and to displace tris-(*p*-nitrophenyl)-methyl radical. Although such negative-ion induced decompositions do not seem to have been observed in the past it is interesting to note the connection, in purely radical displacements, between the electron-donor ability of the attacking radical and the rate of the induced decomposition.[5] It is also to be expected that in the dissociation of a pair of radicals of unequal electronegativity, complexing one of them should reduce the electronegativity difference and accelerate the reaction.

Experimental

Tris-(*p*-nitrophenyl)-methyl Bromide.—This compound is more readily prepared by the method of Ziegler and Boye[6] than by the method of Lewis, Magel and Lipkin.[7] Previous workers report a melting point of 191°. The material used in these experiments was recrystallized many times at room temperature from acetone–petroleum ether until a constant active bromine titer was attained; it then melted at 200–200.5° with decomposition. *Anal.* Calcd. for $C_{19}H_{12}O_6N_3Br$: C, 49.8; H, 2.64; N, 9.2; Br, 17.4. Found: C, 49.93, 50.22; H, 2.72, 2.84; N, 8.35, 8.50, 8.55; Br, 17.2.[8,9]

Kinetic Experiments.—The acetone was dried over calcium chloride and distilled. The kinetic runs were made in a Beckman cell-holder jacketed with circulating water. Precooled sodium iodide solution was rapidly added to an equal volume of tris-(*p*-nitrophenyl)-methyl bromide by means of a hypodermic syringe and the timer started. Extinction coefficients for triiodide ion were determined for each sodium iodide concentration used.

Reactions of Tris-(*p*-nitrophenyl)-methyl Bromide.—With sodium iodide in acetone the free radical is formed very rapidly at room temperature or below. The intense blue color due to the radical is not discharged by acid but is discharged on swirling in air. The reaction with sodium iodide is very much slower in acetone–alcohol mixtures. The radical is still produced even in the presence of 1% acetic acid or excess *p*-nitrobenzaldehyde.

The radical is not produced by acids in acetone but is produced when a few drops of aqueous sodium bicarbonate are refluxed with the acetone solution, the color being discharged when the condenser is removed and air admitted. The color is not discharged by perchloric acid. Refluxing in acetone with sodium *p*-nitrobenzoate, with pyridine, or with dimethylaniline also gives the air-sensitive color.

The radical is also produced on refluxing in benzene with phenol plus pyridine but not with *p*-nitrobenzoic acid plus pyridine. In dioxane it was found that pyridine and pyridine plus phenol gave no color until water was added.

The radical is also produced by a rapid reaction with a mixture of sodium thiosulfate, water and acetone at room temperature. The product after exposure to air melts at 212.5–213° with decomposition. Binaghi reports 208–210° for the peroxide.[10]

Refluxing with a benzene solution of benzoyl peroxide also forms an air-sensitive colored radical.

Boiling with perchloric acid in aqueous acetic acid hydrolyzes the bromide to the carbinol, m.p. 190–191°.

The bromide reacts slowly with a suspension of silver *p*-nitrobenzoate in dry benzene at room temperature giving the ester in small yield. It melts at 191–191.5° and depresses the melting points of both the carbinol and the bromide. *Anal.* Calcd. for $C_{26}H_{16}O_{10}N_4 \cdot C_6H_6$: C, 61.7; H, 3.56. Found: C, 60.82, 61.10; H, 3.50, 3.51.[8] The anisate was made by refluxing the bromide and silver anisate in acetonitrile for about 1.5 hours, filtering, removing the solvent and crystallizing from benzene–petroleum ether. It melts at 264–269°, yield 50%. *Anal.* Calcd. for $C_{27}H_{19}O_9N_3$: C, 61.25; H, 3.62. Found: C, 61.95, 62.04; H, 3.59, 3.62.[11]

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DEPARTMENT OF CHEMISTRY
FLORIDA STATE UNIVERSITY
TALLAHASSEE, FLORIDA

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[5] C. G. Swain, W. H. Stockmayer and J. T. Clarke, THIS JOURNAL, **72**, 5426 (1950).

[6] K. Ziegler and E. Boye, *Ann.*, **458**, 248 (1927).

[7] G. N. Lewis, D. Lipkin and T. T. Magel, THIS JOURNAL, **66**, 1579 (1944).

[8] Analysis by Clark Microanalytical Co., Urbana, Ill.

[9] Bromine by titration of iodine from reaction with sodium iodide.

[10] R. Binaghi, *Gazz. chim. ital.*, **53**, 879 (1923).

[11] Analysis by Weiler and Strauss, Inc., Oxford.

