The blends of perbenzoic acid, benzoic acid, benzaldehyde, and ethyl acetate then were scanned at four 15-min. intervals over the indicated temperature range. The initial spectrum was recorded at −60° and the final one at 30°.

The absorptions of the two acids and benzaldehyde changed concomitantly with the changes of the ethyl acetate absorption and were perfectly consistent with the variations observed from the previous runs due to path length differences.

These results constituted unequivocal evidence that, between −60 and 30°, temperature has no effect upon the benzaldehyde–benzoic acid–perbenzoic acid equilibrium in ethyl acetate.

Acknowledgment.—The author wishes to thank H. L. Spell of the Texas Division Central Laboratory for performing the infrared work herein reported, and Dr. O. C. Dermer for his many helpful discussions.

The Synthesis and Cyclization of 2-(1-Naphthylmethyl)-2′-carboxybenzophenone[1,2]

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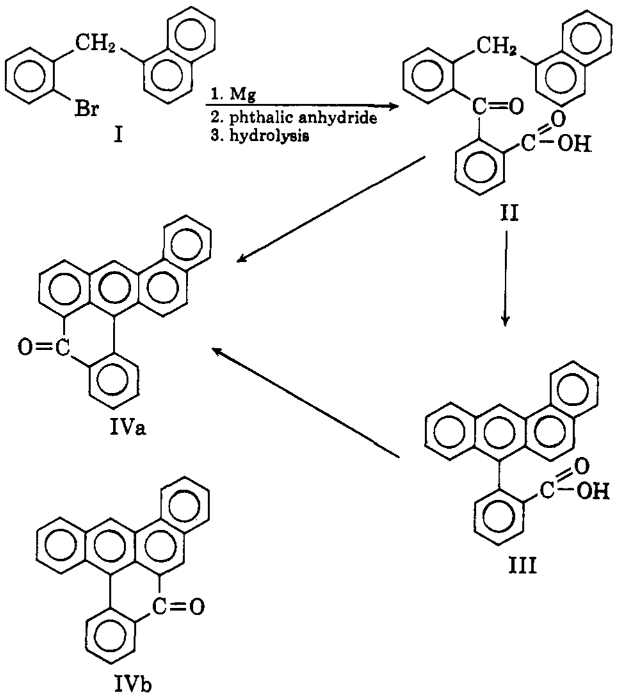
2-(1-Naphthylmethyl)-2′-carboxybenzophenone has been synthesized and cyclized to dibenzo[*hi,l*]chrysen-9-one under one set of conditions, and to 7-(2-carboxyphenyl)benz[*a*]anthracene under different conditions. One of the optically active forms of this acid has been isolated.

A study of the cyclization of 2-(1-naphthylmethyl)-2′-carboxybenzophenone (II) is interesting for several reasons. First, II might lose 1 mole of water to give 7-(2-carboxyphenyl)benz[*a*]anthracene (III). This should be resolvable into optically active forms owing to restricted rotation about the 7-1′ bond as a result of molecular overcrowding; it is of further interest because of its close relationship to 7-phenylbenz[*a*]anthracene.[4] Second, II might lose 2 moles of water to give dibenzo[*hi,l*]chrysen-9-one (IVa) and/or naphtho[3,2,1-*fg*]naphthacen-9-one (IVb).

The keto acid (II) was prepared in satisfactory yield by the addition of the Grignard reagent of 2-(1-naphthylmethyl)bromobenzene[5] (I) to a boiling solution of phthalic anhydride in benzene (see Chart I). The structure of II was established by carbon–hydrogen analysis, neutralization equivalent titration, infrared spectrum, and by conversion to its methyl ester which was characterized by carbon–hydrogen analysis and by its infrared spectrum.

The keto acid (II) lost 1 mole of water when heated with a mixture of hydrobromic and acetic acids for 1 hr. to give 90% of 7-(2-carboxyphenyl)benz[*a*]anthracene (III).[6] It is interesting to note that when Bradsher and Vingiello[7] cyclized an analogous keto acid, 2-benzyl-2′-carboxybenzophenone, to 9-(2-carboxyphenyl)anthracene they obtained an 80% yield after 20 hr. of heating. The greater ease of aromatic cyclodehydration into the 2-position of the naphthyl system as compared with the phenyl system is consistent with a proposed mechanism for aromatic cyclodehydration.[8]

CHART I



The ease of cyclization of II to III was further illustrated when the reaction was accomplished in 60% yield by simply treating II with concentrated sulfuric acid for a few minutes at −40°.

