Reduction with sodium borohydride gave a mixture of the *meta* and *para* alcohols α-cyano-α-ethyl-α′-hydroxy-α′-methyl-*m*- and -*p*-xylene, bp 115–120° (0.6 mm), $n^{25}\mathrm{D}$ 1.5220, having characteristic infrared absorptions at 2.95 (OH), 4.49 ($C\equiv N$), 12.00 (*para* substitution), 12.56, and 14.22 μ (*meta* substitution) and nmr chemical shifts at −60 (ethyl CH_3), −83 (CH_3), −111 (ethyl CH_2), −223 (CHCN), −234 (OH), −286 (CH), and −437 (aromatic CH) cps.[15]

Anal. Calcd for $C_{12}H_{15}NO$: C, 76.15; H, 7.99; N, 7.40. Found: C, 75.90; H, 8.20; N, 7.38.

An alternate preparation of α-cyano-α-ethyl-α′-hydroxy-α′-methyl-*p*-xylene uncontaminated by the *meta* isomer was made by the interaction of ethyl bromide, 13 g, with the sodium salt of *p*-acetylphenylacetonitrile, prepared from 15 g of the nitrile and sodium amide from 2.4 g of sodium, in 100 ml of refluxing ether. The product, α-ethyl-*p*-acetylphenylacetonitrile, 15 g, isolated after washing of the neutral reaction mixture with water, concentration of the ether, and distillation of the residual oil, bp 120–125° (0.6 mm), $n^{25}\mathrm{D}$ 1.5330, has characteristic infrared absorptions at 4.49 ($C\equiv N$), 5.95 ($C=O$), and 12.07 μ (*para* substitution) and nmr chemical shifts of −63 (CH_3), −114 (CH_2), −153 (CH_3CO–), −232 (CH), −445 (CH aromatic), and −476 (CH aromatic *ortho* to acetyl group) cps. Reduction of this ketone in methanol at 10–20° and with an excess of sodium borohydride gave α-cyano-α-ethyl-α′-hydroxy-α′-methyl-*p*-xylene, bp 110–112° (0.3 mm), $n^{25}\mathrm{D}$ 1.5220, having characteristic infrared absorptions at 2.93 (OH), 4.48 ($C\equiv N$), and 12.05 μ (*para* substitution).

Anal. Calcd for $C_{12}H_{15}NO$: C, 76.15; H, 7.99; N, 7.40. Found: C, 76.34; H, 8.10; N, 7.47.

Thionyl chloride, 9 g, was used to convert the mixed alcohol, 18 g dissolved in 100 ml of ether, to 12 g of a mixture of α-cyano-α-ethyl-α′-chloro-α′-methyl-*m*- and -*p*-xylene, bp 120–122° (0.4 mm), having characteristic infrared absorptions at 4.48 ($C=N$), 12.00 (*para* substitution), 12.58, 14.27 (*meta* substitution), and 13.40 μ (C–Cl?) and nmr chemical shifts of −63 (CH_3–CH_2), −109 (CH_3–CHCl–), −115 (CH_2), −225 (CH–CN), −305 (CHCl), and *ca.* −440 (aromatic) cps.

Anal. Calcd for $C_{12}H_{14}ClN$: C, 69.39; H, 6.79; N, 6.75. Found: C, 69.72; H, 7.15; N, 6.62.

To a solution of the mixed chlorides in methanol was added slowly with stirring methanolic potassium hydroxide until the reaction mixture remained basic. Under these conditions the addition of base initially produces a yellow color which fades as polymer is precipitated. The precipitated polymer was washed with methanol, water, and methane. This polymer has a glass transition temperature at 230° and is soluble in chloroform but can be reprecipitated by addition of petroleum ether (bp 30–50°) or methanol. A sample prepared by the addition of the chloride to the base was found to have a reduced viscosity of 3.0 (N,N-dimethylformamide, 0.2 g/100 ml, 25°).

