ment another 75 ml. of water was gradually added and the distillate collected in a solution of 100 ml. of 0.1 *N* hydrochloric acid until complete neutralization was effected. A total quantity of 97 ml. of liquid was thus distilled. The residual solution was cooled, acidified with concd. hydrochloric acid, and the resultant precipitate filtered and air dried. Yield, 1.94 g. (95%). It was recrystallized from boiling water and melted at 196°.

Anal. Calcd. for $C_{10}H_7O_4N$: C, 58.5; H, 3.4; N, 6.8%. Found: C, 58.4; H, 3.7; N, 7.2%.

N-Phthaloyl-L-valine.—A solution of 3 g. (0.0256 mole) of L-valine (Nutritional Biochemicals Corporation) and 2.6 g. of triethylamine in 40 ml. of water was added with stirring to a solution of 3.8 g. of phthalic anhydride in 130 ml. of dioxane. During the addition a small amount of precipitate was formed which dissolved again after 5 min. of vigorous stirring. The resultant homogenous solution was then stirred at room temperature for another 45 min. during which time an additional 2.6 g. of triethylamine was gradually added. Another 130 ml. of dioxane was then added and the solution was subjected to slow distillation for a period of 2 hr. During this time a total of 265 ml. of liquid was distilled and the temperature of the vapor rose slowly until finally the boiling point of pure dioxane was reached. The residual solvent was then evaporated *in vacuo* at room temperature and the resultant glassy residue treated with 10 ml. of pure concd. hydrochloric acid until complete crystallization set in. The precipitate was then filtered, washed with a little cold water, and air dried; yield, 5.7 g. (90%). It was twice recrystallized from cyclohexane. White needles were obtained which melted at 116–117° (for analysis and rotation, see Table II).

An Unusual Reaction of Thionyl Chloride Leading to 10-Dicyanomethyleneanthrone

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Received July 12, 1962

The unusually high electrical conductivities exhibited by several polycyano derivatives[1,2] have stimulated research in recent years on organonitrile compounds. As a part of the study of the electrical properties of organic compounds, 10-dicyanomethyleneanthrone has been synthesized. The reaction of thionyl chloride with anthrone, followed by a treatment with malononitrile, to yield the 10-substituted anthrone is described.

Anthrone was refluxed with excess thionyl chloride (1:10 molar ratio) and the resultant solution was treated with malononitrile (5 moles) in dioxane, producing 10-dicyanomethyleneanthrone (I) in 88% yield. Upon replacing dioxane with tetrahydrofuran as a solvent, only a small yield of I was obtained. Both chloroform and N,N-dimethylformamide failed to yield the dinitrile product. Infrared absorptions for I were observed at 4.48 (CN) and 5.98 μ (quinoid CO).[3]

The dinitrile (I) was recovered unchanged from heating in concentrated sulfuric acid. However, it was converted by hot 90% sulfuric acid, followed by hydrolysis, to 10 - (cyanocarbonamidomethylene)anthrone (II) in 42% yield. Infrared absorptions for II were noted in the 3- and 6-μ regions attributed to a primary amide[3] and carbonyl group, respectively. A nitrile absorption was also observed at 4.54 μ.

Catalytic hydrogenation of I and II yielded 10-dicyanomethylanthrone (III) and 10-(cyanocarbonamidomethyl)anthrone(IV), respectively. Infrared spectra of III and IV exhibited a band at 6.0 μ and a weak band at 4.45 μ. In addition, IV exhibited several bands in 3 μ (primary amide) region similar to that found in II. Hydrolyses of III and IV yielded anthraquinone as the only identifiable product.

The structural assignment of the dicyanomethylene group of I to the 10-position of anthrone was based on elemental analyses, spectral data, and the facile acid or base catalyzed conversions of I to anthraquinone, in yields of 75 and 80%, respectively.

In an effort to study the generality of the reactions leading to the synthesis of I, the anthrone–thionyl chloride reaction product was treated with two other compounds containing active methylene groups. Both ethyl cyanoacetate and phenylacetonitrile failed to yield the corresponding substituted methyleneanthrone derivative; anthraquinone was the only product isolated. Furthermore, the treatment of anthrone with phosphorus oxychloride or phosphorus trichloride followed by malononitrile in dioxane did not yield I. However, replacing thionyl chloride with sulfuryl chloride gave a low yield of I. It may be possible in the latter case that thionyl chloride was present in the sulfuryl chloride as an impurity.

To investigate the possibility that the reaction may be proceeding *via* anthraquinone, this quinone was refluxed with thionyl chloride and then treated with malononitrile in dioxane. The only crystalline compound isolated was the starting material, anthraquinone.

Upon treatment of the reaction product of anthrone and excess thionyl chloride with crushed ice, an unidentified product was obtained. Attempted purification of this product resulted in its decomposition to yield anthraquinone. Since 10,10-dichloroanthrone is reported[4] to be stable in ice–water under highly acidic conditions and is recrystallizable from aqueous ethanol, it appears reasonable that the dichloroanthrone is not an

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intermediate in the reaction leading to 10-dicyanomethyleneanthrone.

