

452. *Metallation and Carboxylation of Chrysene.*

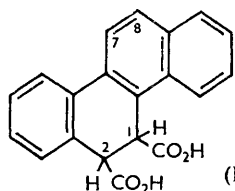
By S. E. HUNT and A. S. LINDSEY.

Carboxylation of the chrysene-sodium adduct leads to 1 : 2-dihydrochrysene-1 : 2-dicarboxylic acid. Oxidation of the diacid yields 1 : 2-chrysoquinone, and of the derived anhydride yields chrysene-1 : 2-dicarboxylic anhydride. Treatment of the chrysene-sodium adduct with ethanol gives 1 : 2-dihydrochrysene. The stereochemistry and ultraviolet absorption spectra of the products are discussed.

THE addition of alkali metals to chrysene in complex-forming or co-ordinating solvents has not hitherto been examined in detail. Mohler and Sorge¹ prepared crystalline dihydrochrysene by treatment of chrysene with lithium in diethyl ether followed by ethanol, but no structure was indicated. The theoretical aspects of this type of addition of alkali metals have been discussed by Paul *et al.*² and by Ubbelohde and his colleagues.³ Chrysene and sodium have now been found to form readily an adduct when stirred together in dimethoxyethane at room temperature, the adduct being deposited as an almost black solid. Carboxylation of the suspended sodio-derivative at about -65° gave a crystalline dihydrochrysenedicarboxylic acid.

The carboxylation product was shown to be 1 : 2-dihydrochrysene-1 : 2-dicarboxylic acid (I) by the analytical data, equivalent-weight determination, and infrared absorption spectrum. With diazomethane it gave a crystalline dimethyl ester. At the melting point (280°) or in hot acetic anhydride it was readily converted into an anhydride which on hydrolysis at room temperature and acidification at 0° yielded a dicarboxylic acid which appeared to differ from the starting material in becoming orange-coloured on storage, possibly owing to aerial oxidation but with diazomethane gave the same dimethyl ester. With chromium trioxide in acetic acid the anhydride furnished the orange crystalline chrysene-1 : 2-dicarboxylic anhydride. Oxidation of the dihydrochrysenedicarboxylic acid with potassium dichromate yielded 1 : 2-chrysoquinone as sole product.

Oxidation of chrysene occurs readily at the 1- and the 2-position, and bromination at positions 2 and 8. Bond-order calculations⁴ agree with the experimental data. Since with other aromatic systems an alkali metal adds to the most reactive positions it seems



¹ Mohler and Sorge, *Helv. Chim. Acta*, 1939, **22**, 229.

² Paul, Lipkin, and Weissman, *J. Amer. Chem. Soc.*, 1956, **78**, 116.

³ Holmes-Walker and Ubbelohde, *J.*, 1954, 720; Slough and Ubbelohde, *J.*, 1957, 982.

⁴ Berthier, Coulson, Greenwood, and Pullman, *Compt. rend.*, 1948, **226**, 1906.

likely that reaction occurs at the 1:2-positions of chrysene in this instance, the vicinal character of the two carboxyl groups being confirmed by the ready anhydride formation. Chrysene-1:2-dicarboxylic anhydride was hydrolysed by alkali at room temperature to the very unstable 1:2-dicarboxylic acid: the initially pale yellow precipitate rapidly reverted to the orange anhydride. Phenanthrene-9:10-dicarboxylic acid behaves similarly.⁵ The instability is even more marked with the chrysene compound since attempts to prepare a dimethyl ester led only to recovery of the anhydride. The instability of the diacid with anhydride formation is markedly different from the properties reported for chrysene-2:8-dicarboxylic acid.⁶

Two *cis*- and two *trans*-forms of 1:2-dihydrochrysene-1:2-dicarboxylic acid are possible but there is insufficient evidence for assignment of a complete configuration. Our acid is probably a *trans*-compound since it is unchanged by concentrated hydrochloric acid at 180°; this is consistent with Jeanes and Adams's observation⁵ that phenanthrene yields a *trans*-product.

