Preparation of Tetrachlorohydroquinone Dibenzyl Ether.—Eight g. (0.03 mole) of tetrachlorohydroquinone was added to 2.6 g. (0.065 mole) of sodium hydroxide in 100 ml. of water. The solution was heated to reflux and 9.0 g. (0.07 mole) of benzyl chloride was added dropwise. After the addition was complete the solution was refluxed for two more hours. On cooling a precipitate formed which was recrystallized from 95% ethanol, m.p. 173.5–173.8°. *Anal.* Calcd. for $C_{20}H_{14}OCl_4$: C, 56.0; H, 3.28; Cl, 33.2. Found: C, 57.8; H, 3.47; Cl, 31.8.

Structure of Tetrachlorohydroquinone Monobenzyl Ether.—The potentiometric titration of the substance in water solution indicated an equivalence point at *p*H 8.4. The neutral equivalent found was 332 as compared with the calculated value of 337. Since the compound could not be made easily by alkylation, the monoether was converted to the diether. A 0.5-g. sample of the product from the decomposition of AIDN in toluene containing chloranil was dissolved in the minimum volume of 5% aqueous sodium hydroxide and heated to reflux. Then 0.2 ml. of benzyl chloride was added dropwise and the solution was refluxed for four hours. A solid separated during the heating period, and after cooling it was extracted with ether. The ether was evaporated and the solid residue was recrystallized from 95% ethanol, m.p. 173–175°, no depression on admixture with authentic material. The infrared spectrum was also identical with that of the authentic material.

Alkylation of Tetrachlorohydroquinone Mono-[3-cyano-3-pentyl] Ether.—The proof of structure of the monobenzyl ether by conversion to the dibenzyl ether involves the assumption that some other ether would not be cleaved and then dibenzylated under the reaction conditions. Since it is especially important to demonstrate that the substance was not the cyanoalkyl ether a small sample of the latter compound, from the reaction of AIDN with chloranil, was benzylated under identical conditions. The white product was recrystallized from methanol and melted at 230–250° but depressed the melting point of authentic dibenzyl ether.

AMES, IOWA

[CONTRIBUTION FROM THE ROHM & HAAS CO.]

Reactive Nitrile Groups. II. The Reaction of Cyanoesters with Aqueous Amines[1]

BY MARVIN J. HURWITZ, LAWRENCE J. EXNER AND PETER L. DE BENNEVILLE

RECEIVED DECEMBER 17, 1954

Methyl cyanoacetate and methyl β-cyanopropionate were found to differ from the corresponding dinitriles, malononitrile and succinonitrile, in their reactions with aqueous amines, in that hindered primary amines, such as 1,1,3,3-tetramethylbutylamine and cyclohexylamine, did not react with the nitrile group but yielded the corresponding salts of the cyanoalkanoic acids. The product from aqueous piperidine and methyl β-cyanopropionate at reflux was piperidinium succinamate. Unhindered primary amines and morpholine gave N,N′-substituted diamides as expected. A comparison of the reaction of a variety of amines in water with, respectively, succinic anhydride, succinimide, methyl β-cyanopropionate and succinonitrile allows the postulation of a consistent cyclic scheme of aminolysis and hydrolysis for succinic acid derivatives. The aminolysis of malonic acid derivatives is thought to result from a chain effect.

In a previous article[2] it was shown that the uncatalyzed attack of an amine on a nitrile group, normally unsuccessful, will take place in the case of structures $NC(CH_2)_xCN$ where x is 1, 2 or 3. The present work was based on the expectation that if one of the –CN groups were replaced with the –COOR group, the nitrile group would react again regardless of whether the driving force were furnished by an inductive effect transmitted through the chain, or by a reaction path involving a cyclic imide intermediate. The study of methyl cyanoacetate and of methyl β-cyanopropionate in reactions of the same type as previously described has led to a further elucidation of the routes by which all of these reactions proceed.

