{24}H_{16}(CO_2H)_2$: Equiv. 197]. Acidification of the above solution of sodium salts in 30% sodium hydroxide gave a mixture of solid acids. Extraction of the dried mixture with cold acetone removed the readily soluble acenaphthene-*trans*-1,2-dicarboxylic acid (1·9 g.), m. p. 234° (decomp.) from the insoluble *acid A* (see text), m. p. 304° (decomp.) (2·3 g.) [Found: C, 78·5; H, 4·7%; Equiv. 195. Calc. for $C_{24}H_{16}(CO_2H)_2$: C, 79·2; H, 4·6%; Equiv. 197]. The action of diazomethane on acid A gave the *dimethyl ester*, m. p. 164° [Found: C, 80·2; H, 5·3%; *M* (Rast), 410. Calc. for $C_{28}H_{22}O_4$: C, 79·6; H, 5·25%; *M*, 422].

Acid B would not dissolve in boiling acetone; but when a few drops of water were added to the suspension, a clear solution was obtained, which when cooled did not at first deposit crystals. Only when this solution had several times been heated to boiling and cooled did the solute crystallise out completely. The product was not, however, the original acid B, but a new *acid C* (see text), m. p. 300° (decomp.) (Found: C, 78·6; H, 4·8%; Equiv. 193). The infrared spectrum (Nujol mull) of acid C differed markedly from those of acids B and A, although there were a number of broad similarities in all three spectra.

Acid B, with diazomethane, gave *dimethyl ester B*, m. p. 158° after recrystallisation from ether (Found: C, 79·4; H, 5·25%). Acid C, similarly treated, gave *dimethyl ester C* (Found: C, 79·4; H, 5·25%; *M*, 432). The infrared spectra of esters A, B, and C (Nujol mulls) showed broad similarities but numerous marked differences in detail. Ester C had an initial m. p. 124°, but the melt resolidified almost immediately, and finally re-melted at 158°. After the ester had cooled to room temperature, the cycle could be repeated. Cooling of ester B from the melt to room temperature gave ester C, which showed the above unusual behaviour when heated. The original form of ester B which existed at room temperature could not again be obtained after having been once melted. The infrared spectra of melts of esters B and C, or of their solutions in carbon disulphide (60 mg./ml.), were identical with one another but differed from the corresponding spectrum of ester A. Hence, esters B and C are chemically identical in the solutions at room temperature, and when molten at 158°, but not identical with ester A.

Oxidation of acids A and C by potassium permanganate in aqueous pyridine gave naphthalic acid (m. p., mixed m. p., infrared spectrum). Attempts to convert the acids to anhydrides thermally or by the action of acetic anhydride led either to recovery of the starting material or to gross decomposition. Acenaphthylene (3 g.) was recovered from neutral products of the carboxylation reaction.

Addition of Sodium to Acenaphthylene.—Sodium wire (6·1 g.) was extruded directly into tetrahydrofuran (50 ml.). The addition of 5 ml. of a solution of acenaphthylene (18·2 g.) in tetrahydrofuran (100 ml.) led to an immediate dark green coloration. The remainder of the acenaphthylene solution was added with stirring over 5 hr. at −70°. After a further 1 hr. at −70°, the product was poured on to an ethereal slurry of solid carbon dioxide. Conventional working-up gave acenaphthene-*trans*-1,2-dicarboxylic acid

(14·5 g.) having the correct m. p. and infrared spectrum. The dimethyl ester had m. p. and mixed m. p. 84°, and the correct infrared spectrum. Acenaphthylene (1 g.) was recovered from the neutral products. In a further very similar experiment, no free acenaphthylene was obtained, so the above small quantity probably represented unreacted starting material.

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