precipitate was removed from the resulting slurry by centrifugation. The supernatant solution was transferred to a graduated storage vessel by means of a nitrogen pressure siphon which excluded air at all times. The concentration of the organomagnesium compound was determined by titration of an acid hydrolyzed aliquot with standard base using phenolphthalein as the indicator. The yields of the dialkylmagnesium compound by this method varied from 62–76%.

Reaction of Grignard reagent and dialkylmagnesium compounds with diisopropyl ketone. In each reaction 11.4 g. (0.1 mole) of diisopropyl ketone, diluted to 50 ml. with anhydrous ether, was added over a period of 2 hours to a rapidly stirred solution of the organomagnesium compound. The concentration of the organomagnesium compound was adjusted before the reaction so that it would be approximately 1 *N*. The number of equivalents[15] of organomagnesium compound per 0.1 mole of ketone can be obtained by multiplying a particular value in column 2, Table I, by 0.1. In reactions involving both Grignard and dialkylmagnesium compounds it was noted that as each drop of ketone hit the solution a faint yellow color developed and immediately disappeared. The temperature of the reaction mixture during addition was maintained between 30 and 35°. After addition was completed, the solution was stirred for two additional hours at room temperature and then allowed to stand overnight. The reaction mixture was hydrolyzed with just enough water so that the magnesium hydroxide formed was crystalline.[16] The ether solution was decanted from the crystals of magnesium hydroxide and the precipitate was washed several times with anhydrous ether. Combined ether solutions were dried over a small amount of anhydrous magnesium sulfate and most of the ether removed by fractionation through a 2 ft. column packed with 1/8-in. Pyrex helices. The product ratios were determined by gas-liquid partition chromatography of the residue. Values were calculated from area per cent in comparison with known standard mixtures. The material balance was obtained in the same way based on the total weight of concentrated reaction mixture. The accuracy of the values for the ratio of the products was slightly better than the values determined for the material balance, as the latter included the determination of the amount of solvent ether in the concentrate which was the major component.

STANFORD, CALIF.

(15) By definition: 1 equivalent of Grignard equals 1 formula weight of $RMgX$ or $^1/_2$ formula weight of $R_2Mg \cdot MgX_2$; 1 equivalent of dialkylmagnesium equals $^1/_2$ formula weight of R_2Mg.

(16) B. F. Landrum and C. T. Lester, *J. Am. Chem. Soc.*, **74**, 4954 (1952).

[CONTRIBUTION FROM THE DEWEY & ALMY A.-G.]

Reaction of Metallic Sodium with Naphthalene.[1] Dihydronaphthalenedicarboxylic Acids-1,4 and -1,2 and Related Compounds

THEODOR M. LYSSY[2]

Received August 21, 1961

The reaction product of the carbonation of sodiumnaphthalene was investigated. It consists of an isomeric mixture of dihydronaphthalenedicarboxylic acids, the carboxyl groups being in position 1,4 and 1,2, in agreement with the mechanism proposed by D. E. Paul, D. Lipkin, and S. I. Weissmann.[3] The isomers of dihydronaphthalene-and tetralindicarboxylic acid-1,4 and -1,2 and the anhydrides of the 1,2-acids were isolated and/or prepared, and the configuration thereof demonstrated. The ΔpK^*_{MCS} values of the dicarboxylic acids are discussed.

J. F. Walker and N. D. Scott[4] were the first to describe the preparation of dihydronaphthalenedicarboxylic acids from sodiumnaphthalene and carbon dioxide in ethereal solvents. In the course of their investigation they found two product fractions. One contained a dicarboxylic acid, m.p. 230°, which is practically insoluble in hot or cold water. The authors claimed to have isolated 1,4-dihydronaphthalenedicarboxylic acid-1,4 (IIa/IIIa); however, it was later shown by Stanley Hsi-Kwei Jiang[5] that the acid in question was 1,2-dihydronaphthalenedicarboxylic acid-1,4 (IVa). None of the authors reported any stereo isomers. The other acid fraction (m.p. range 140–180°) which is readily soluble in hot water and organic solvents was said to consist of 1,2-dihydronaphthalenedicarboxylic acid-1,2.[4]

1,2-Dihydronaphthalenedicarboxylic acid-1,2 and related compounds are described extensively by K. Alder and K. Triebeneck[6] who treated maleic anhydride with α-bromostyrene in boiling toluene to receive, after subsequent elimination of hydrogen bromide, followed by saponification, 1,2-dihydronaphthalenedicarboxylic acid-1,2 (XIIIa/XVIIa).

Methods. Ultraviolet spectroscopy was used to establish the position of double bonds. *Infrared spectroscopy* was helpful in isolated cases. The *micro titrations* of the dicarboxylic acids were carried out by the method of W. Simon and E.

(1) Part of this work was presented at the spring meeting of the Swiss Chemical Society, February 1960, in Geneva, Switzerland.

(2) Present address: Department of Chemistry, Swiss Federal Institute of Technology, Zurich, Switzerland (ETH).

(3) D. E. Paul, D. Lipkin, and S. I. Weissmann, *J. Am. Chem. Soc.*, **78**, 116 (1956).

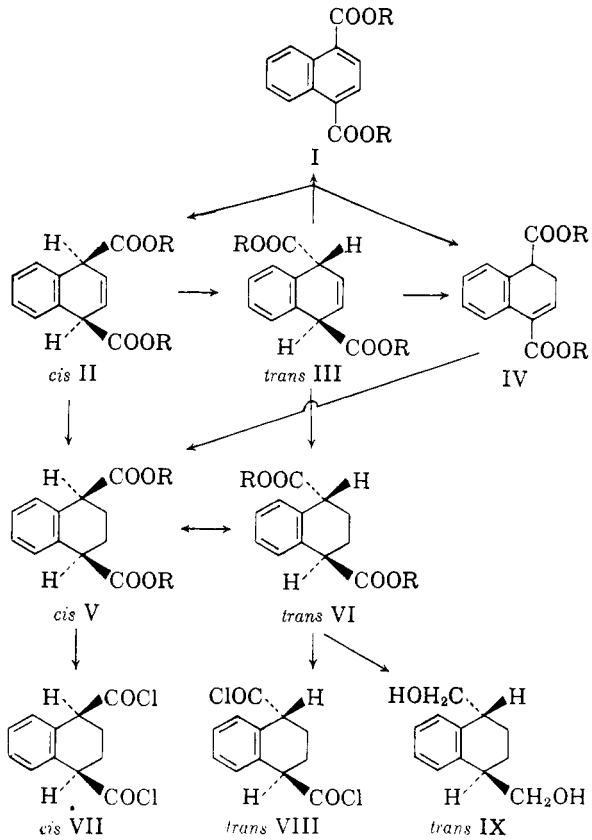
(4) J. F. Walker and N. D. Scott, *J. Am. Chem. Soc.*, **60**, 951 (1938).

(5) Stanley Hsi-Kwei Jiang, *Hua Hsüeh Pao*, **23**, 351 (1957); *Chem. Abstr.*, 15481 (1958).

(6) K. Alder and K. Triebeneck, *Ber.*, **87**, 237 (1954).

CHART I

1,4-Acids
a. R = H
b. R = CH_3



Heilbronner[7] who have shown that an "apparent dissociation constant" pK^*_{MCS}, which can be determined in Methyl Cellosolve (MCS), is a valuable tool in the characterization of dicarboxylic acids. It was possible to confirm the configuration of corresponding *cis* and *trans* isomers by their ΔpK^*_{MCS} values. Moreover, interesting information was gained concerning pK values of 1,4- and 1,2-dicarboxylic acids.

RESULTS AND DISCUSSION

Investigating the two product fractions described above, we have found that the water-insoluble fraction consists mainly of *trans*-1,4-dihydronaphthalenedicarboxylic acid-1,4 (IIIa) but is still contaminated with 1,2-dihydronaphthalenedicarboxylic acid-1,2 (XIIIa/XVIIa). The water-soluble acid fraction contains all isomers of the dihydronaphthalenedicarboxylic acid-1,2, as well as the highly water-soluble *cis* isomer of the 1,4-dihydronaphthalenedicarboxylic acid-1,4 (IIa) which has not been described so far. The present paper is concerned with the isomers of dihydronaphthalene- and tetralindicarboxylic acids-1,4 and -1,2 and the configuration as well as some derivatives thereof.