Anal. Calcd for $C_{12}H_{13}N$: C, 84.17; H, 7.65; N, 8.18. Found: C, 84.20; H, 7.71; N, 8.36.

The nmr spectrum of a 3% polymer solution in deuteriochloroform showed broad overlapping peaks centered at −46, −65, and −128 cps of relative intensity 8.0 (CH_3, CH_3–CH_2–), a single broad peak at −187 cps of relative intensity 0.95 (C–H), and broad overlapping peaks at −405, −426, and −445 cps of relative intensity 4.0 (aromatic CH). Characteristic infrared peaks are those found at 4.48 ($C=N$) and 11.96 μ (*para* substitution).

From the mother liquors of the dehydrohalogenation was obtained by concentration *in vacuo* and distillation α-cyano-α′-chloro-α′-methyl-*m*-xylene, bp 120–122° (0.4 mm), having characteristic infrared absorptions at 4.46 ($C\equiv N$), 12.5, and 14.3 μ (*meta* substitution), and nmr chemical shifts virtually identical with those of the mixed chlorides except for the aromatic proton resonances which consisted of two major peaks at about −437 and −445 cps (neat).[15]

Anal. Calcd for $C_{12}H_{14}ClN$: C, 69.39; H, 6.79; N, 6.75. Found: C, 69.50; H, 7.02; N, 6.87.

Dehydrohalogenation of α-Carbomethoxy-α′-chloro-α′-methylxylene.—Methyl *p*-acetylphenylacetate was prepared as a mixture of isomers by adding 450 g of aluminum chloride (anhydrous) at 0–10° to a stirred solution of 400 g of methyl phenylacetate, 240 g of acetyl chloride, and 1000 ml of carbon disulfide, refluxing the mixture for 16 hr, pouring into ice and hydrochloric acid, extracting with ether, washing the ether extracts with water, drying, and distilling to yield 86 g. This product was reduced with 10 g of sodium tetrahydridoborate in 400 ml of methanol to yield 43 g of alcohol. The alcohol was dissolved in 90 ml of benzene, and 0.3 ml of pyridine and 35 g of thionyl chloride were added with cooling. After refluxing for 2 hr, the reaction was concentrated *in vacuo*, washed, and distilled, bp 90–107° (0.5 mm). This chloride (4 g) added to a methanolic potassium hydroxide solution gave a low yield of amorphous high molecular weight polymer, insoluble in acetone, containing some potassium as –COOK groups (flame test) and the COOR, C–CH_3 *para*-substituted benzene groups (by infrared).

Dehydrohalogenation in Deuterated Solvents.—All deuterium analyses were made by Josef Nemeth, Urbana, Ill. (A) *p*-(α-Chloroethyl)phenylacetonitrile, 1.7 g (0.0095 mole), was added to 0.4 g of potassium hydroxide (less than 0.01 mole) in 8 ml of deuterium oxide at room temperature. After 1 hr the polymer was removed by filtration, washed with deuterium oxide and with acetone, and dried. The residual polymer, 0.50 g, was found to contain 1.94 atom % excess deuterium (calcd for complete exchange of one proton, 10.5%). (B) To 5.40 g of a solution of potassium hydroxide (0.0075 mole) in methanol-*d* containing 88% of exchangeable protons as deuterium by nmr (made from 3.56 g of "85%" potassium hydroxide and 37.31 g. of methanol-*d*) was added at room temperature 231 g (0.0013 mole) of chloronitrile I (R_1 = CN, R_2 = H) as an undiluted liquid. After 5 min the reaction was washed successively with methanol-*d*, deuterium oxide, acetone, and methanol-*d*, and air dried to yield 90 mg (49%) of polymer containing 5.75 atom % excess deuterium (calcd for complete exchange of one proton, 9.7 atom %). (C) Reaction B was repeated except that the product was allowed to stand 24 hr at room temperature. The polymer was found to contain 8.95 atom % excess deuterium. (D) To 0.4 g of "85%" potassium hydroxide in 10 ml of methanol-*d* at −20° was added 2.0 g (0.0095 mole) of chloronitrile I (R_1 = CN, R_2 = C_2H_5). Upon warming, polymer formed which, after the usual washing and drying, produced polymer having 0.11 atom % excess deuterium.

