

995, 1030, 1070, 1095, 1130, 1175, 1200, 1220, 1240, 1290, 1360, 1380, 1420, 1450, 1720, 2850, 2920 cm^{-1} .

Norcedrenedicarboxylic Acid Isomonomethyl Ester (38). A.—Dimethyl norcedrenedicarboxylate (110 mg.) was dissolved in 20 ml. of methanolic potassium hydroxide containing 1 ml. of water and subsequently refluxed for 4 hours. The volume of the mixture was reduced to one-quarter on a rotary evaporator and worked up in the usual manner to give a crystalline compound which after two recrystallizations from hexane had m.p. 130.5–132.0° (lit.³³ m.p. 130–131°), $[\alpha]^{25D} -39^\circ$ (*c* 1.29, CHCl_3); infrared spectrum (10% in CCl_4): 708, 850, 920, 966, 995, 1032, 1077, 1105, 1137, 1163, 1186, 1210, 1245, 1304, 1352, 1376, 1395, 1425(sh), 1439, 1467, 1700, 1725 cm^{-1} , broad O–H region characteristic of carboxylic acids. Hydrolysis of norcedrenedicarboxylic acid isomonomethyl ester (100 mg.) by refluxing in 5 *N* methanolic potassium hydroxide solution for 20 hours yielded 92 mg. of crude norcedrenedicarboxylic acid. Recrystallization from formic acid gave pure norcedrenedicarboxylic acid, m.p. 214–215°, pure and mixed with authentic material.

B.—To a solution of 10 ml. of methanol in which *ca.* 50 mg. of sodium had been dissolved was added norcedrenedicarboxylic acid anhydride (117 mg., 0.52 mmole). After 14 minutes at room temperature, the mixture was poured into water and extracted with ether. Work up in the usual manner yielded 130 mg. (97%) of an oil which crystallized when seeded with norcedrenedicarboxylic acid isomonomethyl ester. Recrystallization from hexane gave a pure sample.

3-Carbomethoxy-2,2,6-*exo*-trimethylbicyclo[3.3.0]oct-4-ene (39).—A mixture of norcedrenedicarboxylic acid monomethyl ester (1.52 g., 6.0 mmoles) and lead tetraacetate (4.5 g., 10.2 mmoles, 95% active lead) in 300 ml. of benzene was refluxed under nitrogen for 14 hours. The mixture was poured into an aqueous solution of ferrous sulfate, extracted with ether, the ether layer washed with water, with a solution of sodium carbonate, again with water, dried over magnesium sulfate and concentrated to yield 1.22 g. of neutral material. The product was fractionated and the portion (750 mg.) that distilled at bath temperature 110° (0.4 mm.) was separated into two components by gas chromatography using a packing of 15% Dow Corning compound no. 11 on firebrick. 3-Carbomethoxy-2,2,6-*exo*-trimethylbicyclo[3.3.0]oct-4-ene (105 mg.) was eluted first and was purified further by filtration in hexane solution through a small column of Woelm alumina (neutral, activity III) followed by distillation through a micro-Hickman

column under high vacuum; $[\alpha]^{30D} -283^\circ$ (*c* 2.05, CHCl_3), n_D^{20} 1.4696; nuclear magnetic resonance spectrum (60 mc.): 4.54, 6.16, 6.70, 8.72, 8.85, 8.95 τ ; infrared spectrum (10% in CCl_4): 650, 846, 915, 950, 980, 1023, 1036, 1156, 1197, 1245, 1275, 1335, 1367, 1387, 1438, 1455, 1663, 1732, 2880, 2960, 3060(sh) cm^{-1} .

Anal. Calcd. for $\text{C}_{13}\text{H}_{20}\text{O}_2$: C, 74.96; H, 9.68. Found: C, 75.20; H, 9.75.

3-Carbomethoxy-2,2,6-trimethylbicyclo[3.3.0]oct-5(6)-ene (41).—The other compound obtained by gas chromatographic separation of the above product was purified by the same procedure to give a liquid ester $[\alpha]^{25D} +36^\circ$ (*c* 2.13, CHCl_3), n_D^{25} 1.4792; nuclear magnetic resonance spectrum (60 mc.): 6.40, 7.66, 8.37, 9.07, 9.17 τ ; infrared spectrum (10% in CCl_4): 835, 882, 913, 940, 1041, 1063, 1202, 1228, 1260, 1297, 1324, 1355, 1372, 1382, 1390, 1441, 1450, 1735, 2860, 2960 cm^{-1} .

Anal. Calcd. for $\text{C}_{13}\text{H}_{20}\text{O}_2$: C, 74.96; H, 9.68. Found: C, 75.46; H, 9.92.

3-Carbomethoxy-2,2,6-*endo*-trimethylbicyclo[3.3.0]octane (40).—3-Carbomethoxy-2,2,6-trimethylbicyclo[3.3.0]oct-5(6)-ene (64 mg., 0.31 mmole) was reduced in absolute alcohol over a platinum catalyst prepared from 30 mg. of platinum oxide. After 10.2 ml. had been absorbed the catalyst was removed by filtration and the alcohol solution concentrated. The residue was dissolved in hexane containing 5% benzene and filtered through a column of 3 g. of Merck alumina (acid-washed, activity III). Distillation through a micro-Hickman column gave 3-carbomethoxy-2,2,6-*endo*-trimethylbicyclo[3.3.0]octane (61 mg., 95%), $[\alpha]^{28.5} -47^\circ$ (*c* 0.95, CHCl_3) as a colorless oil. Both the mass spectrum and the infrared spectrum (32 peaks) of this compound were identical in every respect with those of the product obtained by catalytic reduction of 3-carbomethoxy-2,2,6-*endo*-trimethylbicyclo[3.3.0]oct-8-ene derived from patchouli alcohol; mol. wt. 210 (mass spectrum).