The dihydro-anhydride is considered to have a *cis*-configuration from its mode of formation. A molecular model shows that a *trans*-anhydride is sterically unlikely and the ultraviolet absorption (see Table) suggests that the molecule is essentially planar. Further the infrared absorption bands (at 1858 and 1771 cm.⁻¹) are close to those for succinic anhydride⁷ (1866 and 1783 cm.⁻¹), and indicate that the anhydride ring is not under undue strain.

Treatment of the chrysene-sodium adduct with ethanol gave a crystalline dihydrochrysene, the m. p. and ultraviolet absorption spectrum of which agreed with those reported by Mohler and Sorge.¹ In view of the carboxylation products derived from the same adduct it appears reasonable to assume that the 1:2-dihydrochrysene is obtained.

Ultraviolet absorption spectra.

Chrysene		1:2-Dihydrochrysene		1:2-Dimethylchrysene ^a		2-Phenyl-naphthalene ^b	
λ	$\log \epsilon$	λ	$\log \epsilon$	λ	$\log \epsilon$	λ	$\log \epsilon$
220	4.50	216	4.48	—	—	—	—
241	4.32	—	—	—	—	—	—
257	4.86	255	4.73	—	—	251	4.8
266.5	5.13	264	4.88	274	4.95	272	4.1
281	4.08	282	3.96	—	—	—	—
293	4.07	292—293	4.07	—	—	288	4.1
304	4.10	303	4.15	304	3.96	—	—
317	4.10	316	4.06	323	4.08	—	—
6:7 Dihydro-3-methyl-cholanthrene ^b		1:2-Dihydrochrysene-1:2-dicarboxylic acid		1:2 Dihydrochrysene-1:2-dicarboxylic anhydride		Chrysene-1:2-dicarboxylic anhydride	
λ	$\log \epsilon$	λ	$\log \epsilon$	λ	$\log \epsilon$	λ	$\log \epsilon$
—	—	216	4.43	216	4.43	222	4.52
—	—	238	4.28	239	4.32	—	—
~263	4.67	—	—	247	4.66	—	—
272	4.7	264	4.81	266	4.77	270	4.91
—	—	293	4.02	293	4.03	—	—
—	—	302	4.09	304	4.08	302—303	4.04
314	4.1	314	4.00	316	4.00	314—315	4.08

^a Jones, *J. Amer. Chem. Soc.*, 1941, **63**, 313. ^b Fieser and Herschberg, *ibid.*, 1938, **60**, 940.

Brode and Patterson⁸ report that comparison of the ultraviolet spectra of 1- and 12-methylchrysene with that of chrysene reveals bathochromic and hypochromic shifts

⁵ Jeanes and Adams, *J. Amer. Chem. Soc.*, 1937, **59**, 2608.

⁶ Funke, Müller, and Vadasz, *J. prakt. Chem.*, 1936, **144**, 265; Funke and Ristic, *ibid.*, 1936, **146**, 151.

⁷ Randall, Fowler, Fuson, and Dangl, "Infrared Determination of Organic Structures," Van Nostrand Co. Inc., New York, 1949, p. 163.

⁸ Brode and Patterson, *J. Amer. Chem. Soc.*, 1941, **63**, 3253.

greater than those observed for the other monomethylchrysenes, owing to steric interference between the 1-hydrogen atom and the 12-methyl group. These differences are more marked in the case of 1:2-dimethylchrysene,⁹ and a similar effect is shown by chrysene-1:2-dicarboxylic anhydride, the spectrum of which is similar to that of 1:2-dimethylchrysene. On the other hand the ultraviolet spectra of 1:2-dihydrochrysene and its 1:2-dicarboxylic acid and anhydride do not greatly differ from that of chrysene itself in the 200—320 $m\mu$ region, the most intense band being found about 266 $m\mu$. In the substituted compounds the intensities of the absorption bands are, however, somewhat lower. These results suggest that there is little steric interference by tetrahedrally directed substituents at positions 1 and 2 and this is confirmed by molecular models.

EXPERIMENTAL

Microanalyses were carried out by Miss M. Corner, Mrs. A. Grant, and Mrs. D. Butterworth of this laboratory. Ultraviolet absorption spectra of solutions in EtOH were measured by means of a Unicam S.P. 500 spectrophotometer.