Nucleophilic Displacement of Vinylic Halogen in Fluorinated Cycloalkenes. I. Reaction with Pyridines

S. E. ELLZEY, JR., AND WILMA A. GUICE

Southern Regional Research Laboratory,[1]
New Orleans, Louisiana 70119

Received October 11, 1965

Reaction of the fluorinated olefins Ia or Ib (Chart I) and tertiary alkylamines has been reported to give trialkyl (3,3-difluoro-2,4-dioxocyclobutyl)ammonium betaines (II).[2] From the *solvent-free* reaction of Ia and pyridine or substituted pyridines, Pruett and coworkers[3] obtained a mixture of olefin dimers, an olefin trimer, or, in some cases, a quaternary adduct of an olefin dimer. Only from 3-bromopyridine and Ia did they isolate a betaine (IIIf) in low yield after an aqueous work-up.

Herein is reported a more general method for the preparation of fluorinated dioxocycloalkyl pyridinium betaines (III), and the reaction of pyridines with the olefins I has now been extended to the five- and six-membered ring compounds.[4]

---

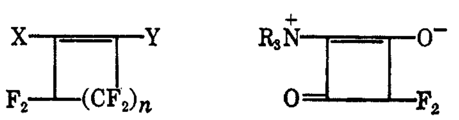
[1] One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

[2] (a) K. E. Rapp, *J. Am. Chem. Soc.*, **73**, 5901 (1951); (b) R. L. Pruett, C. T. Bahner, and H. A. Smith, *ibid.*, **74**, 1633 (1952).

[3] R. L. Pruett, C. T. Bahner, and H. A. Smith, *ibid.*, **74**, 1638 (1952).

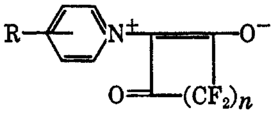
[4] While this paper was in manuscript, F. H. Megson, M. T. Beachem, and R. F. Stockel [Abstracts, 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965, p 11P] reported the preparation of IIIb from 1-chloro-2-methoxyhexafluorocyclopentene.

CHART I



Ia, $n = 1$; X=Y=F
b, $n = 1$; X=F, Y=Cl
c, $n = 1$; X=Y=Cl
d, $n = 2$; X=Y=Cl
e, $n = 3$; X=Y=Cl

II



IIIa, $n = 1$; R=H
b, $n = 2$; R=H
c, $n = 3$; R=H
d, $n = 1$; R=4-CO$_2$Et
e, $n = 2$; R=4-CO$_2$Et
f, $n = 1$; R=3-Br
g, $n = 2$; R=3-Br.

After mediocre success (because of tar formation) using several solvents, it was unexpectedly found that acetic acid was a good solvent for the reaction of I and pyridines, usually giving products of excellent purity. This solvent apparently lowers the basicity of the reaction medium sufficiently to prevent tar formation but yet not enough to inhibit the olefin–pyridine reaction. In support of this, lack of stability toward base was demonstrated in the case of IIIb when tarry material and an ammonia odor were obtained upon refluxing the compound with 10% sodium hydroxide for 30 min. Upon heating at 65° for 2 hr in the base about 90% recovery of IIIb was realized.

In the reaction of the olefins with pyridine it was noted that olefin reactivity decreased with increasing ring size, an effect probably attributable to the degree of ring strain.

The two reactive substituted pyridines examined, 3-bromopyridine and ethyl isonicotinate, were less reactive than pyridine itself, probably due to the lower order of nucleophilicity of these compounds. 2-Chloropyridine failed to react with Id during 4 days at reflux in acetic acid–water.

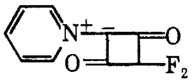
Vinylic fluorine in Ia is also highly reactive since a quantitative yield of the corresponding betaine IIIa was obtained upon reaction with pyridine in acetic acid containing water.

