NOTES

Effect of Salt Concentration and Temperature on the Ultraviolet Absorption Spectra of Aqueous Thiosulfate and Sulfite

By Donald P. Ames and John E. Willard

Incidental to another investigation[1] we have observed that the molar extinction coefficients of thiosulfate in the range of 250 to 270 mμ: (1) are progressively decreased by increasing concentrations of lithium, sodium, potassium and magnesium salts; (2) are increased by increased temperature; (3) are independent of the ionic strength (in the range from 2 to 3) and of pH (in the range from 5 to 12). It seems probable that the spectra observed are electron transfer spectra,[2] and that the changes in extinction coefficients are due to changes in the concentration of the absorbing species (probably $S_2O_3^-\cdot xH_2O$) caused by shifting its equilibria with ion pairs[3] and other hydrated species. We are reporting our exploratory observations here because they seem to offer a new method for obtaining information about certain ionic interactions in aqueous solution.

Measurements were made with a Beckman DU spectrophotometer using a hydrogen discharge lamp and matched quartz cells with 1 cm. light paths. The reference cell solution was, in each case, identical in concentration of added salt and pH with the thiosulfate solution being measured. The thiosulfate concentration was determined iodometrically. All measurements except those designed to test temperature effects were made at room temperature.

Results

Effect of Normality of Sodium Salts.—Three solutions of identical thiosulfate concentration (0.0102 M), ionic strength (2.00) and pH (12.1) were prepared by making them 0.353 M in Na_3PO_4, 0.657 M in Na_2SO_4 and 1.97 M in NaCl, respectively. The molar extinction coefficients[4] of these solutions, plotted as curves III, IV and V of Fig. 1, decreased with increasing normality of salt at all wave lengths tested.

Other solutions (Fig. 1) with sodium salt concentrations which varied from 2 $\times$ 10^{-3} N to 10 N

(1) D. P. Ames and J. E. Willard, This Journal, **73**, 164 (1951).

(2) (a) E. Rabinowitch, Rev. Modern Phys., **14**, 112 (1942); (b) L. Farkas and F. S. Klein, J. Chem. Phys., **16**, 886 (1948).

(3) Other types of observation which have been interpreted in terms of significant ion-pair formation in solutions of "strong" electrolytes include: (1) activity coefficient measurements, H. S. Harned and B. B. Owen, "Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1950, p. 423; (2) conductance measurements, I. L. Jenkins and C. B. Monk, This Journal, **72**, 2695 (1950); (3) the solubility of BaS_2O_3 in aqueous solutions of different chlorides, T. O. Denney and C. B. Monk, Trans. Faraday Soc., **47**, 992 (1951); (4) rates of ionic reactions in aqueous solution, A. R. Olson and T. R. Simonsen, J. Chem. Phys., **17**, 1167 (1949).

(4) Molar extinction coefficients of $S_2O_3^-$, at unspecified concentration have been reported by A. D. Awtrey and R. E. Connick, This Journal, **73**, 1842 (1951); L. Lorenz and R. Samuel, Z. physik. Chem., **B14**, 219 (1931); H. Ley and E. Konig. ibid., **B41**, 365 (1938).

(while the ionic strength varied by a similar factor) always showed a decrease in molar extinction coefficient with increase in the normality of the added salt.
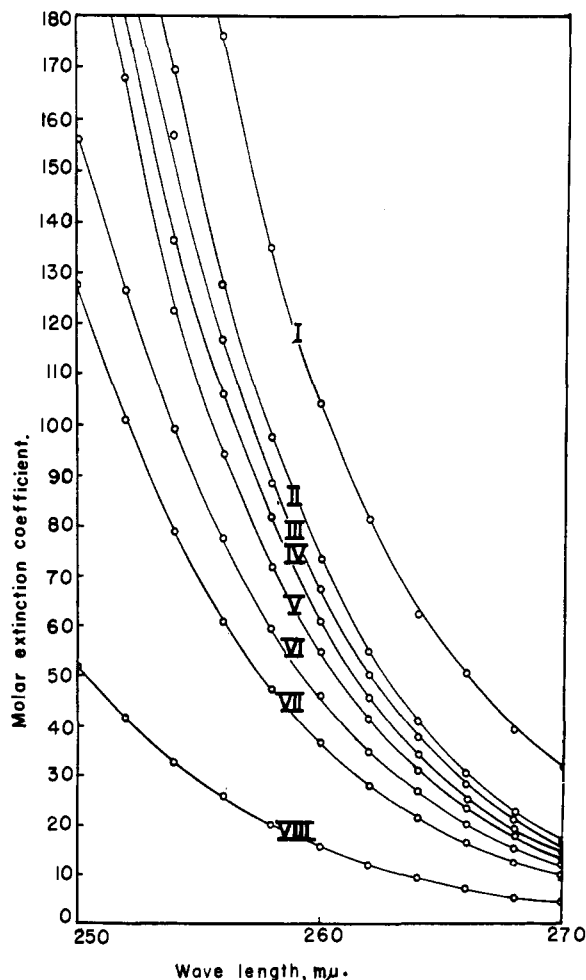

Fig. 1.—The effect of salt concentration on the molar extinction coefficients of thiosulfate solutions. The data opposite the roman numerals below give the conditions represented by the corresponding curves in the figure.

	Na^+ moles/l.	Ionic strength	pH	Anion	$S_2O_3^-$ mole/l.
I	0.002	0.003	9.4	$S_2O_3^-$	0.001
II	0.12	0.13	12.8	Cl^-	.0106
III	1.08	2.0	12.2	PO_4^-	.0102
IV	1.33	2.0	12.1	SO_4^-	.0102
V	1.99	2.0	12.0	Cl^-	.0102
VI	3.77	5.6	12.3	SO_4^-	.0102
VII	5.48	5.5	12.0	Cl^-	.0104
VIII	10.0	10.0	12.0	ClO_4^-	.0100

Effect of Ionic Strength.—Two solutions of identical thiosulfate concentration (0.0106 M) and pH (12.8) were made up to have the same normality (1.91 N) by using sodium chloride in one case and sodium sulfate in the other. In the first

case the ionic strength was 1.9 and in the second 2.9. The extinction coefficients were identical within 2% throughout the range from 250 to 270 mμ.

Effect of pH.—Two solutions of identical thiosulfate concentration (0.0106 M), sodium chloride concentration (2.0 N) and ionic strength (2.0) but with a pH of 4.6 in one case and 12.0 in the other were found to have identical molar extinction coefficients within 2% from 250 to 270 mμ.

Effect of Changing Cation Species.—A comparison of columns 2, 3 and 4 of Table I indicates that equal concentrations of lithium, sodium or potassium chloride have equal effect in reducing the thiosulfate extinction coefficient. Columns 5 and 6 show that magnesium sulfate exerts about the same effect (possibly slightly greater) as a solution of lithium chloride of the same normality. A similar result was obtained when a 1 M solution of magnesium sulfate was compared with a 2 M solution of sodium chloride.

TABLE I

EFFECT OF THE CATION SPECIES ON THE THIOSULFATE ABSORPTION SPECTRUM

mμ	Li[+a]	Na[+b]	K[+c]	Mg[++d]	Li[+e]
		Molar extinction coefficients			
250		184.0	187.3	144.2	156.9
2	155.7	150.9	153.9	114.4	124.5
4	119.8	119.8	118.6	89.9	97.1
6	92.0	94.3	91.2	70.4	74.5
8	68.9	69.8	68.6	54.7	56.9
260	51.7	52.8	52.0	42.1	43.1
2	38.6	39.6	38.7	32.9	32.7
4	28.8	29.6	28.8	25.5	24.7
6	21.1	22.1	21.1	19.2	18.6
8	15.5	16.1	15.5	14.7	14.0
270	11.3	11.8	11.3	11.4	10.3

[a] $S_2O_3^- = 0.0106$ M; LiCl $= 1.91$ M; pH $= 12.5$. [b] $S_2O_3^- = 0.0106$ M; NaCl $= 1.91$ M; pH $= 12.7$. [c] $S_2O_3^- = 0.0102$ M; KCl $= 1.91$ M; pH $= 12.5$. [d] $S_2O_3^- = 0.0104$ M; MgSO$_4 = 1.91$ M. [e] $S_2O_3^- = 0.0102$ M; LiCl $= 3.82$ M; pH $= 12.5$.

Effect of Sodium Salt Concentration on Sulfite Spectrum.—The molar extinction coefficient of sulfite is low in the wave length range above 260 mμ but rises rapidly below 250 mμ and depends on sodium salt concentration in a manner similar to that observed for thiosulfate. For example, a pure 0.010 M sulfite solution gave an extinction coefficient of 180 at 238 mμ. This was lowered to 110 when the solution was made 1 M in sodium chloride.

Effect of Temperature.—If the decrease in the extinction coefficients of thiosulfate and sulfite produced by increased salt concentration in solutions is due to ion pair formation, the coefficients might be expected to increase with increase in temperature. The effect of temperature has been tested qualitatively by determining the extinction coefficients of 0.010 M thiosulfite solutions in 2 M sodium chloride on a Cary recording spectrophotometer with the cell at room temperature and immediately after the cell was removed from a bath of boiling water. At 255 mμ the extinction coefficient increased from 111 to 145 and at 260 mμ from 54 to 76 at the elevated temperature. A

spectrum taken after cooling was identical with that obtained before heating.

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The Rearrangement of 9α,11α-Oxido-Δ⁷,²²-ergostadiene-3β-ol Acetate with Magnesium Bromide

By WERNER E. BACHMANN,[1] JEROME P. HORWITZ,[2] AND RAYMOND J. WARZYNSKI[2]

It has previously been reported that the monoepoxide derived from Δ⁷,⁹(¹¹),²²-ergostatriene-3β-ol acetate (ergosteryl D acetate) (I) may be rearranged to the corresponding α,β-unsaturated ketone III by the action of boron trifluoride etherate.[3] We have found that the rearrangement of I, as induced by magnesium bromide etherate, affords the non-conjugated ketone, Δ⁷,²²-ergostadiene-3β-ol-11-one 3-acetate (II) in yields of 60–73%. On passing a benzene–petroleum ether solution of II over a column of activated alumina, the β,γ-unsaturated ketone II was isomerized to the known Δ⁸(⁹),²²-ergostadiene-3β-ol-11-one acetate (III). In addition, it was found that the isomeriza-

tion of the non-conjugated ketone II to the conjugated isomer III may be induced with a trace of hydrochloric acid in alcohol and it is possible to observe the transformation spectrophotometrically.
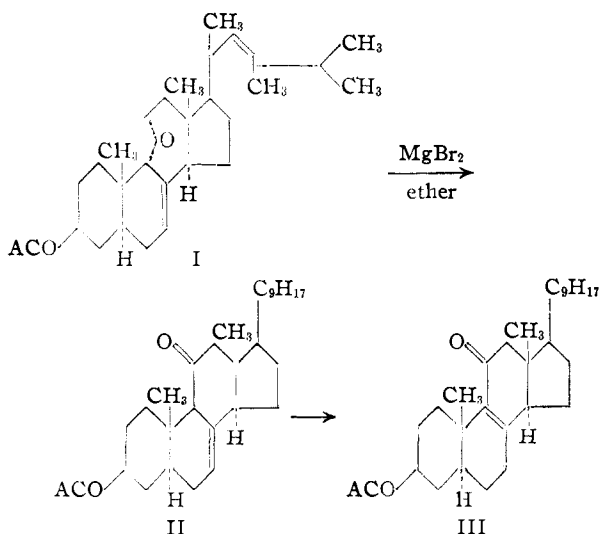
In the early stages of this investigation it became apparent that the methods available in the litera-

(1) Deceased, March 22, 1951.
(2) Parke, Davis Postdoctoral Fellow, 1950–1951.
(3) H. Heusser, et al., Helv. Chim. Acta, **34**, 2106 (1951).

ture for the selective reduction of ergosterol to 5,6-dihydroergosterol were of little synthetic value.[4] The importance of 5,6-dihydroergosterol, as an intermediate in the preparation of I, caused us to investigate a host of reducing agents. Accordingly, it was found that this selective reduction may conveniently be accomplished by refluxing an ethyl acetate solution of ergosteryl acetate in the presence of one-half to one equivalent of W-7 Raney nickel.[5,6] Furthermore, this method was successfully applied to the reduction of 7-dehydrocholesterol to Δ^7-cholesterol. The Δ^7-allosteroids were obtained in 55–65% yield.

Experimental[7]

5,6-Dihydroergosteryl Acetate.—Hydrogenation was accomplished with 40 g. of commercial ergosterol in 1600 cc. of reagent ethyl acetate in the presence of 8 level teaspoonfuls (approx. 20 g.) of W-7 Raney nickel. After one hour of reflux the mixture was filtered, and taken to dryness under reduced pressure. The white residue crystallized from 1 liter of 95% denatured alcohol to give 24 g. (60%) of 5,6-dihydroergosterol, m.p. 170–173° (lit.[5] 174°).

Δ^7-Cholesterol.—Hydrogenation was accomplished in the manner described for ergosteryl acetate with the substitution of absolute ethanol for ethyl acetate. Thus 19.2 g. of 7-dehydrocholesterol and 3 to 5 level teaspoonfuls of W-7 Raney nickel (approx. 10–15 g.) in 800 cc. of absolute ethanol gave 11.4 g. (59%) of Δ^7-cholesterol, in the form of fine white needles, after recrystallization from methanol, m.p. 120–122° (lit.[8] 122–123°).

9α,11α-Oxido-$\Delta^{7,22}$-ergostadiene-3β-ol acetate was prepared by the perphthalic acid epoxidation of $\Delta^{7,9(11),22}$-ergostatriene-3β-ol acetate in a manner essentially the same as that already described by Heusser and co-workers,[3] m.p. 204–206°, $[\alpha]^{29}$D −39° (lit.[4] m.p. 204–206°, $[\alpha]^{20}$D −39.5°).

Magnesium Bromide Etherate.—To a mixture of 60 cc. of anhydrous ether and 30 cc. of dry, reagent benzene was added 0.3 g. of magnesium dust (0.012 g. atom) followed by the addition of 2.16 g. of reagent grade mercuric bromide (0.006 mole). The mixture was then refluxed for two hours, filtered and used immediately in the rearrangement.