The reaction of methyl cyanoacetate with aqueous benzylamine at reflux gave a 92% yield of N,N′-dibenzylmalonamide. Cyanoacetamide gave a 95% yield of the same compound.[3] These aminolytic reactions should involve a polarizing effect transmitted through the chain[4]; a reaction path involving a four-membered ring is not favored. Neither benzonitrile[2] nor phenylacetonitrile reacted under the same conditions with benzylamine, indicating that the activation would have to be of a major sort. Methyl cyanoacetate reacted with 1,1,3,3-tetramethylbutylamine in the presence of water to give a 50% yield of 1,1,3,3-tetramethylbutylammonium cyanoacetate by simple hydrolysis of the ester group. Cyanoacetamide also gave the same product. No further base attack on the negatively charged cyanoacetate ion is seen to take place. As in the case of succinonitrile[2] with this hindered primary amine, no products of amine attack were obtained.

Reactions of methyl β-cyanopropionate with aqueous amines were not entirely analogous to reactions of succinonitrile with the same amines. The usual aliphatic amines did give the diamides, in better yields and more rapidly than with succinonitrile (Table I). Again morpholine gave the dimorpholide in 23% yield, and piperidine gave piperidinium succinamate in 40% yield. However, 1,1,3,3-tetramethylbutylamine gave 1,1,3,3-tetramethylbutylammonium β-cyanopropionate, and cyclohexylamine gave only a small yield (3%) of the diamide, and as the major product cyclohexylammonium β-cyanopropionate (80%). Benzylamine yielded the diamide as the major product (Table I) but also a small amount of some intractable benzylammonium salt, probably also that of β-cyanopropionic acid.

In the two groups of reactions, with methyl β-cyanopropionate and with succinonitrile, respectively, there are thus some rather surprising differences with small changes in base strength, along with other differences which are obviously the result of the steric nature of the amine. If the reac-

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[1] Given in part at the 126th Meeting of the American Chemical Society, New York, N. Y., September 14, 1954.

[2] L. J. Exner, M. J. Hurwitz and P. L. de Benneville, THIS JOURNAL, **77**, 1103 (1955).

[3] The high yields clearly indicate that the lower yields with malononitrile[2] were due to base-catalyzed self-condensation reactions.

[4] The reaction of ammonia with cyanogen is known to proceed at quite low temperatures; H. M. Woodburn, B. A. Morehead and C. M. Chih, *J. Org. Chem.*, **15**, 535 (1950).

TABLE I

N,N'-DIALKYLAMIDES FROM METHYL β-CYANOPROPIONATE

$RNHCOCH_2CH_2CONHR$

R	Mole ratio ester	amine	H_2O	Time, hr.	Temp., °C.	Yield, %	M.p., °C.
CH_3	1.0	3.1	2.2	8	100[a]	98	170–173[c]
C_2H_5	1.0	2.1	2.2	8	100[a]	41	190–192[d]
n-C_4H_9	1.0	2.1	2.2	24	90[b]	44	186–188[e]
n-C_8H_{17}	1.0	2.3	2.0	28	90–95[b]	73	160–162[f]
2-Et-hexyl	1.0	2.1	1.0	48	90[b]	28	88–90[g]
C_6H_5	1.0	2.3	2.0	48	94[b]	0	[h]
$C_6H_5CH_2$	1.0	4.0	12.0	48	Reflux[b]	68	209–211[i]

[a] Reaction run in autoclave. [b] Reaction run at reflux at atmospheric pressure. [c] H. J. Backer, *J. Chem. Soc.*, 111, 596 (1912), reports m.p. 175°. Mixed m.p. with authentic sample from diethyl succinate (m.p. 170–173°) did not depress. [d] *Anal.* Calcd. for $C_8H_{16}N_2O_2$: N, 16.3. Found: N, 16.1. [e] Mixed m.p. with authentic sample from diethyl succinate (m.p. 186–188°) did not depress. [f] Mixed m.p. with the same product prepared from succinonitrile[2] did not depress. [g] *Anal.* Calcd. for $C_{20}H_{40}N_2O_2$: N, 8.2. Found: N, 8.2. [h] No ammonia was evolved and 84% of starting aniline was recovered. [i] Mixed m.p. with the same product obtained from succinonitrile[2] did not depress.