Structures have been assigned to the products III on the basis of elemental analysis, molecular weight, infrared spectrum, and by analogy to the products formed from trialkylamines and Ia.[2] In support of these assignments, oxidation of IIIb with acidic dichromate gave the expected perfluorosuccinic acid. Using alkaline permanganate 38% of the starting material was recovered after refluxing 30 min.

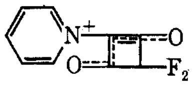
The infrared spectrum of (3,3-difluoro-2,4-dioxocyclobutyl)pyridinium betaine (IIIa) showed a very strong band at 5.60 μ which is attributed to C=O stretching. A poorly resolved doublet at 5.95 and 6.10 μ may be ascribed to C=C stretching of the four-membered ring and a pyridinium ring absorption, respectively.[5] In the five-membered ring compound IIIb two very weak bands are present at 5.80 and 5.89 μ and may represent C=O absorption; one very strong, broad band is also present at 6.13 μ. In the six-membered ring betaine IIIc absorption in the 5–6 μ region is practically absent but two strong bands at 6.22 and 6.35 μ are present.

The strong absorption at 5.60 μ which distinguishes IIIa from IIIb and IIIc is also present at 5.60 μ in the spectrum of IIId in addition to the ester C=O band at 5.97 μ. By way of contrast a weak band at 5.81 μ is present in IIIe in addition to ester absorption at 5.74 μ and a band of medium intensity is present at 5.87 μ in the bromo compound IIIg.

A structure such as IV would tend to relieve strain present in the structures IIIa or V. Contrary to expectations IIIa failed to react with methyl iodide in refluxing acetone or to yield a 2,4-dinitrophenylhydrazone. No evidence for protonation of IIIa upon addition of trifluoroacetic acid was obtained from its proton magnetic resonance (nmr) spectrum in dimethyl sulfoxide (aryl protons at τ 0.67–2.02). Likewise, in trifluoroacetic acid as solvent only the aromatic protons were observed (τ 0.5–1.97). However obscure the true structure of the four-membered ring compounds remains, it appears probable that resonance of the type indicated for V may be important in explaining the lack of strong absorption in the C=O stretching region for the betaines IIIb and IIIc and may account for one of the two infrared bands in the 6.1–6.3-μ region observed in IIIb and IIIc (the other being due to a pyridinium ring vibration).[6]



IV



V

Striking differences were observed in the reactivities of the betaines IIIa–c with acids. The four-membered ring compound IIIa yields two products with hydrochloric acid. On the basis of analysis, infrared spectra, and by analogy to the behavior of II[2b] these products are assigned the structures VIa and VII (Scheme I). Compounds of the type II have been reported to yield the decarboxylated quaternary chlorides with hydrochloric acid, probably *via* the carboxy betaine hydrochlorides as intermediates.[2b] In the case of IIIa the major product from the reaction is the water-soluble VII with a small amount of the water-insoluble VIa being formed also. About 96% recovery of IIIb was realized from similar treatment of this compound, while the six-membered ring compound IIIc gave a moderate yield of VIc. With 50% sulfuric acid, however, IIIb was converted into VIb upon prolonged heating. The latter in trifluoroacetic acid exhibited a proton nmr spectrum having a singlet attributable to the CH$_2$ protons and a multiplet assignable to the aromatic protons.

---

[5] In the spectra of II (R$_3$N = Et$_3$N or Et$_2$NMe) a band of medium intensity appears in the range 5.5–6.0 μ but apparently was unassigned. A strong band at 6.0–6.2 μ in the compounds II was compared with absorption in this region shown by the electronically similar acetylacetone.[2b]

[6] One of the referees pointed out that as the size of the fluorinated ring increases, steric repulsions to coplanarity increase with consequent decreased overlap of the rings and weaker C=O absorption.

