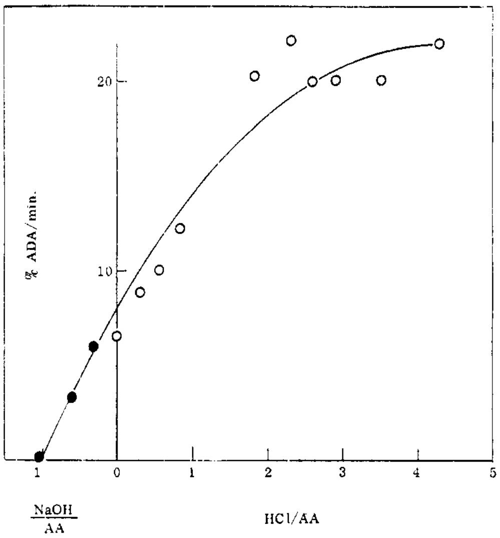


Figure 1.—Hydrogenative dimerization of acrylic acid (AA). Dependence of rate on molar ratio of AA to NaOH and HCl.

As part of our study on the hydrodimerization of acrylic monomers by means of alkali metal amalgams,[2,3] we have also attempted to dimerize acrylic acid. When the reaction was carried out in water, dioxane, or diglyme, the only product was propionic acid (PA). However, when dimethyl sulfoxide (DMSO) was used as solvent, adipic acid (ADA) was the main product.

The reaction was carried out by stirring a solution of 2–5% AA and 10% water in DMSO with a sodium amalgam. To achieve high conversion, it was necessary to add hydrochloric acid during the reaction. Under these conditions, it was possible to obtain a yield of about 70% ADA, and as by-product 20–25% propionic acid. The interesting point is that the addition of hydrochloric acid increased the rate of the reaction but did not increase the PA/ADA ratio.

The following standard technique was used to measure the reaction rate. A sodium amalgam (60 ml, the sodium content being 15 mmol/100 g of mercury) was placed into a reaction flask equipped with an efficient mechanical stirrer. To this was then introduced 50 ml of a DMSO solution containing 5% AA and 10% water, and stirring was continued for 30 additional sec. The amalgam was then separated and the acids formed were esterified with a boron trifluoride–methanol mixture and injected into an F & M gas chromatograph (column, LAC 446 polyester on Chromosorb W).

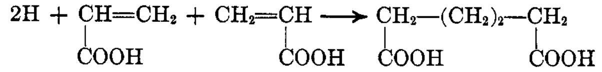
The results may be seen from Figure 1.

When sodium acrylate is the reacting species, no reaction is occurring. However, upon addition of hydrochloric acid to the medium, the rate of reaction gradually increases due to the equilibrium

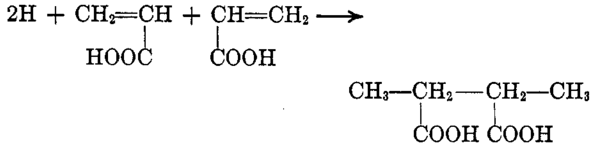
$$\text{acrylate}^- + H^+ \rightleftarrows \text{acrylic acid}$$

The large excess of hydrochloric acid is required because of the strongly alkaline conditions existing at the double layer. This shows clearly that the active species interacting with the amalgam is the undissociated acid and not the acrylate anion.

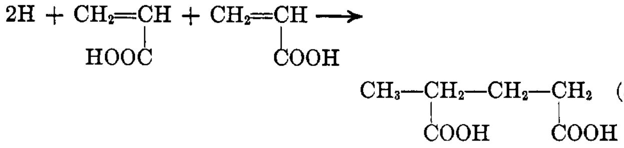
Hydrodimerizations were also carried out with methacrylic and crotonic acids. In these cases, however, one does not obtain the tail-to-tail addition that was the exclusive reaction made for AA (eq 1), but mainly head-to-head (eq 2) and head-to-tail (eq 3) addition.



$$2H + \underset{COOH}{CH}=CH_2 + CH_2=\underset{COOH}{CH} \longrightarrow \underset{COOH}{CH_2}-(CH_2)_2-\underset{COOH}{CH_2} \qquad (1)$$



$$2H + CH_2=\underset{HOOC}{CH} + \underset{COOH}{CH}=CH_2 \longrightarrow CH_3-\underset{COOH}{CH_2}-\underset{COOH}{CH_2}-CH_3 \qquad (2)$$



$$2H + CH_2=\underset{HOOC}{CH} + CH_2=\underset{COOH}{CH} \longrightarrow CH_3-\underset{COOH}{CH_2}-CH_2-\underset{COOH}{CH_2} \qquad (3)$$

Codimerizations of these two acids with AA were also carried out to yield mixtures of isomeric saturated dicarboxylic acids.