A. Dihydronaphthalenedicarboxylic acids-1,4 and related compounds. Sodium reacted with naphthalene in ethylene glycol dimethyl ether (EGDME),[8] and the product was carbonated at low temperatures. Acidification of the aqueous sodium salt solution precipitated *trans*-1,4-dihydronaphthalenedicarboxylic acid-1,4 (IIIa), m.p. 220–223°. (The mother liquor will be described below.) On prolonged heating of the melt of IIIa, the double bond shifted to the 1-position, and the compound crystallized again to melt at 231–233° (IVa). The same isomerization is achieved by subliming IIIa and/or by treating it with a 1*N* sodium hydroxide solution.[5] This shift of the double bond from position 2 to 1 resulted in a displacement and an enhancement of the ultraviolet absorption from 263 mμ (ε 408) to 271 mμ (ε 5170).[5]

Hydrogenation of IIIa gave *trans*-tetralindicarboxylic acid-1,4 (VIa), m.p. 226–228°. Hydrogenation of IVa gave *cis*-tetralindicarboxylic acid-1,4 (Va) in quantitative yield. The *cis* isomer Va is much more soluble in water than the corresponding *trans* derivative VIa and thus can be crystallized from hot water, m.p. 188–189°. The assignment of the *trans* and *cis* configuration, respectively, to the two tetralindicarboxylic acid-1,4 isomers is supported by its physical properties which are analogous to those of the cyclohexanedicarboxylic acids-1,4 and the isomers of Δ^2-tetrahydroterephthalic acid (see Table I) as well as by their genesis. While the hydrogenation of IIIa to VIa is a straightforward reduction with no influence on the configuration (which evidently was *trans*) of the two carboxyl groups, the catalytic hydrogenation of IVa produces a new asymmetric center; the hydrogen-bearing catalyst is more likely to approach the molecule from the side opposite the noncoplanar carboxyl group to yield *cis*-tetralindicarboxylic acid-1,4 (Va) (Fig. 1).

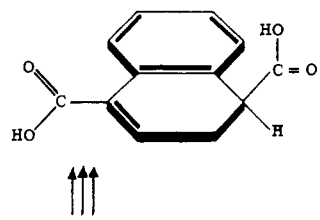


Figure 1

Moreover, the assigned configurations were strongly supported by the difference of the corresponding ΔpK^*_{MCS} values.[7] The titration curve of the *trans* derivative VIa showed only one break (like a monobasic acid) and the ΔpK^*_{MCS} of 1.27 was calculated by an approximation method.[7]

(7) W. Simon, *Helv. Chim. Acta*, **41**, 1835 (1958); and references cited therein.

(8) N. D. Scott, J. F. Walker, and V. L. Hansley, *J. Am. Chem. Soc.*, **58**, 2442 (1936).

CHART II

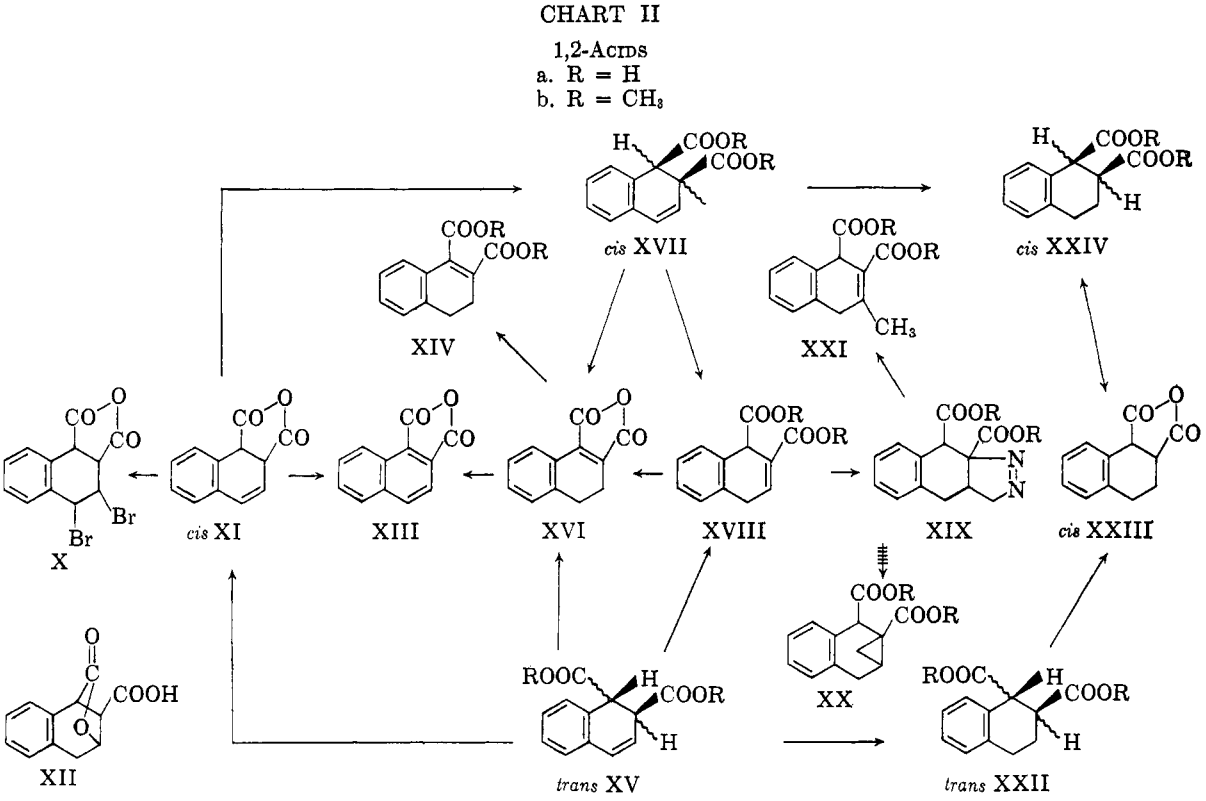


TABLE I

Compound	M.P.	ΔpK	Solubility in Water, % 20–24°	95–100°
1. *trans*-Tetralindicarboxylic acid-1,4 (VIa)	226–228	1.27[a]	0.22	3.05
2. *cis*-Tetralindicarboxylic acid-1,4 (Va)	188–189	1.77[a]	0.89	93.5
3. *trans*-Δ^2-Tetrahydrotereph-thalic acid[c]	228	0.995[b]	0.17	Good[e]
4. *cis*-Δ^2-Tetrahydroterephthalic acid[c]	161	1.05[b]	2.70	Inf.[e]
5. *trans*-Cyclohexanedicarboxylic acid-1,4	312–313	1.23[b,d]	0.086	0.135[e]
6. *cis*-Cyclohexanedicarboxylic acid-1,4	170–171	1.48[b,d]	Better than No. 5	

[a] ΔpK^*_{MCS}. [b] ΔpK_{H_2O}. [c] See ref. 9. [d] R. Kuhn and A. Wassermann, *Helv. Chim. Acta*, **11**, 65 (1928). [e] A. v. Baeyer, *Ann.*, **251**, 308 (1894).

The *cis* acid Va exhibited a double break curve from which a ΔpK^*_{MCS} of 1.77 was deduced. Finally, the configurations of the two isomers Va and VIa were proved by separating the *trans*-tetralindicarboxylic acid-1,4 (VIa) into its optical antipodes by way of the brucine salt.[9] It was possible to isolate the 1-isomer, m.p. 239–242°, $[\alpha]_D^{20}$ −45° in pure form.

The *cis*-tetralindicarboxylic acid-1,4 (Va) was isomerized to the *trans*-tetralindicarboxylic acid-1,4 (VIa) by refluxing with concentrated hydrochloric acid for sixteen hours.[10] However, treatment of a sodium salt solution (*p*H 8.5) of *trans*-tetralindicarboxylic acid-1,4 (VIa) for three hours at 270° led, after acidification, to a mixture of the *cis* and *trans* isomers, m.p. 170–178°. It was possible to separate the two isomers analytically by paper chromatography.[11] R_F [*cis*-tetralindicarboxylic acid-1,4 (Va)] 0.059; R_F [*trans*-tetralindicarboxylic acid-1,4 (VIa)] 0.0225.