tion were to proceed through a cyclic intermediate, either a succinimide or a succinimidine, these differences also should result from the reaction of the same amines with succinic anhydride and with succinimide under the same conditions. This has proved to be the case. In Table II are listed the major products of the reaction of these four succinic acid derivatives with three groups of amines in the presence of water. These are: class I—piperidine, representing strong bases (K_b 1.6 × 10^{-3})[5]; class II—weaker unhindered bases of ionization constant 5 × 10^{-4} or less (methylamine,[6] benzylamine[7] and morpholine[5]); class III—amines of the same base strength as class II amines, but of such a structure as to make the direct formation of amides difficult (1,1,3,3-tetramethylbutylamine[9] and, to a lesser extent, cyclohexylamine[10]).

TABLE II

PRODUCTS FROM SUCCINIC ACID DERIVATIVES AND AMINES

Amine class	Anhydride	Imide	Cyano ester	Dinitrile
I	Mixed salts	Amide salt	Amide salt	Amide salt[2]
II	Dialkylamide	Dialkylamide	Dialkylamide	Dialkylamide[2]
III	Di-salt	Amide salt	Cyano salt	Amide salt[2]

It is now obvious that whereas aminolytic reactions on succinic acid derivatives are favored by amines of class II, hydrolytic reactions take place with amines of classes I and III. Those hydrolytic reactions which affect the cyano group could occur, like the aminolytic reactions of class II, either *via* a cyclic intermediate or through the operation of an inductive chain effect.[11]

Since succinamic acid is essentially a hydrated succinimide, it was worthwhile to test whether or not if it were formed at an intermediate stage, further reaction with amines of class II would occur. Benzylamine was found to react rapidly with succinamic acid to give a 70% yield of N,N'-dibenzylsuccinamide. However, since amines of class III cannot carry the hydrolysis of methyl β-cyanopropionate to the amide-salt stage as does the stronger base, piperidine, the conclusion must be that amines of class II having the same base strength as amines of class III, react not by a hydrolytic mechanism, but by the direct attack of the amine on the –CN group.

Experimental[12]

Aqueous Aminolysis of Methyl β-Cyanopropionate. A. General Procedure for Atmospheric Pressure Reactions.—Methyl β-cyanopropionate, the amine and water were mixed in the molar ratio listed in Table I for each reaction. The mixture, which was a homogeneous solution, was refluxed for the given number of hours (see Table I). Rapid evolution of ammonia commenced soon after heating was begun. At the end of the reflux period, the evolution of ammonia was very slow. The reaction was then stripped of excess water and amine under aspirator vacuum, and at a pot temperature of up to 120°. The residue was recrystallized from either isopropyl alcohol or ethyl acetate. Yields and melting points are listed in Table I. **B. General Procedure for Pressure Reactions.**—The mixture of methyl β-cyanopropionate, amine and water were charged to the autoclave, and the mixture heated at 100° for the given amount of time. This pressure reaction was only used in the case of methylamine and ethylamine. The products with their yields and melting points are listed in Table I.