3-Carbomethoxy-2,2,6-*exo*-trimethylbicyclo[3.3.0]octane (42).—3-Carbomethoxy-2,2,6-*exo*-trimethylbicyclo[3.3.0]oct-4-ene (102 mg., 0.49 mmole) was reduced in absolute alcohol over a platinum catalyst prepared from 16 mg. of platinum oxide. The reaction was worked up as described above to yield 92 mg. (89%) of 3-carbomethoxy-2,2,6-*exo*-trimethylbicyclo[3.3.0]octane, $[\alpha]^{30.4} -75^\circ$ (*c* 0.94, CHCl_3), mol. wt. 210 (mass spectrum); infrared spectrum (10% in CCl_4): 705, 915, 932, 973, 1035, 1140, 1158, 1185, 1202, 1225, 1241, 1258, 1297, 1374, 1394, 1417, 1464, 1735, 2880, 2960 cm^{-1} .

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA, MINNEAPOLIS 14, MINN., AND THE DEPARTMENT OF CHEMISTRY, IOWA STATE UNIVERSITY, AMES, IOWA]

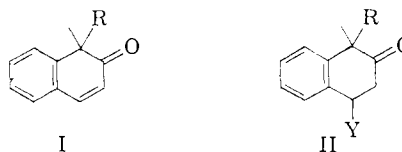
Alkali-induced Reactions of 1-Methyl-1-dichloromethyl-2(1H)-naphthalenone and Related Compounds

BY R. M. DODSON,^{1a} JOHN R. LEWIS,^{1b} WILLIAM P. WEBB,^{1a} ERNEST WENKERT^{1b} AND R. D. YOUSSEFYEH^{1b}

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Base treatment of 1-methyl-1-dichloromethyl-2(1H)-naphthalenone yields 1-methyl-2-naphthol, 1-methyl-3-naphthoic acid and a cinnamic acid. Similar treatment of 1-methyl-1-dichloromethyl-2-tetralone produces 1-methyl-3,4-dihydro-3-naphthoic acid and 1-methyl-3-naphthoic acid. Rational mechanisms for these and similar rearrangements involving cyclobutanone intermediates are presented. The trapping of a bridged cyclobutanone is described.

It has been noted in two previous studies that 1-methyl-1-dichloromethyl-2(1H)-naphthalenone (Ia), the Reimer-Tiemann product of 1-methyl-2-naphthol, and its dihydro derivative IIa undergo a chemical change in alkaline media.^{2a,b} The present report represents an extension of these observations.

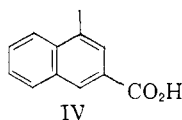
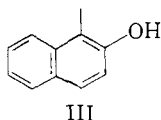


- I, R = CHCl_2 , Y = H
 b, R = CH_2Cl , Y = H
 c, R = CHCl_2 , Y = OH
 d, R = CHCl_2 , Y = OEt
 e, R = CHClOH
 f, R = CHO

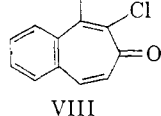
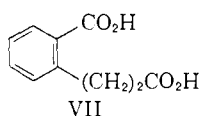
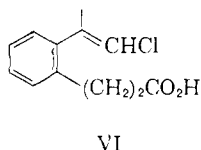
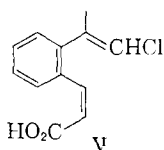
(1) (a) University of Minnesota; (b) Iowa State University.

(2) (a) R. M. Dodson and W. P. Webb, *J. Am. Chem. Soc.*, **73**, 2767 (1951); (b) E. Wenkert and T. E. Stevens, *ibid.*, **78**, 5627 (1956).

Treatment of the unsaturated ketone Ia with refluxing aqueous potassium hydroxide solution led to a mixture containing mostly an acid, $C_{12}H_{11}O_2Cl$, 1-methyl-2-naphthol (III), and a small amount of 1-methyl-3-naphthoic acid (IV).³ When the reaction was carried out in aqueous ethanol, the yields of the unknown acid and the naphthol dropped drastically, while the naphthoic acid became the major product.



The acid proved to be V on the basis of its spectral properties, its transformation on catalytic hydrogenation to a hydrocinnamic acid (VI) and the latter's oxidation to *o*-carboxyhydrocinnamic acid (VII). When it was exposed to concentrated sulfuric acid, it was transformed into a ketone whose spectral properties were suggestive of the benzotropone derivative VIII. Permanganate oxidation of the ketone to phthalic acid confirmed this formulation. This cyclodehydration of an *o*-vinyl-*cis*-cinnamic acid into a benzotropone system represents a novel tropone synthesis which may have general applicability.



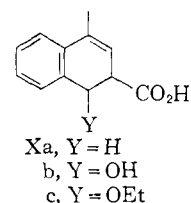
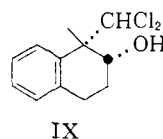
In attempts to prepare the saturated ketone IIa^{2a} by palladium-charcoal catalyzed hydrogenation of Ia the desired β -tetralone was obtained along with small quantities of a crystalline alcohol. It was shown to be the β -tetralol IX when the same compound proved to be the sole product of lithium aluminum hydride as well as lithium aluminum tri-*t*-butoxyhydride reductions of IIa.

Treatment of the β -tetralone IIa with refluxing aqueous alcoholic sodium hydroxide solution gave a high yield of an acid, $C_{12}H_{12}O_2$. A similar reaction, however, with higher alcohol concentration, led to a mixture of the same acid and the naphthoic acid IV and a neutral fraction with 5.85μ carbonyl infrared absorption. Sodium methoxide-methanol runs yielded mixtures of both acids and neutral fractions exhibiting 5.60 and 5.85μ carbonyl peaks. Finally, a potassium *t*-butoxide run afforded a similar mixture of uncharacterized neutral substances, but only one acidic product, the $C_{12}H_{12}O_2$ compound.

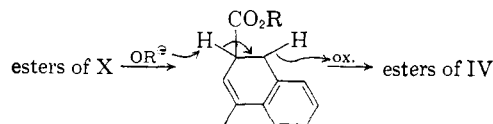
The structure of the acid could be shown to be Xa on the basis of its spectral properties and its ready dehydrogenation to 1-methyl-3-naphthoic acid (IV).