In addition, the following derivatives of tetralindicarboxylic acid-1,4 were prepared: *trans*- and *cis*-tetralindicarboxylic acid-1,4 dichloride (VIII and VII); *trans*- and *cis*-tetralindicarboxylic acid-1,4-dimethyl ester (VIb and Vb); *trans*-1,4-bis(hydroxymethyl)tetralin (IX).

The acidified mother liquor of the carbonation product of sodiumnaphthalene (water-soluble fraction) was continuously extracted with diethyl ether. Treatment of the resinous material with diisopropyl ether yielded a white, insoluble powder, which will be discussed under B. From the diisopropyl ether, it was possible to isolate *cis*-1,4-

(9) W. H. Mills and G. H. Keats, *J. Chem. Soc.*, 1374 (1935).

(10) (a) A. v. Baeyer, *Ann.*, **251**, 308 (1894); *Ann.*, **251**, 257 (1894). (b) F. Ramirez and T. Sargent, *J. Am. Chem. Soc.*, **74**, 5785 (1952).

(11) Separated in the laboratory of PD Dr. A. Dreiding at the University of Zurich by the ascending method, using butanol-ammonia (1:1) as solvent mixture at 21.5°.

dihydronaphthalenedicarboxylic acid-1,4 (IIa), m.p. 154.5–156.5°. IIa does not absorb in the ultraviolet region; hence the double bond was assigned to the 2- position. Despite the high ΔpK^*_{MCS} number of 5.26 (which is unexpected for a 1,4-dicarboxylic acid), the *cis*-1,4-dihydronaphthalenedicarboxylic acid-1,4 (IIa) does not give an anhydride on refluxing with acetic anhydride. Proof of the *cis* structure IIa was accomplished by the catalytic reduction of IIa which gave *cis*-tetralindicarboxylic acid-1,4 (Va). On heating above the melting point, the substance IIa crystallized again, melted at 213–216° and crystallized a third time to melt finally at 233–234°. Titrations (ΔpK^*_{MCS}), ultraviolet and mixed melting point of the purified isomerized substances showed that the isomerization produced successively *trans*-1,4-dihydronaphthalenedicarboxylic acid-1,4 (IIIa) and 1,2-dihydronaphthalenedicarboxylic acid-1,4 (IVa).

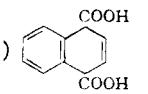
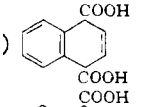
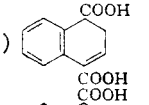
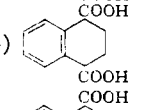
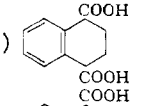
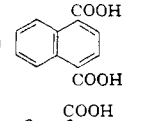
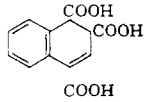
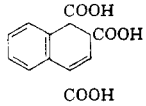
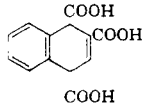
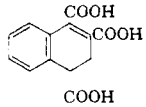
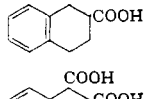
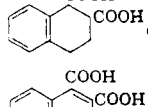
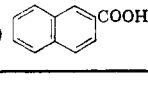
B. Dihydronaphthalenedicarboxylic acids-(1,2) and related compounds. The mother liquor of the acidified carbonation product of sodiumnaphthalene was continuously extracted with diethyl ether and the solvent removed. Treatment of the resinous material with diisopropyl ether yielded *trans*-1,2-dihydronaphthalenedicarboxylic acid-1,2 (XVa) as an insoluble white powder. The product XVa is obtained from the above mother liquor, if the latter is allowed to stand after removal of the *trans*-1,4-dihydronaphthalenedicarboxylic acid-1,4 (IIIa), m.p. 182–184°. The ultraviolet spectrum with maxima at 216–217 mμ (ε 19,300) and 262 mμ (ε 9280) showed that the double bond is in conjugation with the aromatic ring. Proof of the *trans* configuration of XVa was obtained by the catalytic reduction of XVa with Raney Nickel, which gave *trans*-tetralindicarboxylic acid-1,2 (XXIIa). The low ΔpK^*_{MCS} of 1.75 is in agreement with above findings. Treatment of XXIIa with acetic anhydride, followed by saponification, gave *cis*-tetralindicarboxylic acid-1,2 (XXIVa).[12]

Treatment of *trans*-1,2-dihydronaphthalenedicarboxylic acid-1,2 (XVa) with acetic anhydride yielded 3,4-dihydronaphthalenedicarboxylic acid-1,2 anhydride (XVI), m.p. 125–126° (λ_{max} 290 mμ; ε 14,040),[6] with comcomitant shifting of the double bond. Treatment of XVa with acetyl chloride at room temperature gave a mixture of anhydrides consisting to the extent of 80% of 1,2-dihydronaphthalenedicarboxylic acid-1,2 anhydride (XI) as calculated from the intensity of the ultraviolet absorption. Saponification of the yellow anhydride XVI with strong alkali gave the corresponding dicarboxylic acid XIVa (λ_{max} 290 mμ; ε 15,920).

Distillation of the resinous material from the mother liquor of the *trans*-1,4-dihydronaphthalenedicarboxylic acid-1,4 (IIIa) gave a mixture of isomeric anhydrides originating from the 1,2-dicarboxylic acids. Recrystallization from diisopropyl ether yielded *cis*-1,2-dihydronaphthalenedicarboxylic acid-1,2 anhydride (XI). The dibromo derivative X melted at 204–205°.[6] Hydrolysis of XI gave *cis*-1,2-dihydronaphthalenedicarboxylic acid-1,2 (XVIIa), which, on treatment with acetic anhydride in the heat, yielded the anhydride XVI. Reduction of XVIIa produced *cis*-tetralindicarboxylic acid-1,2 (XXIVa),[13] m.p. 180–182°. Hydrogenation of the crude extracted material from the mother liquor (see above), followed by distilla-

TABLE II

TABLE OF COMPOUNDS

Compound		UV-spectra λ_{max} (mμ)	ε	M.P.	ΔpK^*_{MCS}
1) 	*trans*	263	408	220–222	1.37
2) 	*cis*	263	195	154.5–156.5	5.25
3) 		271	5,170	235–236	1.19
4) 	*trans*	263	205	227.5–228.5	1.27
5) 	*cis*	264	208	188–189.5	1.77
6) 		310	7,300	319–321	1.76
7) 	*trans*	262	9,280	182–184	1.79
8) 	*cis*	263	8,820	179–181	3.12
9) 		—	—	219–221	2.51
10) 		290	15,920	131.5–132.5	2.66
11) 	*trans*	—	—	163–164	2.02
12) 	*cis*	268 273	296 257	180–182	3.24
13) 		272 284 294	5,770 6,980 5,600	164–166	2.04

(12) R. D. Haworth and F. H. Slinger, *J. Chem. Soc.*, 1321 (1940).

(13) K. Alder and R. Schmitz-Josten, *Ann.*, 595, 10 (1955).

tion gave directly *cis*-tetralindicarboxylic acid-1,2 anhydride (XXIII) which, on hydrolysis, led to the corresponding acid XXIVa.