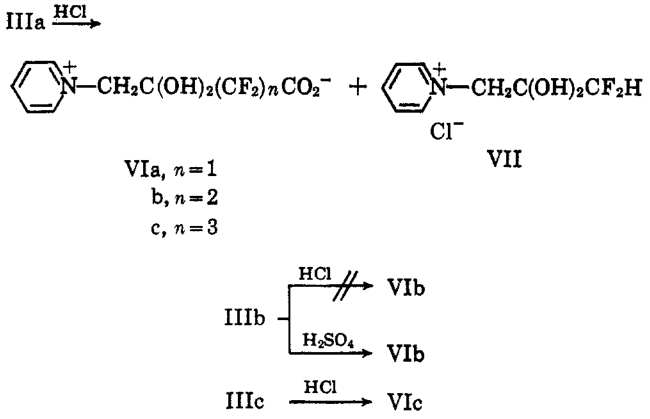
TABLE I

(PERFLUORODIOXOCYCLOALKYL)PYRIDINIUM BETAINES

Structure	Time, hr	Temp, °C	Yield, %[a]	Mp, °C[b]	Carbon, % Calcd	Carbon, % Found	Hydrogen, % Calcd	Hydrogen, % Found	Fluorine, % Calcd	Fluorine, % Found	Nitrogen, % Calcd	Nitrogen, % Found	Molecular weight Calcd	Molecular weight Found
IIIb	1	120	97	229–231	48.59	48.80	2.04	2.27	30.75	31.00	5.67	5.83	247	252
IIIc	24	120	87	191–192	44.46	44.69	1.70	1.93	38.36	38.18	4.71	4.57	297	300
IIId	6	25	84	236	53.54	53.52[c]	3.37	3.47	14.12	14.29	5.20	5.19	269	269
IIIe	24	120	36[d]	235–236	48.91	49.03	2.84	2.74	23.81	23.73	4.39	4.59	319	315
IIIg[e]	24	25	33	184–185	36.83	37.05	1.24	1.37	23.31	23.30	4.30	4.31	326	320

[a] Crude product. [b] Analytical sample. [c] Residue, 1.45%. [d] Additional product, contaminated with isonicotinic acid, isolated. [e] Dilute HCl used to remove excess amine.

SCHEME I



In the infrared spectrum of VIa–c and VII a strong band at 6.10, 6.06, 6.09, or 6.11 μ, respectively, is probably due to a pyridinium ring absorption. In addition, carboxylate absorption in VIa–c occurs at 6.10 μ (unresolved from pyridinium ring absorption), 5.96, or 6.00 μ, respectively. VIa–c and VII were all characterized by strong OH stretching bands at about 3.2 μ.

Experimental Section[7]

Infrared spectra were obtained from KBr disks using the Perkin-Elmer Models 21 or 137B spectrophotometers. Nmr spectra were run at 25° using the Varian A-60 or A-60A spectrometers. Molecular weights were determined in acetone with the Mechrolab vapor pressure osmometer.

1,2-Dichlorohexafluorocyclopentene was a gift of Hooker Chemical Corp.; the other olefins were from Peninsular Chem-Research, Inc.

(3,3-Difluoro-2,4-dioxocyclobutyl)pyridinium Betaine (IIIa).—A mixture of 19.78 g (0.25 mole) of pyridine, 25 ml of glacial acetic acid, and 1 ml of water was cooled to 25°. With stirring was added 4.87 g (0.025 mole) of 1,2-dichlorotetrafluorocyclobutene. Within 20 min the temperature rose to 56° and slowly began to fall. After a reaction time of 1 hr, 100 ml of water was added and the mixture was cooled. After filtering and washing with water, the yield of an orange product was 4.77 g (97%), mp 241–243°. Recrystallization from aqueous acetone (Norit) gave colorless needles, mp 241–242°.

Anal. Calcd for $C_9H_5F_2NO_2$: C, 54.83; H, 2.56; F, 19.28; N, 7.11; mol wt, 197. Found: C, 55.01; H, 2.65; F, 19.13; N, 6.96; mol wt, 199.

A quantitative yield of IIIa was obtained from hexafluorocyclobutene and pyridine in acetic acid–water at 15–35°.