Sorbic acid can also be hydrodimerized in DMSO by the use of sodium amalgam to yield three different isomeric dicarboxylic acids. This, however, can be accomplished in an ether solvent such as diglyme as well as in DMSO, which emphasizes the effect of DMSO on the reduction potential of the unconjugated acids.

The effect of DMSO is probably due to its donor character. It is known that DMSO can bind acids through strong hydrogen bonding. It thus avoids the direct reduction of the acid and enables it to undergo hydrodimerization. The detailed mechanism of the reaction is at present under study.

Registry No.—Acrylic acid, 79-10-7.

Acknowledgment.—The authors are indebted to U. C. B. (Union Chimique-Chemische, Bedrijven) S. A., Brussells, Belgium, for financial support of this work.

[2] Y. Arad, M. Levy, I. R. Miller, and D. Vofsi, *J. Electrochem. Soc.*, **114**, 889 (1967).

[3] Y. Arad, M. Levy, H. Rosen, and D. Vofsi, *J. Polym. Sci.*, in press.

Acid-Catalyzed Reactions of 1,4-Dihydro-1-methyl-4-oxo-1-naphthonitrile. Self-Condensation to a 13-Oxapicene Derivative[1]

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Received March 17, 1969

Certain cyclohexadienones have been found to undergo the dienone–phenol rearrangement with difficulty or with the formation of unusual reaction products if one of the *gem* substituents is an electron-attracting group.[2] We now find that another similarly con-

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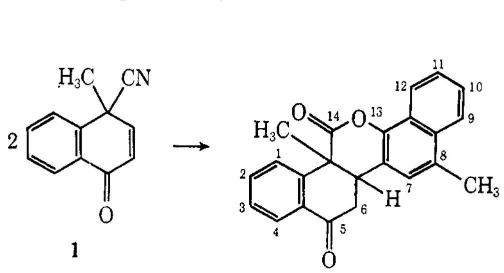
[1] The author is indebted to Lafayette College for a 1968 Summer Research Fellowship. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support (1905-B) of this research.

[2] (a) T. G. Miller, *J. Org. Chem.*, **27**, 1549 (1962). (b) H. Pleininger and T. Suehiro, *Chem. Ber.*, **89**, 2789 (1956). (c) M. S. Newman and L. L. Wood, Jr., *J. Amer. Chem. Soc.*, **81**, 6450 (1959).

stituted compound, 1,4-dihydro-1-methyl-4-oxo-1-naphthonitrile (1)[3], does not undergo a dienone–phenol type rearrangement when treated with strong acids, but instead undergoes a unique self-condensation reaction involving lactone formation and bridging of the two ring systems to give the oxapicene derivative, 2. The process is accompanied by loss of carbon dioxide.



1

2

The yield of crude 2 is high when the condensation is carried out by heating 1 in either polyphosphoric acid or pure *p*-toluenesulfonic acid hydrate. Somewhat lower yields result when 80–85% sulfuric acid is used. Losses due to low returns of even rather pure samples from any of a number of crystallizing solvents reduced the yields of pure lactone, however.

Although the 13-oxapicene ring system has apparently not been reported previously, a combination of chemical and spectrometric evidence clearly confirms the designated structure for compound 2. 2,4-Dinitrophenylhydrazine reacts as expected with 2, but the orange derivative was difficult to purify and was not analyzed. The lactone structure is hydrolyzed slowly by aqueous sodium hydroxide (more rapidly if some alcohol is present to increase solubility) to give a solution from which, as predicted for a carboxylic acid salt,[4] the free acid is precipitated by strong acids but not by carbon dioxide. The free acid reverts spontaneously to 2 and hence could not be isolated in pure condition; however, infrared absorption bands characteristic of the free carboxylic acid were noted (see below).