The dimethyl ester of the *trans*-1,2-dihydro acid XVb was prepared from(a) methanol and sulfuric acid and(b) diazomethane. Alkaline hydrolysis gave 1,4-dihydronaphthalenedicarboxylic acid-1,2 (XVIIIa), m.p. 219–221° (under evolution of gas).[14] The same product XVIIIa was obtained (a) by treating the free acid XVa with 2*N* sodium hydroxide solution in the heat and (b) by treating the anhydride XI with 2*N* sodium hydroxide solution at room temperature. XVIIIa does not absorb in the ultraviolet region. The infrared absorption spectrum exhibited bands at 1700 and 1665 cm.$^{-1}$ (carbonyl groups: saturated and α,β-unsaturated) which rule out the possibility of the lactone XII. Esterification of the acid XVIIIa with methanol and sulfuric acid gave the dimethyl ester XVIIIb (lit.[4] m.p. 71–72°), however, treatment of the acid XVIIIa with diazomethane led to the pyrazoline derivative XIXb which is further proof of the structure of the 1,4-dihydronaphthalenedicarboxylic acid-1,2 (XVIIIa).[15] The infrared spectrum of the pyrazoline derivative XIXb exhibited a band at 1745 cm.$^{-1}$ (nonconjugated ester carbonyl). Bands at 3320 cm.$^{-1}$ (N—H), 1715 cm.$^{-1}$ (conjugated ester carbonyl) and 1570 cm.$^{-1}$ (C=N) are missing. The N=N absorption is too weak to be detected.[16]

Distillation of the crystalline pyrazoline product XIXb gave 1,4-dihydro-3-methyl-naphthalenedicarboxylic acid-1,2-dimethyl ester (XXIb) as a water-white liquid. The infrared spectrum showed a new absorption band at 1660 cm.$^{-1}$ which can be assigned to the double bond. Maxima at 3340 cm.$^{-1}$ and 1555 cm.$^{-1}$ indicating the presence of a cyclopropane ring (XXb), are absent. Maxima at 1380 cm.$^{-1}$ and 2960 cm.$^{-1}$ are due to the methyl group vibrations. Final proof of the structure XXIb was obtained from the NMR spectrum.[17]

Analogous to the *cis*- and/or *trans*-1,2-dihydronaphthalenedicarboxylic acid-1,2 (XVIIa and XVa, respectively), sublimation, distillation, and/or treatment with acetic anhydride yielded in all cases 3,4-dihydronaphthalenedicarboxylic acid-1,2-anhydride (XVI). Dehydrogenation of XI and/or XVI with sulfur[4] gave 1,2-naphthalenedicarboxylic acid anhydride (XIII).

EXPERIMENTAL[18]

Melting points are corrected and were determined in an open capillary tube in a Tottoli melting point apparatus, (silicone oil) made by W. Büchi, Flawil, Switzerland. *Infrared spectra* were taken on a Perkin-Elmer 21 double-beam spectrograph, the *ultraviolet spectra* on a Beckman DK 1 spectrograph. Analyses were made by Mr. W. Manser (Swiss Federal Institute of Technology (ETH), Zurich).

(1) *trans-1,4-Dihydronaphthalenedicarboxylic acid-1,4* (IIIa). Naphthalene (512 g., 4 moles) and 2000 ml. of dry ethyleneglycol dimethyl ether were charged to a 4-l. three necked flask, equipped with stirrer and gas inlet. The reaction flask was kept under positive nitrogen pressure and stirred until the naphthalene was completely dissolved. Sodium (97 g., 4.218 g.-atoms) was added in form of shavings; the solution turned green and the temperature rose to about 40°. Stirring was continued for 16 hr. The sodiumnaphthalene solution was added by means of a syphon system under rapid stirring to a slurry of Dry Ice in ethyleneglycol dimethyl ether at −70°. After the excess carbon dioxide had evaporated, the sodium salt suspension was filtered, dissolved in water, extracted with petroleum ether (b.p. 30-60°) (to remove naphthalene), filtered, and acidified at 0–5° with concd. hydrochloric acid in the presence of little diisopropyl ether which promotes crystallization. The crude, light yellow *trans*-1,4-dihydronaphthalenedicarboxylic acid-1,4 (IIIa) which precipitated at once, melted in the range of 190–200°; yield 227 g. (52%). Repeated recrystallization from hot glacial acetic acid yielded colorless needles which melted at 220–222° and then crystallized again to melt at 230–232° (IVa). (Very slow heating results in a lower melting point of 208–212°, most probably due to a partial shift of the double bond to Δ1, the melting point actually being a mixed melting point.) The mother liquor, containing other acid fractions, was separately investigated (see below): ultraviolet; λ_{max} 263 mμ, ε 408. The infrared spectrum (in Nujol) shows broad maxima at 1700 cm.$^{-1}$ (C=O) and in the range of 3000 cm.$^{-1}$ (Carboxyl-OH). Titration: $pK^*_{1(MCS)}$ 6.10; $pK^*_{2(MCS)}$ 7.47; $\Delta pK^*_{(MCS)}$ 1.37.

Anal. Calcd. for $C_{12}H_{10}O_4$: C, 66.05; H, 4.62. Found: C, 66.01; H, 4.58.

(2) *trans-1,4-Dihydronaphthalenedicarboxylic acid-1,4-dimethyl ester* (IIIb). Dicarboxylic acid IIIa (7.3 g.) was dissolved in 100 ml. of absolute methanol and refluxed with 2 ml. of concd. sulfuric acid for 18 hr. Half of the solvent was removed *in vacuo;* the reaction mixture was poured in a mixture of ice water and extracted with ether. The ethereal solution was washed three times with 1*N* sodium carbonate solution under ice cooling, neutralized with sulfuric acid, washed three times with water, and dried over sodium sulfate. The ether was distilled and the oily, colorless dimethyl ester IIIb distilled *in vacuo*, b.p. 110–112°/0.02 Torr., n_D^{20} 1.5418. The dimethyl ester crystallized slowly from seeding points, m.p. 75–79°; clustering, white needles from petroleum ether m.p. 83.5–84.5°.

Anal. Calcd. for $C_{14}H_{14}O_4$: C, 68.28; H, 5.73. Found: C, 68.05; H, 5.84.

(3) *1,2-Dihydronaphthalenedicarboxylic acid-1,4* (IVa). *trans*-1,4-Dihydronaphthalenedicarboxylic acid-1,4 (IIIa) (10 g.) was dissolved in 100 ml. of a 1*N* sodium hydroxide solution and heated for 3 hr. on the steam bath. Acidification with concd. hydrochloric acid yielded a white precipitate, m.p. 224–228°. Recrystallization from glacial acetic acid gave white crystals, m.p. 235–236°. Ultraviolet: λ_{max} 271 mμ; ε 5170. Titration: $pK^*_{1(MCS)}$ 6.38; $pK^*_{2(MCS)}$ 7.57; $\Delta pK^*_{(MCS)}$ 1.19.

Anal. Calcd. for $C_{12}H_{10}O_4$: C, 66.05; H, 4.62. Found: C, 65.65; H, 4.62.

(4) *1,2-Dihydronaphthalenedicarboxylic acid-1,4 dimethyl ester* (IVb). Dicarboxylic acid IVa (10 g.) was dissolved in 50 ml. of absolute methanol, refluxed with 1 ml. of concd. sulfuric acid for 6 hr. and worked up as usual [see (2)]. The oily dimethyl ester IVb was distilled through a Vigreux

(14) Lit.[6] m.p. 237–239°.

(15) T. L. Jacobs and R. C. Elderfield, *Heterocyclic Compounds*, Vol. 5, J. Wiley & Sons, Inc., New York, 1957, Chap. 2.

(16) W. M. Jones, *J. Am. Chem. Soc.*, **81**, 5153 (1959).

(17) A band at 7.68 p.p.m. (TMS = 10.0 p.p.m.) is assigned to a methyl group, attached to a double bond. Protons of a three-membered ring (approx. 9.5 p.p.m.) are missing.

(18) Thanks are due to Mr. Reto Gredig for excellent technical assistance.

column, b.p. 115°/0.02 Torr., n_D^{20} 1.5602. Scratching induced slow crystallization, m.p. 51.2–52° (from petroleum ether).

Anal. Calcd. for $C_{14}H_{14}O_4$: C, 68.28; H, 5.73. Found: C, 68.15; H, 5.82.

(5) *trans-Tetralindicarboxylic acid-1,4* (VIa). *trans*-1,4-Dihydronaphthalenedicarboxylic acid-1,4 (IIIa) (50 g.) was suspended in a solution of 200 ml. of water plus 25 ml. of methanol. The mixture was cooled externally and an ice-cooled solution of 25 g. of sodium hydroxide in 100 ml. of water was added dropwise under vigorous stirring and cooling (to prevent any shifting of the double bond from the 2- to the 1-position). The dicarboxylic acid IIIa dissolved slowly under formation of its sodium salt. The *p*H of the sodium salt solution was kept between 7 and 8 by the addition of glacial acetic acid, the turbid solution filtered and the resulting clear solution diluted with water up to a volume of 425 ml. Hydrogenation was carried out at 120 atm., the temperature being kept between 45 and 75° for 16 hr., using 10–15% of freshly prepared Raney-nickel as catalyst. After completion of the reduction, the catalyst was removed by filtration and the *trans*-tetralindicarboxylic acid-1,4 (VIa) precipitated with concd. hydrochloric acid; white powder, m.p. 222–228°. Recrystallization from glacial acetic acid or methanol-water (1:1) raised the melting point to 227.5–228.5°. Ultraviolet: λ_{max} 263 mμ; ε 205. Titration: $pK^*_{1(MCS)}$ 6.60; $pK^*_{2(MCS)}$ 7.87; ΔpK^*_{MCS} 1.27.