2,3,6,7-Tetramethylnaphthalene

BY WILLIAM L. MOSBY[1]

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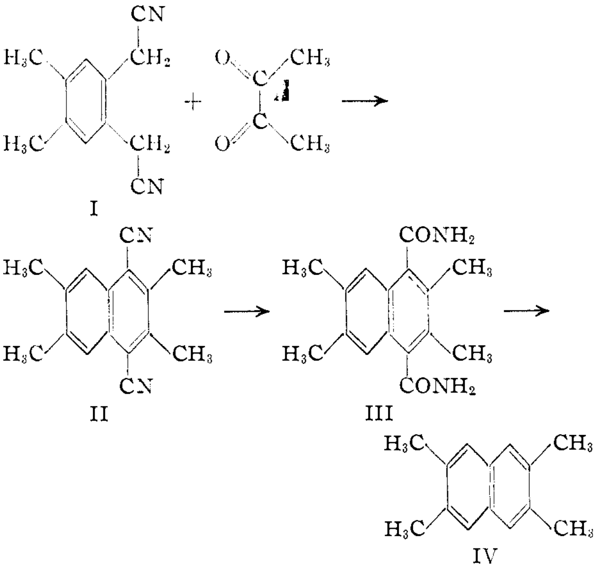
The hitherto unknown 2,3,6,7-tetramethylnaphthalene (IV) was obtained *via* the route



The dinitrile II was prepared by Dr. P. E. Hoch for another purpose, and advantage was taken of its availability to complete the rest of the sequence. The diamide III was obtained from the dinitrile II in excellent yield by refluxing II with potassium hydroxide in aqueous ethylene glycol. When heated at 200° with 100% phosphoric acid,[2] III readily afforded a 79% yield of IV.

The condensation of a substituted *o*-phenylenediacetonitrile with a 1,2-diketo compound is an extension of the synthesis employed by Moureu, Chovin and Rivoal[3] and by Orchin and Reggel.[4] The complete removal of two carboxamide groups from a benz[k]fluoranthene analog of III by hot 100% phosphoric acid was described by Orchin and Reggel.[4] This reagent had previously been recommended[2] for the saponification of hindered amides. Since it seemed probable that hot 100% phosphoric acid would act as a dehydrating agent, converting an amide to a nitrile, treatment of II directly was attempted. When II was heated to 200° with polyphosphoric acid, a good yield of IV was readily obtained. This procedure may offer a more convenient general method of removing such difficultly

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[1] Calco Chemical Division, American Cyanamid Company, Bound Brook, New Jersey.

[2] G. Berger and S. C. J. Olivier, *Rec. trav. chim.*, **46**, 600 (1927).

[3] H. Moureu, P. Chovin and G. Rivoal, *Bull. soc. chim. France*, [5] **13**, 106 (1946); *Compt. rend.*, **223**, 951 (1946); *ibid.*, **225**, 501 (1947).

[4] M. Orchin and L. Reggel, THIS JOURNAL, **73**, 436 (1951).

saponifiable nitrile groups in stable aromatic systems.

Experimental

2,3,6,7-Tetramethylnaphthalene-1,4-dinitrile (II).—The author is indebted to Dr. P. E. Hoch for a sample of this material which he prepared by a standard Knoevenagel reaction of biacetyl with 3,4-dimethyl-*o*-phenylenediacetonitrile. This product, when decolorized with charcoal and recrystallized from cyclohexane, formed felted yellow needles which appear greenish in reflected light as a result of a blue fluorescence. It decomposed at about 240° without melting.

Anal. Calcd. for $C_{16}H_{14}N_2$: C, 82.0; H, 5.98; N, 11.96. Found: C, 81.9; H, 5.88; N, 11.75.

2,3,6,7-Tetramethylnaphthalene-1,4-dicarboxamide (III).—A mixture of 250 mg. of the dinitrile II, 4.0 g. of potassium hydroxide, 40 ml. of ethylene glycol and 5 ml. of water was refluxed one hour. The solid II slowly dissolved to a clear yellow solution, which, when it was poured onto ice and filtered, gave 260 mg. (97% yield) of pale buff solid, m.p. above 320°.

2,3,6,7-Tetramethylnaphthalene (IV).—To a solution of 3.0 g. of phosphorus pentoxide in 7.0 g. of reagent 85% phosphoric acid was added 250 mg. of the diamide III. The mixture, contained in a small flask with reflux condenser, was heated at 200° for one hour with occasional shaking. White micro-platelets of product sublimed into the upper part of the flask and into the condenser. The mixture was cooled, diluted with water and extracted well with cyclohexane. The cyclohexane solution was dried and chromatographed on an 80 × 8 mm. column of alumina. The product, recovered from the effluent liquid by vacuum stripping, weighed 145 mg. (79% yield). One recrystallization from methanol gave shining, fluffy platelets, m.p. 191.2–191.8°.

Anal. Calcd. for $C_{14}H_{16}$: C, 91.25; H, 8.75. Found: C, 91.14; H, 8.80.

The **TNF derivative**, when recrystallized from benzene, gave scarlet microneedles, m.p. 176.0–176.6°.