The mechanism and the scope of the above reaction are currently under investigation. Although both anthrone and malononitrile contain extremely reactive methylene groups, the former compound is a tautomer of 9-anthrol. The facile interconversion of anthrone and 9-anthrol would indicate that the reaction path may proceed through either structure. While there are papers pertaining to reactions of thionyl chloride with hydroxy aromatic[5,6] and active methylene compounds,[7] their direct applicability to the present reaction is not obvious. Although further work on this system is necessary before a logical mechanism can be advanced, it appears that the reaction is not proceeding *via* anthraquinone or dichloroanthrone. Furthermore, there is no evidence to indicate that I results from the chlorination of malononitrile by thionyl chloride, followed by alkylation of anthrone.

Experimental[8,9]

10-Dicyanomethyleneanthrone.—A mixture of 4 g. of anthrone and 25 g. (15 ml.) of thionyl chloride was refluxed 3 hr. To the refluxing mixture, a solution of 6 g. of malononitrile in 60 ml. of dioxane was added. The resulting solution was heated and approximately 30 ml. of distillate was removed from the system under reduced pressure. The remaining solution was refluxed for an additional 2 hr. The remaining thionyl chloride and dioxane were then removed under reduced pressure leaving a brown solid. The solid was triturated twice with 75 ml. of acetonitrile, and once with acetone leaving a green solid. This solid was then placed in a Soxhlet extraction apparatus and extracted with toluene for 24 hr. The toluene was concentrated to approximately 150 ml. and allowed to cool. The yellow crystals were collected and dried, yielding 4.65 g. (88%) of 10-dicyanomethyleneanthrone, m.p. 289°.

Anal. Calcd. for $C_{17}H_8N_2O$: C, 79.68; H, 3.15; N, 10.93. Found: C, 80.00; H, 3.17; N, 10.81.

10-(Cyanocarbonamidomethylene)anthrone.—A solution of 6 g. of 10-dicyanomethyleneanthrone, 20 ml. of concentrated sulfuric acid and 2 ml. of water was heated to 100°. The resulting red solution was poured onto 300 g. of crushed ice. The yellow precipitate was collected, taken up in 200 ml. of hot ethanol, and filtered. The filtrate was poured into 500 ml. of cold water and the crystals collected. These yellow crystals were recrystallized from ethyl acetate yielding 2.7 g. (42%) of 10-(cyanocarbonamidomethylene)-anthrone, m.p. 246°.

Anal. Calcd. for $C_{17}H_{10}N_2O_2$: C, 74.44; H, 3.66; N, 10.21. Found: C, 74.53; H, 3.80; N, 10.25.

10-Dicyanomethylanthrone.—A mixture of 3 g. of 10-dicyanomethyleneanthrone and 200 ml. of toluene was catalytically hydrogenated with 0.3 g. of Adams catalyst on a Parr apparatus for 1 hr. The contents were then removed from the Parr shaker, heated to near boiling, and filtered free of catalyst while hot. The toluene was concentrated, cooled, and the crystals collected, yielding 2.4 g. (80%) of 10-dicyanomethylanthrone, m.p. 220–225°. Recrystallizations from toluene yielded an analytical sample of white crystals, m.p. 225°.

Anal. Calcd. for $C_{17}H_{10}N_2O$: C, 79.06; H, 3.91; N, 10.85. Found: C, 79.13; H, 3.70; N, 10.80.

10-(Cyanocarbonamidomethyl)anthrone.—A mixture of 2.7 g. of 10-(cyanocarbonamidomethylene)anthrone and 300 ml. of ethanol was catalytically hydrogenated with 0.5 g. of 5% palladium on charcoal on a Parr shaker. The mixture was removed from the Parr apparatus and heated to effect solution. The hot solution was filtered free of catalyst. The alcohol solution was concentrated and allowed to cool Upon cooling 1.6 g. (60%) of 10-(cyanocarbonamidomethyl)-anthrone, m.p. 205–210°, crystallized. An analytical sample was recrystallized from ethanol, yielding white needles, m.p. 213–115°.

Anal. Calcd. for $C_{17}H_{12}N_2O_2$: C, 73.90; H, 4.38; N, 10.14. Found: C, 73.88; H, 4.35; N, 10.10.

Acknowledgment.—The authors are indebted to Dr. L. Schieler for the helpful interest in this work and to Mr. G. B. Charlan for infrared measurements.

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Anodic Decarboxylation of Isostevic Acid

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Received August 8, 1962

Evidence has been recently presented supporting structures I and II for steviol and isosteviol, respectively.[1,2] Prior to these communications, work in this laboratory had been directed toward decarboxylation of the steviol–isosteviol system to ascertain whether the carboxyl group was at position 4 or 10. If the carboxyl were at C-4, decarboxylation should lead to a compound having a methyl resonance split by spin coupling to a lone proton on an adjacent carbon atom.

To achieve decarboxylation, chemical procedures were initially investigated. Hunsdiecker reaction[3] was found inapplicable because I and II failed to give silver salts. In the hope of replacing the carboxyl group by an acetoxy group which might subsequently be removed, isostevic acid (III)[4] was converted *via* the acid chloride to the methyl ketone.[5] The latter, however, failed to undergo Baeyer–Villiger oxidation in trifluoroperacetic acid.[6]

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