

then cooled to 5° in a salt-ice-bath. The crude yellow product was collected on a büchner funnel and dissolved in 200 ml. of water at 75°, and 20 ml. of concentrated hydrochloric acid was added with rapid stirring. The red solution became pale yellow, and a pale yellow precipitate began to separate in a few minutes. The mixture was cooled to 5° and the yellow solid was collected on a cold büchner funnel. After drying for three days in a vacuum desiccator over calcium chloride, the product weighed 30.6 g. (93% yield) and melted to an orange liquid at 258–263°, after slight previous sintering. By recrystallization from water, an analytical sample was obtained in the form of flat white needles which melted at 265–266°.

*Anal.* Calcd. for  $C_8H_3N_3O_3$ : C, 43.65; H, 1.83; N, 25.45. Found: C, 43.74; H, 2.10; N, 25.31.

**5-Nitro-2-pyridone-3-carboxylic Acid (II).**—A solution of 1.65 g. (0.01 mole) of the nitrile in a mixture of 20 g. of concentrated sulfuric acid and 10 ml. of water was refluxed for one and two-thirds hours. A crude product was obtained by diluting the reaction mixture with water, neutralizing the sulfuric acid with strong aqueous sodium hydroxide and cooling to 5°. Recrystallization from 50 ml. of water gave an analytically impure sample in the form of short, light tan needles which sintered at 246° and melted at 247–248°.

*Anal.* Calcd. for  $C_6H_4N_2O_5$ : C, 39.14; H, 2.19; N, 15.22. Found: C, 38.68; H, 2.35; N, 15.00; ash, 0.53.

A purer sample of II was obtained when the ethoxy derivative V was refluxed for 30 minutes with 50% aqueous sulfuric acid. Successive recrystallizations of the crude hydrolysis product from acetone-water and water gave short, thick, colorless needles which melted at 250–251°.

*Anal.* Calcd. for  $C_6H_4N_2O_5$ : C, 39.14; H, 2.19; N, 15.22. Found: C, 39.64; H, 2.12; N, 15.24.

**Decarboxylation of 5-Nitro-2-pyridone-3-carboxylic Acid (II).**—A 0.1-g. sample of the acid was heated in a side-arm test-tube at 330° and atmospheric pressure for three minutes, then sublimed to a cold finger at 60 mm. pressure. The crude yellow product was purified by another sublimation at 0.2 mm. and 180–200°, followed by two recrystallizations from water. The 5-nitro-2-pyridone obtained in this way melted at 182.5–184.5°. The previously reported value is 186°.²

**2-Chloro-5-nitronicotinonitrile (IV).**—A mixture of 16.51 g. (0.10 mole) of the pyridone (I), 41.6 g. (0.20 mole) of phosphorus pentachloride and 20 ml. of phosphorus oxychloride in an all-glass apparatus was refluxed by heating in an oil-bath at 130–140° for three hours and evaporated to dryness on the steam-bath at water aspirator pressure. One hundred ml. of cold water was added cautiously to the residue. The solid was crushed with a spatula and cold concentrated aqueous sodium hydroxide was added to bring the pH to 6. The crude product was collected on a büchner funnel and extracted in an erlenmeyer flask with two 200-ml. portions of boiling 95% alcohol. The combined extracts were diluted with 100 ml. of water and cooled overnight in the refrigerator, giving 15.30 g. (83% yield) of yellowish-brown crystalline product which sintered at 117–118° and melted at 118–120°. The analytical sample was prepared by sublimation at 0.1 mm. followed by crystallization from 50% aqueous alcohol, when it was obtained in the form of white platelets which melted at 121–122°.

*Anal.* Calcd. for  $C_6H_2ClN_3O_2$ : C, 39.26; H, 1.10; N, 22.89. Found: C, 39.65; H, 1.38; N, 22.50.

**2-Ethoxy-5-nitronicotinonitrile (V).**—To a solution of 1.38 g. (0.06 g. atom) of sodium in 60 ml. of absolute alcohol was added 10.98 g. (0.06 mole) of the chloropyridine IV. The reddish-brown solution was allowed to stand for one hour at room temperature, diluted with 60 ml. of water and cooled to –3°. A brown precipitate formed which was collected, dried and sublimed at 90° and 0.3 mm. pressure, giving 7.86 g. (67%) of nearly colorless product, m.p. 51–53°. After another sublimation and two recrystallizations from aqueous alcohol, an analytical sample was obtained in the form of fine, colorless, leaf-like crystals which melted at 62.5–63°.