Anal. Calcd. for $C_{27}H_{21}N_3O_7$: C, 65.0; H, 4.21; N, 8.42. Found: C, 65.5; H, 4.62; N, 8.32.

When 20 mg. of the dinitrile II and 2.0 g. of polyphosphoric acid were heated at 200° for a short time, white crystals sublimed into the upper part of the tube. The identity of these crystals with IV was confirmed by melting point and mixed melting point.

A comparison of the ultraviolet absorption spectrum and physical properties of this material with those of other tetramethylnaphthalenes has been made.[5]

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[5] W. L. Mosby, This Journal, **75**, 3348 (1953).

Central Research Laboratory
General Aniline and Film Corporation
Easton, Pennsylvania

On the Starch–Iodine Complex

By Sôzaburo Ono, Shinpei Tsuchihashi and Takashi Kuge

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This paper presents a quantitative study of the relationship between iodide concentration and wave length of maximum absorption of amylose–iodine complex. The authors attempt to explain the manner in which the iodide ion influences the starch–iodine complex formation.

Rundle and his co-workers[1] have found that the nature of the absorption spectra of the colored iodine in the starch–iodine complex is something quite different from that of iodine in any other medium. The structure of the amylose–iodine complex has been established as a helical amylose chain in which the iodine molecules are arranged in a linear array parallel to the helix axis, and resonance structures have been proposed for the polyiodine chains.[2] We may expect that this polyiodine chain has a structure similar to that of polyenes. The corresponding two p-electrons (those having the same symmetry) of each iodine atom may form a π-orbital along the polyiodine chain. The iodine chain may have two such π-orbitals, because each iodine atom possesses two pairs of such p-electrons, and these π-electrons may be responsible for the light absorption of the complex. We applied to our experimental results the relation which has been proposed by Kuhn[3] for polyenes. Kuhn's relation is expressed by

$$\lambda_{\max} = \left[\frac{V_0}{hc}\left(1 - \frac{1}{N}\right) + \frac{h}{8mc}\,\frac{N+1}{L^2}\right]^{-1} \quad (1)$$

where $\lambda_{\max}$ is the wave length of maximum absorption, L, the resonating chain length, N, the number of π-electrons, h, Planck's universal constant, m, the mass of the electron, c, the velocity of light, V_0, the perturbation parameter.

The results obtained indicate that the $\lambda_{\max}$ shifts toward the shorter wave lengths and the resonating chain length becomes shorter with the increasing iodide concentrations. Our data are also in good agreement with those obtained by Rundle and co-workers[4] and Swanson,[5] concerning the relationship between starch chain length and $\lambda_{\max}$. Potentiometric[6] and spectrophotometric titrations[4] suggested that iodide enters the helix with iodine. Our suggested explanation for the shift of $\lambda_{\max}$ with the change of iodide concentration is that iodide ions enter into the polyiodine chains and break the resonating chains into shorter lengths.

Experimental

Amylose used was obtained from potato starch by hot water extraction (at 60°), and it had the following characteristics: intrinsic viscosity was $[\eta] = 0.80$. Using this value, the degree of polymerization was calculated to be D.P. = 480 glucose units.[7]

Absorption spectra were measured with a G. E. Recording Spectrophotometer at room temperature, using a cuvette 10 mm. thick. Amylose concentration used in this investigation was 0.01%. Iodide concentrations were varied from zero to 0.5 M at constant iodine concentration (13% of theoretical maximum complex formation). A parallel investigation was conducted using ethanol instead of iodide.

Results and Discussion

In our study, N is equal to twice the number of iodine atoms, n, and L is equal to $6.2(n/2 - 1)$ Å., based on the average I–I distance of 3.1 Å. in the polyiodine chain.[8] It was postulated that in the complex free of iodide, 80 iodine molecules form one polyiodine chain, since D.P. of the amylose used was 480 glucose units and 6 glucose units take up one iodine molecule.[4,9] At zero iodide concentration, all terms in equation (1) are known except V_0. V_0 is then calculated to be 3.09×10^{-12} erg (1.9 e.v.).

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[1] R. E. Rundle, J. F. Foster and R. R. Baldwin, This Journal, **66**, 2116 (1944).

[2] R. S. Stein and R. E. Rundle, *J. Chem. Phys.*, **16**, 195 (1948).

[3] H. Kuhn, *ibid.*, **17**, 1198 (1949).

[4] R. R. Baldwin, R. S. Bear and R. E. Rundle, This Journal, **66**, 111 (1944).

[5] M. A. Swanson, *J. Biol. Chem.*, **172**, 825 (1948).

[6] F. L. Bate, D. French and R. E. Rundle, This Journal, **65**, 142 (1943).

[7] A. L. Potter and W. Z. Hassid, *ibid.*, **73**, 593 (1951).

[8] C. D. West, *J. Chem. Phys.*, **15**, 689 (1947).

[9] R. E. Rundle and D. French, This Journal, **65**, 1707 (1943).