The acid (III) was first isolated as an alcoholate as indicated by carbon, hydrogen analysis, neutralization equivalent titration, and gas chromatographic analysis. Heating *in vacuo* at 110° for 48 hr. gave the acid III.

The acid III should be optically active owing to restricted rotation about the 7-1′ bond, and preliminary experiments using brucine as a resolving agent confirm this.

On dehydration, III might be expected to give IVa and/or IVb. However, if one assumes that the reaction proceeds *via* an attack of the positive carboxylic acid carbon on an electron-rich ring position, one would predict ring closure at C-8 in preference to C-6. The calculation of the localization energies for the 7-(2-carboxyphenyl)benz[*a*]anthracene system (III) is com-

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[1] The nomenclature used in this paper is that presented in the "Definitive Rules for Nomenclature of Organic Chemistry," *J. Am. Chem. Soc.*, **82**, 5545 (1960).

[2] Presented before the Division of Organic Chemistry at the Southeastern Regional Meeting of the American Chemical Society, Gatlinburg, Tenn., Nov., 1962.

[3] Abstracted from the M.S. thesis of E. J. Greenwood presented to the Virginia Polytechnic Institute, 1961.

[4] This compound, NSC #14080, showed slight activity against S-180 and L-1210 (private communication from the National Institutes of Health, Bethesda, Md.).

[5] For an improved method of preparation see P. Polss, Ph.D. dissertation, Virginia Polytechnic Institute, Blacksburg, Va., 1962.

[6] This compound, NSC #76322, which is currently being tested, showed activity against S-180 (private communication from the National Institutes of Health, Bethesda, Md.).

[7] C. K. Bradsher and F. A. Vingiello, *J. Org. Chem.*, **13**, 786 (1948).

[8] C. K. Bradsher and F. A. Vingiello, *J. Am. Chem. Soc.*, **71**, 1434 (1949).

plex and remains to be attempted. Since the attached phenyl ring would not contribute a mesomeric effect because of lack of conjugation due to steric inhibition of resonance,[9] it may be assumed that the localization energy values for III are nearly the same as those of the benz[*a*]anthracene system which are known.[10] The electron localization energy is smaller for position 8 than for position 6 and one might expect that III would give IVa. This reasoning is also applicable to the *frontier* electron density method,[11] and again one would predict ring closure at C-8 in preference to C-6.

Acid-catalyzed dehydration of III gave only one product. This fact was substantiated by gas chromatographic analysis. On the basis of elemental analysis, analysis of the trinitrofluorenone (TNF) adduct, and analysis of the reduction product $C_{25}H_{16}$, the compound could have been either IVa or IVb. An analysis of the infrared absorption spectrum of the compound made a choice possible. A detailed study of the infrared spectra of benz[*a*]anthracenes has been made.[12] Of interest here is the fact that the region between 790 and 850 cm.$^{-1}$ contains at least one strong band for all compounds except 5- and 6-substituted benz[*a*]anthracenes. The infrared spectrum of 7-(2-carboxyphenyl)benz[*a*]anthracene (III) has two bands in this region which are located at 820 and 845 cm.$^{-1}$. If cyclization of III took place at C-6 to give IVb, these bands should disappear. Since the spectrum of the product still retained the bands in question, shifted slightly to 813 and 835 cm.$^{-1}$, it was assumed that cyclization took place at C-8 to give dibenzo[*hi,l*]chrysen-9-one (IVa).

The keto acid (II) was transformed to IVa with polyphosphoric acid and with liquid hydrogen fluoride. The cyclization of III to IVa was effected in 90% yield using liquid hydrogen fluoride and in 17% yield using 100% phosphoric acid.

The reduction of IVa, which failed using zinc dust and alkali, was effected using lithium aluminum hydride and aluminum chloride giving 9H-dibenzo[*hi,l*]chrysene. This structure is consistent with the elemental analysis and the infrared spectrum, which reveals the absence of the carbonyl band at 1650 cm.$^{-1}$ found in the starting material (IVa) and the appearance of the adsorption band for aliphatic carbon–hydrogen linkages at 2900 cm.$^{-1}$.