Formation of the unexpected oxidation product IV in only the ethanol and methanol runs, despite

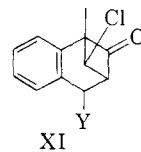
(3) G. Darzens, *Compt. rend.*, **183**, 749 (1926).



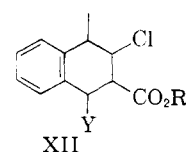
the attempted exclusion of air in all experiments, suggested that aldehydic impurities in these alcohol solvents were responsible for the conversion of the dihydronaphthoyl into the naphthoyl systems.⁴ While no proof of the presence of these oxidizing agents was attempted, the nature of likely oxidizable intermediates was briefly inspected. A methoxide treatment of the acid Xa, for half the reaction time of the previous alkali treatments, gave starting material, whereas its methyl ester afforded some unreacted ester, some ester of IV and a 45% yield of the naphthoic acid IV. These results imply that the esters of Xa, rather than Xa itself, and hence readily enolizable substances were responsible for the oxidative side reaction.⁵ This is in accord with the following representation of the oxidation.



As the above data indicate, in contrast to the complex nature of the base-induced dehydrochlorinative rearrangement of the unsaturated ketone Ia, that of the β -tetralone IIa gave a singular result. It is best explained by the assumption of the base first converting IIa into its anion and the latter undergoing an internal chloride displacement. The resulting cyclobutanone XIa appears to be unstable in basic medium, although the 5.60μ infrared band of the neutral fractions of the reaction mixture undoubtedly indicates its survival to a small extent. The breakdown of the intermediate cyclobutanone finally to product Xa can take place either by a one-step concerted 1,3-elimination⁶ or by a two-step process involving a base-catalyzed solvolytic ring cleavage to XIIa, analogous to the Haller-Bauer reaction,⁷ followed by an elimination of hydrogen chloride. However, three facts speak against the first mechanistic possibility.



a, Y = H
b, Y = OH
c, Y = OEt



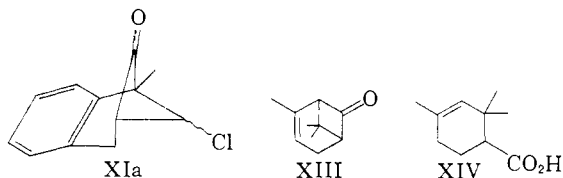
(4) The absence of any tetralin derivatives among the reaction products precluded the possibility of the occurrence of an oxidation-reduction disproportionation of Xa or its esters.

(5) These data also suggested that the production of Xa instead of its esters in the methanol and *t*-butyl alcohol runs was a consequence of the inadvertent presence of small amounts of water. However, the formation of the naphthoic acid IV from its methyl ester by methoxide displacement on the ester's methyl group represents an alternative reaction path not to be overlooked [cf. J. F. Bunnett, M. M. Robison and F. C. Pennington, *J. Am. Chem. Soc.*, **72**, 2378 (1950)].

(6) Cf. C. A. Grob, *Experientia*, **13**, 126 (1957).

(7) Cf. K. E. Hamlin and A. W. Weston, in "Organic Reactions," Vol. IX, John Wiley and Sons, Inc., New York, N. Y., 1957, p. 1.

First of all, the necessary all-*trans* coplanar alignment of all atoms involved in a concerted 1,3-elimination cannot be readily attained in either of the two possible epimers of XIa (*cf.* the conformational representation of XIa below). Secondly, in a study of the base-induced rearrangements of products derived from the "abnormal" Reimer-Tiemann product of *o*-cresol von Auwers reported the isolation of chloroacids, presumably analogous to XII.⁸ Finally, it has been shown recently that chrysanthenone⁹ ("Δ³-carene-1,2-epoxide"¹⁰) (XIII), a natural product functionally greatly akin to the chlorocyclobutanone XI but possessing no chlorine leaving group, undergoes ready base-catalyzed cleavage to a cyclogeranic acid (XIV).¹¹



Definitive proof for the lack of dependence of the ketone ring opening in our systems on the presence of a halogen atom came from a study of the base-catalyzed rearrangement of the monochloroketone IIb, prepared by the catalytic hydrogenation of Ib.¹² Treatment of the β-tetralone IIb with potassium *t*-butoxide under conditions identical with those of the *t*-butoxide run on Ia yielded a mixture of neutral substances, exhibiting 5.60 and 5.85 μ infrared bands, and acids. The latter afforded the tetralin acid XV, identical with a sample obtained from the hydrogenation of Xa.¹³ It appears that the cyclobutanone XVI is no more stable than its chloro derivative XIa. Undoubtedly the neighboring benzene ring facilitates the ring rupture in XIa as well as XVI by giving the transition state benzyl anion character. While the benzene ring's molecular π-orbital is not parallel with the incipient *p*-orbital of the breaking carbon-carbon bond, the geometry of the tricyclic ring systems is such as to permit fair amount of overlap.

It is noteworthy that the present conversion of α,α-dialkyl-β-haloketones to acids represents a

(8) K. von Auwers and M. Hessenland, *Ber.*, **41**, 1816 (1908); K. von Auwers and F. von der Heyden, *ibid.*, **42**, 2404 (1909).

(9) M. Kotake and H. Nonaka, *Ann.*, **607**, 153 (1957).

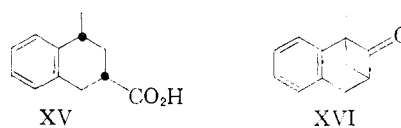
(10) E. P. Blanchard, Jr., *Chemistry & Industry*, 293 (1958).

(11) It is of interest that this conversion involves not only ring opening but also double bond migration. While the suggestion of a prior rearrangement of chrysanthenone to ⁹ can be dismissed on the basis of the latter representing a steric impossibility, the argument in favor of the intermediacy of an allyl carbanion ¹¹ appears more attractive. However, the unipositional protonation of the latter is quite surprising, even though it occurs at the slightly less hindered site. Hence, it is conceivable that the ring rupture and protonation occur concerted in a mechanism approximating an S_E2' type.