In the mass spectrum of 2 the molecular ion peak at *m/e* 342 is quite strong, which is generally the case with large aromatic molecules.[5] Isotopic contributions to the molecular ion give M + 1 and M + 2 peaks whose intensities are consistent with the $C_{23}H_{18}O_3$ formula for 2.[6] The base peak is at *m/e* 314 (M − 28) resulting probably from loss of CO from the molecular ion. It has been found recently that the principal fragmentation peak of 1-tetralone at M − 28 results from loss of the 2 and 3 carbon atoms as ethylene and not from loss of CO.[7] In the case of 2, however, such a cleavage would require breaking both bonds to the 6a carbon and rearrangement of an H atom. It seems more likely, therefore, that a cleavage at the 13–14 bond followed by loss of C-14 as CO, or loss of C-5 as CO in the manner of 1-indanone,[7] is the principal mode of formation of the M − 28 fragment.

The infrared spectrum of 2 contains two C=O bands. One is at 1690 cm^{-1}, the characteristic region for a carbonyl group conjugated with one aromatic ring,[8] but at too high a frequency for double conjugation as exemplified by the starting material (1).[9] A second band occurs at 1761 cm^{-1}, the expected frequency for the lactone C=O in 2.[10] A strong band at 761 cm^{-1} represents the terminal *ortho*-disubstituted rings. There are also several much weaker bands in the 860–900-cm^{-1} region where the out-of-plane deformation absorption for the lone aromatic hydrogen in the 7 position should occur,[11] but a definite assignment of any of them cannot be made. As noted above, the free acid obtained by hydrolysis of the lactone ring could not be isolated in pure condition because it reverted so readily to the lactone. Infrared spectra of some acid–lactone mixtures, obtained by acidification of a basic solution of the lactone and air drying the precipitate, differed from that of the starting material in the expected ways, *i.e.*, strong diminution of the lactone C=O band at 1761 cm^{-1}, new absorption in the 1700-cm^{-1} region resulting in distortion of the ketonic C=O band, and introduction of the broad OH stretching absorption of carboxylic acids in the 3000-cm^{-1} region.[12] The oxime of 2, although difficult to purify by crystallization and hence not submitted for elemental analysis, gave an ir spectrum resembling in most features that of 2, but differing in ways helpful in structural assignments, *i.e.*, loss of the ketonic C=O band at 1690 cm^{-1}, retention of the lactone C=O band, and appearance of OH stretching absorption at 3200 cm^{-1}.

Additional evidence for the structure assigned to 2 is found in its ultraviolet spectrum. Absorption maxima at 230 and 294 mμ undergo bathochromic shifts to 254 and 342 mμ, respectively, when the spectrum is run in the presence of sodium hydroxide to effect opening of the lactone ring, demonstrating that the heterocyclic oxygen is indeed phenolic in nature.[13,14]

The nmr spectrum of 2 is entirely consistent with the designated structure. A complex of bands represents the nine aromatic hydrogens, and singlets at 2.63 and 1.80 ppm represent the methyl groups in the 8 and 14a positions, respectively. One well-resolved peak at the extreme upfield end of the aromatic complex integrates for one proton and may represent the hydrogen atom in the 7 position, but this assignment cannot be made with certainty. The chemical shifts of the axial and equatorial protons in the 6 position must be virtually the same, for the splitting pattern with the 6a proton is first order, a triplet at 3.69 ppm

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(3) R. C. Fuson and T. G. Miller, *J. Org. Chem.*, **17**, 886 (1952).

(4) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th ed, John Wiley & Sons, Inc., New York, N. Y., 1956, pp 81, 335.

(5) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Interpretation of Mass Spectra of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1964, Chapters 9 and 11.

(6) J. H. Beynon and A. E. Williams, "Mass and Abundance Tables for Use in Mass Spectrometry," Elsevier Publishing Co., Amsterdam, The Netherlands, 1963, p 242.

(7) J. A. Bowie, *Aust. J. Chem.*, **19**, 1919 (1966).

(8) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., p 137, 1958.

(9) The starting material absorbs at 1675 cm^{-1} ($CHCl_3$). For other examples, see "Handbook of Organic Structural Analysis," Y. Yukawa, Ed., W. A. Benjamin, Inc., New York, N. Y., 1965, p 332.

(10) Reference 7, p 185.

(11) Reference, pp 75–81.

(12) Reference, pp 161–165.

