[CONTRIBUTION FROM THE FLUORINE RESEARCH CENTER, UNIVERSITY OF FLORIDA]

The Acid Hydrolysis of Fluorocarbon Carboxylic Acid Cyanide Dimers and the Products Thereof

BY R. H. PATTON AND J. H. SIMONS

RECEIVED AUGUST 23, 1956

It has been found that fluorocarbon carboxylic acid cyanide dimers react readily with concentrated hydrochloric acid to yield approximately equivalent amounts of the original fluorocarbon carboxylic acid and an α-hydroxyfluorocarbonmalonamide. The preparation and some of the physical and chemical properties of these new α-hydroxyfluorocarbonmalonamides are given.

In a previous communication[1] the preparation of fluorocarbon carboxylic acid cyanide dimers was described. The chemical behavior of these compounds in reactions with water, alcohols and silver fluoride is such as to yield, respectively, the acid, esters and acid fluoride of the parent fluorocarbon carboxylic acid plus hydrogen cyanide or silver cyanide.

It has now been determined that the acid cyanide dimers react readily with concentrated hydrochloric acid to yield approximately equivalent amounts of the original fluorocarbon acid and an α-hydroxyfluorocarbonmalonamide. The chemical equation suggested by this reaction is, for the first member of the series

$$(CF_3COCN)_2 \xrightarrow{\text{CON, HCl}} CF_3C(OH)(CONH_2)_2 + CF_3COOH$$

This paper will be concerned with this reaction and with some of the physical and chemical properties of the α-hydroxyfluorocarbonmalonamides.

Experimental

α-Hydroxytrifluoromethylmalonamide.—To 50 ml. of cold concentrated hydrochloric acid in a 250-ml. erlenmeyer flask was added 22 g. (0.09 mole) of trifluoroacetyl cyanide dimer. The flask was stoppered, placed in an ice-bath and allowed to stand overnight. The white crystalline precipitate that formed was broken apart with a glass rod and 50 ml. of cold water added. The mixture was cooled in an ice-bath and filtered. The white crystals were washed several times with cold water and dried. The yield of crude product was 7.3 g. (0.04 mole). Two recrystallizations from benzene afforded pure α-hydroxytrifluoromethylmalonamide in the form of white needles, m.p. 150–151°.

The acid filtrate from above was extracted with three 20-ml. portions of ethyl ether, the ether removed by distillation and the residue fractionated from an equal volume of concentrated sulfuric acid. This gave 3.6 g. (0.03 mole) of trifluoroacetic acid.

The other α-hydroxyfluorocarbonmalonamides were prepared by the same procedure. These compounds are summarized in Table I.

TABLE I

α-HYDROXYFLUOROCARBONMALONAMIDES

$RC(OH)(CONH_2)_2$ R	M.p., °C.	Nitrogen, % Theory	Nitrogen, % Found	Fluorine, % Theory	Fluorine, % Found	Carbon, % Theory	Carbon, % Found
CF_3–	150–151	15.05	15.22	30.64	30.12	25.81	25.77
CF_3CF_2–	124–125	11.86	11.61	40.25	39.96	25.42	25.32
$CF_3CF_2CF_2$–	159–160	9.79	9.16	46.50	46.41	25.17	25.05
$CF_3(CF_2)_4$–	170–171	7.25	7.03	54.14	53.44	24.87	24.42

The Sodium Salt of α-Hydroxytrifluoromethylmalonamide.—A solution, formed by adding 0.1 g. of sodium to 10 ml. of 95% ethanol, was added to a solution of 1.0 g. of α-hydroxytrifluoromethylmalonamide in 10 ml. of 95% ethanol. A white precipitate formed immediately. This was filtered, washed several times with cold ethanol and dried. This salt is readily soluble in water and gives a strongly alkaline solution. Acidification of this aqueous solution with dilute mineral acid returned the original α-hydroxytrifluoromethylmalonamide.

The sodium salts of the other malonamides were prepared by the same procedure. A summary of these compounds is presented in Table II.

TABLE II

SODIUM SALTS OF α-HYDROXYFLUOROCARBONMALONAMIDES

$RC(O)(CONH_2)_2Na$ R	M.p., °C.	Sodium, % Theory	Sodium, % Found	Nitrogen, % Theory	Nitrogen, % Found
CF_3–	170–175 d.	11.06	11.21	13.46	13.29
CF_3CF_2–	160–170 d.	8.91	9.10	10.84	10.71
$CF_3CF_2CF_2$–	173–178 d.	7.46	7.63	9.09	8.88

Mercury Derivative of α-Hydroxytrifluoromethylmalonamide.—To a solution of 0.11 g. of α-hydroxytrifluoromethylmalonamide in 10 ml. of 95% ethanol was added 0.2 g. of red mercuric oxide and the solution refluxed for 30 minutes. The hot solution was then filtered and the alcohol evaporated on a steam-bath. The hard glass-like product was pulverized, leached several times with hot water and dried. The yield of pure product, m.p. 212–215° dec., was 0.14 g. The mercury derivative was soluble in hot ethanol and ethyl ether, and insoluble in water.