$\Delta^{7,22}$-Ergostadiene-3β-ol-11-one 3-Acetate (II).—To a solution of 1.23 g. of 9,11-epoxide described above (0.003 mole) in 140 cc. of dry ether was added 75 cc. of freshly prepared magnesium bromide etherate. After refluxing the mixture for two hours, an equal volume of water was added and the mixture shaken vigorously. The ether–benzene layer was drawn off, dried over anhydrous sodium sulfate and evaporated to dryness in a steam-bath in a stream of dry air. The residue crystallized from 100 cc. of methanol to give 0.9 g. (73% yield) of the non-conjugated ketone (II), m.p. 148–155°, $[\alpha]^{25}$D −160°. Two recrystallizations from methanol furnished the analytical sample, m.p. 155–157.5°, $[\alpha]^{25}$D −182°, λ_{max}^{Nujol} 5.85 μ.

Anal. Calcd. for $C_{30}H_{46}O_3$: C, 79.29; H, 10.13. Found: C, 79.84; H, 10.47.

$\Delta^{8,22}$-Ergostadiene-3β-ol-11-one 3-Acetate.—A solution of 40 mg. of II, m.p. 150–155°, in 6 cc. of petroleum ether (60–75°), was put on a column of activated alumina (10 × 40 mm.). The solid was then eluted with 5-cc. mixtures of petroleum ether–benzene, the concentration of the latter being gradually increased until pure benzene was used. The fractions eluted from 40% benzene to pure benzene were combined and evaporated to dryness to give 33.6 mg. of white, crystalline material. This residue was crys-

(4) A. Windaus and J. Brunken, *Ann.*, **460**, 225 (1923); A. Windaus and R. Langer, *ibid.*, **58**, 108 (1934); M. Heilbron and W. A. Sexton, *J. Chem. Soc.*, 921 (1929).

(5) H. Adkins and H. Billica, THIS JOURNAL, **70**, 695 (1948).

(6) After the present study had been completed, a general catalytic method was reported in which $\Delta^{5,7}$-steroids are reduced to Δ^7-allosteroids with Raney nickel in benzene: W. V. Ruyle, *et al.*, *ibid.*, **74**, 5929 (1952).

(7) All melting points are uncorrected. Analyses by Micro-Tech Laboratory, Skokie, Illinois. Rotations were determined in chloroform.

(8) Fr. Schenk, K. Buchholz and O. Wiese, *Ber.*, **69**, 2696 (1936).

tallized from approximately 1 cc. of methanol to give 15 mg. of isomerized product, m.p. 129–131°, $[\alpha]^{27}$D +109°, λ_{max}^{EtOH} 254 (log ε 3.91) λ_{max}^{Nujol} 6.05 and 6.30 μ (lit.[9] m.p. 131.5–134°, $[\alpha]$D +110°, λ_{max}^{EtOH} 254 (log ε 3.82)).

The appearance of the maximum 254 mμ was also observed spectrophotometrically by adding a drop of hydrochloric acid to a 10^{-5} M solution of II in alcohol.

(9) E. Schoenwaldt, *et al.*, THIS JOURNAL, **74**, 2697 (1952).

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Heat Capacities of Multimolecular Layers of Methane Adsorbed on Rutile

BY KENT S. DENNIS, E. L. PACE AND CHARLES S. BAUGHMAN

Multilayer heat capacities of helium on jeweler's rouge and argon on rutile have been reported by Frederikse[1] and Morrison,[2] respectively. The heat capacities of the helium were for three to twelve monolayers and covering a range from 1 to 3°K.; those of the argon were for 1.6 to 4.6 monolayers covering a range from 65 to 86°K. In each case the heat capacity curves exhibited maxima near a transition point (the lambda-point for helium and the melting point for argon). These maxima became higher and the peaks moved nearer the transition point for each increase in the number of layers. The peaks at high coverages were less diffuse than those at lower coverages.

This Laboratory recently investigated the multilayer heat capacities of methane adsorbed on rutile. Coverages of 1.0 to 5.8 monolayers over a temperature range from 72 to 116°K. were used. The apparatus and procedure have been described.[3] The surface area of the adsorbent was determined from a BET plot,[4] and it was found that 0.03106 mole constituted a monolayer. At high coverages pressures were quite large after a series of measurements, and there was danger of condensing gas in the tube used for the introduction of the gaseous sample. This was remedied by continually heating the tube while the calorimeter was being cooled prior to beginning a set of measurements. During the measurements, all portions of the tube were as warm as or warmer than the calorimeter vessel containing the solid adsorbent.

The data are graphed in Fig. 1. Individual points are not shown because then the figure would be too crowded. The experimental points for the curves θ = 3.8, 4.8 and 5.8 fall exactly on the curves as drawn. The points for the curves θ = 1.0, 1.9, and 2.9 are scattered (each curve progressively more so). However, these latter three curves as shown do correctly indicate the trend of the data. This graph exhibits maxima, each one higher and closer to the transition, just as do Morrison's[2] and Frederikse's.[1] It is to be expected that above one monolayer the adsorbed gas will

(1) H. P. R. Frederikse, *Physica*, **XV**, No. 10, 860 (1949).

(2) J. A. Morrison and L. E. Drain, *J. Chem. Phys.*, **19**, 1063 (1951).

(3) E. L. Pace, D. J. Sasmor and E. L. Heric, THIS JOURNAL, **74**, 4413 (1952).

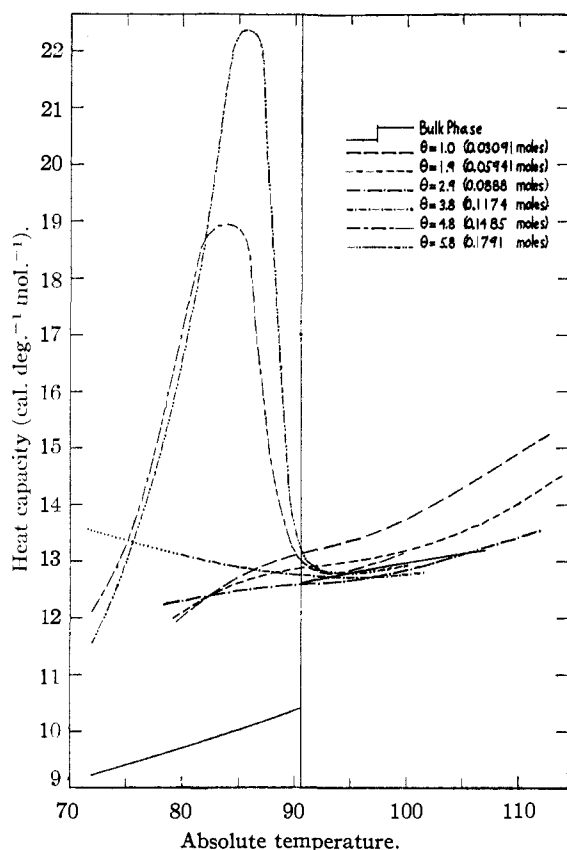(4) S. Brunauer, P. H. Emmett and E. Teller, *ibid.*, **60**, 309 (1938).

Fig. 1.—Multilayer heat capacities of methane adsorbed on rutile.

begin to exhibit bulk properties. The maxima are interpreted as indicating a rearrangement in the adsorbed film corresponding to melting in the bulk phase. Morrison[2] suggests that the melting point is lowered because a distortion of the normal lattice makes solidification more difficult, and that the spreading of the effect over a temperature range might be due to the small thickness of the absorbed films. The graphs show two noticeable differences between argon and methane. For argon, bulk properties begin between 1.6 and 2.9 monolayers; for methane they begin between about three and four monolayers. There is quite a difference in the shape of the 1.6 monolayer curve of argon and the one and two monolayer curves of methane. The argon curve is practically a straight line with only a small slope. The methane curves rise steeply to about 85°K., level off between 85 and 95°K., and then rise rather sharply again. The three monolayer curve of methane more closely approximates the argon curve in shape between 80 and 95°K. Mastrangelo[5] proposes that the shifts in the helium maxima are caused by pressure effects—high pressures at low coverages, and lower pressures at higher coverages. However, this will not explain the shifts for argon and methane, because their melting points are raised by increases in pressure. It is interesting to notice that the heat capacities of methane and argon adsorbed in the monolayer region are above or nearly the same as those of the liquid phases above the melting

(5) S. V. R. Mastrangelo, *J. Chem. Phys.*, **18**, 896 (1950).

point; but one monolayer of nitrogen has heat capacities decidedly below those of the bulk liquid phase.[6]

If the differential heat capacities $(\overline{C_{N_s}})$ at 5.3 monolayers are plotted, using the data of 4.8 and 5.8 monolayers, the integral

$$\int_{72}^{90.6} (\overline{C_{N_s}} - C_{P_{\text{solid}}}) = 230 \text{ cal.}$$

which is very nearly equal to the heat of fusion of methane (*cf.* ref. 2).

This work has been sponsored in part under ONR Contract No. 182(00), Project NR 057 173, and in part under AEC Contract No. AT(30-1)-824.

(6) J. A. Morrison and G. J. Szasz, *ibid.*, **16**, 280 (1948).

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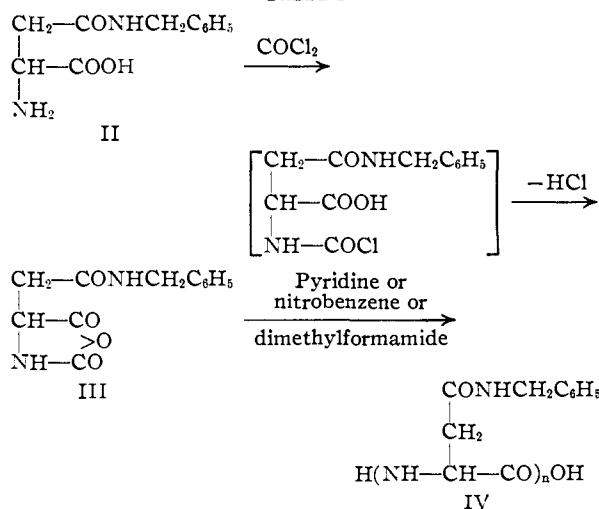## Synthesis of Poly-N$^\beta$-benzyl-*dl*-asparagine

BY MAX FRANKEL, Y. LIWSCHITZ AND A. ZILKHA

In continuation of previous work on syntheses of polyfunctional polyamino acids and derivatives,[1] the synthesis of poly-N$^\beta$-benzyl-*dl*-asparagine is reported in the present paper.

This polymer was prepared by the following series of reactions (Table I), starting from N$^\alpha$,N$^\beta$-dibenzylasparagine (I),[2,3] which was catalytically hydrogenolyzed to N$^\beta$-benzyl-*dl*-asparagine (II). This on being suspended in dioxane and treated with phosgene, yielded the N-carboxy anhydride (III), probably through N$^\alpha$-chloroformyl-N$^\beta$-benzylasparagine. III represented a white crystalline, comparatively stable compound, decomposing at 225°.

TABLE I

CH_2—$CONHCH_2C_6H_5$
|
CH—$COOH$ $\xrightarrow{COCl_2}$
|
NH_2

    II

$\left[\begin{array}{c} CH_2\text{—}CONHCH_2C_6H_5 \\ | \\ CH\text{—}COOH \\ | \\ NH\text{—}COCl \end{array}\right] \xrightarrow{-HCl}$

CH_2—$CONHCH_2C_6H_5$
|
CH—CO Pyridine or
| $>O$ $\xrightarrow{\text{nitrobenzene or}}$
NH—CO dimethylformamide

    III

                $CONHCH_2C_6H_5$
                |
                CH_2
                |
    $H(NH$—CH—$CO)_n OH$
                IV

(1) M. Frankel and A. Berger, *Nature*, **163**, 213 (1949); *J. Org. Chem.*, **16**, 1513 (1951); M. Frankel, M. Breuer and S. Cordova, *Experientia*, **VIII**, 299 (1952); M. Frankel and M. Halmann, *J. Chem. Soc.*, 2735 (1952); M. Frankel, M. Harnik and Y. Levin, *Experientia*, **VIII**, 98 (1952); E. Katchalski, I. Grossfeld and M. Frankel, THIS JOURNAL, **69**, 2564 (1947); **70**, 2094 (1948).
(2) F. H. McMillan and N. F. Albertson, *ibid.*, **70**, 3778 (1948).
(3) M. Frankel, Y. Liwschitz and Y. Amiel, *ibid.*, **75**, 330 (1953).

As, in this instance, the method of thermal polymerization *in alto vacuo* was not feasible because of the high decomposition temperature, polymerization was carried out in solution, using pyridine,[4] nitrobenzene[5] and dimethylformamide as solvents.

III, on being dissolved in dry pyridine or nitrobenzene, polymerized rapidly and the solution turned into a gel. Owing to the sparse solubility even of low-chain polymers of N^β-benzyl-*dl*-asparagine (IV) in these solvents, the resulting substances had an average chain length of 10 to 13 only. As these were, however, soluble in dimethylformamide, polymerization was carried out in the latter solvent leading to polymer preparations with an average chain length of 24 units (molecular weight about 5000), which were already insoluble in dimethylformamide and precipitated on standing.

The above polymers were soluble in hot glacial acetic acid, but practically insoluble in water, as well as in dilute mineral acids and alkali. A positive biuret reaction could, therefore, be obtained only on prolonged contact of the substance with the reagent solution, or when adding some dimethylformamide which dissolved lower fractions. On boiling with ninhydrin solution, the solid particles of the substance attained a blue color.

Attempts to remove the benzyl group have, so far, not been successful.

Experimental

Microanalyses are by Drs. Weiler and Strauss. Melting points were determined in a Fisher–Johns apparatus.

N-Carboxy Anhydride of N^β-Benzylasparagine (III).— N^β-Benzylasparagine (II) was obtained from N^α,N^β-dibenzylasparagine (I),[3] by hydrogenolysis with a palladium chloride on carbon catalyst (30%) in glacial acetic acid at 60°. A 10% catalyst[2] gave only poor results. After reduction, the organic material which adhered to the catalyst was extracted with cold formic acid. Removal of the latter *in vacuo* gave II in 77% yield.