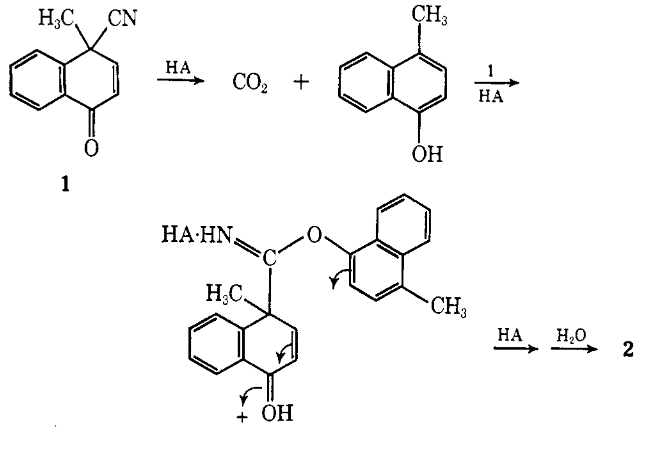
(13) R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1967, p 163.

(14) For comparison, the similar chromophore in 4-methyl-1-naphthol in the same solvent (methanol) has bands at 238 and 302 mμ which are shifted to 251 and 339 mμ, respectively, when the naphtholate ion is formed by the addition of sodium hydroxide. The uv spectrum of 4-methyl-1-naphthol in chloroform has been reported previously. See A. Ebnother, T. M. Meijer, and H. Schmid, *Helv. Chim. Acta*, **35**, 910 (1952).

representing the 6a proton, and a doublet at 3.13 ppm the two protons in the 6 position. Both the pattern and the distortion of intensities correspond very closely to those of an $A_2'B'$ system where $\Delta\nu/J_{AB\ \mathrm{average}}$ is 5–6.[15] Expected differences between J_{A_1B} and J_{A_2B} have no effect on the pattern, and the observed coupling constant of 6.5 Hz represents $J_{AB\ \mathrm{average}}$.[15] It must be entirely fortuitous that both methylene protons have the same chemical shift, for averaging of the shifts by rapid interconversion of conformers, a process observed in certain ring compounds,[16] seems precluded in this case by fusion with the benzene ring which limits four of the atoms to one plane and introduces considerable resistance to rotation of the other two.

Fisher–Taylor–Hirschfelder models permit the construction of 2 with *cis* but not *trans* fusion between the two saturated rings. Two conformations of the *cis* form can be made but are not readily interconvertible. One has the two aromatic systems in roughly the same plane but inclined to each other at about 30°. The other has the two aromatic systems folded back toward each other at an angle of less than 90°. Although the entirely inflexible bond angles in the models used make it impossible to construct 2 with a *trans* ring fusion, the degree of strain is not large, and it seems likely that this configuration is also possible. Other ring systems similar to 2 but not having the two sp^2 carbon atoms of the carbonyl groups and the heterooxygen atom can be constructed easily from the models with either *cis* or *trans* ring fusion.

The mechanism by which 1 is converted into 2 is not known. A logical sequence of steps would first involve removal of the cyano group from 1 by hydrolysis and decarboxylation to give 4-methyl-1-naphthol (or an intermediate resembling it), condensation of the naphtholic hydroxyl with a cyano group to give an imido ester salt, and ring closure by substitution of the β-carbon atom of the carbonyl group on the naphthalene nucleus. Water used in the work-up would convert the imido lactone into the lactone. Polyphosphoric acid, which can affect the condensation, does not usually cause removal of cyano groups;[17] however, in this case carbon dioxide is evolved immediately upon warming the solution. The increase in stabilization energy in going from 1 to the naphthalene aromatic system may provide the driving force for this reaction. More ordinary acidic hydrolytic conditions usually cause the formation of 4-methyl-1-naphthol from 1 (see below). The second step proposed is the familiar reaction of alcohols and nitriles useful in preparing esters, and the ring closure resembles other known aromatic substitution reactions.[18] It would also be possible for the last two steps to occur in reverse order. Supporting the proposed reaction scheme is the fact that an equimolar mixture of 1 and 4-methyl-1-naphthol, when heated in *p*-toluenesulfonic acid hydrate, gives a yield of 2 that is more than theory for its formation from 1 alone. However, two other phenols, α-naphthol and 2,4-xylenol, did not undergo a similar reaction with 1 under the same conditions.