Experimental[13,14]

2-(1-Naphthylmethyl)-2′-carboxybenzophenone (II).—The Grignard reagent, prepared from 1.64 g. (0.067 g.-atom) of magnesium and 20 g. (0.067 mole) of 2-(1-naphthylmethyl)bromobenzene[5] in ether, was added slowly to a boiling solution of 8.95 g. (0.061 mole) of phthalic anhydride in benzene. After acid hydrolysis and the usual work-up, the product was recrystallized twice from a 1:3 mixture of petroleum ether (b.p. 30–60°) and benzene to yield 11.4 g. (52%) of white feathery needles, m.p. 159–160°.

Anal. Calcd. for $C_{25}H_{18}O_3$: C, 81.95; H, 4.95. Found: C, 81.54; H, 5.09.

A 0.200-g. sample of this acid dissolved in ethanol required 5.4 ml. of 0.104 *N* sodium hydroxide for neutralization (bromthymol blue); neut. equiv. 356, calcd. neut. equiv. 366.

The infrared spectrum[15] of II revealed the acid carbonyl band at 1680 cm.$^{-1}$, the ketone carbonyl band at 1665 cm.$^{-1}$, and the carboxylic hydroxyl bands at 2660 and 2550 cm.$^{-1}$.

The methyl ester of II was prepared in 87% yield using methyl alcohol and sulfuric acid, m.p. 88–89°. Its infrared spectrum showed bands at 1730, 1360, and 1300 cm.$^{-1}$.

Anal. Calcd. for $C_{26}H_{20}O_3$: C, 82.08; H, 5.30. Found: C, 82.09; H, 5.41.

7-(2-Carboxyphenyl)benz[*a*]anthracene (III) and Its Alcoholate.—A mixture of 0.50 g. of 2-(1-naphthylmethyl)-2′-carboxybenzophenone, 4 ml. of 48% hydrobromic acid, 1 ml. of water, and 15 ml. of glacial acetic acid was heated under reflux for 1 hr. Upon cooling to room temperature, white crystals formed. The product was filtered, washed with water, and recrystallized from ethanol giving an essentially quantitative yield of the alcoholate of III, m.p. 133–135°.

Anal. Calcd. for $C_{27}H_{22}O_3$: C, 82.21, H, 5.62. Found: C, 81.87; H, 5.65.

A 0.200-g. sample of this acid dissolved in ethanol required 5.3 ml. of 0.0972 *N* sodium hydroxide for neutralization (bromthymol blue); neut. equiv. 388, calcd. neut. equiv. 394. A g.p.c. analysis showed an ethyl alcohol peak.[16]

Heating the alcoholate *in vacuo* at 110° gave fine white crystals of III which melted at 199–200°.

Anal. Calcd. for $C_{25}H_{16}O_2$: C, 86.19; H, 4.63. Found: C, 86.12; H, 4.54.

The infrared spectrum showed the characteristic carboxylic acid absorption bands in the 1350–1450- and 1660–1740-cm.$^{-1}$ regions.

The ultraviolet spectrum, as would be expected, was very similar to that of benz[*a*]anthracene. A slight bathochromic shift was observed which can be attributed to the attached carboxyphenyl group.[17]

A 0.200-g. sample of III dissolved in ethanol required 5.8 ml. of 0.101 *N* sodium hydroxide for neutralization (bromthymol blue); neut. equiv. 341, calcd. neut. equiv. 348.

The methyl ester of III was prepared in 90% yield using diazomethane, m.p. 138–139°. Its infrared spectrum showed bands at 1730, 1260, and 1125 cm.$^{-1}$ characteristic of the ester group. The ultraviolet spectrum was similar to that of III.

Anal. Calcd. for $C_{26}H_{18}O_2$: C, 86.16; H, 5.01. Found: C, 85.72; H, 5.01.

Brucine, 9.52 g. (0.0241 mole), was added to a boiling solution of 8.4 g. (0.0241 mole) of 7-(2-carboxyphenyl)benz[*a*]anthracene (III) in 250 ml. of ethanol. The volume was reduced to 200 ml. and, on cooling to room temperature, 7.6 g. of salt crystallized. The salt was recrystallized five times from ethanol to give crystals with a constant specific optical rotation of −10.77°[18] in benzene.

Anal. Calcd. for $C_{48}H_{42}N_2O_6$: C, 77.61; H, 5.70; N, 3.77. Found: C, 77.39; H, 5.76; N, 3.88.

The brucine salt was decomposed with dilute hydrochloric acid. The optically active acid was recovered and recrystallized from ethanol to give white needles, m.p. 227–228°, which had a specific optical rotation of +18.84° in benzene.