Infrared absorption spectra of solids dispersed in potassium chloride discs were measured on a modified Hilger D 209 double-beam instrument¹⁰ with rock-salt prism; only the strong and the medium-strength bands are reported, these being correct to ± 3 cm^{-1} .

Purification of Chrysene.—A commercially available sample was passed in benzene through a column of decolorising charcoal. Concentration of the eluate gave white leaflets of chrysene, m. p. 255—256 (ultraviolet absorption, see Table), showing blue-violet fluorescence in ultraviolet light superior in this property to a sample refined by zone-melting.

Comparison of Reaction of Chrysene with Sodium in Various Solvents.—A qualitative estimation of this reaction by colour formation was made as follows: Chrysene (100 mg.) was dissolved in 50 ml. portions of dry (i) tetrahydrofuran, (ii) 1:2-dimethoxyethane, (iii) diethyl ether. Complete dissolution was achieved with the first two solvents, but only partial in the third, by bubbling dry nitrogen through each solution. A 20% dispersion of sodium in xylene (4 ml.) was added, and the tubes were stoppered and left at room temperature. The observations are summarised.

Time	Dimethoxyethane	Tetrahydrofuran	Diethyl ether
20 min.	Pale green	Colourless	Colourless
18 hr.	Pale green	Slight colour	Colourless
40 hr.	Pale green	Dark green	Colourless
113 hr.	Dark green	Dark green	Colourless

Treatment of the Sodium-Chrysene Addition Compound with Carbon Dioxide.—A suspension of chrysene (20 g.) in 1:2-dimethoxyethane (400 ml.) was added to a sodium dispersion (50% of sodium in decalin; 18 ml.) stirred under nitrogen, the temperature being kept at 19—24° by cooling. A deep green colour developed and in 4 hours' stirring the solid product was deposited. The mixture was cooled to -65° and dry carbon dioxide was passed over the stirred mixture for 1.5 hr., during which the green colour became discharged and a yellow suspension was formed. After filtration and washing with benzene, the product was dried in a vacuum-desiccator. Cautious treatment with ice-water and filtration removed unchanged chrysene (7.9 g.). Addition of hydrochloric acid to the filtrate precipitated the crude acid, which was filtered off, washed with water, and dried at 100° (yield 15 g.). Recrystallisation from acetic acid gave the 1:2-dihydrochrysene-1:2-dicarboxylic acid, m. p. 280° (decomp.) (Found: C, 75.4, 75.3; H, 4.45, 4.5%; equiv., 161.5. $C_{20}H_{14}O_4$ requires C, 75.5; H, 4.4%; equiv., 159), ν ca. 3066, ca. 2893, ca. 2650, 1732, 1699, 1606, 1410, 1287, 1239, 1225, 1198, 1166, 1149, 812, 762, and 735 cm^{-1} .

Treatment of the acid in methanol-ether with ethereal diazomethane gave the *dimethyl ester* which, recrystallised from light petroleum (b. p. 60—80°), had m. p. 165.5° (Found: C, 76.3; H, 5.2. $C_{22}H_{18}O_4$ requires C, 76.3; H, 5.2%). Hydrolysis of the ester with aqueous-methanolic alkali regenerated the starting material.

Treatment of the Sodium-Chrysene Adduct with Ethanol.—The sodium adduct was prepared from chrysene (8 g.) as described above, and the bulk of the dimethoxyethane removed by

⁹ Jones, *J. Amer. Chem. Soc.*, 1941, **63**, 313.

¹⁰ Hales, *J. Sci. Instr.*, 1949, **26**, 359; 1953, **30**, 52.

distillation. Ethanol (100 ml.) was added and the mixture warmed. After cooling, unchanged chrysene (5 g.) was filtered off and concentration of the filtrate gave the dihydrochrysene (2.8 g.), m. p. 171—173° (from ethanol; charcoal) (Found: C, 94.0; H, 5.9. Calc. for $C_{18}H_{14}$: C, 93.9; H, 6.1%), ν 1612, 1484, 1431, 1381, 1270, 1205, 1029, 864, 817, 763, 758, and 734 cm^{-1} .