Attempts to make 1 undergo the dienone–phenol rearrangement in other acidic systems such as sulfuric acid in acetic anhydride, perchloric acid in acetic anhydride, and *p*-toluenesulfonic acid in acetic acid resulted in no reaction except for very small conversions of the ketone into a phenolic substance. This was isolated in the *p*-toluenesulfonic acid–acetic acid experiment and identified by its ir spectrum as 4-methyl-1-naphthol.

Experimental Section[19]

5,6,6a,14a-Tetrahydro-8,14a-dimethyl-13(14H)-oxapicene-5,14-dione (2).—A mixture of 1.00 g of 1[3] and 8.0 g of *p*-toluenesulfonic acid monohydrate[20] was heated in an oil bath at 115–120° for 1.3 hr. Carbon dioxide[21] began to evolve as soon as the mixture became hot. The light brown solution was poured into water and the resulting pinkish colored solid was collected on a filter, washed acid free, and dried *in vacuo* to give 0.88 g (94%) of a crude product which melted at 205–212° and showed only one component of any significance by tlc (Eastman Chromagram Sheet K301R, $CHCl_3$, uv visualization, R_f 0.57). Crystallization from ethanol–ethyl acetate gave 0.45 g (48%) of pure lactone (2):[22] mp 223–224°; mass spectrum (70 eV) *m/e* (rel intensity) 342 M^+ (83), 315 (25), 314 (100), 299 (19), 281 (15), 157 (19), 128 (20), 115 (22), 103 (25), 77 (28); $M^+ + 1$ and $M^+ + 2$ as per cent of M^+, 25.5 and 3.7% (calcd for $C_{23}H_{18}O_3$, 25.3 and 3.7%[6]); ir ($CHCl_3$ and CS_2) 1761 (lactone C=O), 1690 (conjugated C=O), 1605 (ar C=C), 1390, 1300, 1218, 1133, 1090, and 761 cm^{-1} (4 adjacent aromatic H); nmr ($CDCl_3$, TMS) δ 1.80 (s, 3, CH_3), 2.63 (s, 3, CH_3), 3.13 (d, 2, $=CH_2$, $J_{\mathrm{average}} = 6.5$ Hz), 3.69 (t, 1, $\equiv CH$, $J_{\mathrm{average}} = 6.5$ Hz), 7.19–8.37 ppm (complex, 9 H); uv max (CH_3OH) 294 (ϵ 1.18×10^4), 230 (ϵ 7×10^4), sh 323, 309, 285 mμ; in presence of NaOH uv max (CH_3OH) 342 (ϵ 1.08×10^4), 254 mμ (ϵ 6×10^4).

Anal. Calcd for $C_{23}H_{18}O_3$: C, 80.68; H, 5.30. Found: C, 80.30, H, 5.30.

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(15) R. H. Bible, Jr., "Interpretation of Nmr Spectra," Plenum Press, New York, N. Y., 1965, pp 84–85.

(16) J. W. Emsley, J. Feeny, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 1, Pergamon Press, New York, N. Y., 1965, pp 575–581.

(17) F. Uhlig and H. R. Snyder in Advances in Chemistry. Methods and Results, Vol. I, R. A. Raphael, E. C. Taylor, and H. Wynberg, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, pp 44–70.

(18) (a) R. C. Fuson, "Reactions of Organic Compounds," John Wiley & Sons, Inc., New York, N. Y., 1962, pp 79 and 128. (b) E. P. Kohler, *Amer. Chem. J.*, **31**, 642 (1904).

(19) Elemental analyses were carried out by the Weiler and Strauss Microanalytical Laboratory, Oxford, England. Melting points were taken on a Fisher-Johns apparatus and are corrected. Uv spectra were recorded on a Beckman DK-2A instrument, and ir spectra were recorded on either a Beckman IR-5 or IR-10. The mass spectrum was determined by the Morgan-Schaeffer Corp., Montreal, Canada, using a Hitachi Perkin-Elmer RMU-6D. Nmr spectra were determined by the Sadtler Research Laboratories, Philadelphia, Pa., using a Varian A-60A instrument.

(20) Purified by crystallization from chloroform and drying in a desiccator over $CaSO_4$.