The mercury derivatives of the other α-hydroxyfluorocarbonmalonamides were prepared by the same procedure. These compounds are summarized in Table III.

TABLE III

MERCURY DERIVATIVES OF α-HYDROXYFLUOROCARBONMALONAMIDE

$[RC(OH)(C_2O_2N_2H_3)]_2Hg$ R	M.p., °C.	Mercury,[a] % Theory	Mercury,[a] % Found	Nitrogen, % Theory	Nitrogen, % Found
CF_3–	212 d.	35.09	34.82	9.82	9.71
CF_3CF_2–	246 d.	29.85	29.79	8.36	8.28
$CF_3CF_2CF_2$–	282 d.	25.97	25.67	7.27	7.16

[a] The mercury analysis was performed according to the procedure of Rauscher.[2]

The Sodium Salt of the Mercury Derivative of α-Hydroxytrifluoromethylmalonamide.—A solution of 0.1 g. of the mercury derivative of α-hydroxytrifluoromethylmalonamide in 10 ml. of hot 95% ethanol was added to a solution made by adding 0.1 g. of sodium to 10 ml. of 95% ethanol. A precipitate formed immediately. This was filtered, washed several times with hot ethanol and dried. The yield of product, m.p. >360°, was 0.1 g.

The sodium salts of other mercury derivatives were formed by the same procedure. These compounds are summarized in Table IV.

To demonstrate experimentally the malonic acid-like decarboxylation behavior of the product obtained from the basic hydrolysis of the α-hydroxyfluorocarbonmalonamides, the following experiment was performed.

Reaction of α-Hydroxypentafluoroethylmalonamide with Strong Aqueous Sodium Hydroxide, Followed by Acidification.—To 5.0 g. of α-hydroxypentafluoroethylmalonamide was added 30 ml. of 30% aqueous sodium hydroxide solution in an apparatus similar to that used for Kjeldahl nitrogen determination. The mixture was refluxed gently for

---

[1] R. H. Patton and J. H. Simons, THIS JOURNAL, **77**, 2016 (1955).

[2] W. H. Rauscher, *Ind. Eng. Chem., Anal. Ed.*, **10**, 331 (1938).

TABLE IV

SODIUM SALTS OF THE MERCURY DERIVATIVES OF α-HYDROXYFLUOROCARBONMALONAMIDES

$[RC(O)-(C_2O_2N_2H_3)]_2HgNa_2$ R	M.p., °C.	Mercury,[a] % Theory	Found	Nitrogen, % Theory	Found
CF_3-	>360	32.57	32.11	9.12	8.95
CF_3CF_2-	>360	28.01	27.63	7.84	7.79
$CF_3CF_2CF_2-$	>360	24.57	24.19	6.87	6.63

[a] The mercury analysis was performed according to the procedure of Rauscher.[2]

2 hr. with the tip of the receiving condenser immersed in 25 ml. of standard hydrochloric acid. The solution was then steam distilled until the total volume in the receiving flask was 150 ml. This was titrated with standard sodium hydroxide solution, using methyl red indicator. The results indicated approximately two equivalents of ammonia for each equivalent of α-hydroxypentafluoroethylmalonamide.

After steam distillation, the alkaline residue was acidified with 50% sulfuric acid. The carbon dioxide that evolved was passed immediately through a calcium chloride drying tube and collected in a U-tube containing Ascarite. The weight of carbon dioxide corresponded approximately to one equivalent of the original α-hydroxypentafluoroethylmalonamide.

The acidic solution from above was extracted with ethyl ether and the ether removed. The colorless liquid that remained was very acid to *p*H paper. This liquid was added to 20 ml. of water containing 2.0 g. of silver oxide, the mixture refluxed for 30 minutes, filtered and the water evaporated under reduced pressure. A white crystalline, ether soluble, silver salt remained. This compound did not contain nitrogen. A gravimetric silver chloride analysis of an aqueous solution of this salt indicated 35.70% silver. This salt was not identified further, although it was believed to be a silver salt of the corresponding α-hydroxy or α-keto acid.

The authors wish to acknowledge the sponsorship of the Minnesota Mining and Manufacturing Co. for the work reported in this paper.