1 : 2-Dihydrochrysene-1 : 2-dicarboxylic Anhydride.—(i) Heating 1 : 2-dihydrochrysene-1 : 2-dicarboxylic acid (2 g.) at 280—290° for 2 hr. caused a loss in weight of 0.25 g. The solid product, recrystallised twice from benzene as yellow prisms (1.2 g.), was the *anhydride*, m. p. 251—252° (Found: C, 79.7; H, 4.25. $C_{20}H_{12}O_3$ requires C, 80.0; H, 4.0%), ν 1858, 1771, 1492, 1234, 1205, 1198, 1070, 1038, 1028, 1001, 924, 898, 879, 859, 825, 769, 755, and 716 cm^{-1} .

(ii) The dicarboxylic acid (2 g.) was refluxed with acetic anhydride (50 ml.) for 6 hr. Most of the acetic acid was removed by distillation, the remainder by azeotropic distillation with benzene, to give the solid anhydride, m. p. and mixed m. p. 251—252° (from benzene) (1.35 g.) (Found: C, 80.1; H, 4.2%).

The anhydride (280 mg.) was treated with 10% sodium hydroxide solution (50 ml.) at room temperature for 48 hr. A little insoluble material was filtered off and the solution acidified with dilute hydrochloric acid at 0°. The white precipitate, which was immediately filtered off and washed with water, gradually became buff, had m. p. 267—268° (decomp.) and was orange after being kept overnight [m. p. 250—255° (decomp.)]. The bulk of the precipitate, however, was immediately treated in methanol with ethereal diazomethane. The diester recrystallised from light petroleum (b. p. 80—100°) as prisms, m. p. and mixed m. p. 163—165°.

Dichromate Oxidation of 1 : 2-Dihydrochrysene-1 : 2-dicarboxylic Acid.—To the acid (1.35 g.) in refluxing acetic acid (50 ml.) was added portionwise solid potassium dichromate (7 g.). After 1 hr. part of the acid was distilled off and the residue poured into ice-water. The precipitated solid (0.75 g.) was recrystallised from acetone (m. p. 237—238°) and was shown to be 1 : 2-chrysoquinone by comparison with an authentic specimen (mixed m. p. and infrared spectrum) (Found: C, 83.6; H, 3.8. Calc. for $C_{18}H_{10}O_2$: C, 83.7; H, 3.9%).

Chromium Trioxide Oxidation of 1 : 2-Dihydrochrysene-1 : 2-dicarboxylic Anhydride.—Chromium trioxide (1.3 g.) in acetic anhydride (20 ml.) was added to a solution of 1 : 2-dihydrochrysene-1 : 2-dicarboxylic anhydride (1.0 g.) in the same solvent at 80°, and heated for 15 min. on the steam-bath, whereafter a little insoluble material was filtered off and the solution cooled in ice, to give orange crystals. Recrystallisation from benzene gave orange needles of *chrysene-1 : 2-dicarboxylic anhydride*, m. p. 218—219° (Found: C, 80.4; H, 3.35. $C_{20}H_{10}O_3$ requires C, 80.5; H, 3.35%), ν 1816, 1756, 1274, 1227, 1193, 1160, 933, 828, 806, 785, 755, 745, and 726 cm^{-1} .

This anhydride (1.0 g.) was treated with aqueous sodium hydroxide (4 g. in 120 ml. of water) at room temperature for 48 hr. The pale buff insoluble matter was removed by filtration and washed with water. Addition of the washings to the filtrate caused precipitation of a white solid, which on filtration, dissolution in water, and acidification by hydrochloric acid gave a pale yellow precipitate, recrystallising from acetic acid as orange needles, m. p. 218—219°. A mixed m. p. with the starting anhydride gave no depression.

We thank Dr. J. Idris Jones for his interest and encouragement, and Mr. W. Kynaston for measurement of the infrared spectra. The work described formed part of the research programme of the Chemical Research Laboratory and is published by permission of the Director.