allowed to cool. The product was dissolved in hot benzene, then glacial acetic acid was added to neutralize the catalyst, and the benzene solution was washed several times with water. Upon concentration of the benzene solution 0.5 g. of crystals of the dimer, m.p. 245–246°, was obtained. The benzene filtrate was then concentrated, an equal volume of pentane was added, and upon standing there was deposited 6.2 g. of crystals of hexaphenyl-1,3,5-cyclohexanetrione, m.p. 176°.

Tetraphenyl-1,3-cyclobutanedione (VIII). *Cleavage by phenyllithium.* To 100 ml. of an ethereal solution of phenyllithium, prepared from 1.46 g. of lithium and 16.2 g. of bromobenzene, was added in portions 5 g. of VIII. After the reaction had subsided the reaction mixture was refluxed for 1.5 hr., allowed to stand overnight, and then hydrolyzed with iced hydrochloric acid. The ether extract was washed with water, dried, and evaporated almost to dryness leaving 8.5 g. of a residue which gave 2.3 g. of crystals upon the addition of a small quantity of pentane. After recrystallization from alcohol this material was identified as triphenylcarbinol, m.p. 161–163°, mixed m.p. 161.5–163°. Upon the addition of more pentane there was deposited 4.7 g. of a second crop of crystals, which were recrystallized once from an ether-pentane mixture, and twice from alcohol to yield 4.5 g. of material, m.p. 133–134.5°, which was identified as *sym*-tetraphenylacetone. A mixed m.p. with an authentic sample of *sym*-tetraphenylacetone was 132–134°. The solvents from the mother liquors were removed, and the residue was steam distilled to yield a trace of benzophenone, m.p. 47–48°, and a residue which, after recrystallization from alcohol, gave 0.9 g. of triphenylcarbinol. The total yield consisted of 3.2 g. (95%) of triphenylcarbinol, 4.5 g. (96%) of *sym*-tetraphenylacetone, and a trace of benzophenone.

Treatment of VIII *with phenylmagnesium bromide* failed to give an appreciable reaction, and VIII was recovered unchanged. When 1 g. of VIII was added to an ethereal solution of phenylmagnesium bromide, prepared from 0.95 g. of magnesium and 6.12 g. of bromobenzene, and the solution was refluxed for 1.5 hr. and then hydrolyzed, 0.8 g. of VIII was recovered. In another experiment, using the same quantities of materials, the ether was partially replaced by benzene, and the solution was refluxed at 66° for 6 hr. Upon working up the product, 0.6 g. of VIII, m.p. 245–247°, was recovered.

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[CONTRIBUTION FROM THE PFISTER CHEMICAL WORKS, INC.]

The Action of Perchloryl Fluoride on Acylamidomalonates

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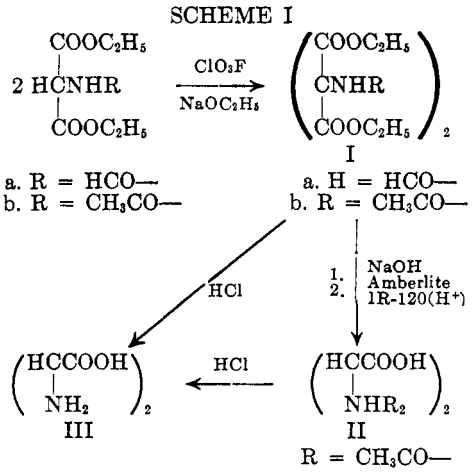
Received August 10, 1961

Acylamidomalonates were oxidatively dimerized by perchloryl fluoride in the presence of strong base. These dimers were hydrolyzed to diaminosuccinic acid.

It was reported by Inman, Oesterling, and Tyczkowski[1] that compounds containing active methylene groups could, in the presence of strong base, be fluorinated by perchloryl fluoride. Since, in our work on amino acid synthesis, extensive use of the aminomalonates is made, it was desired to ascertain the effect of perchloryl fluoride on this group of reagents which possesses active methylene groups.