Data for other betaines prepared by this procedure are summarized in Table I.

Oxidation of IIIb.—To a suspension of 3.73 g (0.015 mole) of IIIb in 25 ml of water was added a solution of 8.82 g (0.03 mole) of potassium dichromate in 30 ml of concentrated sulfuric acid and 45 ml of water. After 2 hr at reflux, excess dichromate was destroyed with sodium bisulfite and the product was continuously extracted with ether for 5 hr. After evaporation of the ether and recrystallization from benzene there was obtained 1.70 g (60%) of perfluorosuccinic acid, mp 116–119°,[8] neut equiv 96 (calcd 95). Its infrared spectrum was identical with that of an authentic sample.

Reaction of IIIa with Hydrochloric Acid.—The betaine, 2.00 g (0.01 mole), was refluxed for 4 hr with 15 ml of concentrated hydrochloric acid. Upon dilution with water and cooling no solid separated. The solution was evaporated on a water bath (70°) with an air stream and the residue, after washing with acetone and ether, was dried and weighed 2.28 g. The solid was suspended in about 50 ml of boiling acetone and a few drops of water were added to bring it into solution. Upon cooling to −35° overnight, 0.22 g (9%) of water-insoluble (1-carboxy-1,1-difluoro-2,2-dihydroxypropyl)pyridinium betaine (VIa) separated, mp 131–132° dec. After recrystallization from aqueous acetone the melting point of the yellow plates was 133–135° (dec).

Anal. Calcd for $C_9H_9F_2NO_4$: C, 46.36; H, 3.89; F, 16.30; N, 6.01. Found: C, 46.54; H, 3.90; F, 16.37; N, 5.85.

An unsuccessful attempt was made to determine the equivalent weight of VIa by back-titration with hydrochloric acid of a sodium hydroxide solution of the compound. Under such conditions VIa apparently rapidly decarboxylates, giving VII.

The filtrate from the above separation was evaporated to dryness and the water-soluble residue was recrystallized from a large volume of acetone containing a few drops of water to aid dissolution. Upon cooling to −35° colorless needles, 1.32 g (58%), mp 158–160° dec, of (1,1-difluoro-2,2-dihydroxypropyl)pyridinium chloride (VII) separated. Further recrystallization gave an analytical sample, mp 161–162° dec.

Anal. Calcd for $C_8H_{10}ClF_2NO_2$: C, 42.58; H, 4.47; F, 16.84; N, 6.21. Found: C, 42.67; H, 4.53; F, 17.01; N, 6.00.

In a similar manner IIIc and hydrochloric acid gave a 45% yield of (1-carboxy-1,1,2,2,3,3-hexafluoro-4,4-dihydroxypentyl)pyridinium betaine (VIc), mp 170–171° dec, upon recrystallization from hot water; about 5% of the unchanged starting material was recovered.

Anal. Calcd for $C_{11}H_9F_6NO_4$: C, 39.65; H, 2.72; F, 34.22; N, 4.20. Found: C, 39.54; H, 2.76; F, 34.06; N, 4.02.

By back-titration with hydrochloric acid of a sodium hydroxide solution of the product, its equivalent weight was found to be 330 (calcd 333).

Upon similar treatment of the five-membered ring betaine IIIb there was recovered 96% of the starting material. Refluxing IIIb with 50% sulfuric acid for 15 hr gave a 50% yield of (1-carboxy-1,1,2,2-tetrafluoro-3,3-dihydroxybutyl)pyridinium betaine (VIb), mp 204–205° dec (recrystallized from hot water), in addition to 28% of the starting material.

Anal. Calcd for $C_{10}H_9F_4NO_4$: C, 42.41; H, 3.20; F, 26.84; N, 4.95; neut equiv, 283. Found: C, 42.60; H, 3.25; F, 26.77; N, 4.91; neut equiv, 261.