*Anal.* Calcd. for  $C_8H_7N_3O_3$ : C, 49.74; H, 3.65. Found: C, 50.12; H, 3.62.

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## 2,7-Di-*t*-butyl-1,4-naphthoquinone and Related Compounds

By H. MARJORIE CRAWFORD

RECEIVED OCTOBER 2, 1954

Two di-*t*-butylnaphthalenes, the 1,4-quinone corresponding to the higher melting hydrocarbon, and the diacetate made by the reductive acetylation of the quinone have been known for some time. Recently the 103° hydrocarbon was shown to be 2,7-di-*t*-butylnaphthalene¹ and the 146° hydrocarbon was shown to be 2,6-di-*t*-butylnaphthalene.² The latter paper also established the structure of the 86° quinone as 2,6-di-*t*-butyl-1,4-naphthoquinone and the corresponding 139° compound as the diacetate of 2,6-di-*t*-butyl-1,4-naphthalenediol.

To complete this series of compounds the quinone and diacetate corresponding to the 103° hydrocarbon have been prepared.

**2,7-Di-*t*-butyl-1,4-naphthoquinone.**—Half a mole (50 g.) of chromium trioxide dissolved in a mixture of 80 ml. of glacial acetic acid and 40 ml. of water was added slowly to a suspension of 0.1 mole (24 g.) of 2,7-di-*t*-butylnaphthalene in 200 ml. of glacial acetic acid. The solution became warm and the temperature was maintained at 40–50° by regulating the rate of addition of the chromium trioxide solution. After standing at room temperature for three hours the mixture was poured onto ice. The resulting gummy, yellow solid was collected and crystallized from ethanol. The yield was 18 g. (67%) and the melting point 55–57°.

*Anal.* Calcd. for  $C_{18}H_{22}O_2$ : C, 80.0; H, 8.2. Found: C, 80.6; H, 8.5.

**Phenylhydrazone of 2,7-Di-*t*-butyl-1,4-naphthoquinone.**—Five drops of glacial acetic acid was added to a solution of the quinone (3.5 g.) and phenylhydrazine (3 ml.) in 50 ml. of ethanol. The solution was allowed to stand for a few minutes after being heated to boiling. The resulting solid crystallized from ethanol as dark red needles with a greenish luster, d. 197–198°.

*Anal.* Calcd. for  $C_{21}H_{28}ON_2$ : C, 80.0; H, 7.8. Found: C, 80.3; H, 8.0.

**The Diacetate of 2,7-Di-*t*-butyl-1,4-naphthalenediol.**—Two grams of the quinone was refluxed for two hours with 5 g. of zinc, 1 g. of fused sodium acetate and 15 ml. of acetic anhydride. The addition of ice and water to the colorless solution gave a white precipitate which was collected and crystallized from ethanol. The yield was 2.2 g. (84%) and the melting point was 123–124°.

*Anal.* Calcd. for  $C_{22}H_{28}O_4$ : C, 74.1; H, 7.9. Found: C, 73.8; H, 7.9.

(1) H. E. Nursten and A. T. Peters, *J. Chem. Soc.*, 729 (1950).

(2) H. M. Crawford and M. C. Glesmann, *This Journal*, **76**, 1108 (1954).

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## Copolymerization by Carbanion and Radical Mechanisms

By RALPH L. DANNLEY AND EDWARD L. KAY<sup>1,2</sup>

RECEIVED DECEMBER 5, 1953

The copolymerization of several monomer pairs has been found<sup>3</sup> to be very susceptible to the nature

(1) Standard Oil Company (Ohio) Fellow, 1953–1954. This paper is based on a portion of the thesis to be submitted by Edward L. Kay in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Western Reserve University.

(2) Presented at the New York City meeting of the American Chemical Society, September, 1954.