Ethyl formamidomalonate and ethyl acetamidomalonate, respectively, were subjected to the action of perchloryl fluoride in the presence of sodium ethoxide. The reaction products were identified by hydrolysis to diacetamidosuccinic acid and to diaminosuccinic acid according to scheme I. Product Ia was obtained in 39.5% yield and melted at 141–142°; product Ib was obtained in 54% yield and melted at 151.5–152.5°. On saponification of Ib by sodium hydroxide at 35° overnight, followed by passage through a column of Amberlite IR-120(H^+), carbon dioxide evolution on the column was observed. Compound II, 2,3-diacetamidosuccinic acid, was obtained in 14.8% yield and melted at 237–238° dec., lit.[2] m.p. 235°

SCHEME I



dec. On hydrolysis of Ia with concentrated hydrochloric acid under reflux for two hours, compound III, 2,3-diaminosuccinic acid, was obtained in 6.8% yield, and it decomposed at 310–315°. Although no stereochemical studies were made, the diaminosuccinic acid obtained was undoubtedly in the meso form. The decomposition point of (+)-2,3-diaminosuccinic acid was reported by Hochstein[3] to be 240–290°. The *dl*-form, according to

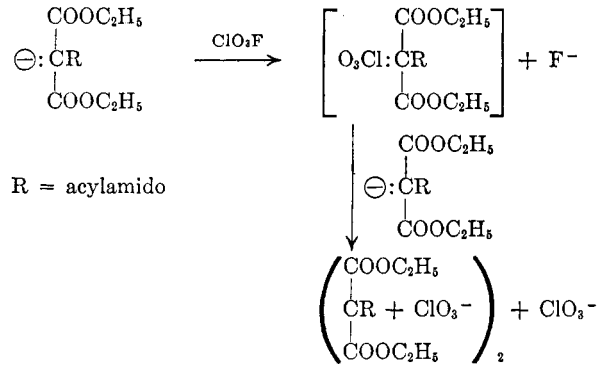
(1) C. E. Inman, R. E. Oesterling, and E. A. Tyczkowski, *J. Am. Chem. Soc.*, **80**, 6533 (1958).
(2) Beilstein, **IV**, p. 487.
(3) F. A. Hochstein, *J. Org. Chem.*, **24**, 679 (1959).

McKennis and Yard,[4] decomposed at 295° and the meso form at 304°. Wenner[5] reported decomposition points of 303–305° and 305–306° for the meso form. Furthermore, it was demonstrated by Kuhn and Zumstein[6] that *dl*-diaminosuccinic acid was converted to the meso form by refluxing for three hours in 15% hydrochloric acid. In addition to the diaminosuccinic acid, a significant percent of ammonium chloride was also recovered from the acid hydrolyzate, indicating extensive degradation. This was in agreement with the instability of (+)-2,3-diaminosuccinic acid as observed by Hochstein.[3] Since the preparation of 2,3-diaminosuccinic acid was not the object of these experiments, but merely a means of establishing the structures of compounds Ia and Ib, optimal conditions for the hydrolysis of these intermediates was not sought.

Upon examination of the reaction conditions of perchloryl fluoride on ethyl formamidomalonate, it was observed that there was a positive heat of reaction only until half of the gas was passed into the reaction mixture, and that at that point the *p*H of the mixture was no longer alkaline. In a second run, the concentration of base was doubled, but no increase in yield was observed. After removal of the oxidative dimer, a sirupy residue, which could not be identified, was obtained by evaporation of the crystallization solvent. No starting material, ethyl formamidomalonate, could be recovered by attempts to vacuum distil the sirupy product. No glycine was detected on acid hydrolysis of the sirup.

When the perchloryl fluoride and sodium ethoxide were replaced by equimolar concentrations of sodium fluoride and potassium chlorate or by sodium fluoride and potassium perchlorate, no reaction was observed, even at reflux temperature.