Eight grams of II (which had been dried at 100°), was suspended in 250 ml. of dry dioxane in a three-necked flask to which a reflux condenser, a gas inlet tube and a stirrer had been attached. Phosgene was bubbled into the suspension and stirring commenced, while the bath temperature was maintained at 55°. After about 30 minutes, a clear solution resulted. Excess of phosgene and the dioxane were removed *in vacuo* at 40° and the resulting white crystalline substance was washed with ether and dried over phosphorus pentoxide. The yield was 7 g. (78.5%).

Anal. Calcd. for $C_{12}H_{12}O_4N_2$: C, 58.1; H, 4.8; N, 11.3. Found: C, 58.0; H, 4.8; N, 11.4.

Polymerization of the N-Carboxy Anhydride of N^β-Benzylasparagine (III) in Pyridine.— III was dissolved in varying amounts of pyridine (which had been dried by reflux with potassium hydroxide) and left at room temperature (*cf.*, Table II). The solutions became gradually more viscous while CO_2 was evolved and finally turned into gels. The polymers were isolated, after different periods of time, by precipitating them through addition of ether or water. They were then filtered, washed with some more ether or water respectively and dried *in vacuo*. The average chain length of all polymeric preparations was determined by analysis of amino-nitrogen in a Van Slyke manometric apparatus.

Polymerization in Nitrobenzene.— The procedure was similar to the above and polymers were precipitated by the addition of ether.

Polymerization in Dimethylformamide.— Polymerization was carried out at temperatures of about 5° and isolation of the polymer effected by addition of water.

(4) V. Go and H. Tani, *Bull. Chem. Soc. (Japan)*, **14**, 510 (1939); W. E. Hanby, S. G. Waley and J. Watson, *Nature*, **161**, 132 (1948); *J. Chem. Soc.*, 3239 (1950).

(5) W. E. Hanby, S. G. Waley and J. Watson, *ibid.*, 3009 (1950).

Results are summarized in Table II.

TABLE II

Amt. III, g.	In pyridine			In nitro-bz.	In dimethylformamide	
Amt. III, g.	1	0.5	1	3	5	1
Sol., ml.	4	20	15	20	40	10
Isold. after, days	15 min.	9	19	18	24 hr.	21
Amino {Calcd.	0.62	0.68	0.68	0.52	0.75	0.29
N, % {Found	0.62	0.67	0.71	0.53	0.75	0.30
Carbon,[6] {Calcd.	64.3	64.1	64.1	64.3	64.1	64.5
% {Found	63.1	63.9	62.8	62.6	64.2	62.0
Hydrogen,[6] {Calcd.	5.9	5.9	5.9	5.9	5.9	5.9
% {Found	5.8	5.9	6.0	5.9	6.6	6.0
Nitrogen,[6] {Calcd.	13.6	13.6	13.6	13.6	13.6	13.6
% {Found	14.2	12.9	13.6	13.5	13.3	13.1
Chain length	11	10	10	13	9	24

Hydrolysis of Poly-N^β-benzyl-*dl*-asparagine.— 0.019 g. of the polymer ($n = 24$) was boiled under reflux with 5 ml. of hydrochloric acid (6 N) for 19 hours. The resulting clear solution was transferred quantitatively into a 25-ml. volumetric flask, neutralized with 6 N sodium hydroxide solution against methyl orange and water added up to the 25-ml. mark. Aliquot parts of this solution were analyzed for free amino-nitrogen and values of 13.0% obtained (theor. 13.7%). This indicated complete hydrolysis to aspartic acid and benzylamine. Confirmation of this fact was obtained by paper partition chromatography of the hydrolysate (phenol–water as mobile phase), giving the characteristic spots for aspartic acid and benzylamine.

(6) As is generally known, analyses of polymers, especially as regards carbon, are not always satifactory (see for instance ref. 5 and C. S. Marvel, Cooke and J. C. Cowan, THIS JOURNAL, **62**, 3497 (1940)).

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Syntheses from 4-Phenyl-2-piperidone[1]

BY C. F. KOELSCH AND ROBERT W. DeNET

Having developed a method for preparing 4-phenyl-2-piperidone (I),[2] we considered it of some interest to investigate various chemical transformations of the substance. The present note describes conversion of I through II, III and IV, into V.
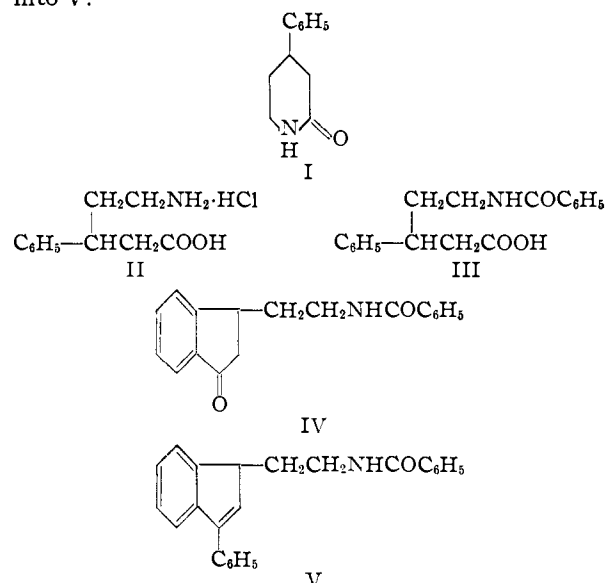
(1) From the M.S. Thesis of R. W. DeNet, December, 1947.

(2) C. F. Koelsch, THIS JOURNAL, **65**, 2459 (1943).

Reduction of ethyl α-carbethoxy-γ-cyano-β-phenylbutyrate to I[2] was found to proceed much better in a larger amount of solvent than used formerly. Thus, 60 g. of cyano-ester in 300 g. of alcohol gave 21 g. of crystalline I, m.p. 138°.

Experimental

δ-Amino-β-phenylvaleric Acid Hydrochloride (II).—A solution of 60 g. of I in 600 ml. of 6 N hydrochloric acid was boiled for three hours and then evaporated. Crystallization of the residue from alcohol–ether gave 57 g. of colorless plates, m.p. 184–186°.

The same hydrochloride was obtained by similar treatment of the sirupy by-product from the preparation of I. From 90 g. of sirup there was obtained 25 g. of pure amino-acid hydrochloride.

Anal. Calcd. for $C_{11}H_{16}ClNO_2$: C, 57.5; H, 7.0. Found: C, 57.8; H, 7.2.

Benzoylation.—Thirty grams of II, shaken with 250 ml. of 16% sodium hydroxide and 18 g. of benzoyl chloride, gave 26 g. of the benzoyl derivative III, crystals from ether–ligroin, m.p. 110–112°.

Anal. Calcd. for $C_{18}H_{19}NO_3$: C, 72.7; H, 6.4. Found: C, 72.8; H, 6.5.

N-Benzoyl-1-keto-3-indanethylamine (IV).—An attempt to cyclize III with concd. sulfuric acid at 90° gave only water-soluble products. However, a Friedel–Crafts cyclization was successful.

A mixture of 29.7 g. of III and 12.5 g. of thionyl chloride was heated in a water-bath at 60–70° for one hour at atmospheric pressure, and then for 15 minutes at 20 mm. The residue was dissolved in 400 ml. of benzene and treated with 28 g. of aluminum chloride. The mixture was stirred for one hour at 60–70° and then poured on ice. The product was washed with sodium carbonate and crystallized from benzene giving 24.5 g. of colorless crystals, m.p. 106–107°.

Anal. Calcd. for $C_{18}H_{17}NO_2$: C, 77.4; H, 6.1. Found: C, 77.3; H, 6.3.

The **2,4-dinitrophenylhydrazone** formed red plates from nitromethane, m.p. 220–221°.

Anal. Calcd. for $C_{24}H_{21}N_5O_5$: C, 62.7; H, 4.6. Found: C, 62.7; H, 4.5.

N-Benzoyl-3-phenyl-1-indene-ethylamine (V).—A solution of 10 g. of IV in 100 ml. of benzene was added to 130 ml. of 1 N ethereal phenylmagnesium bromide, and the mixture was stirred and heated in a water-bath at 70° for one hour. Hydrolysis was effected with iced dilute sulfuric acid, and the crude product was washed with aqueous sodium carbonate. Volatile materials were removed by steam distillation, but the glassy residue could not be crystallized. It was therefore dehydrated by boiling it for five minutes with 50 ml. of acetic acid containing one drop of sulfuric acid. Crystallization from ether–ligroin and then from benzene gave 1.7 g. of V, colorless needles, m.p. 132–134°.

Anal. Calcd. for $C_{24}H_{21}NO$: C, 84.9; H, 6.2. Found: C, 85.4; H, 6.3.

Attempts to hydrolyze compounds IV and V, using either acids or bases, were all unsuccessful.

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Polymerization of Esters of Cinnamic Acid[1]

By C. S. MARVEL AND G. H. McCAIN

In 1878 Erlenmeyer[2] reported that on heating ethyl cinnamate he obtained a powdery white solid which was insoluble in most solvents and decom-

(2) E. Erlenmeyer, *Ber.*, **11**, 150 (1878).

posed before it melted. Liebermann[3] confirmed this observation and showed that this solid was not one of the possible dimeric truxillic esters. Later it was established[4] that other esters of cinnamic acid behaved similarly and the high melting products were described as cyclic trimers. More recently Shapiro, Linstead and Newitt[5] heated ethyl cinnamate for 240 hours at 125° under 4000 atmospheres pressure, and reported that they obtained, in 58% yield, a white powdery product which melted above 320°. They did not establish the molecular weight of this product but did demonstrate that it was non-crystalline.

We have now polymerized ethyl cinnamate by the usual bulk free-radical-initiated procedure and found that this polymer has the structure which one would expect in a vinyl-type polymerization product. By heating ethyl cinnamate to 60° with either benzoyl peroxide or 2,2'-azobisisobutyronitrile for varying times the yield of polymer was 10–11%. The product seems to be identical with the high melting products described as resulting from the thermal polymerizations. When 2,2'-azobisisobutyronitrile was used as the initiator the nitrogen content of the polymer approached the nitrile nitrogen content of the initiator used. Assuming that the polymerization is terminated by coupling of the growing radical chains, the nitrogen content of the polymer indicates a molecular weight of 7600. This product showed an amorphous X-ray pattern.[6] The infrared absorption spectrum of the polymer showed the non-conjugated ester carbonyl band at 1736 cm.$^{-1}$, the ester carbon–oxygen band at 1166 cm.$^{-1}$, and the monosubstituted phenyl ring bands at 744 and 699 cm.$^{-1}$.[7]

Under comparable conditions methyl cinnamate gave a low yield of a similar white solid which melts above 300°. This solid also gave an amorphous X-ray pattern.[6] Its infrared absorption spectrum shows the non-conjugated ester carbonyl band at 1733 cm.$^{-1}$, the ester carbon–oxygen band at 1194 cm.$^{-1}$, and the monosubstituted phenyl bands at 744 and 700 cm.$^{-1}$. In addition there is a very weak carbon–carbon double bond band at 1637 cm.$^{-1}$. The molecular weight calculated from the nitrogen content of the polymer made by initiation with 2,2'-azobisisobutyronitrile was about 2300.

An old laboratory sample of methyl cinnamate which had stood in a partly-filled brown bottle for at least a year was found to be partially polymerized to a white product of fibrous appearance. Its molecular weight was not determined. The polymers prepared in our laboratory were soluble in the corresponding monomers.

Experimental

Polyethyl Cinnamate.—Twenty grams of ethyl cinnamate, 0.10 g. of 2,2'-azobisisobutyronitrile and 0.025 g. of technical lauryl mercaptan were heated to 60° for about a month.

(3) C. Liebermann, *ibid.*, **22**, 2240 (1889).

(4) C. Liebermann and M. Zsuffa, *ibid.*, **44**, 841 (1911); C. Liebermann, G. Mühle and M. Kardos, *ibid.*, **48**, 1645 (1915).

(5) R. H. Shapiro, R. P. Linstead and D. N. Newitt, *J. Chem. Soc.*, 1784 (1937).

(6) We are indebted to Mr. W. E. Thatcher for this information.

(7) The infrared data reported in this work were determined by the Anderson Physical Laboratory, Champaign, Illinois.

The solution became somewhat viscous during this time. The solution was poured into ethanol to precipitate the polymer. A white powdery product which did not darken, decompose or melt below 300° was obtained in 10% yield. This product was insoluble in benzene, chloroform, ethyl acetate, dioxane, dimethyl formamide, ether and hot trichloroethylene. It was soluble in ethyl cinnamate.

Anal.[8] Calcd. for $C_{11}H_{12}O_2$: C, 75.02; H, 6.87. Found: C, 74.95; H, 7.04; N, 0.37.

This nitrogen content is equivalent to the nitrile nitrogen in 0.087 g. of 2,2′-azobisisobutyronitrile.

Polymer of a similar nature was obtained in low yield in cyclohexane solution.

Ten grams of ethyl cinnamate, 0.12 g. of benzoyl peroxide and 0.025 g. of technical lauryl mercaptan were heated at 60° for about a week. On isolation as before an 11.3% yield of polymer was obtained.

Polymethyl Cinnamate.—Twenty grams of methyl cinnamate and 0.10 g. of 2,2′-azobisisobutyronitrile were heated at 60° for about 10 days and then to 85° for 3 days. When the solution was poured into ethanol a white powder was obtained in 2% yield. This product was insoluble in common solvents and did not darken, melt or decompose when heated to 300°.

Anal. Calcd. for $C_{10}H_{10}O_2$: C, 74.04; H, 6.22. Found: C, 71.08; H, 6.43; N, 1.17.

The nitrogen content corresponds to that of 0.055 g. of initiator.

A sample of fibrous polymethyl cinnamate was isolated from an old sample of methyl cinnamate. Its physical properties and infrared spectrum were similar to those of the material made by 2,2′-azobisisobutyronitrile polymerization, except that it was obviously of higher molecular weight. Its low solubility has interfered with proper evaluation of this material.