Anal. Calcd. for $C_{12}H_{12}O_4$: C, 65.44; H, 5.49. Found: C, 65.43; H, 5.49 (sublimed at 172°/0.05 Torr.).

(6) *trans-Tetralindicarboxylic acid-1,4 dimethyl ester* (VIb). One gram of dicarboxylic acid VIa was dissolved in 200 ml. of dry ether and esterified under ice cooling with diazomethane which was distilled into the reaction flask from an ethereal diazomethane solution. A bright yellow color indicated the presence of an excess of esterifying agent. The solution was allowed to warm up to room temperature, then the excess diazomethane and the solvent were removed *in vacuo*. The ester VIb was distilled, yielding a colorless, oily liquid, n_D^{20} 1.5287. Esterification by means of methanol and sulfuric acid [see (2)] gave a colorless oil, b.p. 115–118°: 0.01 Torr., n_D^{20} 1.5298.

Anal. Calcd. for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50. Found: C, 67.51; H, 6.26.

(7) *cis-Tetralindicarboxylic acid-1,4* (Va). 1,2-Dihydronaphthalenedicarboxylic acid-1,4 (IVa) (9 g.) was suspended in a solution of 40 ml. of water and 4.5 ml. of methanol. The mixture was treated with a solution of 4.5 g. of sodium hydroxide in 20 ml. of water as described under (5). A total volume of 80 ml. of sodium salt solution was submitted to hydrogenation at 50°/120 atm. for 16 hr., using 1.35 g. Raney nickel as catalyst. Acidification of the filtered solution with 6.3 ml. of concd. hydrochloric acid yielded slowly crystallizing (not precipitating) white, felty needles; yield 6.5 g. (72%), m.p. 185–187°. Continuous extraction of the mother liquor with ether gave 2 g. more of slightly impure *cis*-tetralin acid Va, m.p. 188–189.5° (from acetone-water). Ultraviolet: λ_{max} 264 mμ; ε 208. Titration: $pK^*_{1(MCS)}$ 6.15; pK^*_{2MCS} 7.92; ΔpK^*_{MCS} 1.77.

Anal. Calcd. for $C_{12}H_{12}O_4$: C, 65.44; H, 5.49. Found: C, 65.34; H, 5.44.

(8) *cis-Tetralindicarboxylic acid-1,4 dimethyl ester* (Vb). Dicarboxylic acid Va was treated with diazomethane as described under (6), yielding a colorless, oily liquid, n_D^{20} 1.5292; b.p. 97/100°/0.01 Torr.

(9) *Transformation of cis-acid Va into trans-acid* VIa. (a) *cis*-Acid Va (1 g.) was refluxed overnight in concd. hydrochloric acid. On cooling, a product crystallized from the solvent, melting at 222–227°; mixed m.p. with the *trans*-acid VIa gave no depression. (b) Sublimation of the *cis*-acid Va at 172°/0.05 Torr., yielded a compound of unchanged brutto formula, m.p. 158–172°, obviously a mixture of *cis*- and *trans*-acid. The two isomers could be separated analytically by paper chromatography.[11] R_F *cis*-acid Va: 0.059; R_F *trans*-acid VIa: 0.0225.

(10) *trans-Tetralindicarboxylic acid-1,4 dichloride* (VIII). *trans*-Acid VIa (20 g.) was mixed with 100 ml. of thionyl chloride at room temperature. Dimethylformamide (0.5 ml.) was added as catalyst, and the reaction mixture allowed to stand overnight. The acid VIa went slowly into solution. The excess thionyl chloride was removed *in vacuo*, and the crude, practically white diacid chloride VIII was recrystallized from petroleum ether yielding thick prisms, m.p. 79–80°; yield, 80%.

Anal. Calcd. for $C_{12}H_{10}O_2Cl_2$: C, 56.05; H, 3.92. Found: C, 56.06; H, 3.98.

(11) *cis-Tetralindicarboxylic acid-1,4 dichloride* (VII). *cis*-Acid Va (6.6 g.) was treated with 50 ml. of thionyl chloride and 0.3 ml. of dimethylformamide as described above. The reaction is fast, and the acid goes into solution within 3–5 min., whereby the reaction mixture cools down. The clear solution was filtered and the solvent removed *in vacuo*. The light yellow, partly crystalline diacid chloride VII was dissolved in hot petroleum ether, leaving some insoluble oily resin which was filtered off and discarded. Needles from petroleum ether, m.p. 55.5–56°.

Anal. Calcd. for $C_{12}H_{10}O_2Cl_2$: C, 56.05; H, 3.92. Found: C, 56.08; H, 3.98.

(12) *trans-1,4-Bis(hydroxymethyl)tetralin* (IX). Lithium aluminum hydride (6.25 g.) and 200 ml. of dried ether were charged to a three-necked flask, equipped with stirrer, dropping funnel, and reflux condenser. Dimethyl ester VIb (25 g.), dissolved in 200 ml. of dried ether, was slowly added to the agitated suspension so as to keep the solvent boiling gently. Stirring was continued overnight under positive nitrogen pressure. Then the reaction mixture was cooled with ice and 27 ml. of water was added with caution. Sulfuric acid (132 ml., 5*N*) was added, the ethereal solution separated, washed three times with water, dried over sodium sulfate, and the solvent removed. The oily diol IX (19.45 g.) was distilled, b.p. 151–152°/0.01 Torr. The water-white, oily liquid (15.15 g.) (78%) crystallized in the form of needles, m.p. 121–122° (from ether).

Anal. Calcd. for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.85; H, 8.45.

(13) *1,4-Naphthalenedicarboxylic acid* (Ia).[4] *trans*-1,4-Dihydronaphthalenedicarboxylic acid-1,4 (IIIa) was refluxed in 50 ml. of glacial acetic acid whereby not everything dissolved. Bromine (2 ml.), dissolved in 5 ml. of acetic acid, was added slowly to the boiling mixture. The precipitating product was filtered hot yielding 6.62 g. (84%), m.p. 319–321°. Ultraviolet λ_{max} 310 mμ, ε 7300. Titration: $pK^*_{1(MCS)}$ 5.36; $pK^*_{2(MCS)}$ 7.12; ΔpK^*_{MCS} 1.76.

Anal. Calcd. for $C_{12}H_8O_4$: C, 66.67; H, 3.73. Found: C, 66.52; H, 3.68.

(14) *cis-1,4-Dihydronaphthalenedicarboxylic acid-1,4* (IIa). The acidified mother liquor of the carbonation product of sodium naphthalene [see (1)] was continuously extracted with diethyl ether (yield, 90.4 g.). The sticky, light brown product was now treated with boiling diisopropyl ether, yielding an insoluble white precipitate which was filtered off. The ethereal solution was concentrated to give slowly crystallizing, hard, tiny, clustering crystals, deposited on the wall of the flask (22 g.). The *cis*-acid IIa, which is extremely soluble (68.6%) in hot water, was recrystallized from diisopropyl ether, m.p. 154.5–156.5°. Ultraviolet: λ_{max} 263 mμ, ε 195. Titration: $pK^*_{1(MCS)}$ 4.16; $pK^*_{2(MCS)}$ 9.42; ΔpK^*_{MCS} 5.26.

Anal. Calcd. for $C_{12}H_{10}O_4$: C, 66.05; H, 4.62. Found: C, 66.04; H, 4.69.

(15) *Rearrangement of cis-acid* IIa *to trans-acid* IIIa. *cis*-Acid IIa (850 mg.) was heated in an open tube for 2 hr. at 180°. The resulting product melted at 210–218°. Recrystallization from (a) methanol-water and (b) glacial acetic acid gave fine needles, m.p. 213–216° (under evolution of gas). Mixed m.p. with a sample of *trans*-1,4-dihydronaphthalenedicarboxylic acid-1,4 (IIIa) gave no depression. Ultraviolet: λ_{max} 263 mμ, ε 422. Titration: $pK^*_{1(MCS)}$ 6.11; $pK^*_{2(MCS)}$ 7.48; ΔpK^*_{MCS} 1.37.