Oxidative dimerization was observed by Shechter and Roberson,[7] as minor reactions in their study of the action of perchloryl fluoride on secondary nitro alkanes. Freeman[8] pointed out from a survey of the literature that fluorination can take place only with resonance stabilized anions with enhanced charge distribution or with neutral nucleophilic agents possessing a fair degree of resonance stabilization. On the other hand, nucleophiles with a high degree of charge localization or uncharged nucleophiles with nonbonding electrons yield products which arise from an initial attack upon the chlorine. The acylamidomalonate anions appear to be of the latter type, and the course of the reaction may be as follows:



EXPERIMENTAL

Diethyl 2,3-dicarbethoxy-2,3-diformamidosuccinate (Ia). To a solution of 18.4 g. (0.8 g.-atom) of sodium in 600 ml. of absolute ethanol was added 162.8 g. (0.8 mole) of ethyl formamidomalonate. After cooling the mixture to 6 ± 2°, 85.0 g. (0.83 mole) of perchloryl fluoride[9] was passed in during 2 hr. The mixture of inorganic salts which formed was removed by filtration, and the alcohol was evaporated *in vacuo*. The residue was dissolved in methylene chloride and washed with water. Again the solvent was removed by vacuum distillation, and the residue was crystallized from isopropyl alcohol. The yield of product was 64.0 g., 39.5%, and melted at 137–140°. After two additional recrystallizations from isopropyl alcohol an analytical sample was obtained, m.p. 141–142°.

Anal. Calcd. for $C_{16}H_{24}N_2O_{10}$: C, 47.52; H, 5.99; N, 6.93. Found: C, 47.67; H, 6.24; N, 6.88.

Diethyl 2,3-dicarbethoxy-2,3-diacetamidosuccinate (Ib). The title compound was prepared in 54.0% yield by the same procedure as described for the diformamido compound. The product melted at 148–150°, and an analytical sample was prepared by recrystallization three times from isopropyl alcohol, m.p. 151.5–152.5°.

Anal. Calcd. for $C_{18}H_{24}N_2O_{10}$: C, 49.99; H, 6.54; N, 6.48. Found: C, 50.16; H, 6.44; N, 6.53.

meso-2,3-Diacetamidosuccinic acid (II). A solution of 12.0 g. (0.52 mole) of sodium hydroxide in a mixture of 100 ml. of water and 50 ml. of methanol was prepared in a stainless steel beaker. To this solution, at room temperature, was added 21.4 g. (0.05 mole) of Ib. The mixture was stirred for about 20 min. until the ester went completely into solution and was allowed to stand overnight. The hydrolyzate was decolorized with charcoal and freed of cations by passage through a column of Amberlite IR-120(H^+). The effluent was evaporated to dryness in a flash evaporator below 40°, and the residue was suspended in acetone and filtered. The product weighed 1.7 g. (14.8%), m.p. 235–237° dec. For analysis, a sample was prepared by crystallization from water followed by recrystallization from methanol, m.p. 237–238° dec., (lit.[2] m.p. 235° dec.).

Anal. Calcd. for $C_8H_{12}N_2O_6$: C, 41.37; H, 5.22; N, 12.07; neut. equiv., 116.11. Found: C, 41.08; H, 5.51; N, 11.91; neut. equiv., 112.

meso-2,3-Diaminosuccinic acid (III). A suspension of 5.0 g. (0.012 mole) of Ia in 50 ml. of concd. hydrochloric acid was heated under reflux for 2 hr. The solution was decolorized with charcoal, and the acid was removed by vacuum evaporation. The residue was crystallized from a small volume of water and yielded 100 mg. (6.75%) of product, m.p. 310-

(4) H. McKennis, Jr., and A. S. Yard, *J. Org. Chem.*, **23**, 980 (1958).
(5) W. Wenner, U. S. Patent **2,389,099**, Nov. 13, 1945.
(6) R. Kuhn and F. Zumstein, *Ber.*, **59**, 479 (1926).
(7) H. Shechter and E. B. Roberson, Jr., *J. Org. Chem.*, **25**, 175 (1960).
(8) J. P. Freeman, *J. Am. Chem. Soc.*, **82**, 3869 (1960).

(9) Perchloryl fluoride was obtained from Pennsalt Chemicals Corp., Philadelphia 2, Pa., along with technical pamphlet DC-1819, "Perchloryl Fluoride" on details of safety and handling.

315° dec. An analytical sample was obtained from water, m.p. 310–315° dec., (lit.[4,5] m.p. 304, 303–305, 305–306). The ninhydrin reaction was positive for the product as indicated by a purple color.