Anal. Calcd. for $C_{10}H_{10}O_2$: C, 74.04; H, 6.22. Found: C, 73.46; H, 6.37.

Attempts to use standard emulsion polymerization procedures for making these products are contemplated.

(8) We are indebted to Mrs. Ester Fett and Mr. Joseph Nemeth for the microanalyses reported here.

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Anion Exchange Studies. VIII.[1,2] Separation of Iron and Aluminum in Sulfate Solutions

BY KURT A. KRAUS AND FREDERICK NELSON

It had been shown in an earlier paper that Fe(III) can be strongly adsorbed from chloride solutions by the quaternary amine polystyrene divinyl benzene "strong base" anion-exchange resin Dowex-1.[3] A similar study of the adsorbability of Fe(III) from sulfuric acid and ammonium sulfate solutions has now been carried out. For these media, conditions of strong adsorption were found. However, in contrast with the behavior in chloride solutions, the maximum adsorption found was considerably smaller for sulfate than for chloride solutions, and adsorption was found to decrease greatly with acidity and slightly with sulfate concentration.

The sulfate form of the resin was prepared by washing the chloride form with 1–2 M H_2SO_4 until the effluent was chloride-free and then washing the resin with distilled water until the pH of the

(1) This document is based on work performed for the Atomic Energy Commission at the Oak Ridge National Laboratory.

(2) Previous paper, K. A. Kraus, F. Nelson and J. F. Baxter, THIS JOURNAL, **75**, 2768 (1953).

(3) G. E. Moore and K. A. Kraus, *ibid.*, **72**, 5792 (1950).

effluent was larger than 5. Since elution of the acid from the resin tends to tail strongly,[2] large volumes of water are necessary.

The adsorbability of Fe(III) was investigated by determining distribution coefficients D (amount Fe per kg. of resin/amount Fe per 1. of solution) by shaking iron sulfate solutions with known amounts of resin, and determining the change in iron concentration spectrophotometrically.

In the sulfuric acid solutions significant adsorption was found only for M $H_2SO_4 < 0.1$. This adsorption increased rapidly with decreasing sulfuric acid concentration reaching values of $D =$ *ca.* 100 in 0.001 M H_2SO_4.

Adsorbabilities in ammonium sulfate solutions were measured with some acid added (initially 0.01 M H_2SO_4) to prevent extensive hydrolysis of Fe(III) and possible hydrolytic polymerization. D was found to decrease from *ca.* 35 in 0.01 M $(NH_4)_2SO_4$ to *ca.* 10 in 4 M $(NH_4)_2SO_4$, and to be essentially independent of iron concentration in the range 10^{-5} to 10^{-3} M Fe(III) under conditions where loading of the resin with respect to iron is small.

The color of the adsorbed iron complex varies somewhat with concentration in the resin phase, becoming red-brown at high concentrations. The adsorbed species cannot readily be identified since, as pointed out in an earlier paper,[2] the resin adsorbs sulfuric acid, hence causing significant changes in the acidity of the solutions and in the composition of the resin phase. The strong dependence of adsorption on acidity suggests that a basic sulfate complex is involved.

The adsorption of Fe(III) can be utilized for separations. The principles of these separations are illustrated in experiments with Al(III) which is only weakly adsorbed under conditions where Fe(III) is strongly adsorbed. Thus, an Fe(III)–Al(III) solution containing 0.005 M $Fe_2(SO_4)_3$, 0.005 M $Al_2(SO_4)_3$ and 0.010 M H_2SO_4 was passed through a 0.488 cm.^{2} × 15.9 cm. Dowex-1 column in the sulfate form with flow rate 0.34 cm. min.$^{-1}$. Aluminum appeared in the effluent after *ca.* 4.2 cc. of solution had been passed through the column. The iron concentration of the solution was $< 10^{-6}$ M. Iron was adsorbed at first at the top of the column, slowly moved through it, and appeared after *ca.* 95 ml. in the effluent. Since the interstitial volume of the column is *ca.* 3.3 cc., while Al(III) appeared in the effluent after 4.2 cc., it appears that Al(III) is slightly adsorbed under these conditions. Possibly for these reasons Fe(III) appears in the effluent somewhat earlier when the same separation is carried out with more concentrated Al(III) solutions (*e.g.*, after 44 ml. with a 0.005 M $Fe_2(SO_4)_3$–0.48 M $Al_2(SO_4)_3$–0.005 M H_2SO_4 solution in a similar though slightly shorter column (15.0 cm.)).

Fe(III) can be eluted from the column by increasing the sulfuric acid concentration of the eluent. The experiments described in Fig. 1 illustrate the procedure. In these experiments, iron was adsorbed from 0.5-ml. samples of 5 × 10^{-3} M $Al_2(SO_4)_3$–5 × 10^{-3} M $Fe_2(SO_4)_3$–10^{-2} M H_2SO_4 solutions on 0.187 cm.^{2} × 9.3 cm. columns.
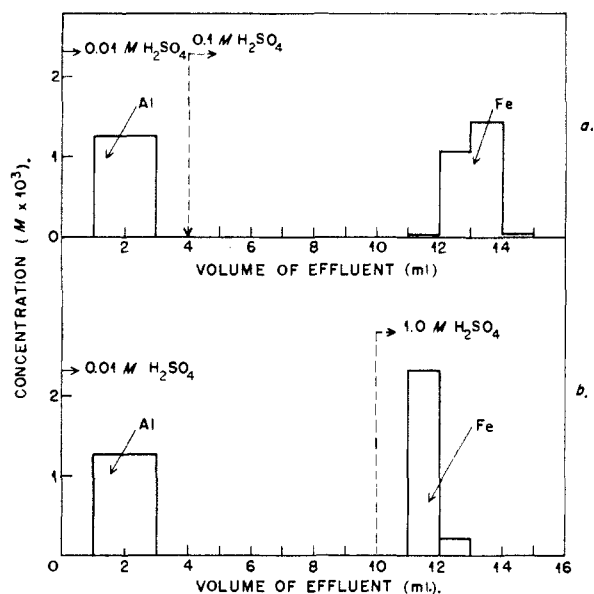
Fig. 1.—Separation of Al(III) and Fe(III) by anion exchange in sulfate solutions (0.187 cm.^{2} $\times$ 9.3 cm. Dowex-1 column).

Al(III) rapidly appeared in the effluent while Fe(III) was adsorbed (iron concentration in effluent $< 10^{-6}\ M$). The appearance of Fe(III) in the effluent is considerably delayed when elution is carried out with 0.1 M H$_2$SO$_4$, (Fig. 1a) but is quite rapid when elution is carried out with 1.0 M H$_2$SO$_4$. In both experiments, the Fe(III) band is narrow and shows little tailing. The long delay in the appearance of the Fe(III) band in the effluent with 0.1 M H$_2$SO$_4$ is probably connected with the adsorption of sulfuric acid by the resin and its partial conversion to the bisulfate form. The sulfuric acid concentration thus remains considerably less than that of the eluent until the column has been equilibrated with the new medium.

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The Refractive Indices and Molecular Dispersion of cis- and trans-Decahydronaphthalene

BY S. MIZUHARA AND WM. F. SEYER

In the course of a series of measurements dealing with the physical–chemical properties of cis- and trans-decahydronaphthalene it became desirable to ascertain their refractive indices in the temperature range of 0 to 85°.

For this purpose a Pulfrich refractometer was used with two sources of light, a bunsen burner sodium chloride flame for the D line and a guild type of hydrogen tube for the C(Hα) and F(Hβ) lines. The results are given in the form of graphs in Figs. 1 and 2.

The refractive index–temperature relationship is linear for the trans compound within the limits of accuracy obtainable. In the case of the cis compound there appeared to be a slight change in slope above 50°. It should be noted that between 50.0

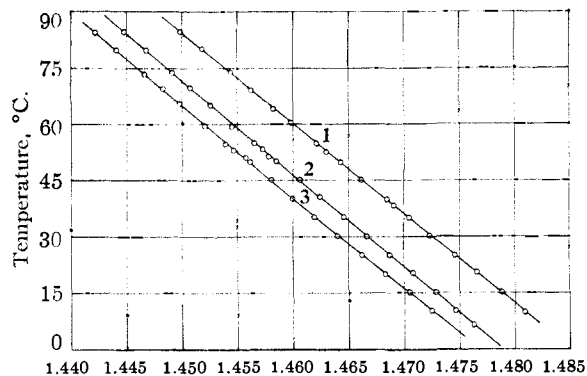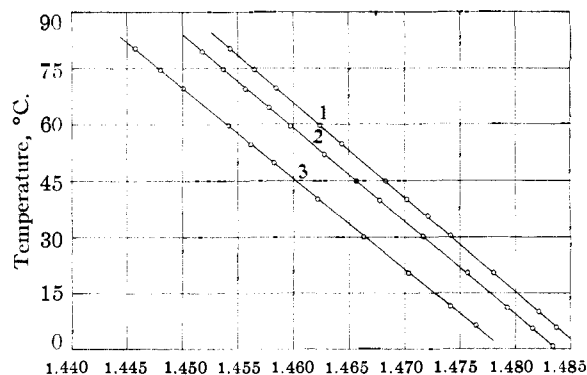Fig. 1.—Refractive index of trans-decahydronaphthalene: 1, n^tF; 2, n^tD; 3, n^tC.

Fig. 2.—Refractive index of cis-decahydronaphthalene: 1, n^tF; 2, n^tD; 3, n^tC.

and 50.9° for this compound no readings of the refractive index could be made because of a persistent turbidity, normally associated with all measurements when the temperature of the liquid in the test cup was not constant. This observation appeared significant because other physical properties indicated some change in liquid structure between these temperature regions in the case of the cis isomer.

The refractive indices of the trans isomer over the temperature interval from 10–90° were used to test the validity of the molar refraction R as calculated from the Gladstone–Dale (R_G), Lorentz–Lorenz (R_L) and Eykman (R_e) equations. The drift in the value of R per degree with rise in temperature for all three wave lengths is shown in Table I.

TABLE I

	nC	nD	nF
$\Delta R_G \times 10^{-3}$	1.6	6.4	5.9
$\Delta R_L \times 10^{-3}$	4.0	6.2	8.1
$\Delta R_e \times 10^{-3}$	52.0	59.0	60.6

Thus for this compound Eykman's empirical equation is far less valid than the other two. Attempts have been made to correlate refractive index with surface tension, notably by Tripathi.[1] However, his equation cannot hold for trans-decahydronaphthalene for the molar refraction R increases with temperature while that of the parachor decreases 0.075 unit per degree.[1] Using Eisenlohr's values of carbon and hydrogen the

(1) R. C. Tripathi, J. Indian Chem. Soc., 18, 411 (1941).

TABLE II

DISPERSION AND SPECIFIC DISPERSION

	Temp.	n^t_D .	$n^t_{H\beta}$	n^t_{Hd}	$\Delta^t_{\beta} - \alpha$	$\delta^t_{\beta} - \alpha$
trans-cyclohexane	20°	1.4254	1.43053	1.42307	74.6 × 10⁴	95.9 × 10⁴
	80°	1.3953	1.40022	1.39345	67.7	93.9
trans-decalin	20°	1.46934	1.47501	1.46669	83.2	95.6
	80°	1.44577	1.45109	1.44297	81.2	98.3
cis-decalin	20°	1.48098	1.48694	1.47844	85.0	91.6
	80°	1.45841	1.46353	1.45582	77.1	90.5

value of R_D calculated by the Lorentz–Lorenz formula was 43.98. Based on the refractive indices as measured at 20° that of the *trans* isomer was 44.25 and 43.87 for the *cis* isomer. Whether this difference is significant in respect to ring structure is at this time uncertain.

It is interesting to compare the dispersion, Δ, the specific dispersion δ and the temperature-refractive index coefficient of these bicyclic saturated hydrocarbons with those compounds listed by Grosse and Wackher.[2]

In the case of both hydrocarbons the temperature coefficients of Δ and δ are extremely small.

(2) A. V. Grosse and R. C. Wacker, *Ind. Eng. Chem., Anal. Ed.*, **31**, 614 (1939).

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The Addition of Nitryl Chloride to Some Simple Olefins[1,2]

BY CHARLES C. PRICE AND CARLTON A. SEARS[2]

The addition of nitryl chloride to a number of unsaturated compounds has been reported in the literature.[3] In many cases, the reaction is complicated by addition of the. elements of chlorine, N_2O_3 or N_2O_4 across the double bond, depending on the solvent used and the olefin studied.

In the simple examples reported herein, all of these reactions have been observed, suggesting that nitryl chloride can easily disproportionate to chlorine and N_2O_4.

$$2ClNO_2 \rightleftharpoons N_2O_4 + Cl_2$$

$$N_2O_4 \longrightarrow N_2O_3 + \text{oxidation}$$
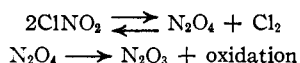
In general, we found dry ether as a solvent superior to carbon tetrachloride or no solvent. We do not have an explanation for the wide difference in the nature of products formed from the four simple olefins studied, but since the work has been discontinued we wish to report the results obtained.

Experimental

The Addition of Nitryl Chloride to Cyclohexene.—A solution of 24.6 g. (0.3 mole) of cyclohexene in 200 cc. of

(1) Abstracted from a thesis presented by Carlton A. Sears in partial fulfillment of the requirements for the Ph.D. degree at the University of Notre Dame.

(2) This work was presented in part at the 119th National Meeting of the American Chemical Society at Cleveland, Ohio. We are indebted to the Navy Department, Bureau of Ordance, for a Grant, Contract NOrd-10273, which made this work possible.

(3) (a) W. Steinkopf and M. Kuhnel, *Ber.*, **75**, 1323 (1942); (b) Brintzinger and K. Pfannsteil, *Z. anorg. Chem.*, **256**, 324 (1948); (c) M. Kuhnel, German Patent 739,538 [July 25, 1940); (d) C. M. Himel, U. S. Patent 2,511,915 (June 20, 1950).

anhydrous ether was added to the reaction flask and 0.35 mole of nitryl chloride was distilled in over a period of two hours at ice temperature. After addition of the inorganic halide the solution was allowed to come slowly to room temperature. The solvent was removed and the cyclohexene pseudo-nitrosite isolated by filtration, 1.2 g. After recrystallization from glacial acetic acid, it melted at 149–150° dec. (lit.[4] m.p. 152° dec.).