(21) Identified by its nonreducing (to $KMnO_4$) nature and its precipitation of $CaCO_3$ from limewater.

(22) A number of solvents and solvent pairs were investigated as crystallizing solvents. Several, such as ethanol, carbon tetrachloride, and toluene–petroleum ether had suitable solvent properties when hot and could be used to prepare analytical samples, but none gave a good return of the product when the solution was chilled, even when the sample being crystallized was substantially pure.

Equivalent results were obtained when a proportionate weight of polyphosphoric acid (20% P_2O_5) was used as the solvent-catalyst instead of *p*-toluenesulfonic acid.

Reaction of 4-Methyl-1-naphthol with 1.—A mixture of 500 mg (2.73 mmol) of 1, 432 mg (2.73 mmol) 4-methyl-1-naphthol (K & K Laboratories), and 5.0 g *p*-toluenesulfonic acid monohydrate[20] was heated in a 115° oil bath for 2 hr. In contrast to the reaction of 1 alone in *p*-toluenesulfonic acid no CO_2 evolution was evident. The mixture was poured into water and the precipitated solid collected on a filter, washed acid free and dried *in vacuo* to constant weight to give 915 mg of a pinkish-colored solid which smelled of 4-methyl-1-naphthol. The crude product was triturated with two 25-ml portions of 50% ethanol to extract unreacted 4-methyl-1-naphthol, and the residue dried *in vacuo* to give 685 mg of a product whose ir spectrum showed it to consist almost entirely of 2 along with a small amount of 4-methyl-1-naphthol. Infrared analysis (see below) of this mixture indicated, as a least favorable figure, 89% lactone (2) corresponding to 610 mg (1.79 mmol) of pure 2. This is 66% of theory for the reaction of 1 mol of 1 with 1 mol of the naphthol, or 131% of theory for the self-condensation of 1 alone.

Ir Analysis of the Mixture of 2 and 4-Methyl-1-naphthol.—The 1761- and 1690-cm^{-1} C=O bands of the lactone were calibrated using pure samples of 2 in $CHCl_3$ solution, the absorbance in the 1850–2000-cm^{-1} range serving as base line. 4-Methyl-1-naphthol has only very weak absorption over the whole 1670–2000-cm^{-1} region. Straight-line Beers law plots were obtained for both bands. The mixture referred to in the preceding section was found to have 94% 2 using the 1761-cm^{-1} band and 89% 2 when analyzed by the 1690-cm^{-1} band.

Registry No.—1, 21615-50-9; 2, 21615-51-0.

The Preparation of 3-Arylphthalides by the Clemmensen Reduction of 2-Aroylbenzoic Acids

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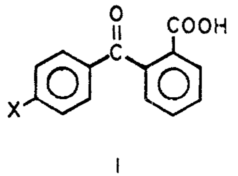
Received March 18, 1969

In the course of our research[2] we carried out a Clemmensen reduction of 2-benzoylbenzoic acid (**1a**), expecting to obtain a high yield of 2-benzylbenzoic acid (**2a**) as reported in the literature.[3,4] We isolated, instead, a compound (80% yield) which was insoluble in base and was identified as 3-phenylphthalide (**3a**). Only a small amount of 2-benzylbenzoic acid was recovered. Clemmensen reduction of several 2-(*p*-substituted benzoyl)benzoic acids gave good yields of the corresponding 3-(*p*-substituted phenyl)phthalides.



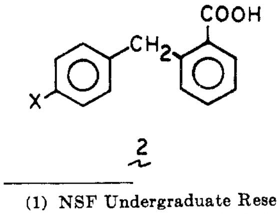
1

a ; X = H

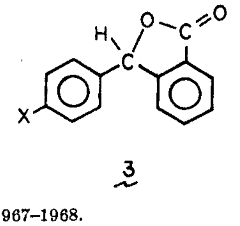
b ; X = Cl

c ; X = OCH_3

d ; X = CH_3



2



3

It is possible that variations in particle size and impurities in the zinc are responsible for these conflicting results.[5] We believe, however, that there was an error in the structure assignment of the Clemmensen reduction product of **1a**, probably due to the almost coincident melting points of **2a** and **3a**. Thus, the melting point of 2-benzylbenzoic acid (**2a**) is reported as 111–113°[6] and 114°[7,8] and the melting point of 3-phenylphthalide (**3a**) as 115°,[7,9] 115.5°,[10] and 117°.[11] Hauser and coworkers[12] found that 3-phenylphthalide is the major product of the Clemmensen reduction of **1a**.