Anal. Calcd. for $C_4H_6N_2O_4$: C, 32.43; H, 5.45; N, 18.91. Found: C, 31.98; H, 5.80; N, 18.45.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

Reactions of α-Dimethylaminophenylacetonitrile and Its Ethylation Product with Basic or Nucleophilic Reagents[1]

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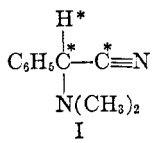
Received August 18, 1961

A study was made of the reactions of α-dimethylaminophenylacetonitrile (I) and its ethylation product (II) with basic or nucleophilic reagents including potassium amide, butyllithium, Grignard reagents, lithium aluminum hydride, and sodium. The reactions of I involved ionization of the α-hydrogen, addition to the nitrile carbon, and displacement of the nitrile group from the α-carbon; those of II occurred at the nitrile carbon and α-carbon. Some interesting comparisons are made between the reactions of phenylacetonitrile and aminonitrile I and between those of aminonitriles I and II.

α-Dimethylaminophenylacetonitrile (I) may be attacked by basic or nucleophilic reagents not only at the α-hydrogen or nitrile carbon as observed with phenylacetonitrile, but also at the α-carbon. Reactions involving each of these vulnerable positions, which are designated by asterisks in I, have been realized in the present investigation or previously as summarized in Table I.



I

TABLE I

REACTIONS OF AMINONITRILE I WITH BASIC OR NUCLEOPHILIC REAGENTS[a]

Reagent	Position Attacked	Product Formed
KNH_2 (NH_3)[b]	α-Hydrogen	Carbanion I′
n-C_4H_9Li	α-Hydrogen	Carbanion I′
	Nitrile carbon	Amino ketone III
Prim. Alkyl-MgX[c] or C_6H_5MgBr[d]	α-Carbon	t-Amines IVa–e
t-C_4H_9MgCl	α-Carbon	Benzyldimethylamine
$LiAlH_4$	Nitrile carbon	Prim. amine VII
	α-Hydrogen ?	Carbanion I′ ?
$Na(NH_3)$	α-Hydrogen	Carbanion I′
	α-Carbon or nitrile carbon	Benzyldimethylamine

[a] Except where designated, the solvent was diethyl ether. [b] Ref. 3 and 4. [c] For result with benzylmagnesium chloride, see ref. 9. [d] Tetrahydrofuran.

Like phenylacetonitrile,[2] I is attacked exclusively at the α-hydrogen by potassium amide or sodium amide in liquid ammonia. This has recently been demonstrated by alkylation of the resulting carbanion I′ with benzyl[3] and alkyl[4] halides to form, for example, II.

I′ II

Ethylation to form II has now been employed to demonstrate ionization of the α-hydrogen of I by certain other reagents (see Table I), and II has served as the starting compound in the second phase of the present work (see Table III). Incidentally, carbanion I′ failed to condense with I under conditions similar to those used previously for the self-condensation of phenylacetonitrile.[5]

Also like phenylacetonitrile,[6] I is attacked partly at the α-hydrogen and partly at the nitrile carbon by n-butyllithium in ether. These two courses of reaction were demonstrated by ethylation of the reaction mixture, followed by hydrolysis with hot hydrochloric acid to form propiophenone and amino ketone III respectively (Equations 1a and 1b). Propiophenone has recently[4] been shown to be the product of acid catalyzed hydrolysis of aminonitrile II, which was formed as an intermediate in course 1a.

The yields of propiophenone and amino ketone III ranged from 21–42% and 34–39%, respectively. No other product was detected. The structure of amino ketone III was supported by its infrared

(1) Supported by National Institutes of Health Grant CY-4455(C2).

(2) C. R. Hauser and W. R. Brasen, *J. Am. Chem. Soc.*, **78**, 494 (1956).

(3) C. R. Hauser, H. M. Taylor, and T. G. Ledford, *J. Am. Chem. Soc.*, **82**, 1786 (1960).

(4) H. M. Taylor and C. R. Hauser, *J. Am. Chem. Soc.*, **82**, 1960 (1960).

(5) G. A. Reynolds, W. J. Humphlett, F. W. Swamer, and C. R. Hauser, *J. Org. Chem.*, **16**, 165 (1951).

(6) See W. I. O'Sullivan, F. W. Swamer, W. J. Humphlett, and C. R. Hauser, *J. Org. Chem.*, **26**, 2306 (1961).