Aqueous Aminolyses of Methyl β-Cyanopropionate with Amines not Listed in Table I.—These reactions were all carried out in a ratio of cyanoester:amine:water of 1:4:12, according to the general procedure for atmospheric reactions described above. The reflux temperatures were between 95 and 105°, and the reflux times were 48 hours in each case. **(a) With Morpholine.**—The stripped reaction mixture crystallized in part upon the addition of isopropyl alcohol. Succinomorpholide, m.p. 177–178°, was isolated in 23% yield; mixed m.p. with authentic sample[2] showed no depression. The mother liquor was stipped to an oil which failed to crystallize further. The residue was insoluble in water and did not release an odor of amine when made alkaline, indicating it not to be an amine salt. **(b) With Piperidine.**—No ammonia was evolved in the reaction. The stripped reaction mixture crystallized upon the addition of isopropyl alcohol. Piperidinium succinamate, m.p. 169–170° dec., was obtained in 40% yield; mixed m.p. with authentic sample[2] showed no depression. The stripped mother liquor did not crystallize further. It was soluble in water and released piperidine when made basic, indicating it to be a salt. **(c) With Cyclohexylamine.**—Trace amounts of ammonia were evolved. N,N'-Dicyclohexylsuccinamide, m.p. 238°, was collected as insoluble material before stripping. *Anal.* Calcd. for $C_{16}H_{28}N_2O_2$: N, 10.0. Found: N, 10.1.

The major portion was identified as cyclohexylammonium β-cyanopropionate obtained in 80% crude yield. In a previous reaction, a purified sample, recrystallized from ethyl acetate, m.p. 126–127°, was obtained in 57% yield.

Anal. Calcd. for $C_{10}H_{18}N_2O_2$: C, 60.6; H, 9.2; N, 14.1; equiv. wt., 198.2. Found: C, 60.7; H, 9.1; N, 14.1; equiv. wt. (by titration with perchloric acid in acetic acid), 205.9.

Addition of this salt to aqueous sodium hydroxide yielded an insoluble organic layer which upon separation and acidification with hydrochloric acid yielded a solid, m.p. 205–206°; mixed m.p. with an authentic sample of cyclohexylammonium chloride gave no depression.

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(5) I. Heilbron and H. Bunbury, "Dictionary of Organic Compounds," Oxford University Press, New York, N. Y., 1953, Vol. IV, p. 217.

(6) K_b 5 × 10^{-4}, *ibid.*, Vol. III, p. 293.

(7) K_b 2.4 × 10^{-5}, *ibid.*, Vol. I, p. 270.

(8) K_b 2.4 × 10^{-6}, A. R. Ingram and W. F. Luder, THIS JOURNAL, **64**, 3043 (1946).

(9) K_b 4.0 × 10^{-4}, "Tertiary Alkyl Primary Amines," Special Products Bulletin No. 33, Rohm & Haas Co., 1952, p. 8.

(10) K_b 1.6 × 10^{-4}, A. Waksmundzki, *Roczniki Chem.*, **18**, 865 (1938); *C. A.*, **33**, 6689 (1939).

(11) Evidence that only the chain effect is operative in the malononitrile series is the fact that amines of class III cannot promote hydrolysis of the –CN group of cyanoacetamide. In the case of succinonitrile only the cyclic path, involving a symmetrical intermediate, permits the participation of both –CN groups and excludes the formation of β-cyanopropionate ion, which is an end-product in solutions of this basicity.

(12) All melting points are uncorrected. Elemental analyses were carried out by the analytical laboratories of the Rohm & Haas Co.

The infrared spectrum of the product showed absorption at 4.44 μ characteristic of a nitrile group and in the region of 6.3 μ indicating a carboxylate ion. The multiple carbonyl absorption characteristic of amides, and the absorption characteristic of an ester group, present in the starting cyanoester, were absent.[13]

(d) **With 1,1,3,3-Tetramethylbutylamine.**—No ammonia was evolved in the reaction. The residue crystallized and 1,1,3,3-tetramethylbutylammonium β-cyanopropionate, m.p. 126–127°, was obtained in 80% yield. *Anal.* Calcd. for $C_{12}H_{24}N_2O_2$: C, 63.1; H, 10.5; N, 12.3; equiv. wt., 228. Found: C, 63.1; H, 10.4; N, 12.0; equiv. wt., 238.