The liquid fraction was vacuum distilled and two products were isolated; b.p. 62–73° (6 mm.), 13.4 g. and b.p. 109–114° (6 mm.), 16.3 g.

A pure sample of the lower-boiling fraction was prepared in the following manner. The liquid was cooled in a Dry Ice–isopropyl alcohol bath and white crystals formed. The supernatant liquid was decanted. The white crystals, which liquified on warming to room temperature, were diluted with an equal volume of alcohol and recooled. The white crystals which formed were quickly separated by filtration and washed with Dry Ice-cooled alcohol. The product was quickly transferred to a clean dry watch glass; n^{25}_D 1.4835, d^{25}_4 1.1655, MR_D calcd., 37.53, found, 37.44. Values reported for 1,2-dichlorocyclohexane are b.p. 75° (15 mm.), $n^{16.6}_D$ 1.4886, corrected to n^{25}_D 1.4834.[5]

The higher boiling fraction proved to be 1-chloro-2-nitrocyclohexane, n^{25}_D 1.4887, d^{25}_4 1.2184, MR_D calcd., 38.20, found, 38.52 (lit.[3a] b.p. 121–122° (9 mm.). Steinkopf and Kuhnel[3a] reported only the chloronitrocyclohexane as the product of this reaction.

Chemical Reduction of 1-Chloro-2-nitrocyclohexane.—Approximately 0.5–1.0 cc. of the product was treated with two drops of 25% sodium hydroxide solution. This was then acidified with a 50% hydrochloric acid solution and a small amount of mossy tin added. The mixture was refluxed for 10 to 15 minutes and the product steam distilled. The distillate was treated with 2,4-dinitrophenylhydrazine in the usual manner. A yellow derivative settled, was separated by filtration, and was recrystallized from alcohol, m.p. 161–163°. A mixture with an authentic sample of cyclohexanone 2,4-dinitrophenylhydrazone melted at 161–162°.

Catalytic Reduction of 1-Chloro-2-nitrocyclohexane.—The reduction was run in a low pressure hydrogenator at room temperature in alcohol as solvent and Raney nickel as catalyst. The reduction was discontinued after six hours at which time the pressure was constant. The Raney nickel was separated by filtration and washed with 95% ethanol. The alcoholic filtrate was made acid with dilute sulfuric acid. The alcohol was distilled from the acidic solution until about 5–10 cc. of brown colored liquid remained. One half of this solution was made alkaline and filtered. The filtrate was treated with benzoyl chloride. A curdy precipitate was formed which was recrystallized from alcohol, m.p. 143–147°. The mixed melting point with the derivative of authentic cyclohexylamine was 144–148°.

General Procedure for the Addition of Nitryl Chloride to 2-Butene, Propene and Isobutylene.—The olefin (ca. 0.25 mole) was passed into a solution of 200 cc. of dry ether and 0.25 mole of nitryl chloride, for about three hours. The ice-bath was then removed and the reaction product came slowly to room temperature. The solvent was removed at the water pump. Any dimeric pseudo-nitrosite was separated by filtration and the oily filtrate distilled. The physical constants for the products and derivatives are recorded below. The derivatives were prepared in a similar manner as described for the cyclohexene derivatives. For

(4) H. Wieland and E. Blumich, *Ann.*, **424**, 8 (1921).
(5) M. Mousseron and R. Granger, *Compt. rend.*, **205**, 327 (1937).

the preparation of N-(2-nitroisopropyl)-aniline hydrochloride see Fourneau.[6]

2-Butene Product.—2-Chloro-3-nitrobutane: b.p. 45–46° (6 mm.), 8.6 g., $n^{25}D$ 1.4421, d^{25}_4 1.1835, MR_D calcd. 30.68, found 31.10; % Cl calcd. 25.59, found 25.47. Derivatives: 2,4-dinitrophenylhydrazone of chemically-reduced product, m.p. 116.5–117°, mixed m.p. with 2,4-dinitrophenylhydrazone of methyl ethyl ketone was 116–117°; benzoyl chloride derivative of catalytically-reduced product, m.p. 72–74°, mixed m.p. with authentic s-butylbenzamide 72–73°.

Propene Products.—Propene pseudo-nitrosite: m.p. 135–135.5°, 5 g., % N calcd. 23.72, found 23.58.

1-Nitro-2-chloropropane: b.p. 32–33° (1 mm.), 16.5 g., $n^{25}D$ 1.4388, d^{25}_4 1.2338, calcd. MR_D 26.55, mol. wt. 123.5, found, MR_D 26.32; mol. wt. 123.1 (lit.[7] b.p. 172° (749 mm.); d^{15}_4 1.2361). Derivatives of 1-nitro-2-chloropropane: N-(2-nitroisopropyl)-aniline hydrochloride, m.p. 139–140°,[6] 2,4-dinitrophenylhydrazone of chemically reduced product, m.p. 142–148°, mixed m.p. with 2,4-dinitrophenylhydrazone of propionaldehyde, m.p. 147–148°. Benzoyl chloride derivative of catalytically reduced product, m.p. 82–83.5°, n-propylbenzamide.

Isobutylene Products.—Isobutylene pseudo-nitrosite; m.p. 87–88°, 8.3 g., % N calcd. 21.21, found 19.66 (lit.[8] m.p. 81°).

1-Nitro-2-chloroisobutane: b.p. 35–38° (1 mm.), 6 g., $n^{25}D$ 1.4530 (reported b.p. 35–42° (2 mm.), $n^{24}D$ 1.4530[3d]).

Nitro-t-butyl nitrite: m.p. 24.5–25.5°, b.p. 82–83° (1 mm.), 3 g., $n^{25}D$ 1.4599, d^{25}_4 1.3022.

Anal. Calcd. for $C_4H_8N_2O_4$: C, 32.43; H, 5.40; N, 18.09; MR_D, 31.91; mol. wt., 148. Found: C, 32.95; H, 5.25; N, 17.35; MR_D, 31.1; mol. wt., 141.1.

The nitrite was converted to isobutyraldehyde (2,4-dinitrophenylhydrazone, m.p. 179–181°) by chemical reduction, with or without prior alkaline treatment. This and the results of the elementary analysis are in accord with the instability ascribed to the nitrite ester function in compounds of this type.[8] Himel[3d] reported only nitro-t-butyl chloride as the product of this reaction.

(6) J. P. Fourneau, *Bull. soc. chim.*, **1**, 603 (1940).

(7) L. Henry, *Chem. Zentr.*, **69**, I, 193 (1898).

(8) N. Levy, C. W. Scaife and A. E. Wilder-Smith, *J. Chem. Soc.*, **52** (1948).

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Nitryl Chloride as a Nitrating Agent[1]

BY CHARLES C. PRICE AND CARLTON A. SEARS

The ease of preparation of nitryl chloride from nitric acid and chlorosulfonic acid has prompted us to investigate its utility as a nitrating agent for some typical aromatic compounds. The results, summarized in Table I, indicate that its activity as a nitrating agent can be promoted with such acids as hydrogen fluoride, aluminum chloride and boron fluoride, but that its useful application seems to be limited to aromatic substances of intermediate reactivity. Highly reactive aromatics like phenol, anisole, dimethylaniline and naphthalene tend to give oxidative degradation and deactivated aromatics like nitrobenzene, benzoic acid and benzaldehyde are recovered unchanged.

Nitryl Chloride.[2]—Anhydrous nitric acid was prepared by adding 644 g. of fuming sulfuric acid (30% sulfur trioxide

TABLE I

REACTION OF NITRYL CHLORIDE WITH VARIOUS AROMATICS

Reactants	Catalyst	Solvent	Product(s)
Benzene	...	...	Nitrobenzene (27–35%)
Benzene	HF[a]	HF	Nitrobenzene (70%)
Benzene	AlCl₃	CS₂	Nitrobenzene (89%)
Toluene	AlCl₃	CS₂	o-Nitrotoluene (47%) p-Nitrotoluene (24%)
p-Bromotoluene	AlCl₃	CS₂	2-Nitro-4-bromotoluene (23%) 3-Nitro-4-bromotoluene (16%)
Bromobenzene	AlCl₃	CS₂	p-Nitrobromobenzene (67%) o-Nitrobromobenzene (8%)
m-Dichlorobenzene	AlCl₃	CS₂	2,4-Dichloronitrobenzene (31%)
Phenol	AlCl₃	CS₂	p-Nitrophenol o-Nitrophenol (trace of both)
Anisole	AlCl₃	CS₂	o-Nitrophenol (trace)
Diphenyl ether	AlCl₃	CS₂	4-Nitrodiphenyl ether 7% Diphenyl ether 5%
N,N-Dimethylaniline	BF₃	CS₂	Tar
Naphthalene	AlCl₃	CS₂	1-Nitronaphthalene 31%
Naphthalene	AlCl₃	C₆H₅NO₂	1-Nitronaphthalene 26%
Salicylic acid	AlCl₃	C₆H₅NO₂	Salicylic acid 10% 5-Nitrosalicylic acid 58%
Benzoic acid	AlCl₃	CS₂	Benzoic acid (73%)
Benzoic acid	BF₃	CS₂	Benzoic acid (82%)
p-Chlorobenzoic acid	AlCl₃	C₆H₅NO₂	p-Chlorobenzoic acid (92%)
p-Toluic acid	AlCl₃	CS₂	p-Toluic acid (67%)
Nitrobenzene	AlCl₃	CS₂	Nitrobenzene (93%)
Nitrobenzene	BF₃	HF	Nitrobenzene (96%)
p-Nitrotoluene	AlCl₃	CS₂	p-Nitrotoluene (86%)
Benzaldehyde	AlCl₃	CS₂	Benzaldehyde (74%)
Acetophenone	AlCl₃	CS₂	Acetophenone (88%)

[a] Benzene (36 g., 0.5 mole) was added to 0.55 mole of nitryl chloride in 250 g. of liquid hydrogen fluoride in a copper beaker.

content) dropwise, with constant stirring, to 400 g. (5.64 moles) of fuming nitric acid (89% acid content), in a 2-liter three-necked, round-bottomed flask, cooled to 0°, equipped with a dropping funnel, a seal glass stirrer, and attached through a wide bore U-tube to a 500-cc. round-bottomed flask serving as receiver. The receiver was then cooled by a Dry Ice–isopropyl alcohol bath and 370 cc. (5.70 moles) of chlorosulfonic acid (fraction boiling at 149–152° (747 mm.) on redistillation) was added dropwise, with vigorous stirring and continued cooling, over a period of about 12 hours. After all of the chlorosulfonic acid had been introduced the cooling bath was removed from the reaction flask and the mixture stirred for one hour at room temperature; 420 g. (91%) of a dense, pale yellow liquid boiling at −16 to −15° was collected.

The Reaction of Benzene with Nitryl Chloride.—Nitryl chloride (0.2 mole) was allowed to distil into 50 cc. of dry benzene slowly at room temperature. The solution became yellow as the inorganic halide was added. After all of the reactant had been added the mixture was heated at reflux for 15 hours, after which the test for escaping inorganic halide was negative. Washing and distillation yielded 8.6 g. (35%) of nitrobenzene.

General Procedure for the Condensation of Nitryl Chloride with an Aromatic Compound.—The reactions were run under anhydrous conditions. The reaction flask was cooled by an ice-bath and a solution of 100 cc. of carbon disulfide and 0.2 mole of the aromatic compound added to the flask. The aluminum chloride (0.25 mole) was then added to this solution with vigorous stirring. Nitryl chloride (0.25 mole) was then allowed to distil into the reaction mixture. After all of the inorganic halide had been added the product was stirred at ice temperature for 1–2 hours, the ice-bath removed, and the reaction stirred at room temperature until inorganic halides were no longer evolved. The product was hydrolyzed by pouring into ice and concentrated hydrochloric acid mixture. The organic layer separated, was washed with water, sodium bicarbonate, again with water, and finally dried. The solvent was re-

moved by a hot water-bath and the resulting product purified by the conventional means of vacuum distillation, steam distillation or crystallization.

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Some Nuclearly Substituted Catechols and their Acid Dissociation Constants

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In the course of other work, the acid dissociation constants in water of certain nuclearly substituted catechols were required. Such values of the constants[1,2] as appeared in the literature were open to question, so that it was decided to determine them for the entire group. In the preparation of the catechols, difficulties unmentioned by previous authors were encountered, which made it desirable to report some of the synthetic procedures in detail.

The attempt to make 4-nitrocatechol according to Benedikt[3] led, at first, to the isolation of a dinitro derivative, identified via its dimethyl ether as 3,4-dinitrocatechol. Reduction in the quantity of nitrosating reagents permitted the desired 4-nitrocatechol to be obtained. Nitration of catechol in ether solution,[4] to produce a mixture of 3- and 4-nitrocatechols, gave evidence of a threshold concentration of reagents, below which no reaction could take place; such a phenomenon has been described by Halberstadt, Hughes and Ingold.[5] After several unsuccessful attempts to isolate 3,4-dihydroxybenzophenone according to the method of Rosenmund and Lohfert,[6] the authors were furnished by Dr. Joseph Corse with a satisfactory modification of that method.[7]

Experimental and Results

3,4-Dinitrocatechol.—A solution of sodium nitrite (16 g., 0.24 mole) and catechol (4.0 g., 0.036 mole) in water (150 ml.) was mixed with sufficient ice to bring the temperature down to 0°. In the course of 3–5 minutes, 75 ml. of 2.5 M H_2SO_4 (0.19 mole) was added, along with more ice and with shaking. The solution was then extracted with ether in two portions (150 and 75 ml.). The combined ether extract was twice washed with 100 ml. of water, dried briefly over anhydrous sodium sulfate and evaporated quickly at room temperature under a stream of nitrogen. When the ether had been removed, the oily residue was left under vacuum until it had crystallized; it was then extracted with xylene at 100° and the crystalline product that separated from the cooled xylene solution was collected, washed with petroleum ether and air-dried. This material was recrystallized twice from 15% ethanol-water (8–11 ml./g.), care being taken not to exceed the temperature required for solution. The air-dried dihydrate thus obtained in 24% yield lost two moles of water on drying for several hours at 59° and a

(1) F. L. Gilbert, F. C. Laxton and E. B. R. Prideaux, *J. Chem. Soc.*, 2295 (1927).