The pmr spectrum of the product VIb in trifluoroacetic acid showed a single peak at τ 3.77 and a complex multiplet at τ 0.97–1.82, relative to internal TMS; the ratio of integrated areas was in fair agreement with the expected 2:5. IIIb itself has a complex multiplet in the range τ 0.50–1.90 in the same solvent.

---

(7) Melting points are uncorrected. Analyses were by Midwest Microlab, Inc., Indianapolis, Ind., and Galbraith Laboratories, Inc., Knoxville, Tenn. Mention of a product or a company does not imply endorsement by the Department to the exclusion of others which may be equally satisfactory.

(8) O. Scherer, German Patent 856,145 (1952).

Acknowledgment.—The authors are grateful to members of Spectroscopy Investigations of this Laboratory for many of the infrared spectra, to Dr. Robert Barker and Gordon J. Boudreaux for the nmr spectra, and to Mrs. Ann Alford for the molecular weights.

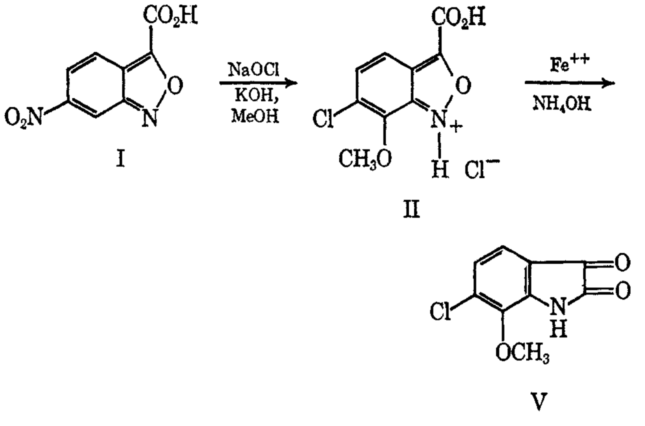
Application of the Haloalkoxy Reaction to 6-Nitroanthroxanic Acid[1a]

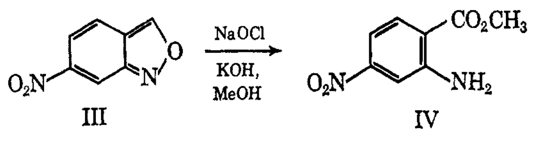
D. R. ECKROTH,[1b] T. G. COCHRAN, AND EDWARD C. TAYLOR

Department of Chemistry, Princeton University, Princeton, New Jersey

Received November 10, 1965

In a series of papers Mallory[2] and co-workers investigated a novel conversion, called the "haloalkoxy substitution reaction," in which the replacement of a nitro group by a chlorine and of an adjacent ring hydrogen by a methoxy group is effected by treatment of certain aromatic nitro compounds with aqueous sodium hypochlorite in alkaline methanol solution. Mallory demonstrated that this reaction takes place with nitro-substituted benzofurazans and their corresponding N-oxides, with 5-nitro-2-phenylbenzotriazole, and with 6-nitro-2,3-diphenylquinoxaline, and he suggested that the reaction may be general for molecules having a nitrogen heterocycle fused to the ring bearing the replaceable nitro group.





In support of this suggestion, we have found that 6-nitroanthroxanic acid (I) also undergoes the "haloalkoxy substitution reaction." Compound I is converted under the conditions described by Mallory to 6-chloro-7-methoxyanthroxanic acid hydrochloride (II). The structure of II was confirmed by its nmr spectrum, which exhibited two doublets of an AB system due to the two adjacent ring protons ($J = 9.0$ cps). Attempts to carry out an analogous conversion on 6-nitroanthranil (III) were unsuccessful because III is easily ring opened under the basic reaction conditions to methyl 4-nitroanthranilate (IV).

Since anthroxanic acids are easily converted to isatins by reductive cleavage of the isoxazole ring,[3] the "haloalkoxy substitution reaction" applied to nitro-substituted anthroxanic acids is potentially useful as a means of synthesizing certain isatins with adjacent ring substituents. Illustrative of this synthetic potential is the conversion of II to 6-chloro-7-methoxyisatin (V) with ferrous sulfate and ammonia.