Dibenzo[*hi,l*]chrysen-9-one (IVa). A. From 2-(1-Naphthylmethyl)-2′-carboxybenzophenone (II).—(1) To 0.5 g. (0.0014 mole) of 2-(1-naphthylmethyl)-2′-carboxybenzophenone was added 5 ml. of 85% phosphoric acid. Phosphorus pentoxide was added until the mixture became pasty. The mixture was heated in a metal bath at 190–200° for 4.5 hr., and at 250° for an additional 1.25 hr. The mixture was worked up in the usual way and the resulting red crystals, 0.29 g. (64%), were recrystallized from benzene–ethanol giving red needles, m.p. 221–222°.

Anal. Calcd. for $C_{25}H_{14}O$: C, 90.89; H, 4.27. Found: C, 90.42; H, 4.53.

The infrared spectrum showed the carbonyl absorption band at 1650 cm.$^{-1}$ and peaks at 813 and 835 cm.$^{-1}$. These data are

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[9] F. A. Vingiello and A. Borkovec, *J. Am. Chem. Soc.*, **77**, 3413 (1955).

[10] M. J. S. Dewar, *ibid.*, **74**, 3357 (1952).

[11] K. Fukui, T. Yonezawa, C. Nagata, and H. Shinger, *J. Phys. Chem.*, **22**, 1433 (1954).

[12] N. Fuson and M. L. Josien, *J. Am. Chem. Soc.*, **78**, 3049 (1956).

[13] Melting points were taken on a Fisher-Johns melting point block and are corrected.

[14] Analyses were performed by Geller Laboratories, Bardonia, N. Y.

[15] The infrared spectra of all solids were taken using the KBr disk method employing a Beckman Model IR-5 spectrophotometer.

[16] This analysis was performed by Mr. Jose Yanez using a Micro-Tek Model 2500R gas chromatograph with a 6 ft. × 1/4 in. column packed with 3.5% SE-30 on Gas-Chrom Z operated at a column temperature of 85°, inlet temperature of 305°, and using a hydrogen flame detector.

[17] The ultraviolet and visible spectra were taken with a Model 3000 Spectracord at a concentration of 10 mg./l. in 95% ethanol. The wavelength maxima for III are (in mμ) λ 222, 231, 259, 271, 281, 292, 321, 335, 352, and 365; and for IVa are λ 225, 249, 273, 312, 370, 405, 425, and 475.

[18] Optical measurements were made at 25° on a Rudolph Model No. 70 polarimeter using a 4-dm. jacketed tube.

consistent with structure IVa as are the ultraviolet and visible spectra.[17]

(2) The same product, IVa, was obtained in 85% yield when II was treated with anhydrous hydrogen fluoride at room temperature.

B. From 7-(2-Carboxyphenyl)benz[*a*]anthracene (III).—The same product, IVa, was obtained in 91% yield when III was treated with anhydrous hydrogen fluoride at room temperature.

Trinitrofluorenone Adduct of Dibenzo[*hi,l*]chrysen-9-one.—A hot solution of 0.048 g. of trinitrofluorenone in 15 ml. of ethanol was added to a hot solution of 0.050 g. of dibenzo[*hi,l*]chrysen-9-one in 15 ml. of benzene. On cooling, deep red crystals formed. Recrystallization from benzene–ethanol gave fine red needles, m.p. 201.5–202°.

Anal. Calcd. for $C_{38}H_{19}N_3O_8$: C, 70.69; H, 2.97; N, 6.51. Found: C, 70.73; H, 2.69; N, 6.35.

9H-Dibenzo[*hi,l*]chrysene.—A solution of 0.2 g. (0.0006 mole) of IVa and 0.081 g. (0.0006 mole) of aluminum chloride in 25 ml. of benzene was added slowly to a warm slurry of 0.029 g. (0.0008 mole) of lithium aluminum hydride and 0.100 g. (0.0008 mole) of aluminum chloride in 4 ml. of dry ether. After 20 min., the mixture was decomposed with 3 ml. of 6 *N* sulfuric acid and worked up in the usual way. The desired product, 0.11 g. (58%), was obtained as fine orange needles, m.p. 157–158°. Its infrared spectrum, in contrast to the spectrum of IVa, showed the absence of a carbonyl band at 1650 cm.$^{-1}$ and the appearance of the band for aliphatic carbon–hydrogen linkages at 2900 cm.$^{-1}$.