(2) H. Pauly, K. Schübel and K. Lockemann, *Ann.*, 383, 309 (1911).

(3) R. Benedikt, *Ber.*, 11, 362 (1878).

(4) M. J. Astle and S. P. Stephenson, THIS JOURNAL, 65, 2402 (1943).

(5) E. S. Halberstadt, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 2441 (1950).

(6) K. W. Rosenmund and H. Lohfert, *Ber.*, 61, 2601 (1928).

(7) Private communication from Dr. Joseph W. Corse of the Western Regional Research Laboratory, Albany, California. A sample of this material was kindly made available to us by Dr. Corse.

pressure of 8 mm. The anhydrous compound was somewhat hygroscopic (m.p. 147–148°).

Anal. Calcd. for $C_6H_4O_6N_2$: C, 36.0; H, 2.0; N, 14.0; mol. wt., 200. Found: C, 35.2; H, 2.39; N, 13.4; mol. wt. (Rast), 197.

In 1 N aqueous HCl this compound showed an absorption maximum at 352 mμ, ϵ 7.1 × 10^3, and a minimum at 266 mμ.

3,4-Dinitroveratrole.—Anhydrous 3,4-dinitrocatechol (0.45 g., 0.00225 mole) was mixed with methyl sulfate (0.60 ml., 0.0063 mole) and 1.09 N NaOH (4.8 ml., 0.0052 mole) and subjected to vigorous shaking and gentle heating for about five minutes at which time the initially red color of the aqueous phase had been nearly discharged. Additional NaOH solution (3.1 ml., 0.0034 mole) caused reappearance of the red color, which persisted on further heating and shaking. A solid phase soon appeared to take the place of the liquid methyl sulfate layer. The mixture was cooled and extracted with ether. The ether layer was extracted with several portions of a dilute aqueous NaOH solution until the aqueous phase was colorless, then washed twice with water and dried over Na_2SO_4. Evaporation of the ether left a white residue which was recrystallized from methanol-water. The product so obtained was isolated and dried with a stream of air (m.p. 90.5°). Of the four possible dinitroveratroles, all of which are known,[8] only the 3,4-isomer has the m.p. found.

4-Nitrocatechol.[3]—A solution of sodium nitrite (5.5 g., 0.08 mole) and catechol (4.0 g., 0.036 mole) in water (150 ml.) was mixed with sufficient ice to bring the temperature down to 0°. In the course of 3–5 minutes, 25 ml. of 2.5 M H_2SO_4 (0.063 mole) was added, along with more ice and with shaking. The solution was then extracted with ether in two portions (150 and 75 ml.). The combined ether extract was twice washed with 100 ml. of water, dried briefly over anhydrous sodium sulfate and evaporated quickly at room temperature under a stream of nitrogen. The residue was subjected to vacuum sublimation at a pressure of 6 mm. The first small fraction, somewhat oily, was removed at a bath temperature of 100–150° and probably consisted mostly of 3,4-dinitrocatechol. The second fraction, removed at a bath temperature of 160–190°, was nearly pure 4-nitrocatechol (m.p. 172–174°); its weight was 1.63 g. (29% yield). When somewhat greater amounts of sodium nitrite (8.25 g., 0.12 mole) and sulfuric acid (37.5 ml., 0.09 mole) were used a yield of 2.11 g. (37%) of 4-nitrocatechol was obtained.

3- and 4-Nitrocatechol.—Previous authors[4] treated a solution of 10 g. of catechol in 500 ml. of ether with 4 ml. of fuming nitric acid, allowed the resulting solution to stand 24 hours, washed the ether solution with water and proceeded with the isolation of 3- and 4-nitrocatechol. The present authors recovered mostly catechol by this procedure. Neither refluxing nor addition of water induced the reaction when the recommended quantity of ether was employed, but distillation of a portion of the ether prior to washing with water caused the desired reaction to take place. When the amount of ether was reduced to 250 ml. the reaction proceeded rapidly and the products were isolated; when 375 ml. of ether was employed, the reaction proceeded in three out of the four times it was tried. When 375 ml. of ether was used, isolation was carried out by evaporation of the washed ether solution, vacuum sublimation of the residue (bath temperature being raised gradually from 100 to 200°), and continuous extraction of the sublimate with 30–60° petroleum ether. The petroleum ether-soluble fraction consisted of nearly pure (m.p. 84°, reported 86°) 3-nitrocatechol, while the residue, consisting mostly of 4-nitrocatechol, was purified (m.p. 176°, reported 174°) by recrystallization from water. The yield of impure mononitrocatechols was approximately 65–70%, the product consisting of 56–62% 3-nitrocatechol and 38–44% 4-nitrocatechol. Variation of the temperature of reaction did not produce significant difference in the ratio of the 3- to 4-isomer. Spectral absorption maxima for 4-nitrocatechol in 1 M aqueous HCl occurred at 240 and 346 mμ, while the 3-isomer showed a single maximum at 298 mμ. Isobestic points for the first dissociation of 4-nitrocatechol were found at 229, 252, 280 and 370 mμ, while those of 3-nitrocatechol were found at 268 and 320 mμ.

(8) I. M. Heilbron, "Dictionary of Organic Compounds," Vol. I, Oxford University Press, New York, N. Y., 1934, p. 640.

TABLE I
ACID DISSOCIATION CONSTANTS

Compound	K_1	K_2	Melting point, °C. Lit.	Found
3-Nitrocatechol	2.2×10^{-7}	....	86	84
4-Nitrocatechol	1.3×10^{-7}	....	174	176
3,4-Dinitrocatechol	4.1×10^{-5}	5.4×10^{-9}	.....	147–148
Protocatechualdehyde[13]	4.4×10^{-8}	....	153–154	152
Protocatechualdoxime[14]	2.1×10^{-9}	....	157	156
Protocatechunitrile[14]	1.9×10^{-8}	....	156	156
3,4-Dihydroxybenzophenone	1.8×10^{-8}	....	145[6]	147–148
3-Methoxycatechol[15]	5.3×10^{-10}	....	.....	.....
3-Methylcatechol	5.3×10^{-10}	....	45, 47, 68	58–62

3,4-Dihydroxybenzophenone.[7]—Sixty-five grams of catechol dibenzoate, 185 ml. of nitrobenzene and 56 g. of anhydrous aluminum chloride were heated on the steam-bath for six hours. Ice and hydrochloric acid were then added, and, after the decomposition was complete, the nitrobenzene was steam distilled. The remaining solution was chilled and the solid material collected, dried and dissolved in 400 ml. of methanol. The resulting solution was saturated with anhydrous hydrogen chloride, and refluxed for 3.5 hours. Methanol was removed on the steam-bath, water was added to the residue, and the mixture was steam distilled to remove methyl benzoate. The residual mixture was boiled, enough water was introduced to effect solution, and decolorizing charcoal was added. After being boiled for several minutes, the solution was filtered and chilled. The product was collected and recrystallized four times from hot water. The resulting colorless crystalline material melted at 147–148°, and showed no melting point depression when mixed with an authentic specimen.[7] The substance appeared to contain a small amount of water of crystallization, which was not determined exactly.

3-Methylcatechol.—Orthovanillin was reduced[9] to 2-hydroxy-3-methoxytoluene in 45% yield. The latter was converted to 3-methylcatechol by the de Vries[10] demethylation procedure. The viscous oil obtained by distillation (130–139° (20 mm.)) of the crude product solidified on standing in the refrigerator. Vacuum sublimation at 0.8 mm. gave a white substance melting at 58–62°. The melting point has been reported[11] as 45, 47 and 68°. The compound gave a negative test for aldehydes with 2,4-dinitrophenylhydrazine.

Dissociation constants were obtained by potentiometric titration[12] of 10^{-3} M solutions of the substances in question with 0.02 N NaOH at 25° against a Beckman Model G pH meter. In each case the dissociation constant was an average of values calculated from data near the mid-point of the titration (Table I). The figures for the last three compounds are only approximate, since the titration curves were poor.

Spectrophotometric data were determined on the Beckman Model DU spectrophotometer at 2×10^{-4} M concentrations. From some of these data it was possible to calculate[16] dissociation constants in confirmation of the potentiometrically derived values. Thus, 4-nitrocatechol in 1.25 M HCl and in 0.04 M phosphate buffers, had extinction coefficients at 430 mμ of 200, 1.0 × 10⁴ and 1.375 × 10⁴ at pH's 0.11, 7.1 and 8.0, which yield a value of 1.8 × 10⁻⁷ for the apparent dissociation constant. The constant for 3-nitrocatechol has been derived similarly.[16]

Discussion

The dissociation constants of several of the present group of compounds have been determined

(9) J. Koetschet and P. Koetschet, *Helv. Chim. Acta*, **13**, 474 (1930).

(10) M. O. de Vries, *Rec. trav. chim.*, **28**, 276 (1909).

(11) Beilstein, "Handbuch der organischen Chemie," Vol. VI 4th Ed., Julius Springer Verlag, Berlin, 1923, p. 872; 1st supplement, 1931, p. 426.

(12) D. D. Van Slyke, *J. Biol. Chem.*, **52**, 549 (1922).

(13) J. S. Buck and F. J. Zimmermann, "Organic Syntheses." Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 549.

(14) K. Hoesch and T. v. Zarzecki, *Ber.*, **50**, 465 (1917).

(15) A. R. Surrey, *Org. Syntheses*, **26**, 90 (1946).

(16) D. H. Rosenblatt, paper in preparation.

in 40% dioxane–water by Corse and Ingraham[17] and show excellent qualitative agreement with the present results, especially when the difference in the dielectric constants of the media is considered. The present values for 3- and 4-nitrocatechol are significantly lower than those found by Gilbert, Laxton and Prideaux[1]; no evident reason can be shown for this discrepancy. The value found for protocatechualdehyde is of the same order of magnitude as that of Pauly, *et al.*[2]

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(17) J. Corse and L. L. Ingraham, THIS JOURNAL, **73**, 5706 (1951).

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Substitution Reactions of 2- and 3-Methylthianaphthene

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The nitration of 2-methylthianaphthene gave a mononitro derivative in 48% yield. This was shown to be the 2-methyl-3-nitrothianaphthene by reduction and acetylation to 2-methyl-3-acetamino-thianaphthene which was desulfurized by the useful technique of Mozingo[2] with Raney nickel catalyst to form 1-acetamino-1-phenylpropane. This last compound was identical with an authentic sample.

Bromination of 2-methylthianaphthene gave 2-methyl-3-bromothianaphthene in 88% yield. The structure of the product was proved by conversion through the Grignard reagent to 2-methyl-3-thianaphthenecarboxylic acid which was desulfurized as above to the known α-phenylbutyric acid. The 2-methyl-3-thianaphthenecarboxylic acid was identical in melting point with an acid obtained by Gaertner[3] and shown to be 2-methyl-3-thianaphthenecarboxylic acid by oxidation to 2,3-thianaphthenedicarboxylic acid.

(1) Department of Chemistry, University of Tennessee, Knoxville, Tennessee.

(2) R. Mozingo, D. E. Wolf, S. A. Harris and K. Folkers, THIS JOURNAL, **65**, 1013 (1943).

(3) R. Gaertner, *ibid.*, **74**, 766 (1952).

Metalation of 3-methylthianaphthene with *n*-butyllithium gave, subsequent to carbonation, 3-methyl-2-thianaphthenecarboxylic acid which was again proved by desulfurization to the known β-phenylbutyric acid. The same desulfurization product would have been obtained from metalation in the methyl group giving thianaphthene-3-acetic acid. However, this product has been prepared several times by different workers[4] and there is general agreement on its melting point of 109°, whereas our acid melts at 244.5–245°. Desulfurization therefore constitutes rigorous structure proof. 3-Methyl-2-thianaphthenecarboxylic acid is mentioned by Gaertner[5] as the product from the action of carbon dioxide on the Grignard reagent from 3-chloromethylthianaphthene.

Nitration of 3-methylthianaphthene gave 2-nitro-3-methylthianaphthene in 25% yield. The structure of this compound was indicated as above by reduction, acetylation, desulfurization and hydrolysis giving the known 2-phenyl-1-aminopropane. Here again the desulfurization technique does not distinguish nitration in the 2-position from substitution in the methyl group. This latter type of substitution is however highly unlikely under the conditions employed.

Acknowledgment.—The authors wish to express appreciation to the Research Corporation for financial aid in this work.

Experimental[6]

2-Methyl-3-bromothianaphthene.—A solution of 5 g. (0.034 mole) of 2-methylthianaphthene[7] in 30 ml. of chloroform was cooled in an ice-bath and a dilute solution of bromine in chloroform added dropwise with stirring until a permanent bromine color was obtained in the reaction mixture. Evaporation of the solvent gave a solid which was pressed between filter paper to produce 7.0 g. (88%) of 2-methyl-3-bromothianaphthene, m.p. 42–42.5°. Recrystallization from 95% ethanol did not change the melting point.

Anal. Calcd. for C_9H_7BrS: S, 14.11. Found: S, 14.19, 14.08.

The above bromo compound was converted to the Grignard reagent and carbonated in normal fashion except that formation of the Grignard reagent was initiated by use of considerable methyl iodide. There was obtained a 50% yield of 2-methyl-3-thianaphthenecarboxylic acid, m.p. 194–195°. Gaertner[3] reports m.p. 196°. Since this work had been completed before the appearance of Gaertner's work,[3] the acid was desulfurized to α-phenylbutyric acid, m.p. 33.5–35°, identical in melting point and mixed melting point with a commercial sample. The amide derivatives, m.p. 85–86°, were prepared from both samples and were also identical.

2-Methyl-3-nitrothianaphthene.—Ten grams (0.067 mole) of 2-methylthianaphthene dissolved in 65 ml. of acetic acid was cooled in an ice-bath while 30 ml. of concentrated nitric acid was added over a five-minute period. The reaction mixture was allowed to stand 30 minutes in the ice-bath and the precipitated solid removed by filtration, washed and dried to give 5.75 g. (48%) of nitro compound, m.p. 96–98°. Recrystallization from ethanol raised the melting point to 98–98.5°.