Anal. Calcd. for $C_{12}H_{10}O_4$: C, 66.05; H, 4.62. Found: C, 65.97; H, 4.67.

(16) *Rearrangement of cis-1,4-dihydroacid* IIa *to 1,2-dihydroacid* IVa. One gram of *cis*-acid IIa was dissolved in 20 ml. of a 2*N* sodium hydroxide solution and heated on the steam bath for 2 hr. Acidification with concd. hydrochloric acid yielded 800 mg. of 1,2-dihydronaphthalenedicarboxylic acid-1,4 (IVa), m.p. 230–232°. Recrystallization from water raised the melting point to 233–234°; mixed m.p. with an original sample of IVa gave no depression. Ultraviolet: λ_{1max} 223 mμ, ε 12,240; λ_{2max} 271 mμ, ε 5038. Titration: $pK^*_{1(MCS)}$ 6.47; $pK^*_{2(MCS)}$ 7.63; ΔpK^*_{MCS} 1.16.

(17) *Hydrogenation of cis-1,4-dihydroacid* IIa *to cis-tetralin acid* Va. *cis*-1,4-Dihydro acid IIa (1.5 g.) was suspended in a solution of 40 ml. of water and 4 ml. of methanol. The mixture was treated with a solution of 0.75 g. sodium hydroxide in 20 ml. of water as described under (5). A total volume of 80 ml. of sodium salt solution (*p*H 7.5) was hydrogenated at 50°/120 atm. for 16 hr. using 0.5 g. Raney-nickel as catalyst. Acidification of the filtered solution with concd. hydrochloric acid yielded slowly crystallizing needles (0.85 g.) m.p. 185–187°. A mixed m.p. with a sample of *cis*-tetralindicarboxylic acid-1,4 (Va) gave no depression. Recrystallization from water raised the m.p. to 188–189.5°. Ultraviolet: λ_{max} 263 mμ, ε 230. Titration: $pK^*_{1(MCS)}$ 6.47; $pK^*_{2(MCS)}$ 8.11; ΔpK^*_{MCS} 1.64.

(18) *cis-1,4-Dihydronaphthalenedicarboxylic acid-1,4 dimethyl ester* (IIb). The dimethyl ester IIb was prepared from the acid IIa and diazomethane as described under (6). The water-white liquid could not be brought to crystallization, n_D^{20} 1.5497. The compound seems to isomerize into the *trans*-ester VIb on distillation, n_D^{20} 1.5427 after two distillations.

(19) *Decomposition of trans-tetralindicarboxylic acid-1,4* (VIa) *in optically active components by the brucine salt method.*[9] *trans*-Tetralin acid VIa (11.2 g., 0.051 mole) and 47.5 g. (0.102 mole) of brucine were heated in 515 ml. of water. On cooling, 19.55 g. of salt crystallized, m.p. 149–152°, $[\alpha]_D$ −58° (*c*, 0.92 in chloroform). Recrystallization of 18.55 g. of above salt from 162 ml. of hot water gave 13.9 g. salt, $[\alpha]_D$ −61° (*c*, 1.05 in chloroform). Further crystallization of 12.9 g. of salt ($[\alpha]_D$ −61°) from 113 ml. of hot water gave 11.17 g. of salt, $[\alpha]_D$ −63° (*c*, 1.09 in chloroform). A final recrystallization of 10.2 g. of salt from 180 ml. of hot water gave 7.34 g. of salt of unchanged rotation $[\alpha]_D$ −63°. Brucine salt, 6.34 g. recrystallized four times, ($[\alpha]_D$ −63°), was dissolved in 300 ml. of hot water and an excess of ammonium hydroxide was added. The brucine was extracted with chloroform three times and with ether once, the ammonium salt solution of the dicarboxylic acid acidified, and extracted with diethyl ether. White crystals, 1.27 g. (93%), were formed; m.p. 236–238°, $[\alpha]_D$ −45° (*c*, 1.36 in ethanol), representing 1-*trans*-tetralindicarboxylic acid-1,4. The mother liquor of the first brucine salt crystallization was concentrated *in vacuo* to yield 16.15 g., 4.82 g., and finally 4.64 g. of brucine salt. From the fourth mother liquor, the solvent was completely removed and the residue (13.5 g.) treated with ammonium hydroxide as described above; yield: 1.35 g. of *d-trans*-tetralindicarboxylic acid-1,4, m.p. 200–210°. Recrystallization from water gave m.p. 228–230°, $[\alpha]_D$ +24.5°. The impure *d-trans*-acid was not further purified.

(20) *trans-1,2-Dihydronaphthalenedicarboxylic acid-1,2* (XVa). The acidified mother liquor of the carbonation product of sodium naphthalene [after removal of the *trans*-1,4-dihydronaphthalenedicarboxylic acid-1,4 (IIIa)] was continuously extracted with diethyl ether (yield, 90.5 g.). The sticky, light brown product was now extracted with diisopropyl ether, yielding *trans*-1,2-dihydronaphthalenedicarboxylic acid-1,2 (XVa) as an insoluble, white precipitate (yield, 30.3 g.), m.p. 171–175.5°. Recrystallization from water (2 g./20 ml.) raised the m.p. to 182–184°. Ultraviolet: λ_{max} 262 mμ; ε 9050. Titration: $pK^*_{1(MCS)}$ 6.28; $pK^*_{2(MCS)}$ 8.03; ΔpK^*_{MCS} 1.75.

Anal. Calcd. for $C_{12}H_{10}O_4$: C, 66.05; H, 4.62. Found: C, 66.04; H, 4.68.

(21) *trans-1,2-Dihydronaphthalenedicarboxylic acid-1,2* (XVa). Acidification of the sodium salt solution of the carbonated sodiumnaphthalene precipitated *trans*-1,4-dihydronaphthalenedicarboxylic acid-1,4 (IIIa), which was removed by filtration. On standing, from the mother liquor precipitated *trans*-1,2-dihydronaphthalenedicarboxylic acid-1,2 (XVa) (10% yield based on the yield of *trans*-1,4-dihydronaphthalenedicarboxylic acid-1,4 (IIIa)), m.p. 175–179°. Recrystallization from ether-hexane raised the m.p. to 182–184°. Ultraviolet: λ_{1max} 216–217 mμ, ε 19,300; λ_{2max} 262 mμ, ε 9280. Titration: $pK^*_{1(MCS)}$ 6.23; $pK^*_{2(MCS)}$ 8.02, ΔpK^*_{MCS} 1.79.

Anal. Calcd. for $C_{12}H_{10}O_4$: C, 66.05; H, 4.62. Found: C, 65.98; H, 4.73.

(22) *Treatment of* XVa *with acetic anhydride. trans*-1,2-Dihydronaphthalenedicarboxylic acid-1,2 (XVa) (1 g.) was refluxed in 20 ml. of acetic anhydride for 8 hr. Removal of the solvent *in vacuo* yielded yellow crystals, m.p. 120.5–123.5°. Recrystallization from diisopropyl ether gave 3,4-dihydronaphthalenedicarboxylic acid-1,2 anhydride (XVI) in form of light green needles, m.p. 125–126°. Ultraviolet: λ_{1max} 227 mμ, ε 15,150; λ_{2max} 232 mμ, ε 14,150; λ_{3max} 290 mμ, ε 14,040.

Anal. Calcd. for $C_{12}H_8O_3$: C, 71.99; H, 4.03. Found: C, 72.07; H, 4.05.

(23) *Treatment of* XVa *with acetyl chloride. trans*-1,2-Dihydronaphthalenedicarboxylic acid-1,2 (XVa) (1 g.) was treated with 20 ml. of acetyl chloride for 12 hr. at 50°. Removal of the solvent gave a brownish oil which crystallized slowly, m.p. 106–112°. Recrystallization from diisopropyl ether gave a crystalline product (m.p. 100–104°) which consisted of 80% of 1,2-dihydronaphthalenedicarboxylic acid-1,2 anhydride (XI), calculated from the ε of the ultraviolet spectrum. Ultraviolet: λ_{max} 265 mμ, ε 6100.