(3) C. Walling, E. R. Briggs, W. Cummings and F. R. Mayo, *This Journal*, **72**, 48 (1950).

of the catalyst. Thus the initial polymer formed from an equimolecular mixture of styrene and methyl methacrylate was found to vary from 99±% polystyrene using boron trifluoride as catalyst, to equimolecular copolymer using benzoyl peroxide, to 99±% polymethyl methacrylate using metallic sodium. The variation in polymer composition was ascribed to a shift in mechanism from carbonium ion, to free radical, to carbanion type respectively.

Both carbanion<sup>4</sup> and free radical<sup>5</sup> mechanisms had previously been proposed for sodium-catalyzed polymerizations. The quoted variation in copolymerization obtained from sodium and benzoyl peroxide led to the conclusion<sup>3</sup> that as the peroxide catalyst is known to be free-radical in nature, the sodium-catalyzed reaction must be carbanion.

This explanation was based upon the premise that all free radicals react in an identical manner. Recent investigations,<sup>6</sup> however, have shown that this is certainly not always true, and that varying the nature of a free radical may alter the course of a reaction. Therefore, both sodium and benzoyl peroxide could theoretically function as free radical catalysts in polymerization and the differences observed might be due to the electron-donating nature of the sodium atom in contrast to the greater tendency of either the phenyl radical or benzoyloxy radical to seek electrons.

As the determination of the mechanism of sodium catalysis is of considerable importance, the present work was undertaken to test the hypothesis that it is carbanion in nature.

First, an equimolecular mixture of methyl methacrylate and styrene was treated with triphenylmethyl sodium to determine the product formed by a catalyst undeniably carbanion in nature. The initial copolymer formed contained 98.3 to 99+% polymethyl methacrylate, corresponding within experimental error to that obtained using sodium metal. Therefore, sodium metal does yield the same copolymer as a carbanion catalyst.

Second, the effect of a change of type of chain-initiating free radicals upon the copolymerization of the same monomer mixture was determined to eliminate this explanation of the difference in action of benzoyl peroxide and sodium. Both *t*-butyl peroxide and *p*-chlorobenzoyl peroxide (which decompose to give the electron-seeking *t*-butoxy and *p*-chlorobenzoyloxy free radicals, respectively) were found to give 49 to 51% styrene in the initial polymer. Therefore, considerable variation of the type of the catalyst free radicals does not affect the composition of the initial copolymer. Supporting evidence is therefore offered that sodium does not function as a free radical catalyst for polymerization. An unequivocal proof could be obtained if the effects of catalysts yielding only electron-donating free radicals could be studied,

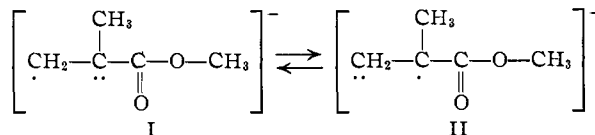
(4) (a) C. C. Price, "Reaction at Carbon-Carbon Double Bonds," Interscience Publishers, Inc., New York, N. Y., 1946, p. 117; (b) R. G. Beaman, *THIS JOURNAL*, **70**, 3115 (1948); (c) R. E. Robertson and L. Marion, *Can. J. Research*, **26B**, 657 (1948).

(5) J. L. Bolland, *Proc. Roy. Soc. (London)*, **A178**, 24 (1941).

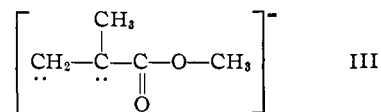
(6) R. L. Dannley and M. Sternfeld, Abstracts of Papers, 124th Meeting of the American Chemical Society, Chicago, Ill., September, 1953, p. 37-0.

but none are available. For example, when anisoyl peroxide thermally decomposes to give the electron-donating *p*-anisoyl radical, it simultaneously forms an electron accepting anisoyloxy radical.

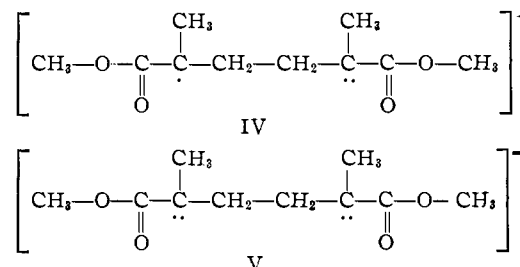
An examination of the possible structures which could be formed in the mechanism of polymerization is now appropriate. The transfer of an electron from a sodium atom to a methyl methacrylate molecule would produce the radical-ion represented by I and II. Each of these structures would be



stabilized by resonance of the unshared electrons of the  $\alpha$ -carbon atom with the carbonyl group. In addition, there would be a very unusual resonance relationship between I and II, for this three electron system has more than one electron-pairing arrangement. It is possible, of course, that a second atom of sodium may react either at this step (to form III) or at a succeeding step of chain growth to convert a radical-ion to a divalent ion.