Anal. Calcd. for $C_9H_7NO_2S$: N, 7.25. Found: N, 7.25, 7.06.

(4) For example see E. M. Crook and W. Davies, *J. Chem. Soc.*, 1698 (1937).

(5) R. Gaertner, This Journal, **74**, 2185 (1952).

(6) All melting points were taken on a Fisher–Johns apparatus and are uncorrected.

(7) D. A. Shirley and M. D. Cameron, This Journal, **74**, 664 (1952).

2-Methyl-3-acetaminothianaphthene.—The nitro compound (5 g. or 0.028 mole) was reduced in acetic acid–acetic anhydride solvent with Raney nickel catalyst at 50 p.s.i. hydrogen pressure in the normal fashion. There was obtained 2.73 g. (51%) of 2-methyl-3-acetaminothianaphthene, m.p. 186–186.5°.

Anal. Calcd. for $C_{11}H_{11}NOS$: N, 6.82. Found: N, 6.89.

The acetamino compound was desulfurized[2] to N-acetyl-1-phenylpropylamine m.p. 77–78°, identical in melting point and mixed melting point with a sample prepared from the Leuckart reaction with propiophenone according to the method of Crossley and Moore.[8]

Metalation of 3-Methylthianaphthene.—To a solution of 6.6 g. (0.044 mole) of 3-methylthianaphthene[5] in 30 ml. of ether was added slowly with stirring an ethereal solution containing 0.045 mole of *n*-butyllithium, the concentration of which was determined by the procedure of Gilman and Haubein.[9] The mixture was stirred and heated to reflux for 45 minutes and carbonated with crushed solid carbon dioxide in the usual manner. After hydrolysis and addition of excess dilute hydrochloric acid the ether layer was separated and the aqueous layer extracted twice with ether. The combined ether solutions were extracted with 10% aqueous sodium hydroxide and the extracts acidified to precipitate 5.1 g. (65%) of 3-methyl-2-thianaphthenecarboxylic acid, m.p. 244–246°. Gaertner[5] reports m.p. 244–244.5°. Reprecipitation from aqueous base changed the melting point to 244.5–246°.

Anal. Calcd. for $C_{10}H_8O_2S$: S, 16.67; neut. equiv., 192. Found: S, 16.78; neut. equiv., 189.

3-Methyl-2-thianaphthenecarboxamide.—The amide was prepared from the above acid in usual fashion involving treatment with thionyl chloride and ammonia. There was obtained after crystallization from ethanol 2.1 g. (70%) of amide, m.p. 181–183°.

Anal. Calcd. for $C_{10}H_9NOS$: N, 7.33. Found: N, 7.55.

The amide was desulfurized[2] in 85% yield to β-phenylbutyramide, m.p. 105–106°. This amide has been reported to melt 105°[10] and 106–107°.[11] The β-phenylbutyramide was further characterized by nitration to its *p*-nitro derivative by the method of Schroeter.[12] The product melted at 164° which is in agreement with the literature value.[12]

2-Nitro-3-methylthianaphthene.—To a solution of 5 g. (0.034 mole) of 3-methylthianaphthene in 10 ml. of glacial acetic acid was added slowly with stirring a solution of 10 ml. of concentrated nitric acid and 10 ml. of acetic acid. The mixture was allowed to stand at room temperature for 15 hours and then poured into excess water. The precipitated solid was separated and crystallized from ethanol to give 1.65 g. (25%) of 2-nitro-3-methylthianaphthene, m.p. 148–149°.

Anal. Calcd. for $C_9H_7NO_2S$: N, 7.25. Found: N, 7.46.

2-Acetamino-3-methylthianaphthene.—Reduction of the nitro compound as described previously gave the acetamino compound, m.p. 182.5–183° in 55% yield.

Anal. Calcd. for $C_{11}H_{11}NOS$: N, 6.86. Found: N, 7.05.

Desulfurization[2] of a small amount of the acetamino compound followed by alkaline hydrolysis of the product gave 2-phenylpropylamine identified as its picrate, m.p. 184–185°, and its N-benzoyl derivative, m.p. 87.5–88°. Both of these derivatives have been prepared previously and the melting points reported approximately as above.[10,13,14]

N-Benzoyl-2-amino-3-methylthianaphthene.—This compound was prepared by reduction of 2-nitro-3-methylthianaphthene with Raney nickel at 50 p.s.i. hydrogen pressure. The reduction was carried out in ether solution and the ether evaporated followed by immediate treatment of the amine with benzoyl chloride in the presence of aqueous alkali. The product was crystallized once from ether and

(8) M. L. Crossley and M. L. Moore, *J. Org. Chem.*, **9**, 529 (1944).

(9) H. Gilman and A. H. Haubein, This Journal, **66**, 1515 (1944).

(10) B. B. Day and V. S. Ramanathan, *Proc. Nat. Inst. Science India*, **9**, 193 (1943).

(11) J. F. Eijkman, *Chem. Zentr.*, **79**, II, 1100 (1908).

(12) G. Schroeter, *Ber.*, **40**, 1596 (1907).

(13) M. Freund and E. Koenig, *ibid.*, **26**, 2875 (1893).

(14) J. von Braun, J. Grabowski and G. Kirschbaum, *ibid.*, **46**, 1281 (1913).

once from ethanol to give the N-benzoyl-2-amino-3-methyl-thianaphthene melting at 167.5–170°.

Anal. Calcd. for $C_{16}H_{13}NOS$: N, 5.24. Found: N, 5.37.

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Studies on Carcinogenic Hydrocarbons: Dissociation Constants and Free Energies of Formation of Complexes with 2,4,7-Trinitrofluorenone[1]

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The reasons for the synthesis of appreciable amounts (about 20–25 g. of each) of all of the mono-methyl-1,2-benzanthracenes and monomethyl-benzo(c)phenanthrenes have been stated.[2] In an attempt to find some physical or chemical property of these hydrocarbons which might be correlated with their cancer producing activities, we have studied spectrophotometrically the equilibrium of the reaction between these hydrocarbons and 2,4,7-trinitrofluorenone[3] (TNF) in chloroform solution. From the data we have calculated the dissociation constants for the reaction

$$X \cdot TNF \rightleftharpoons X + TNF$$

We also have calculated the free energy of formation of the complexes X·TNF. The results of these calculations are summarized in Table I.
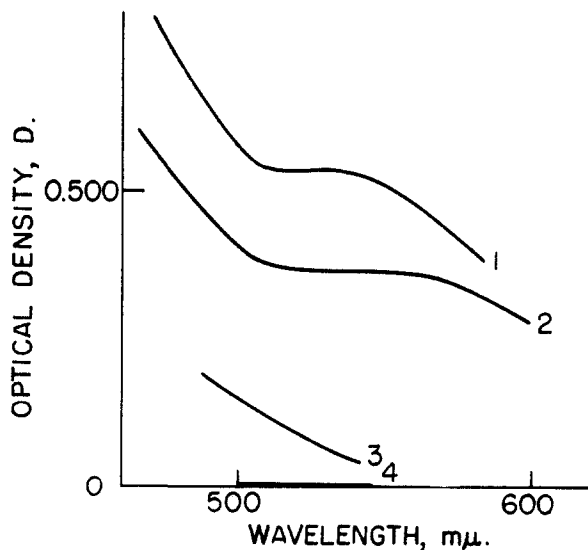

Fig. 1.—Typical absorption curves: initial concentrations in $CHCl_3$, 1, 6-methyl-1,2-benzanthracene 0.999×10^{-3} M, TNF 47.0×10^{-3} M; 2, 9-methyl-1,2-benzanthracene 1.045×10^{-3} M, TNF 46.7×10^{-3} M; 3, benzo(c)phenanthrene 0.750×10^{-3} M, TNF 38.4×10^{-3} M; 4, saturated solution of TNF.

(1) This work was supported by a grant, C-483-C3,4 from the U. S. Public Health Service to whom grateful acknowledgment is made.

(2) M. S. Newman and R. Gaertner, THIS JOURNAL, 72, 264 (1950); M. S. Newman, H. V. Anderson and K. H. Takemura, *ibid.*, 75, 347 (1953).

(3) M. Orchin and O. Woolfolk, *ibid.*, 68, 1727 (1946).

TABLE I

DISSOCIATION CONSTANTS AND FREE ENERGIES OF FORMATION OF THE COMPLEXES OF 1,2-BENZANTHRACENES AND BENZO(C)-PHENANTHRENES IN CHLOROFORM, 25°

1,2-Benzanthracenes	Wave length,[a] mμ	K, mole/l.	F, cal./mole
4-Methyl	517	0.013	−2600
9-Methyl	546	.019	−2400
7-Methyl	517	.019	−2400
6-Methyl[b]	526	.021	−2300
	526	.023	−2200
8-Methyl	517	.023	−2200
10-Methyl[b]	546	.023	−2200
	546	.024	−2200
3-Methyl	517	.029	−2100
3'-Methyl	526	.029	−2100
4'-Methyl	517	.030	−2100
Unsubstituted	517	.034	−2000
5-Methyl[b]	517	.032	−2000
	526	.036	−2000
1'-Methyl	517	.040	−1900
2'-Methyl	526	.059	−1700
Benzo(c)phenanthrenes			
4-Methyl	500	0.035	−2000
2-Methyl[b]	526	.051	−1800
	500	.052	−1800
6-Methyl	500	.054	−1700
5-Methyl	500	.056	−1700
3-Methyl	500	.087	−1400
Unsubstituted[b]	500	.12	−1200
	500	.12	−1200
1-Methyl[b]	500	.15	−1100
	500	.15	−1100

[a] Wave length at which measurements were taken.
[b] Two separate experiments were carried out and the values obtained in each are recorded.

Experimental

The general procedure for spectrophotometric determination is described below.

A solution of the hydrocarbon of known concentration (0.7–1.0×10^{-3} M) in chloroform (C.P.) was prepared. This was transferred to a series of volumetric flasks containing weighed amounts of TNF. The TNF concentrations in the resultant solutions were from 35–47×10^{-3} M. The mixtures were shaken to dissolve the TNF and then were allowed to stand overnight at room temperature. Prior to the photometric measurements the solutions were set for several hours in the spectrographic laboratory where the room temperature was held at 25°.

The solutions of the TNF complexes with the methyl-1,2-benzanthracenes varied in color from a deep red to reddish purple while the methylbenzo(c)phenanthrenes gave orange solutions. For each of the methyl-1,2-benzanthracene solutions there was a region around 517–546 mμ where the optical densities of these solutions were constant (Fig. 1). No such plateaus were found in the absorption curves of benzo(c)phenanthrene and its methyl derivatives. The absorption of TNF alone was very small at the wave lengths studied.

The optical densities of the solutions were measured with a Beckman quartz spectrophotometer, model DU, in 1-cm. quartz cells. Measurements were made at a number of wave lengths in the region of 500–546 mμ. These were taken as rapidly as possible to minimize any temperature changes of the solution in the cell compartment.

The TNF complexes were made by the method described for 1,2-benzanthracene.[3] Recrystallization involved solution in acetone, addition of alcohol, and distillation to incipient crystallization. The melting points recorded in Table II are for once recrystallized samples. All of the TNF derivatives involved a 1:1 ratio of hydrocarbon and

TABLE II

MELTING POINTS OF HYDROCARBONS, TNF COMPLEXES AND PICRATES

Hydrocarbon	M.p.,[a] °C.	M.p. (TNF),[b] °C.	M.p. (picrate),[c] °C.
1,2-Benzanthracene	159.5–160.5[e]	223.6–224.0[d]	141.5–142.5
1'-Methylbenzanthracene	138	241.1–241.4	119[e]
2'-Methylbenzanthracene	150.7–151.7	218.7–219.2	180
3'-Methylbenzanthracene	163.0–163.9	239.0–239.6	146–146.8
4'-Methylbenzanthracene	194	228.2–228.8	139
3-Methylbenzanthracene	155.9–156.9	235.4–235.6	153[f]
4-Methylbenzanthracene	126.2–127.2	221.4–221.8	149–150
5-Methylbenzanthracene	160.6–160.6	243.2–243.6	165.8–166.3
6-Methylbenzanthracene	150.5–151.5	225.1–225.4	152–153
7-Methylbenzanthracene	183.0–183.6	224.8–225.0	159.0–159.4
8-Methylbenzanthracene	118.0–118.5	238.2–238.6	159.5–160.0
9-Methylbenzanthracene	138.6–139.6	209.5–209.7	115
10-Methylbenzanthracene	140.2–140.8	236.1–236.5	173.5–174.0
Benzo(c)phenanthracene	68[e]	170.8–171.1	128–128.5[g]
1-Methylbenzo(c)phenanthrene	141.4–141.9[e]	130.6–131.4[h]	None
2-Methylbenzo(c)phenanthrene	80–81[e]	144.2–144.5	118–118.5
3-Methylbenzo(c)phenanthrene	54–54.5[e]	178.5–178.8	134–134.5
4-Methylbenzo(c)phenanthrene	65–66[e]	180.7–180.9	107–108
5-Methylbenzo(c)phenanthrene	70.4–71.0[e]	157.9–158.5	141.8–143.2
6-Methylbenzo(c)phenanthrene	77–78[e]	171.8–172.2	112.5–113.5

[a] See m.p.'s listed in M. S. Newman and R. Gaertner, THIS JOURNAL, 72, 264 (1950). [b] Melting points taken on short range Anschütz thermometers certified by the U. S. Bureau of Standards. [c] Taken from M. Orchin, J. Org. Chem., 16, 1165 (1951). [d] M. Orchin and E. O. Woolfolk, THIS JOURNAL, 68, 1727 (1946). [e] Dipicrate. [f] In the ref. in a, the m.p. was found to be 146.0–146.8°. [g] See W. E. Bachmann and R. O. Edgerton, THIS JOURNAL, 62, 2970 (1940). [h] M. S. Newman and W. B. Wheatley, ibid., 70, 1913 (1948).