Horning and Reisner[6] have reported that catalytic hydrogenation of 2-benzoylbenzoic acid gives high yields of 2-benzylbenzoic acid.[13] We have successfully repeated this work and believe that catalytic hydrogenation is a superior method for effecting this conversion.

Experimental Section

Melting points are uncorrected. Microanalyses were by Alfred Bernhardt, Germany, and Micro-analysis, Inc., Wilmington, Del.

Reduction procedure A of Bradlow and VanderWerf[3] was followed exactly. The reaction mixture was extracted with benzene and the aqueous layer discarded. The benzene solution was extracted with 5% sodium carbonate solution. The 3-arylphthalide was isolated upon removal of the benzene and was recrystallized from methanol. Acidification of the carbonate solution precipitated a small amount of the benzylbenzoic acid which was recrystallized from methylene chloride.

Reduction of 2-Benzoylbenzoic Acid (1a).—2-Benzoylbenzoic acid, 11.5 g (0.051 mol) yielded 8.4 g (79%) of 3-phenylphthalide (**3a**): mp 114–115° (lit.[11] mp 117°); ir ($CHCl_3$) 1755 cm^{-1} (lactone C=O); nmr ($CDCl_3$) δ 6.38 (s, 1) and 7.28–7.93 ppm (m, 9).

The sodium carbonate extract yielded 2.3 g (21%) of 2-benzylbenzoic acid (**2a**): mp 112–115° (lit.[6] mp 111–113°); ir (Nujol) 1690 cm^{-1} (acid C=O); nmr ($CDCl_3$) δ 4.46 (s, 2) and 7.33–8.00 ppm (m, 9), carboxyl proton not observed.

Reduction of 2-(*p*-Chlorobenzoyl)benzoic Acid (1b).—2-(*p*-Chlorobenzoyl)benzoic acid, 12 g (0.045 mol), yielded 8.8 g (80%) of 3-(*p*-chlorophenyl)phthalide (**3b**): mp 121–122°; ir (Nujol) 1750 cm^{-1}; nmr ($CDCl_3$) δ 6.24 (s, 1) and 6.97–7.86 ppm (m, 8).

Anal. Calcd for $C_{14}H_9ClO_2$: C, 68.73; H, 3.71. Found: C, 68.50; H, 3.68.

Reduction of 2-*p*-Anisoylbenzoic Acid (1c).—2-*p*-Anisoylbenzoic acid, 6 g (0.023 mol), yielded 3.4 g (62%) of 3-*p*-anisylphthalide (**3c**): mp 113–114.5°; ir (Nujol) 1756 cm^{-1}; nmr ($CDCl_3$) δ 3.73 (s, 3), 6.24 (s, 1), and 6.66–7.87 ppm (m, 8).

Anal. Calcd for $C_{15}H_{12}O_3$: C, 74.99; H, 5.04. Found: C, 75.18; H, 5.05.

Reduction of 2-*p*-Toluylbenzoic Acid (1d).—2-*p*-Toluylbenzoic acid, 6 g (0.025 mol), yielded 1.5 g (27%) of 3-*p*-tolyphthalide (**3d**): mp 127–128°; ir (Nujol) 1755 cm^{-1}; nmr ($CDCl_3$) δ 2.28 (s, 3), 6.23 (s, 1), 6.99 (s, 4), and 7.06–7.85 ppm (m, 4).

Anal. Calcd for $C_{15}H_{12}O_2$: C, 80.34; H, 5.39. Found: C, 80.13; H, 5.30.

A large amount of starting material was isolated indicating that the low yield of **3d** was due to low conversion.

Registry No.—**3a**, 5398-11-8; **3b**, 4889-69-4; **3c**, 21615-74-7; **3d**, 21615-75-8.

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(1) NSF Undergraduate Research Fellow, 1967–1968.

(2) D. P. Weeks and J. Cella, Abstracts, 3rd Middle Atlantic Regional Meeting of the American Chemical Society, Philadelphia, Pa., Feb 1968, No. H-58.

(3) H. L. Bradlow and C. A. VanderWerf, *J. Amer. Chem. Soc.*, **69**, 1254 (1947).

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