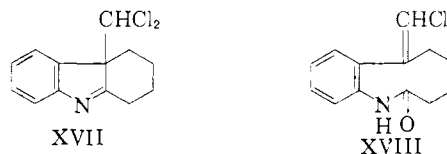


(12) E. Wenkert, R. D. Youssefyeh and R. G. Lewis, *J. Am. Chem. Soc.*, **82**, 4675 (1960).

(13) While these results permit the assignment of a *cis* configuration for XV, no significance should be attached to this fact in regard to the question of the stereochemistry of the ring opening. Both the direction and the stereochemistry of base-catalyzed cyclobutanone rupture is presently under study.



rearrangement closely related to the Favorskii rearrangement, a transformation of α-haloketones to acids or their derivatives. As in our cases, the Favorskii reaction has been shown to proceed through small-ring ketone intermediates.¹⁴ It further is of interest that the rearrangements described so far need not be the only consequence of the interaction of alkali and β-halocarbonyl systems. This is illustrated by the transformations of Ia (*vide infra*) as well as the reported hydrolytic conversion of the indolenines XVII to XVIII.¹⁵



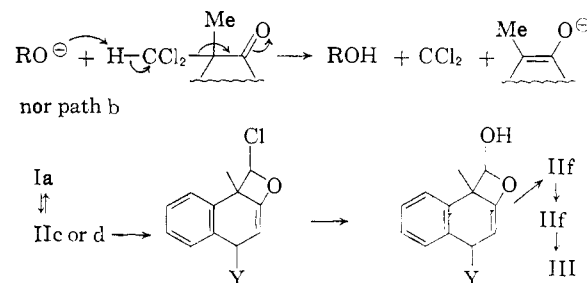
On the basis of the above interpretation of the mechanism of the rearrangements of the β-tetralones it is now possible to explain the more complex results obtained in the study of the naphthalenone Ia. An attack of base on the latter could occur either at the site of the carbonyl group or at its β-carbon atom. In case of the former a 1,3-elimination, analogous to the XVII-XVIII transformation, would follow leading to the cinnamic acid V.¹⁶ On the other hand, β-attack would yield the β-tetralones IIc or d which, in analogy with the behavior of the tetralone Ia, would be converted to cyclobutanones XIb or c, tetralin acids or esters XIIb or c, dihydronaphthoic acids Xb or c or their esters and, finally, to the naphthoic acid IV. β-Addition must be responsible also for the formation of 1-methyl-2-naphthol (III). The initial addition product IIc (present exclusively in aqueous medium while only partly in aqueous alcoholic solution) can be expected to undergo internal chloride displacement toward XIX even more readily than toward XIIb. β-Elimination of XIX and hydrolysis of the resulting naphthalenones Ie and f would finally lead to the phenolic product III.¹⁷

(14) R. B. Loftfield, *J. Am. Chem. Soc.*, **73**, 4707 (1951).

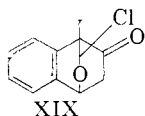
(15) M. F. Bartlett, D. F. Dickel and W. I. Taylor, *ibid.*, **80**, 126 (1958).

(16) In contrast to the elimination of XIa the 1,3-elimination of Ia undoubtedly proceeds in a concerted manner. The geometry of the reversibly formed hydrate of Ia not only greatly favors concerted elimination but also is highly unfavorable for a two-step process (*i.e.*, benzyl anion intermediacy).

(17) Neither path a, a *retro*-Reimer-Tiemann process

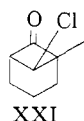
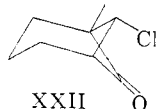
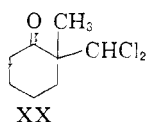


can account for the difference of yields of III and IV in aqueous vs. aqueous alcoholic media. Furthermore, if path b were important,



These arguments are in accord with the observed difference of yields of the naphthol III, naphthoic acid IV and cinnamic acid V in aqueous and aqueous alcoholic solutions. In the former medium hydroxide ion, a small nucleophile, can be envisaged to undergo interaction with the highly sterically hindered carbonyl group of Ia with a rate comparable to attack at its β -carbon. Furthermore, β -addition should lead mostly to phenol. Hence, III and V are the major products. However, in an aqueous alcoholic medium, wherein the larger ethoxide ion would be the more effective nucleophile, attack at the β -position would be preferred and the consequent greater concentration of II_d, rather than of II_c, should result in less phenol. Hence, the major product is IV.

Since cyclobutanones played a vital role as postulated intermediates in most of the above reactions, it became of interest to trap and isolate such an intermediate. However, in view of the observed instability of exocyclic benz-substituted cyclobutanones toward base a saturated derivative was desired. As a consequence, 2-methyl-2-dichloromethylcyclohexanone (XX), prepared by catalytic hydrogenation of the Reimer-Tiemann product of *o*-cresol,¹⁸ was exposed to base treatment. The neutral products of the reaction could be separated by repeated fractional distillation, whereupon a liquid cyclobutanone (XXI), exhibiting solely a 5.60μ carbonyl band in its infrared spectrum, could be isolated. It proved to be only one of the two possible isomers (epimeric at the chlorine-holding carbon atom) since it gave a single crystalline semicarbazone in high yield. The internal chloride displacement thus appears to be stereospecific, which suggests that the unaffected chlorine atom assumed an equatorial orientation in the transition state of its neighbor's extrusion. Hence, XXII represents the most reasonable stereostructure of the product. The isolation of this compound lends further credence to the mechanism of the aforementioned base-induced rearrangements.