TNF, as all gave values for nitrogen which ranged from 7.2 to 7.8% N (calcd. for $C_{32}H_{19}O_7N_3$: N, 7.5). Microanalyses by the Galbraith Laboratories, Knoxville, Tennessee.

Calculations

Calculation of the dissociation constants (Table I) of the complexes was based upon methods previously reported.[4]

For the dissociation $X \cdot TNF \rightleftarrows X + TNF$ in dilute solutions, the dissociation constant, K, may be expressed as

$$K = \frac{[X][TNF]}{[X \cdot TNF]} \quad (1)$$

where $[X]$, $[TNF]$ and $[X \cdot TNF]$ are molar concentrations of hydrocarbon, TNF and complex, respectively. If $[X]_0$ be the initial molar concentration of hydrocarbon and $[TNF]_0$ be the initial molar concentration of TNF, then

$$K = \frac{([X]_0 - (X \cdot TNF))([TNF]_0 - [X \cdot TNF])}{[X \cdot TNF]} \quad (2)$$

From the expression for the molar extinction coefficient of the complex, $\epsilon = D/[X \cdot TNF]$, (where D is the optical density of the solution corrected for the absorption of TNF and l is the cell length), and for the case where $[TNF]_0 \gg [X \cdot TNF]$

$$K = \frac{([X]_0 - D/\epsilon l)([TNF]_0)}{D/\epsilon l} \quad (3)$$

$$1/D = (K/\epsilon l[X]_0)(1/[TNF]_0) + (1/\epsilon l[X]_0) \quad (4)$$

Equation (4) is of the form $y = mx + b$. Figure 2 illustrates the plot of equation (4) in the case of the 9-methyl-1,2-benzanthracene-TNF complex. The constants, $K/\epsilon l[X]_0$ and $1/\epsilon l[X]_0$, for the curve were determined by the method of least squares. From these K is readily obtained. Since

(4) H. A. Benesi and J. H. Hildebrand, THIS JOURNAL, 71, 2703 (1949); J. Landauer and H. McConnell, ibid., 74, 1221 (1952).

the pure hydrocarbon shows no absorption at 500–546 $m\mu$ and the absorption of TNF is very small (Fig. 1), the corrected optical density, D, of the solution is due to the complex alone.
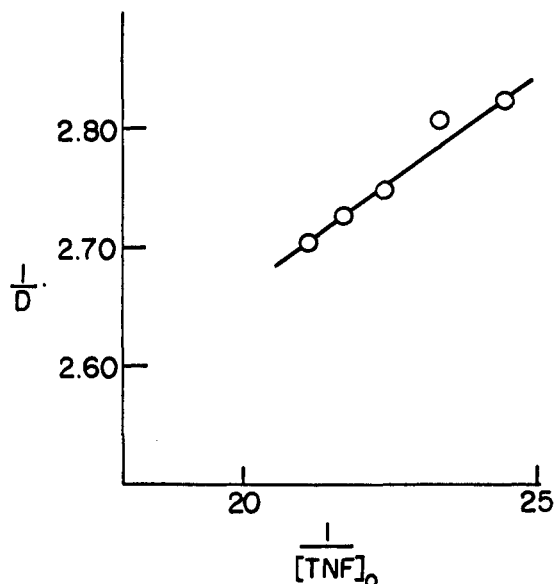
Fig. 2.—Plot of equation (4) for the 9-methyl-1,2-benzanthracene–TNF complex. Initial concentration of hydrocarbon 1.003 × 10⁻³ M. D = optical density of solutions at 546 mμ. [TNF]₀ = initial molar concentration of TNF.

Discussion

In attempting to correlate any physical or chemical property of a compound with its carcinogenic activity it is essential to have at least a semiquantitative measure of this activity. In spite of the large amount of biological testing which has been

done, no study has as yet been reported in which all of the monomethyl-1,2-benzanthracenes and/or -benzo(c)phenanthrenes have been tested under reasonably constant conditions. The difficulties inherent in the attempt to assign the degree of carcinogenic potency to any hydrocarbon are well summarized in the Introduction to the latest survey on carcinogenic activity.[5] Fortunately, work which will provide some of the necessary data[6] on the methyl-1,2-benzanthracenes and -benzo(c)-phenanthrenes is now in progress in the laboratories of E. von Haam (Ohio State University) and I. Berenblum (Weizmann Institute).

Despite this present lack of complete quantitative data on the carcinogenic properties of these hydrocarbons, it is fairly well established that among the monomethyl-1,2-benzanthracenes, the 10-methyl is the most active cancer producing agent, the 5- and 9-methyl derivatives are slightly less active, while the 1'-derivative is comparatively inactive.[5,6]

From this qualitative information it is apparent that there is no correlation between carcinogenic activity of the hydrocarbon and the dissociation constant (or free energy of formation) of its TNF complex. For example, the TNF complex of the 5-methyl derivative is less stable than that of the 10-methyl while the 9-methyl complex is more stable. Furthermore, relatively inactive carcinogens form complexes which are about as stable as the 10- (e.g., the 8-methyl), more stable (e.g., the 7-methyl), or even less stable (e.g., the 1'- and 2'-methyl). There are not enough data on the carcinogenic activity in the benzo(c)phenanthrene series to make any comparisons.

Recently the bathochromic shifts in the ultraviolet absorption of 1,2-benzanthracene produced by the substitution of a methyl group for each of the twelve hydrogens have been determined.[7] A comparison of the observed shifts with the conjugating power (calculated both by the molecular orbital and valence bond methods) of the hydrocarbons was made. The stabilities of the hydrocarbon–TNF complexes given in Table I show no correlation with either the bathochromic shifts or the conjugating power of the hydrocarbon.

Orchin[8] has discussed steric effects in the formation of complexes of tetracyclic compounds. He states that "although substitution of a methyl group on the hydrocarbon usually enhances the ease of formation and stability of the picrate, if the methyl group is located where steric interference (methyl, hydrogen overlap) is possible, complex formation is often made difficult or the complex forms in other than a 1:1 ratio." With the methyl-1,2-benzanthracenes such steric interference is possible in the case of the 9-methyl (overlap with 1'-hydrogen) and 1'-methyl (overlap with the 9-hydrogen); in 1-methylbenzo(c)phenanthrene con-

siderable overlap with the 1'-hydrogen is possible. Orchin used the melting point of the picrate as a criterion of its stability,[9] concluding that the 9-methyl-1,2-benzanthracene picrate, because of its low melting point (see Table II), is unstable; he noted that the 1'-methyl was not a 1:1 complex and that the 1-methylbenzo(c)phenanthrene complex did not form.

Since the TNF compounds with the methyl-1,2-benzanthracenes and -benzophenanthrenes are all formed in a ratio of 1:1, an evaluation of the general applicability of the melting point as a criterion of complex stability is afforded. While these compounds may be arranged into groups which melt fairly closely and have comparable stability, there are notable exceptions. The 9-methyl complex is the lowest melting (209°) of the 1,2-benzanthracenes, but is the second most stable; the 1'-methyl is the second highest melting, but is the next to the least stable.

The effect of the methyl, hydrogen overlap on the stability of the TNF complexes is of interest. The 1'-methyl-1,2-benzanthracene complex is, indeed, relatively unstable, but the 9-methyl complex is the second most stable. As would be expected from steric considerations, the complex compound with 1-methylbenzo(c)phenanthrene is the most unstable of its series.

We are presently engaged in determining the rate of reaction of the hydrocarbons of the 1,2-benzanthracene series with maleic anhydride and the equilibrium constants for these reactions.

(9) See also C. Shinomiya, Bull. Chem. Soc. Japan, 15, 92, 137, 281 (1940).

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Densities and Freezing Points of Sodium Permanganate Solutions

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In the use of strong solutions of sodium permanganate it became necessary to know the densities and phase diagram for the system sodium permanganate–water. The temperature at which a solid phase appears was determined for solutions from 0 to 96 weight per cent. sodium permanganate. The salt received for this work analyzed 88 weight per cent. and when dried in vacuo at 100° the analysis rose to 98.5% sodium permanganate. Further drying did not improve the purity. All compositions are given on the weight basis and corrected to the $NaMnO_4$ and water content only. The 1.5% is considered inert and as playing no part on freezing point curves. Solutions were made up by mixing weighed amounts of salt and water and titrations against standard sodium oxalate were used to check the concentration. The freezing points composition curves were obtained by recording the cooling curves for various concentrations of sodium permanganate in the standard way; i.e., the solutions were mechanically stirred during cooling and seed crystals added where any tendency to under-

(5) "Survey of Compounds which Have Been Tested for Carcinogenic Activity," 2nd Ed., Federal Security Agency, Public Health Service Publication No. 149, U. S. Government Printing Office, Washington, D. C., 1951.

(6) Ibid., 1st Ed. On p. 9 J. L. Hartwell says, "The most obvious need, as is shown by the table, is for more complete investigation of compounds already studied in a preliminary fashion."

(7) G. M. Badger, R. S. Pierce and R. Pettit, J. Chem. Soc., 1112 (1952).

(8) M. Orchin, J. Org. Chem., 16, 1165 (1951).

cool was apparent. The recording was accomplished with a four junction copper–constantan thermocouple and a Leeds and Northrup recording potentiometer. The thermocouple was calibrated over the range used against fixed points using a reference junction at 0°. A smooth curve was obtained over the range.

Difficulty was experienced in obtaining cooling curves for solutions above 89.4 weight per cent. sodium permanganate and reproducible freezing points were not obtained for the eutectic between the monohydrate and anhydrous material.

In Table I, the temperatures are given at which a solid phase appears for a given percentage of sodium permanganate. The compositions of solid phases were calculated from the composition of the solutions at the freezing point. For concentrations below 41.4% the solid phase is ice; between 41.4 and 75.2% the solid phase is sodium permanganate trihydrate with a melting point at 36.0°. Between 75.2 and about 91% the solid phase is monohydrate with a melting point at 68.7°. Above about 89.4% the data are rendered somewhat questionable due to decomposition of the sample; however, the points obtained may indicate the possible existence of hydrate containing $1/2$ molecule of water. No freezing point could be determined above 96% due to decomposition. The phase diagram is shown in Fig. 1. The doubtful part of the diagram is shown by a dotted line. Each solution used is indicated with a different type point.

Concentration of NaMnO₄ in weight per cent.

Fig. 1.

TABLE I

NaMnO₄,[a] Wt. %	F.p., °C.	NaMnO₄, Wt. %	F.p., °C.	NaMnO₄, Wt. %	F.p., °C.
0	0	36	−13.2	70	35.3
2	− 0.5	38	−14.1	72	36.0
4	− 0.9	40	−15.0	74	35.3
6	− 1.4	41.4	−15.8E	75	34.0
8	− 2.0	42	−14.7	75.2	33.7E
10	− 2.5	44	−10.7	76.0	36.4
12	− 3.2	46	− 6.2	78.0	45.6
14	− 3.8	48	− 2.0	80	51.5
16	− 4.6	50	+ 2.25	82	59.0
18	− 5.3	52	6.6	83	62.5
20	− 6.1	54	10.8	84	65.2
22	− 7.0	56	15.0	86	67.7
24	− 7.7	58	18.9	88	68.7
26	− 8.5	60	22.5	90	68.0?
28	− 9.5	62	25.8	90.7	66.2E?
30	−10.3	64	30.7	92	66.5?
32	−11.2	66	31.3	94	67.6?
34	−12.2	68	33.7	96	67.6?

[a] The sodium permanganate content is based on the titratable permanganate and water only.

Density.—The densities of sodium permanganate solutions were determined by the use of water-calibrated 50-cc. dilatometers.

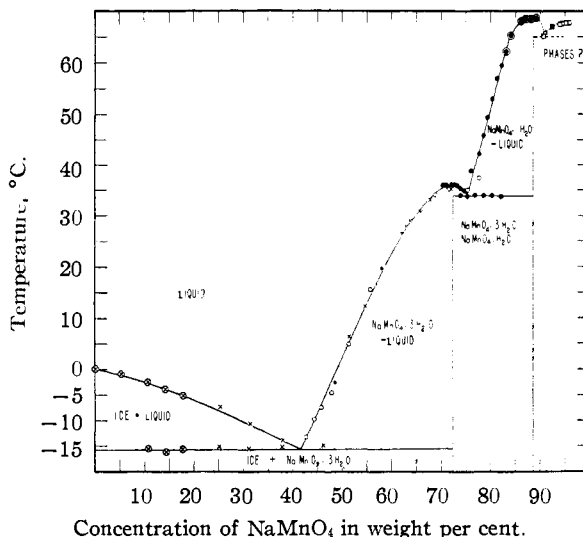Five different concentrations based on the weight of titratable sodium permanganate were used. These were put in the dilatometers by means of a fine capillary tube. Both the solution and dilatometer were kept at 0° during the operation in order to keep the opaque solutions from getting on the upper portion of the calibrated tube. The solutions were apt to cling to the sides of the tube and thereby make it difficult to read the volume as well as lead to error in the volume read. The dilatometers were then placed in the thermostat set at a given temperature and allowed to come to equilibrium. This was ascertained by observing the volume in the capillary. A cathetometer was used to obtain readings on the height in the capillary tubes. The volumes were easily read to 0.0001 cc.

The volumes were determined at 1.35, 13.0, 25.3 and 37.45° for each of the five solutions by use of five dilatometers. In order to be sure the temperatures were constant in each case readings were taken until a constant volume was obtained. To be sure that there was no loss in weight of the solutions during the determinations, they were weighed at frequent intervals. No loss occurred.

The determined densities are given in Table II.

TABLE II

DENSITY OF NaMnO₄ SOLUTIONS (G./CC.)

NaMnO₄, Wt. %	Temperature, °C.			
	1.35	13.00	25.30	37.45
5.32	1.0404	1.0390	1.0361	1.0319
10.58	1.0843	1.0817	1.0776	1.0725
14.05	1.1148	1.1110	1.1062	1.1005
17.62	1.1471	1.1429	1.1371	1.1310
25.60	1.2243	1.2180	1.2110	1.2034

The measurements and values given herein have become available for publication though declassification of part of a program of study pursued in 1939. While more complete data would be desirable those available appear worthy of recording in the published literature.

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