Aqueous Aminolyses of Succinic Anhydride.—These reactions all were carried out in a ratio of succinic anhydride: amine:water of 1:4:12, according to the general procedure for atmospheric reactions described above. The reflux temperatures were between 95 and 105°, and the reflux times were 48 hours in each case. (a) **With Benzylamine.**—N,N'-Dibenzylsuccinamide, m.p. 210–211°, was obtained in 70% yield. A mixed m.p. with authentic sample[2] did not depress. (b) **With 1,1,3,3-Tetramethylbutylamine.**—1,1,3,3-Tetramethylbutylammonium succinate, m.p. 167–168°, was obtained in 87% yield. *Anal.* Calcd. for $C_{20}H_{44}N_2O_4$: C, 63.8; H, 11.7; N, 7.5; equiv. wt., 372. Found: C, 63.9; H, 11.5; N, 7.4; equiv. wt. (by titration with perchloric acid in acetic acid), 382. (c) **With Piperidine.**—The stripped reaction mixture remained an intractable viscous oil after standing one month in the cold. The oil then was taken up in benzene and the solution boiled to remove water. Upon cooling this solution in an ice-bath, a small amount of solid crystallized. After several recrystallizations from isopropyl alcohol, 4 g. (6%) of piperidinium acid succinate, melting at 143–144°, was obtained. *Anal.* Calcd. for $C_9H_{17}NO_4$: C, 53.3; H, 8.1; N, 6.9; equiv. wt., 203. Found: C, 53.2; H, 8.3; N, 6.7; equiv. wt. (by titration with aqueous NaOH), 204; (by titration with perchloric acid in acetic acid), 206. The major portion of the residue did not crystallize. It was water soluble and released piperidine when made alkaline, indicating it to be a piperidine salt, probably the dipiperidinium succinate.

Aqueous Aminolyses of Succinimide.—These reactions were all carried out in a ratio of succinimide:amine:water of 1:4:12, according to the general procedure for atmospheric reactions described above. The reflux temperatures were between 95 and 105°, and the reflux times were 48 hours in each case. (a) **With Benzylamine.**—N,N'-Dibenzylsuccinamide, m.p. 210°, mixed m.p. with authentic sample[2] did not depress, was obtained in 81% yield. (b) **With 1,1,3,3-Tetramethylbutylamine.**—No ammonia was evolved in the reaction. 1,1,3,3-Tetramethylbutylammonium succinamate, m.p. 180–181°, was obtained in 93% yield. A mixed m.p. with authentic sample did not depress. (c) **With Piperidine.**—No ammonia was evolved in the reaction. Piperidinium succinamate, m.p. 170–171°, identified by mixed melting point with an authentic sample,[2] was obtained in 50% yield.

Aqueous Aminolysis of Succinamic Acid with Benzylamine.—Four grams (0.039 mole) of succinamic acid, 16.6 g. (0.155 mole) of benzylamine and 8.4 g. (0.465 mole) of water were mixed and reacted according to the general procedure for atmospheric reactions described above. N,N'-Dibenzylsuccinamide, m.p. 209–210°, was obtained in 70% yield. A mixed m.p. with authentic sample did not depress. *Anal.* Calcd. for $C_{18}H_{20}N_2O_2$: C, 73.0; H, 6.8; N, 9.5. Found: C, 73.6; H, 6.8; N, 8.9.