Acknowledgments.—J. R. L., E. W. and R. D. Y. wish to express their gratitude to the National Science Foundation and Ciba Pharmaceutical Products, Inc., for financial support and to the Institute of Atomic Research, Ames, Iowa, for the use of a Baird infrared spectrophotometer. R. M. D. and W. P. W. are indebted to the Research Corporation for financial support.

it would be expected to predominate also in the alkaline hydrolysis of the saturated ketone II_a.

(18) K. von Auwers and G. Keil, *Ber.*, **35**, 4207 (1902); K. von Auwers and E. Lange, *Ann.*, **401**, 317 (1913).

Experimental

Alkali Treatments of 1-Methyl-1-dichloromethyl-2(1H)-naphthalenone(Ia). (a) **In Aqueous Base.**—A mixture of 5.00 g. of ketone Ia and a solution of 15 g. of potassium hydroxide in 75 ml. of water was refluxed for 24 hr. After cooling, the mixture was extracted exhaustively with ether. The extract was dried over magnesium sulfate and evaporated. The residue, 2.01 g. (50%), was crude starting material which on crystallization from chloroform gave m.p. 64–65°. The aqueous basic reaction mixture then was acidified with 1 *N* hydrochloric acid and extracted with ether. The organic extract was washed with water and extracted with saturated sodium bicarbonate solution. The remaining ether solution was washed with water, dried over magnesium sulfate and evaporated. Chromatography of the residue on Celite-silicic acid and elution with 20:1 petroleum ether-ether yielded 620 mg. (18%) of 1-methyl-2-naphthol (III), m.p. 107–109° after crystallization from hexane. The remaining sodium bicarbonate solution was acidified with 1 *N* hydrochloric acid and extracted with ether. The extract was dried and evaporated, and the residue chromatographed on Celite-silicic acid. Elution with 20:1 petroleum ether-ether led to 840 mg. (20%) of an acid, m.p. 110–112°. Crystallization from aqueous methanol gave crystals of *o*-(α -methyl- β -chlorovinyl)-*cis*-cinnamic acid (V), m.p. 113–114°; ultraviolet spectrum (95% ethanol), λ_{\max} 260 $m\mu$ (ϵ 8800) and λ_{\min} 245 $m\mu$ (ϵ 8400).¹⁹

Anal. Calcd. for $C_{12}H_{11}O_2Cl$: C, 64.73; H, 4.98. Found: C, 64.7; H, 5.01.

Treatment of the acid with thionyl chloride and then with ammonia in the usual manner and crystallization of the product from dilute methanol gave the amide of V, m.p. 147°.

Anal. Calcd. for $C_{12}H_{11}ONCl$: C, 65.00; H, 5.46. Found: C, 64.9; H, 5.83.

Further elution of the chromatogram with 20:1 petroleum ether-ether yielded 70 mg. (2%) of another acid, m.p. 199–203°. Crystallization from aqueous methanol gave 1-methyl-3-naphthoic acid (IV), m.p. 203–205° (lit.³ m.p. 198–199°); ultraviolet spectrum (95% ethanol), λ_{\max} 238 $m\mu$ (ϵ 56,400) and 284 $m\mu$ (ϵ 8280), λ_{\min} 255 $m\mu$ (ϵ 3900).

Diazomethane treatment of the acid and crystallization of the product from hexane gave the methyl ester of IV, m.p. 39–40° (lit.³ m.p. 39°).

Treatment of the acid with thionyl chloride and then with ammonia in the usual manner and sublimation of the product gave the amide of IV, m.p. 163.5°.

Anal. Calcd. for $C_{12}H_{11}ON$: C, 77.80; H, 5.99. Found: C, 77.7; H, 6.12.

Further elution of the chromatogram with 10:1 petroleum ether-ether led to another acid component which gave m.p. 205–210° on repeated crystallizations from aqueous ethanol but whose homogeneity and structure was not investigated.

(b) **In Aqueous Alcoholic Base.**—A mixture of 3.00 g. of ketone Ia and a solution of 4 g. of potassium hydroxide in 15 ml. of water and 30 ml. of ethanol was refluxed for 7 hr. The reaction mixture then was divided into neutral, phenolic and acidic fractions as above. Petroleum ether elution of an alumina chromatogram of the neutral products gave 1.55 g. of starting ketone, m.p. 62–64° after crystallization from chloroform. Elution with 30:1 petroleum ether-ether yielded 50 mg. of a solid, m.p. 55° after crystallization from hexane, which was not investigated further. Petroleum ether-ether (20:1) elution of a Celite-silicic acid chromatogram of the phenolic fraction led to 81 mg. (4%) of 1-methyl-2-naphthol (III), m.p. 107–109°. Crystallization of the acidic fraction twice from aqueous methanol gave 80 mg. (36%) of 1-methyl-3-naphthoic acid (IV). Solvent removal from the crystallization mother liquors, treatment of the residue with an ether solution of ca. 0.5 g. of diazomethane, second solvent removal, alumina chromatography of the residue and petroleum ether elution led to two fractions. Hydrolysis of the separated esters was accomplished by refluxing solutions of 0.5 g. of potassium hydroxide and 2 ml. of water and 10 ml. of ethanol for 2 hr. Crystallization of the products of the first fraction several times from hexane gave 80 mg. (4%) more of 1-methyl-3-naphthoic acid, m.p.

(19) The absorption characteristics are in close agreement with those of compounds possessing only one of the two chromophores in V, compound Xa (λ_{\max} 260 $m\mu$) and *cis*-cinnamic acid (λ_{\max} 264 $m\mu$) [S. Svakula and A. Wasserman, *Z. physik. Chem.*, **A155**, 353 (1931)]

195–198°, and 220 mg. (9%) of the cinnamic acid (V). Crystallization of the products of the second fraction from cyclohexane led to the acidic component of unknown constitution, m.p. 205–209°.