Addition of either I-II or III to a second monomer unit should proceed by an abnormal tail-to-tail arrangement (IV or V, respectively) in order to



form a structure in which both unshared-electron centers would be stabilized by resonance with a carbonyl group. Succeeding steps should proceed by normal head-to-tail additions by the same reasoning. This mechanism yielding abnormal tail-to-tail addition at the dimer step applies to other monomers also and is confirmed by the formation of 1,4-diphenylbutane in the sodium-alcohol reduction of styrene.<sup>7</sup>

If the growing polymer unit is a radical-ion IV and not a divalent ion V, the styrene-methyl methacrylate copolymerization experiments prove that the carbanion center must provide the driving force in the polymerization.

#### Experimental

**Materials.**—The methyl methacrylate and styrene were freshly distilled under an atmosphere of nitrogen. *t*-Butyl peroxide (Shell), *p*-chlorobenzoyl peroxide (Lucidol) and benzoyl peroxide (Lucidol) were used without purification.

Triphenylmethyl sodium (selected as a carbanion catalyst

(7) T. Midgley, Jr., A. L. Henne and H. M. Leicester, *THIS JOURNAL*, **58**, 1961 (1936).

TABLE I  
DATA ON COPOLYMERIZATIONS BY DIFFERENT CATALYSTS OF 0.02 MOLE OF STYRENE AND 0.02 MOLE METHYL METHACRYLATE

Catalyst	Mole % catalyst <sup>a</sup>	Temp., °C.	Time, hr.	Yield, % by wt. of monomers used	C, %	H, %	Mole % styrene in polymer
Na		Room	65	11	60.17 ± 0.04	8.16 ± 0.01	0.6 ± 0.1
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> CNa	1.0	Room	24.5	18.4	60.27 ± .24	8.12 ± .23	0.80 ± 0.65
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> CNa	0.5	Room	65	11.8	60.88	6.11	2.79
(C <sub>6</sub> H <sub>5</sub> COO) <sub>2</sub>	0.1	60	7.7	12.3	76.18	7.99	50.19
( <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> COO) <sub>2</sub>	0.1	60	16	21.3	75.70	8.31	48.70
( <i>t</i> -C <sub>4</sub> H <sub>9</sub> O) <sub>2</sub>	0.1	100	2.5	17.5	75.81 ± .58	8.15 ± .15	49.04 ± 1.80

<sup>a</sup> On shaking machine.

because its solubility in ether ensured separation from excess sodium) was prepared from triphenylmethyl chloride and sodium in ether solution.<sup>8</sup>

**Procedure.**—Techniques previously reported were used for the preparation<sup>9</sup> and purification<sup>10</sup> of the polymers. In the reaction with triphenylmethylsodium, an ether solution of the catalyst was added to the monomer mixture. The degassing process was carried out with a conventional high vacuum system and a pressure of  $2.5 \times 10^{-4}$  mm. was obtained at least three times before the sample was allowed to polymerize for the indicated time. Repetition of polymerizations previously reported<sup>8</sup> was undertaken to determine the accuracy in duplication of the previous work, and good agreement was obtained. The results are given in Table I.

(8) *Org. Syntheses*, **19**, 83 (1939).

(9) F. R. Mayo and F. M. Lewis, *This Journal*, **66**, 1594 (1944).

(10) F. M. Lewis and F. R. Mayo, *Ind. Eng. Chem., Anal. Ed.*, **17**, 134 (1945).