(24) *3,4-Dihydronaphthalenedicarboxylic acid-1,2* (XIVa). Anhydride XVI (500 mg.) was dissolved in acetone and refluxed with water for 5 hr. The solution was treated with charcoal and filtered, yielding a slightly yellow solution from which the dicarboxylic acid XIVa crystallized on scratching, m.p. 131.5–132.5°. Ultraviolet: λ_{max} 290 mμ, ε 15,920. Titration: $pK^*_{1(MCS)}$ 5.55; $pK^*_{2(MCS)}$ 8.21, ΔpK^*_{MCS} 2.66.

Anal. Calcd. for $C_{12}H_{10}O_4$: C, 66.05; H, 4.62. Found: C, 65.99; H, 4.51.

(25) *3,4-Dihydronaphthalenedicarboxylic acid-1,2 dimethyl ester* (XIVb). The anhydride XVI (1.5 g.) was treated with methanol and concd. sulfuric acid. The resulting oily product crystallized slowly, m.p. (crude) 57–58°. Recrystallization from acetone–petroleum ether yielded white plates, m.p. 59–60°. Ultraviolet: λ_{1max} 227 mμ, ε 15,180; λ_{2max} 233 mμ, ε 14,200; λ_{3max} 292 mμ, ε 16,530.

Anal. Calcd. for $C_{14}H_{14}O_4$: C, 68.28; H, 5.73. Found: C, 68.16; H, 5.76.

(26) *Reduction of dicarboxylic acid* XVa *to trans-tetralindicarboxylic acid-1,2* (XXIIa). Dicarboxylic acid XVa was hydrogenated as described before [see (5)]. Acidification of the hydrogenated sodium salt solution yielded two kinds of crystals (small, white clustering needles and large, transparent crystals) after standing for 2 hr., yield, 1.6 g. They both melted at 158–159° and did not depress each other. Recrystallization from water raised the m.p. to 163–164°.[6] Ultraviolet: no absorption. Titration: $pK^*_{1(MCS)}$ 6.43; $pK^*_{2(MCS)}$ 8.45; ΔpK^*_{MCS} 2.02.

Anal. Calcd. for $C_{12}H_{12}O_4$: C, 65.44; H, 5.49. Found: C, 65.39; H, 5.42.

(27) *Transformation of trans-acid* XXIIa *into cis-acid* XXIVa. *trans*-Tetralindicarboxylic acid-1,2 (XXIIa) (400 mg.) was refluxed in 10 ml. of acetic anhydride for 2 hr. The solvent was removed *in vacuo* and the oily anhydride refluxed in water, yielding crystals, m.p. 177.5–180°. Recrystallization from much water gave needles, m.p. 180–182°. A mixed melting point with an authentic sample

of *cis*-tetralindicarboxylic acid-1,2 (XXIVa) gave no depression [see (31)]. Titration: $pK^*_{1(MCS)}$ 6.43; $pK^*_{2(MCS)}$ 9.32; ΔpK^*_{MCS} 2.89.

(28) *1,2-Dihydronaphthalenedicarboxylic acid-1,2 anhydride* (*cis*) (XI). The extraction product of the mother liquor of the *trans*-1,4-dihydronaphthalenedicarboxylic acid-1,4 (IIIa) was distilled *in vacuo*. The accrued yellow anhydride mixture (b.p. 128–130°/0.05 Torr.) was refluxed in diisopropyl ether, yielding *cis*-1,2-dihydronaphthalenedicarboxylic acid-1,2 anhydride (XI) as colorless plates, m.p. 110.5–111.5°. Ultraviolet: λ_{max} 265 mμ, ε 7490.

Anal. Calcd. for $C_{12}H_8O_3$: C, 71.99; H, 4.03. Found: C, 71.91; H, 4.12.

(29) *cis-3,4-Dibromotetralindicarboxylic acid-1,2 anhydride* (X).[6] One gram of anhydride XI was dissolved in 10 ml. of chloroform, and 0.25 ml. of bromine was added under shaking. The brown-red solution discolored slowly and the dibromo derivative X precipitated as white powder, m.p. 202.5–203.5°. Recrystallization from acetone–petroleum ether gave m.p. 204–205°.

Anal. Calcd. for $C_{12}H_8O_3Br_2$: C, 40.02; H, 2.24; Br, 44.39. Found: C, 39.94; H, 2.18; Br, 44.22.

(30) *cis-1,2-Dihydronaphthalenedicarboxylic acid-1,2* (XVIIa). Anhydride XI was dissolved in dry acetone, and water was added until the solution became turbid. Then, more acetone was added to clear up the solution. After 16 hr. standing at room temperature, the acetone was partly removed *in vacuo* until the dicarboxylic acid XVIIa started precipitating. Recrystallization from acetone–diisopropyl-ether gave prisms, m.p. 179–181°. Ultraviolet: λ_{1max} 216 mμ, ε 20,700, λ_{2max} 264 mμ, ε 8620. Titration: $pK^*_{1(MCS)}$ 6.04; $pK^*_{2(MCS)}$ 9.16; ΔpK^*_{MCS} 3.12.

Anal. Calcd. for $C_{12}H_{10}O_4$: C, 66.05; H, 4.62. Found: C, 65.98; H, 4.53.

(31) *cis-Tetralindicarboxylic acid-(1,2)* (XXIVa) *by reduction of* XVIIa. Crude *cis*-1,2-dihydronaphthalenedicarboxylic 1,2 (XVIIa) (2.5 g.) was hydrogenated [see (5)]. After removal of the catalyst, the colorless sodium salt solution was acidified, which precipitated *cis*-tetralin acid XXIVa as a white powder. Recrystallization from water gave needles, m.p. 180–182°. Ultraviolet: λ_{1max} 223 mμ, ε 2100, λ_{2max} 268 mμ, ε 296, λ_{3max} 273 mμ, ε 257. Titration: $pK^*_{1(MCS)}$ 6.21; $pK^*_{2(MCS)}$ 9.55; ΔpK^*_{MCS} 3.24.

(32) *cis-Tetralindicarboxylic acid-1,2 anhydride* (XXIII). The extracted mother liquor of the *trans*-1,4-dihydronaphthalenedicarboxylic acid-1,4 (IIIa) (320 g.) was hydrogenated as sodium salt in water, using 10% Raney-nickel as catalyst. The crude, dark brown tetralin acid mixture was kept under vacuum at 200° to split out water. Distillation yielded 152 g. of a light greenish, fluorescent oil (b.p. 170–180°/0.02–0.04 Torr.). Refractionation gave a light greenish, viscous oil, b.p. 138.5°/0.03 Torr., n_D^{20} 1.5718. Spraying with diisopropyl ether induced immediate crystallization, yielding white, powdery crystals, m.p. 60.5–62.5°.

Anal. Calcd. for $C_{12}H_{10}O_3$: C, 71.28; H, 4.99. Found: C, 71.23; H, 4.98.

(33) *Hydrolysis of anhydride* XXIII *to cis-tetralindicarboxylic acid* XXIVa. The *cis*-tetralin anhydride XXIII was dissolved in hot water, which, on cooling, gave *cis*-tetralindicarboxylic acid-1,2 (XXIVa) as white crystals, m.p. 176–179°. Recrystallization from glacial acetic acid gave m.p. 179–181°. Titration: $pK^*_{1(MCS)}$ 6.23; $pK^*_{2(MCS)}$ 9.31; ΔpK^*_{MCS} 3.08.

Anal. Calcd. for $C_{12}H_{12}O_4$: 65.44; H, 5.49. Found: C, 65.42; H, 5.44.

(34) *Treatment of cis-1,2-dihydronaphthalenedicarboxylic acid 1,2* (XVIIa) *with acetic anhydride. cis*-1,2-Dihydro acid XVIIa was treated with acetic anhydride for 8 hr. as described under (22), which gave 3,4-dihydronaphthalenedicarboxylic acid-1,2 anhydride (XVI) m.p. 117–123°. Recrystallization from diisopropyl ether gave m.p. 124–126°.

(35) *cis-1,2-Dihydronaphthalenedicarboxylic acid-1,2 dimethyl ester* (XVIIb). The dimethyl ester XVIIb was prepared from the acid XVIIa and diazomethane yielding a colorless, oily liquid, n_D^{20} 1.5538.

Anal. Calcd. for $C_{14}H_{14}O_4$: C, 68.28; H, 5.73. Found: C, 68.20; H, 5.78.