GAINESVILLE, FLORIDA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, TULANE UNIVERSITY]

Dehydrogenation of Glyoximes[1]

BY J. H. BOYER AND U. TOGGWEILER

RECEIVED SEPTEMBER 10, 1956

The dehydrogenation of certain quinonoid and non-quinonoid glyoximes with chlorine, sodium hypochlorite or dinitrogen tetroxide was investigated.

Aldoximes and vicinal dioximes but not ketoximes[2] undergo simple intramolecular dehydrogenation. Polymerization of nitrile oxides, from aldoximes, leads to the formation of furoxanes, together with other products. Furoxanes and *ψ-o*-dinitrosoaromatic compounds have been obtained from cyclic non-quinonoid and *o*-quinonoid glyoximes, respectively.

Moderately useful chemical reagents for the dehydrogenation of aldoximes and glyoximes are dinitrogen tetroxide,[3] sodium hypohalite[4] and alkaline ferricyanide.[3,5] Nitric acid and arsenic trioxide[6] have been used less frequently and nitrous acid,[7] nitrogen trioxide[8] or amyl nitrite[9] inefficiently oxidizes aldoximes to nitrile oxides. In contrast, Caro's acid oxidizes both aldoximes and ketoximes to the corresponding nitro compounds.[10]

Hydroxamic acid chlorides resulted from combinations of aldoximes and chlorine[11] or nitrosyl chloride[12] while *gem*-chloro-nitroso compounds have been similarly obtained from ketoximes.[11,12] Dehydrochlorination of the hydroxamic acid chlorides occurs upon formation or upon mild treatment with alkali and the nitrile oxide thereby obtained polymerizes.[12]

The action of chlorine upon glyoximes has now been investigated. In agreement with the earlier work on monoximes, an immediate blue color characteristic of C-nitroso monomers developed upon combination of dialkyl glyoximes and chlorine in benzene or ethanol and disappeared upon warming. An intermediate *gem*-chloro-nitroso derivative apparently was formed. An unstable and impure colorless solid resulted from the combination of chlorine and decalin-2,3-dione dioxime and it gave a positive Beilstein test for halogen. Attempts to purify the compound were unsuccessful. In the treatment of benzil dioxime with chlorine a very dark color developed and faded rapidly. A high yield of diphenylfuroxane (I) was obtained, in sharp contrast to no yield of dialkyl furoxanes from corresponding dioximes.

Earlier attempts to oxidize phenanthrene-9,10-quinone dioxime to *ψ*-9,10-dinitrosophenanthrene (II) failed.[13] Both this quinonoid glyoxime and *o*-benzquinone dioxime were successfully dehydrogenated by chlorine into the corresponding *ψ-o*-

---

[1] The financial support for this work was provided by the Office of Ordnance Research, U. S. Army, under contracts No. DA-01-ORD-331 and DA-01-ORD-428.

[2] A. Mailhe and F. de Godon, *Bull. soc. chim.*, **23**, 18 (1918), reported the formation of nitriles, hydrogen, olefins, ammonia and amines from dialkyl ketoximes over thorium or aluminum oxide catalysts at 350°.

[3] R. Scholl, *Ber.*, **21**, 506 (1888); **23**, 3490 (1890).

[4] G. Panzio, *Atti reale accad. sci. Torino*, **41**, 11/2 (1906); *Chem. Zentr.*, **77**, I, 1700 (1906); J. Meisenheimer, H. Lange and W. Lamparter, *Ann.*, **444**, 94 (1925); P. Robin, *Ann. chim.*, **16**, 77 (1921); E. M. Cherkasova and N. N. Mel'nikov, *Zhur. Obshchei Khim.*, **19**, 321 (1949); *C. A.*, **43**, 6569 (1949).

[5] R. Koreff, *Ber.*, **19**, 176 (1886).

[6] E. Beckmann, *ibid.*, **22**, 1588 (1889).

[7] E. Beckmann, *ibid.*, **22**, 1501 (1889).

[8] R. Ciusa and E. Parisi, *Gazz. chim. ital.*, **55**, 416 (1925).

[9] C. Minunni and R. Ciusa, *Atti accad. Lincei*, **14**, II, 518 (1905).

[10] E. Bamberger, *Ber.*, **35**, 4293 (1902); E. Bamberger and R. Seligman, *ibid.*, **35**, 4299 (1902).

[11] E. Graf, *Annales soc. españ. fís. quím.*, **34**, 91 (1936); *C. A.*, **30**, 4432 (1936).

[12] H. Rheinholdt and M. Dewald, *Ann.*, **455**, 300 (1927), for leading references.

[13] J. H. Boyer, R. F. Reinisch, M. J. Danzig, G. A. Stoner and F. Sahhar, THIS JOURNAL, **77**, 5688 (1955).