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### 1,3,5-Trichloro-2,4,6-tribromocyclohexane

By H. R. FRISCH

RECEIVED MAY 13, 1954

Benzene reacts with chlorine to form a mixture of isomers of benzene hexachloride and with bromine to yield a mixture of the hexabromides, but chlorine does not react with benzene hexabromide with the replacement of any bromine atoms. Under the conditions described below the reaction of benzene with a mixture of chlorine and bromine yields a product which is probably a mixture of isomers of 1,3,5-trichloro-2,4,6-tribromocyclohexane, eight of which are theoretically possible with a cyclohexane of planar configuration. On alkaline hydrolysis 3 moles of the alkali bromide and 1,3,5-trichlorobenzene were obtained. The formation of 1,3,5-trichloro-2,4,6-tribromocyclohexane is best explained if a chemical combination of chlorine and bromine is assumed; the existence of chlorine bromide has been suggested, but not conclusively demonstrated.

The insecticidal potency of the mixture against roaches and mites is about the same as that of crude benzene hexachloride.

#### Experimental

Under actinic irradiation and at temperatures below 10°, benzene reacted quantitatively with stoichiometric amounts of chlorine and bromine to yield a solid product which was recrystallized from hot glacial acetic acid as colorless plates of 1,3,5-trichloro-2,4,6-tribromocyclohexane, m.p. 171° with slight decomposition.<sup>1</sup>

*Anal.* Calcd. for C<sub>6</sub>H<sub>3</sub>Cl<sub>3</sub>Br<sub>3</sub>: C, 16.99; H, 1.43; Cl, 25.07; Br, 58.51; mol. wt., 424.24. Found: C, 16.3; H, 1.47; Cl, 22.38; Br, 56.42; mol. wt., 427.

(1) Tests were carried out by courtesy of Niagara Chemical Division of Food Machinery and Chemical Corporation, Middleport, N. Y.

The compound is soluble in most organic solvents with the exception of carbon tetrachloride. On alkaline hydrolysis it yielded 3 moles of alkali bromide and a water-insoluble oil, 1,3,5-trichlorobenzene; b.p. 208° (760 mm.), Cl 58%.

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### Pyrosynthesis of Aspartic Acid and Alanine from Citric Acid Cycle Intermediates<sup>1</sup>

By SIDNEY W. FOX, JOSEPH E. JOHNSON AND MAVIS MIDDLEBROOK

RECEIVED JUNE 21, 1954

Experiments directed toward synthesis of true protein, and elucidation of its primordial origin<sup>2</sup> and subsequent evolution<sup>3</sup> have been performed. In the course of these experiments, almost all chromatographic evaluations of pyropolymerization of various pairs of DL-amino acids revealed, following hydrolysis, a number of ninhydrin-reactive spots which exceeded the number of reactants. These results indicate that the conditions which produce polymers<sup>2,4</sup> from unsubstituted amino acids lead also to the formation of additional amino acids (and in part possibly to amines).

Attention was diverted to a possible thermal origin of aspartic acid from the citric acid cycle by the postulate that those features of current biochemistry which are biologically relatively ubiquitous were also part of a primordial biochemistry.<sup>5</sup> Over a century ago, aspartic acid had been prepared by heating ammonium fumarate or ammonium malate<sup>6,7</sup> although of course not with reference to the now recognized citric acid cycle.

In the present experiments, ammonium salts of two additional acids from the citric acid cycle were each heated for up to three hours at 200°, chromatographed, and also hydrolyzed and chromatographed. Faint ninhydrin spots were obtained from heated ammonium fumarate and ammonium malate, although there were none from ammonium citrate or ammonium succinate either before or

(1) Journal paper No. J-2546 of the Iowa Agricultural Experiment Station, Ames, Iowa. Project 1111, supported by the Rockefeller Foundation.

(2) S. W. Fox and M. Middlebrook, *Federation Proc.*, **13**, 211 (1954).

(3) S. W. Fox, *Am. Naturalist*, **87**, 253 (1953).

(4) H. Schiff, *Ann.*, **307**, 231 (1899).

(5) Additional reasons for this particular study were the facts that aspartic acid is an *early* or the earliest amino acid in biosynthesis and that its metabolic origin is from the citric acid cycle (see E. Baldwin, "Dynamic Aspects of Biochemistry," the University Press, Cambridge, 1952).

(6) J. Wolff, *Ann.*, **75**, 294 (1850).

(7) Dessaignes, *Compt. rend.*, **30**, 324 (1850).