Reactions of the Cinnamic Acid V.—A mixture of 3.30 g. of the cinnamic acid V and 100 mg. of platinum oxide in 100 ml. of 95% ethanol was shaken with hydrogen under an initial pressure of 38 lb. The reduction was stopped after 5 min., when the pressure had dropped to 17 lb. (1.2 moles of hydrogen uptake), the catalyst filtered and the filtrate concentrated. The resulting solid was crystallized from aqueous methanol yielding 1.89 g. (56%) of colorless crystals, m.p. 76–78°. Recrystallization from petroleum ether gave the hydrocinnamic acid VI, m.p. 79–79.5°; ultraviolet spectrum (95% ethanol), λ_{\max} 270 m μ (ϵ 1000).

Anal. Calcd. for $C_{12}H_{18}O_2Cl$: C, 64.13; H, 5.83. Found: C, 64.52; H, 5.96.

Potassium permanganate, 4.0 g., was added slowly to a solution of 1.22 g. of the hydrocinnamic acid VI and 2.0 g. of sodium carbonate in 150 ml. of water kept at 30°. After disappearance of the red color of the mixture it was acidified to congo red with dilute sulfuric acid. Sodium bisulfite was added in small amounts until the manganese dioxide precipitate had disappeared. The solution then was extracted eight times with 10-ml. portions of ether. The combined extracts were dried over magnesium sulfate, the solvent evaporated and the oily solid residue crystallized from water giving 230 mg. (22%) of a solid, m.p. 142–149°. Washing with benzene, two further crystallizations from water and sublimation at 142° (0.15 mm.) yielded the diacid VII, m.p. 167–168° (lit.²⁰ 166.5–168°).

Anal. Calcd. for $C_{10}H_{10}O_4$: C, 61.84; H, 5.19. Found: C, 61.9; H, 5.18.

The cinnamic acid V, 1.25 g., was mixed with 19 ml. of concentrated sulfuric acid with stirring and the black solution allowed to stand for 45 min., at room temperature. The solution was poured into 285 ml. of water with rapid stirring and left standing at room temperature for 18 hr. The resulting precipitate was filtered, air-dried, mixed with stirring with 5% sodium hydroxide solution and refiltered. The solid, 560 mg. (49%), m.p. 96–99°, was crystallized from aqueous methanol leading to light tan crystals of 2-chloro-3-methyl-4,5-benzotropone (VIII), m.p. 102–103°; spectra: ultraviolet (95% ethanol), λ_{\max} 225 m μ (ϵ 27,200), 228 m μ (ϵ 25,000), 233 m μ (ϵ 28,800), 276 m μ (ϵ 26,600) and $\lambda_{\text{shoulder}}$ 333–338 m μ (ϵ 3,560)²¹; infrared (CCl₄), C=O 6.06 (s) μ .²¹

Anal. Calcd. for $C_{13}H_9OCl$: C, 70.41; H, 4.43. Found: C, 70.32; H, 4.52.

Its 2,4-dinitrophenylhydrazone was crystallized from acetone-ethanol yielding bright red crystals, m.p. 230°.

Anal. Calcd. for $C_{13}H_{13}O_4N_4Cl$: C, 56.20; H, 3.41. Found: C, 56.3; H, 3.54.

A mixture of 1.00 g. of the tropone VIII and 6.20 g. of potassium permanganate in 125 ml. of water was refluxed for 8 hr. The cooled mixture was acidified to congo red with dilute sulfuric acid and the precipitated manganese dioxide dissolved by the slow addition of sodium bisulfite. The clear solution was extracted twelve times with 10-ml. portions of ether, the combined extracts dried over magnesium sulfate and the solvent evaporated. Two crystallizations of the residue from water gave 100 mg. (11%) of phthalic acid, m.p. and m.m.p. 210–212°. Conversion to its anil and crystallization of the latter from aqueous alcohol yielded phthal-anil, m.p. 205°, m.m.p. 206°.

1-Methyl-1-dichloromethyl-2-tetralol (IX). (a).—A mixture of 2.00 g. of ketone Ia and 100 mg. of 5% palladium-charcoal in 20 ml. of ethanol was hydrogenated at atmospheric pressure and room temperature. After cessation of hydrogen uptake the catalyst was filtered, the filtrate evaporated *in vacuo* and the oily residue chromatographed on alumina. Petroleum ether elution led to 1.30 g. (65%) of a

solid, which on crystallization from chloroform-petroleum ether gave the tetralone IIa, m.p. 72–73°. Elution with 3:1 petroleum ether-benzene yielded 550 mg. (27%) of a solid, m.p. 68–70°, which on crystallization from chloroform-petroleum ether afforded the tetralol IX, m.p. 75–76°.

Anal. Calcd. for $C_{12}H_{14}OCl_2$: C, 58.8; H, 5.77; Cl 28.95. Found: C, 58.6; H, 5.74; Cl, 29.10.

(b).—A solution of 500 mg. of ketone IIa and 500 mg. of lithium aluminum hydride in 20 ml. of tetrahydrofuran was stirred for 2 hr. The excess hydride was decomposed with ethyl acetate, the mixture acidified with 1 *N* hydrochloric acid and extracted with ether. The extract was dried over magnesium sulfate and the solvent evaporated. Alumina chromatography of the residue and elution with 5:1 petroleum ether-benzene gave 420 mg. (82%) of a solid which on crystallization from hexane afforded the tetralol IX, m.p. and m.m.p. 75°.

(c).—Anhydrous *t*-butyl alcohol, 1.5 ml., was added slowly to a stirred mixture of 200 mg. of lithium aluminum hydride in 10 ml. of ether. After vacuum removal of the solvent, 10 ml. of diglyme and then a solution of 200 mg. of ketone IIa in 5 ml. of diglyme were added. After stirring for 2 hr., dilute hydrochloric acid was added and the mixture extracted with ether. The extract was dried, evaporated and the residual solid, 185 mg. (93%), m.p. 70–73°, crystallized from hexane. This afforded crystalline tetralol IX, m.p. 73–74°, m.m.p. 73–75°.