Experimental Section[4]

The preparations of 6-nitroanthroxanic acid and 6-nitroanthranil have been described in a previous paper.[5]

6-Chloro-7-methoxyanthroxanic Acid Hydrochloride (II).—A solution of 0.5 g (0.0024 mole) of 6-nitroanthroxanic acid (I) and 0.8 g of potassium hydroxide (0.014 mole) in 50 ml of methanol was stirred magnetically and heated at reflux during the dropwise addition of 65 ml of aqueous sodium hypochlorite solution.[6] The solution was maintained at 60–65° during the addition, over 15 min, of the hypochlorite solution and for 20 min more, after which time most of the methanol was removed at aspirator pressure on a rotating flash evaporator. The flask was cooled in ice and acidified with 2 *N* hydrochloric acid. The yellow crystals of II were collected by filtration and washed with ice-cold water to give 0.25 g (40%): mp 182°; $\lambda_{\max}^{\mathrm{EtOH}}$ 229 mμ (ϵ 26,900); $\nu_{\max}$ 3535, 3450, 1690, 1637, 1546, 1520, 1275, 800, and 780 cm^{-1}.

Anal. Calcd for $C_9H_7N_4Cl \cdot HCl$: C, 40.91; H, 2.67; N, 5.31. Found: C, 40.61; H, 2.36; N, 5.11.

6-Chloro-7-methoxyisatin (V).—To a solution containing 5 ml of water and 1.5 ml of concentrated ammonium hydroxide was added 0.15 g of 6-chloro-7-methoxyanthroxanic acid hydrochloride (II) followed by 1.0 g of $FeSO_4 \cdot 7H_2O$. The solution was allowed to stand at room temperature for 30 min, after which time 20 ml of water was added. The mixture was shaken and filtered, and the filtrate was acidified with 15 ml of 2 *N* hydrochloric acid. The orange crystals of V which separated on standing were collected by filtration to give 0.09 g (74%): mp 179°; $\lambda_{\max}^{\mathrm{EtOH}}$ in mμ (ϵ) 216 (21,600), 248 (17,000), 255 (15,200), 311 (6100); $\nu_{\max}$ 3225, 1770, 1736, 1615, 1325, 1275, 1040, and 760 cm^{-1}.

Anal. Calcd for $C_9H_6NO_3Cl$: C, 51.09; H, 2.86; N, 6.62; Cl, 16.75. Found: C, 50.92; H, 3.00; N, 6.67; Cl, 17.03.

---

(1) (a) This work was supported in part by a grant (CA-02551) to Princeton University from the National Cancer Institute, National Institutes of Health, Public Health Service. (b) National Institutes of Health Predoctoral Fellow, 1962–1965.

(2) Part IV: F. B. Mallory, C. S. Wood, and B. M. Hurwitz, *J. Org. Chem.*, **29**, 2605 (1964).

(3) A procedure for reducing anthroxanic acid to isatin was described by A. Reissert, *Ber.*, **41**, 3921 (1908).

(4) All melting points are corrected.

(5) D. R. Eckroth, T. G. Cochran, and E. C. Taylor, in press.

(6) The aqueous sodium hypochlorite solution used in this work was the commercial product Clorox.

Protonolysis of 2-Isopropoxy-2-methyl-1-methylenecyclopropane. A Stable Unsaturated Carbonium Ion

T. C. SHIELDS, B. A. SHOULDERS, AND P. D. GARDNER[1]

Department of Chemistry, University of Texas, Austin, Texas

Received November 1, 1965

The study of carbonium ion structures was greatly facilitated by the discovery that nmr data can be obtained quickly and simply for solutions in strong acids.[2] Ions studied in this way are usually produced by protonation of a double bond or by protonolysis of a hy-

---

(1) Department of Chemistry, University of Utah, Salt Lake City, Utah.

(2) *Cf.* N. C. Deno, *Chem. Eng. News*, **42**, 88 (1964).