Anal. Calcd. for $C_{25}H_{16}$: C, 94.90; H, 5.10. Found: C, 94.62; H, 5.31.

Acknowledgment.—We wish to thank Dr. John D. Vaughan for constructive suggestions regarding the electron localization energies and frontier electron density correlations. This investigation was supported in part by Research Grant No. CY-4412(C2) from the National Institutes of Health, U. S. Public Health Service.

Definition of "Inductive" Substituent Constants

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The definition of σ_I constants may conveniently be made by means of the equation $\sigma_{I,X} = m(pK_{a,X}) + c$, where $pK_{a,X}$ is that of a substituted acetic acid in water. In general, no steric effects are observed. Ionization constants of 2- or 3-substituted propanoic acids, substituted methylamines, 2-substituted ethylamines, and substituted methyl phosphonic acids in water and of acetic acids in 80% Methyl Cellosolve–water have also been examined as secondary reference series for the definition of σ_I constants. Data available in the literature have permitted the definition of more than 100 σ_I values.

The Hammett equation has been used extensively for the correlation of rate and equilibrium data and of certain physical properties with substituent effects. In its most general form the Hammett equation may be written

$$Q_X = \rho\sigma_X + Q_H \qquad (1)$$

where Q is the quantity correlated, σ is a constant representing the electrical effect of the X substituent, ρ is the slope, and Q_H is the intercept. The nature of the substituent constant σ_X appears to depend upon the hybridization state of the carbon atom to which the substituent is bonded. The electrical effect of a substituent X bonded to an sp^3 hybridized carbon atom is best represented by the σ_I constants.[1] These constants were originally defined by Taft[1a] from the equation

$$\sigma_I = \left[\log\left(\frac{k}{k^0}\right)_{OH^-} - \log\left(\frac{k}{k^0}\right)_{H^+}\right]/6.23 \qquad (2)$$

where OH$^-$ and H$^+$ denote the base- and acid-catalyzed hydrolyses of esters, and k and k^0 are the rates of reaction of the substituted and unsubstituted compounds, respectively. This definition is inconvenient in that it requires two measurements to define a new value of σ_I, and also suffers from the difficulty of obtaining reliable and reproducible rate measurements in different laboratories. The choice of this approach to the definition of σ_I values by Taft[1b] was due to an attempt to eliminate steric effects. The steric effect in both acid- and base-catalyzed hydrolyses of esters is believed to be the same, as the transition states proposed for these reactions differ only by a proton, and of course the steric requirements for a proton must be quite small.

Our need for a convenient source of new σ_I values has led us to consider the alternative definition of σ_I constants in terms of the equation

$$\sigma_{I,X} = b(pK_{a,X}) + d \qquad (3)$$

where b is the slope of the regression line which minimizes deviation on the pK_a values and d is the intercept of this line and where the σ_I values are defined in terms of the pK_a values of the corresponding substituted acetic acids. There is nothing new in this proposal; that substituent effects are "inductive" in nature has been suggested many times before.[2] Taft's definition is based on the assumption that in addition to the polar effects of a substituent in an aliphatic compound there is also a significant steric effect which must be accounted for. If this steric effect is not significant (or, at most, rarely significant), then eq. 3 constitutes a more convenient definition. The advantages of such a definition are threefold. First, only one measurement suffices to define a new value of σ_I; second, the pK_a values may be more reliably and reproducibly determined; third, the definition of σ_I values would now be directly comparable to that of the Hammett[3a,b] substituent constants.

To determine whether such a definition is justifiable, pK_a values of substituted acetic acids in water at 18 and at 25° generally taken from the compendium of

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[1] (a) R. W. Taft, Jr., and I. C. Lewis, *J. Am. Chem. Soc.*, **80**, 2436 (1958); (b) R. W. Taft, Jr., *J. Phys. Chem.*, **64**, 1805 (1960); (c) R. W. Taft, Jr., E. Price, I. R. Fox, I. C. Lewis, K. K. Anderson, and G. T. Davis, *J. Am. Chem. Soc.*, **85**, 709 (1963).

[2] G. E. K. Branch and M. Calvin, "Theory of Organic Chemistry," Prentice-Hall, New York, N. Y., 1941, p. 217.

[3] (a) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940; (b) H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953); (c) R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. S. Newman, John Wiley and Sons, Inc., New York, N. Y., 1956.