Alkali Treatments of 1-Methyl-1-dichloromethyl-2-tetralone (IIa). (a) **Dilute Alcoholic Base.**—A mixture of 24.30 g. of ketone IIa, 200 ml. of 30% sodium hydroxide and 100 ml. of ethanol was refluxed for 8 hr. The cooled mixture was filtered, concentrated, refiltered, extracted with ether and acidified. The resulting red oil was taken up in ether, the extract washed with water and dried over magnesium sulfate. Evaporation of the solvent and crystallization of the oily solid from petroleum ether gave 15.29 g. (81.5%) of solid, m.p. 90–93°, which on recrystallization from methanol and from petroleum ether afforded crystalline 1-methyl-3,4-dihydro-3-naphthoic acid (Xa), m.p. 94.5–95°; ultraviolet spectrum (95% ethanol): λ_{\max} 260 m μ (ϵ 8900).²²

Anal. Calcd. for $C_{12}H_{12}O_2$: C, 76.59; H, 6.43. Found: C, 76.8; H, 6.64.

Its amide was crystallized from dilute methanol, m.p. 146.5–147°.

Anal. Calcd. for $C_{12}H_{13}ON$: C, 76.99; H, 7.00. Found: C, 77.05; H, 6.65.

An intimate mixture of 6.20 g. of the acid Xa and 1.3 g. of sulfur was heated at 196° and 25 mm. for 2 hr. The reaction mixture and sublimate were stirred well into a 5% sodium hydroxide solution. The filtered mixture was acidified and the precipitated acid collected. This led to 5.40 g. (88%) of 1-methyl-3-naphthoic acid (IV), m.p. and m.m.p. 196–198°.

(b) **Sodium Hydroxide in Ethanol-Water.**—A solution of 3.00 g. of ketone IIa, 20 ml. of 20% sodium hydroxide and 25 ml. of ethanol was refluxed under nitrogen for 8 hr. The solution was concentrated under vacuum, diluted with water and extracted with ether. The extract was washed with water, dried over magnesium sulfate and evaporated, leaving 300 mg. of starting ketone IIa. The aqueous solution was acidified with 1 *N* hydrochloric acid and extracted with ether. The extract was dried, evaporated and the resulting solid extracted with hexane. Crystallization of the residue, 650 mg., from aqueous methanol led to the naphthoic acid IV, m.p. 202–204°. Evaporation of the hexane solution gave 1.15 g. of solid which afforded the dihydro-naphthoic acid Xa, m.p. 94–95°, on crystallization from cyclohexane-hexane.

(c) **Sodium Methoxide in Methanol.**—A solution of 2.00 g. of ketone IIa and 0.2 g. of sodium in 40 ml. of dry methanol was refluxed under nitrogen for 8 hr. A work-up identical to the above (b) gave a neutral fraction exhibiting 5.60 and 5.85 μ bands, presumably corresponding to compounds XIa and IIa, respectively; 860 mg. (55%) of the naphthoic acid IV; and 210 mg. of a mixture of acids, m.p.

(20) H. R. Snyder and G. I. Poos, *J. Am. Chem. Soc.*, **71**, 1395 (1949).

(21) This compares favorably with the ultraviolet absorption characteristics of 2-methoxy-4,5-benzotropone, λ_{\max} 238 m μ (ϵ 31,600), 276 m μ (ϵ 38,000), 354 m μ (ϵ 4000) and $\lambda_{\text{shoulder}}$ 233–234 m μ (ϵ 25,600), 241–246 m μ (ϵ 22,000), 303–307 m μ (ϵ 7200) [G. P. Scott and D. S. Tarbell, *ibid.*, **72**, 240 (1950)]. R. M. D. and W. P. W. are most grateful to Professor Tarbell for a sample of the latter compound.

(22) Cf. ultraviolet spectra of 1-methyl-3,4-dihydronaphthalene, λ_{\max} 260 m μ (ϵ 7900) [P. Ramart and M. J. Hoch, *Bull. soc. chim. (France)*, 848 (1938)], 1,4-dihydronaphthalene λ_{\max} 274 m μ (ϵ 850) [R. A. Morton and A. J. A. DeGouveia, *J. Chem. Soc.*, 911 (1934)] and *trans*-cinnamic acid, λ_{\max} 273 m μ (ϵ 20,800).

108–116°, from the hexane extract. The latter was treated with diazomethane and the mixture of esters chromatographed on alumina. Petroleum ether elution gave 160 mg. (10%) of liquid methyl ester of the dihydro acid Xa, whose infrared spectrum was identical with that of an authentic specimen prepared by diazomethane esterification of a pure sample of Xa. Further petroleum ether elution yielded 20 mg. (1%) of methyl 1-methyl-3-naphthoate, m.p. 38–40° after crystallization from hexane.

(d) **Potassium *t*-Butoxide in *t*-Butanol.**—A potassium *t*-butoxide solution (0.2 g. of potassium in 30 ml. of *t*-butyl alcohol) of 1.50 g. of ketone was stirred at room temperature under nitrogen for 24 hr. The reaction mixture was diluted with water and extracted with ether. Drying and evaporation of the extract, alumina chromatography of the oily residue and elution with petroleum ether gave 0.86 g. of an inseparable oily mixture exhibiting 5.60 and 5.85 μ infrared peaks. Repeated alumina chromatography partly destroyed the 5.60 μ absorbing substance. The initial aqueous solution was acidified with 1 *N* hydrochloric acid and extracted with ether. Drying of the extract over magnesium sulfate and evaporation left 320 mg. (27%) of acid, m.p. 89–90°, which on crystallization from hexane afforded the dihydro-naphthoic acid Xa, m.p. 91–92.

Alkali Treatments of 1-Methyl-3,4-dihydro-3-naphthoic Acid (Xa) and Its Ester.—Refluxing of a sodium methoxide solution (10 mg. of sodium in 15 ml. of dry methanol) of 200 mg. of the acid Xa and the aforementioned work-up gave 192 mg. (96%) of starting material.