(36) *cis-Tetralindicarboxylic acid-1,2 dimethyl ester* (XXIVb). The dimethyl ester XXIVb was prepared from the acid XXIVa and diazomethane, yielding an oily water-white liquid, n_D^{20} 1.5284.

Anal. Calcd. for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50. Found: C, 67.65; H, 6.55.

(37) *trans-1,2-Dihydronaphthalenedicarboxylic acid-1,2 dimethyl ester* (XVb). *trans*-1,2-Dihydro acid XVa was treated with (a) methanol and concd. sulfuric acid and (b) with diazomethane which gave the dimethyl ester XVb, b.p. 108°/0.01 Torr., n_D^{20} 1.5510. Ultraviolet: λ_{max} 263 mμ, ε 11,620.

Anal. Calcd. for $C_{14}H_{14}O_4$: C, 68.28; H, 5.73. Found: C, 68.05; H, 5.63.

(38) *Saponification of trans-1,2-dihydro ester* XVb *to 1,4-dihydronaphthalenedicarboxylic acid-1,2* (XVIIIa). One gram of dimethyl ester XVb was refluxed with 25 ml. of a 10% solution of sodium methoxide for 16 hr. Part of the methanol was removed, water added, and refluxing continued for an additional 2 hr. After acidification with concd. hydrochloric acid, the product was extracted with ether, the ethereal solution washed with water, dried over sodium sulfate, and the solvent removed. The crude, crystalline 1,4-dihydro acid XVIIIa melted at 195.5–216° under strong evolution of gas. Recrystallization from methanol-water gave small plates, m.p. 215.5–217° (slowly heated). Fast heating raised the m.p. to 219–221°; mixed m.p. with pure 1,4-dihydro acid XVIIIa, obtained from treatment of *trans*-1,2-dihydro acid XVa with 2*N* sodium hydroxide solution gave no depression. Ultraviolet: no absorption. Titration: $pK^*_{1(MCS)}$ 6.01; $pK^*_{2(MCS)}$ 8.52; ΔpK^*_{MCS} 2.51.

Anal. Calcd. for $C_{12}H_{10}O_4$: C, 66.05; H, 4.62. Found: C, 65.99; H, 4.60.

(39) *1,4-Dihydronaphthalenedicarboxylic acid-1,2 dimethyl ester* (XVIIIb).[6] Acid XVIIIa (1 g.) was refluxed with 50 ml. of methanol and 2 drops of concd. sulfuric acid. The reaction mixture was worked up as usual, yielding 0.95 g. of an oily, water-white liquid which crystallized slowly, m.p. 68–70°. Clustering needles from acetone–petroleum ether, m.p. 71–72°. Ultraviolet: no absorption.

Anal. Calcd. for $C_{14}H_{14}O_4$: C, 68.28; H, 5.73. Found: C, 68.31; H, 5.77.

(40) *Reaction of 1,4-dihydronaphthalenedicarboxylic acid-1,2* (XVIIIa) *with diazomethane.* 1,4-Dihydroacid XVIIIa (2 g.) was dissolved in 400 ml. of dried ether (only slightly soluble) under addition of 50 ml. dried acetone. By gently warming an etheral solution of diazomethane, the latter was passed under swirling into the acid solution, whereby some undissolved dicarboxylic acid reacted and dissolved. After 16 hr., the excess diazomethane was removed by gently shaking the esterified mixture on the steam bath under vacuum until the yellow color had disappeared. Removal of the solvent gave the pyrazoline derivative XIXb as white crystals, m.p. 142–143°. Thick prisms from acetone–petroleum ether m.p. 146–147° under strong evolution of gas. Ultraviolet: λ_{1max} 212 mμ, 685.5; λ_{2max} 265 mμ, ε 727; λ_{3max} 290 mμ, ε 535.

Anal. Calcd. for $C_{15}H_{16}O_4N_2$: C, 62.49; H, 5.59; N, 9.72; OCH_3, 21.58. Found: C, 62.40; H, 5.63; N, 9.64; OCH_3 21.68.

(41) *Pyrolysis of the pyrazoline compound* XIXb *to 1,4-dihydro-3-methylnaphthalenedicarboxylic acid-1,2 dimethyl ester* (XXIb). A sample of the pyrazoline product XIXb was heated in an open tube above its melting point. Gas escaped under foaming, leaving a water-white liquid which was distilled twice *in vacuo*. Ultraviolet: λ_{max} 272 mμ (weak shoulder), ε 435.

Anal. Calcd. for $C_{15}H_{16}O_4$: C, 69.21; H, 6.20; OCH_3, 23.84. Found: C, 69.21; H, 6.20; OCH_3, 23.83.

(42) *Reaction of 1,4-dihydronaphthalenedicarboxylic acid-1,2* (XVIIIa) *with acetic anhydride.* 1,4-Dihydro acid XVIIIa (1 g.) was refluxed with 10 ml. of acetic anhydride for 4 hr. Removal of the solvent gave 0.95 g. of yellow 3,4-dihydronaphthalenedicarboxylic acid-1,2 anhydride (XVI), m.p. 118.5–123.5°. Needles from diisopropyl ether, m.p. 125–126°. Ultraviolet (of crude product): λ_{1max} 226 mμ, ε 13,750; λ_{2max} 287 mμ, ε 12,790.

(43) *Dehydrogenation of 1,2-dihydronaphthalenedicarboxylic acid-1,2 anhydride* (XI) *to 1,2-naphthalenedicarboxylic acid anhydride* (XIII).[4] Anhydride XI (5 g.) and 0.8 g. of sulfur were thoroughly mixed in a mortar and placed in a 50 ml. three necked flask, equipped with cold finger and gas inlet. A slow stream of nitrogen was passed through the inlet and the temperature was slowly raised from 140° to 230°. Hydrogen sulfide started evolving at 180°. After 1 hr., only traces of hydrogen sulfide could be shown by lead acetate paper. The product was sublimed at 120°/0.01 Torr. and the yellow 1,2-naphthalenedicarboxylic acid anhydride (XIII) was recrystallized from acetone–diisopropyl ether, m.p. 164–166°; yield, 2.2 g. Ultraviolet: λ_{1max} 272 mμ, ε 5770; λ_{2max} 284 mμ, ε 6980, λ_{3max} 294 mμ, ε 5600. Titration: $pK^*_{1(MCS)}$ 5.54; $pK^*_{2(MCS)}$ 7.94; ΔpK^*_{MCS} 2.40.

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Some Photochemistry of 1,2,3,4,5-Pentaphenylcyclohexa-1,3-diene[1]

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A study of the photosensitized oxidation of 1,2,3,4,5-pentaphenylcyclohexa-1,3-diene revealed the formation of a 1,4-epidioxide, 2,3-dioxa-1,4,5,6,7-pentaphenylbicyclo[2.2.2]oct-5-ene(II), and pentaphenylbenzene(V), along with a small quantity of an isomer, 1,2,3,5,6-pentaphenylbicyclo[3.1.0]hex-2-ene(XIIb). In the absence of oxygen, the exclusive photochemical formation of XIIb was observed. Some information on the mechanism of formation of these products is presented.

As a foundation for further work on the thermal and photochemical rearrangements of 1,4-epidioxides, in which this laboratory has previously shown special biogenetical interests,[3] some investigations of the photochemistry of 1,3-homoannular dienes and the formation of 1,4-epidioxides from them were undertaken. Because of the availability and known reactivity to light and oxygen of phenyl substituted 1,3-homoannular dienes,[4] and also because of the recent interest in the reactivity of *cis*-stilbene derivatives,[5] the experimental work was centered on 1,2,3,4,5-pentaphenylcyclohexa-1,3-diene (I).

When I, methylene blue, and oxygen were irradiated under photosensitizing conditions,[6] with light of wave lengths greater than 320 mμ, a 54% yield of a colorless crystalline product, $C_{36}H_{28}O_2$, was obtained by chromatography of the irradiation mixture on alumina. Since two oxygen atoms had added to the diene I and the infrared spectrum showed no hydroxyl or carbonyl absorption the product may be considered to be either the 1,4-epidioxide (II), or the diepoxide (III).[7]

Although a carbon-carbon double bond stretching vibration was not detected in the infrared, the Raman spectrum of the $C_{36}H_{28}O_2$ product in chloroform had an emission band at 1625 cm.$^{-1}$, which was ascribed to the presence of a

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