Other Aqueous Aminolyses Carried out with Benzylamine. (a) **On Methyl Cyanoacetate.**—Methyl cyanoacetate, benzylamine and water were mixed in a 1:4:12 molar ratio according to the general procedure for atmospheric reactions described above. N,N'-Dibenzylmalonamide, m.p. 139–140°, identified by mixing melting point with an authentic sample,[2] was obtained in 92% yield. (b) **On Cyanoacetamide.**—N,N'-Dibenzylmalonamide, m.p. 138–139°, was obtained in 95% yield. A mixed m.p. with an authentic sample did not depress. (c) **On Phenylacetonitrile.**—The molar ratio used here was 1:2:6. No ammonia was evolved in the reaction. The cooled reaction mixture was acidified with concentrated hydrochloric. The phenylacetonitrile separated and was distilled to yield 46.5 g. (80% recovery) of nitrile, b.p. 122–123° (22 mm.). The yield of benzylamine hydrochloride, obtained by stripping the aqueous layer, was 126 g. (88% recovery of benzylamine).

Reactions of Aqueous 1,1,3,3-Tetramethylbutylamine. (a) **On Methyl Cyanoacetate.**—Methyl cyanoacetate, 1,1-3,3-tetramethylbutylamine and water were mixed in a 1:4:12 molar ratio according to the general procedure for atmospheric reactions described above. 1,1,3,3-Tetramethylbutylammonium cyanoacetate, m.p. 99–101°, was obtained in 52% yield. *Anal.* Calcd. for $C_{11}H_{22}N_2O_2$: C, 61.8; H, 10.3; N, 13.1; equiv. wt., 214. Found: C, 61.8; H, 10.5; N, 12.7; equiv. wt., 216 (by non-aqueous titration with perchloric acid). (b) **On Cyanoacetamide.**—1,1,3,3-Tetramethylbutylammonium cyanoacetate, m.p. 98–101° after recrystallization in good yield from petroleum ether, was obtained in 60% yield. Mixed m.p. with an authentic sample did not depress below 98°. Equiv. wt., calcd. 214, found (by non-aqueous titration) 218.

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[13] We are indebted to Dr. J. S. Stroupe and Miss Helen Miklas for obtaining and interpreting the infrared curves.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

Reactions of Some Aromatic Acetylenic Carbinols[1]

BY G. F. HENNION AND B. RAYMOND FLECK[2]

RECEIVED DECEMBER 4, 1954

9-Ethynyl-9-fluorenol, diphenylethynylcarbinol and phenylmethylethynylcarbinol have been hydrated to the expected methyl ketones. Some hydroxyl group reactions of the ethynylcarbinols and of the α-ketols obtained by hydration have been studied also. In none of these reactions has rearrangement of the carbon skeleton been observed. The ethynylcarbinols underwent the Meyer–Schuster rearrangement and thus produced fluorenylideneacetaldehyde, β,β-diphenylacrolein and β-methylcinnamaldehyde, respectively, the latter in poor yield. When treated with thionyl chloride or hydrochloric acid, 9-ethynyl-9-fluorenol yielded 9-(chlorovinylidene)-fluorene.

Discussion

It is now well established that certain 17-ethynyl-17-hydroxysteroids and 17-acetyl-17-hydroxysteroids undergo skeletal rearrangement under proper conditions and lead to expanded (six-membered) D rings.[3] The present work was directed to exploring this type of rearrangement. The *t*-ethynylcarbinols, 9-ethynyl-9-fluorenol (I), diphenylethynylcarbinol (VIII) and phenylmethylethynylcarbinol (XII) together with the corresponding acetyl derivatives were chosen as model compounds.

Attempts to hydrate the triple bond of I in acetic

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[1] Paper LXI on substituted acetylenes; previous papers, *J. Org. Chem.*, **18**, 1601 (1953); THIS JOURNAL, **76**, 5160 (1954). Presented at the National A.C.S. Meeting in New York, N. Y., September, 1954.

[2] National Science Foundation Fellow, 1952–1953. Abstracted from the Ph.D. dissertation of Brother Raymond Fleck, C.S.C.

[3] A. W. Johnson, "The Chemistry of the Acetylenic Compounds, Vol. I. The Acetylenic Alcohols," Edward Arnold Co., London, 1946, p. 261; R. Turner, THIS JOURNAL, **75**, 3484 (1953).