A sodium methoxide solution (10 mg. of sodium in 15 ml. of absolute methanol) of the methyl ester of Xa, prepared by diazomethane treatment of 250 mg. of acid Xa, was refluxed under nitrogen for 4 hr. The solution was diluted with water and extracted with ether. Drying of the extract over magnesium sulfate and evaporation led to 95 mg. of neutral oil whose ultraviolet spectrum revealed it to be a mixture of the methyl esters of Xa and IV. The basic aqueous solution was acidified with 1 *N* hydrochloric acid and extracted with ether. Similar work-up of this extract led to 112 mg. (45%) of 1-methyl-3-naphthoic acid, m.p. 195–198° after crystallizations from carbon tetrachloride-hexane and aqueous methanol.

1-Methyl-1,2,3,4-tetrahydro-3-naphthoic Acid (XV).—A solution of 400 mg. of ketone Ib¹² in 20 ml. of ethanol was hydrogenated exhaustively over 20 mg. of 5% palladium-charcoal at room temperature and atmospheric pressure.

Filtration of the catalyst, vacuum removal of the solvent, alumina chromatography of the oily residue and petroleum ether elution gave 230 mg. of liquid tetralone IIB, infrared spectrum (CCl₄), C=O 5.85(s) μ ; orange 2,4-dinitrophenylhydrazone, m.p. 177–178° after crystallization from ethanol-ethyl acetate. The ketone was used in the next experiment without further purification.

A potassium *t*-butoxide solution (60 mg. of potassium in 30 ml. of dry *t*-butyl alcohol) of 200 mg. of ketone IIB was stirred under nitrogen for 8 hr. The usual work-up yielded 94 mg. of an oily neutral mixture exhibiting 5.60 and 5.85 μ infrared peaks and an acidic fraction which on sublimation gave 67 mg. (37%) of an acid, m.p. 105–109°. Two crystallizations of the latter from hexane afforded acid XV, m.p. and m.m.p. 123–125° (*vide infra*).

A solution of 100 mg. of acid Xa in 20 ml. of ethanol was hydrogenated over 10 mg. of palladium-charcoal at room temperature and atmospheric pressure. Filtration of the catalyst and vacuum removal of the solvent yielded 94 mg. (94%) of solid. Crystallization of the product from hexane gave 1-methyl-1,2,3,4-tetrahydro-3-naphthoic acid (XV), m.p. 124–125; ultraviolet spectrum (95% ethanol), λ_{\max} 266 $m\mu$ (ϵ 532), 273 $m\mu$ (ϵ 548) and λ_{\min} 248 $m\mu$ (ϵ 242) and 270 $m\mu$ (ϵ 333).

Anal. Calcd. for C₁₂H₁₄O₂: C, 75.76; H, 7.42. Found: C, 75.94; H, 7.42.

Cyclobutanone XXI–XXII.—A potassium *t*-butoxide solution (4.1 g. of potassium in 200 ml. of *t*-butyl alcohol) of 19.5 g. of 2-methyl-2-dichloromethylcyclohexanone (XX), m.p. 33–35°,¹⁸ was stirred under nitrogen for 24 hr. The usual work-up led to 15.0 g. of neutral products exhibiting 5.60 and 5.85 μ infrared absorption bands. Three vacuum distillations gave 7.0 g. of pure cyclobutanone XXI–XXII, b.p. 45° (0.07 mm.); infrared spectrum (CCl₄), C=O 5.60 (s) μ .

Anal. Calcd. for C₈H₁₁OCl: C, 60.55; H, 6.99. Found: C, 61.00; H, 7.24.

The infrared spectra of all other distillation fractions showed them to contain mostly starting ketone XX and some more product XXI–XXII.

The cyclobutanone could be converted in 80% yield into its semicarbazone, m.p. 234–235° after crystallization from aqueous methanol.

Anal. Calcd. for C₈H₁₄ON₂Cl: C, 50.11; H, 6.54; Cl, 16.44. Found: C, 49.96; H, 6.93; Cl, 16.92.

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Syntheses of 4,12-Dimethyl[2.2]metacyclophane

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Two syntheses of 4,12-dimethyl[2.2]metacyclophane (IV) are described.

Undoubtedly, one of the most stimulating concepts introduced into aromatic chemistry is the generalization from simple molecular orbital theory known as the Hückel rule.⁵ This requirement that aromatic stability in conjugated, planar, monocyclic polyenes is associated with those molecules having $4n + 2\pi$ electrons has been amply confirmed by Doering,⁶ Dauben,⁷ Dewar⁸ and

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(5) E. Hückel, *Z. Elektrochem.*, **43**, 752 (1937).
(6) W. von E. Doering and L. H. Knox, *THIS JOURNAL*, **76**, 3203 (1954). For a summary, see W. von E. Doering, "Theoretical Organic Chemistry (Kekulé Symposium)," Butterworth Scientific Publications, London, 1959, p. 35.

(7) H. J. Dauben, Jr., and H. Ringold, *THIS JOURNAL*, **73**, 876 (1951), and related papers.

Breslow⁹ for small rings and observations by Sondheimer¹⁰ indicate it for large rings. However, testing the Hückel rule with rings of intermediate size presents both synthetic and theoretical difficulties. Molecular models indicate that in the case of compounds such as cyclotetradecaheptaene (I) the steric interference of the *internal* hydrogens would be sufficiently great to cause twisting and result in an appreciable deviation of the conjugate unsaturation from planarity. However, the presence of saturated atoms within a π -electron cloud should not in itself affect appreciably the delocalization energy.

(8) M. J. S. Dewar and R. Pettit, *J. Chem. Soc.*, 2021, 2026 (1956), and related papers.

(9) (a) R. Breslow and C. Yuan, *THIS JOURNAL*, **80**, 5991 (1958); (b) R. Breslow and H. Höver, *ibid.*, **82**, 2644 (1960); see also, D. G. Farnum and M. Burr, *ibid.*, **82**, 2651 (1960).

(10) F. Sondheimer and R. Wolovsky, *Tetrahedron Letters*, **3**, (No. 3) (1959).