4 hr. at reflux temperature. Solution was not observed during this time. The reaction was terminated and the viscous oil on the bottom of the mixture solidified on cooling. This material was recrystallized from absolute ethanol. Four grams (50%) of the starting material (m.p. 137–140.5°) was recovered. The ethanolic filtrate was diluted with a large volume of water. The resulting pale yellow precipitate was dissolved in ether and passed through a 12 × 1.5 in. column of alumina. A white, crystalline solid, 2,3,5,6-tetrafluorobiphenyl (XIX, 1.2 g., 17%), m.p. 102.5–104.5°, was obtained by evaporation of the ether solution. Recrystallization from 90–120° ligroin afforded the analytical sample, white needles, m.p. 104–106° (sublimes while melting).

Anal. Calcd. for $C_{12}H_6F_4$: C, 63.72; H, 2.67; F, 33.6. Found: C, 63.86; H, 2.68; F, 32.8.

The F^{19} nuclear magnetic resonance spectrum in acetone exhibits two multiplets of equal intensity at 62.8 and 67.4 p.p.m.

The Reaction of Stannous Chloride and Pentafluorophenylhydrazine in Concentrated Hydrochloric Acid.—Pentafluorophenylhydrazine (16.0 g., 0.081 mole) and stannous chloride dihydrate (18.3 g., 0.081 mole) were stirred and refluxed in 150 ml. of concentrated hydrochloric acid for 2.5 hr. No azeotrope or volatile distillate was obtained. Pentafluorophenylhydrazine hydrochloride (13.4 g., 71%), m.p. 238–240° (lit.[10] m.p. 239–241°), precipitated from the cooled reaction solution.

F^{19} Nuclear Magnetic Resonance Data.—The F^{19} spectra were run on a Varian V-4300-2 D.P. spectrometer at 40.0 Mc./sec. Chemical shifts are reported in parts per million from trifluoroacetic acid.

Acknowledgment.—The authors wish to thank J. V. Pustinger, Jr., of the Monsanto Research Corporation, for the determination and interpretation of the nuclear magnetic resonance spectra reported in this work.

1,1,2,2-Ethanetetracarboxaldehyde and Its Reactions

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Contribution No. 972 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington 98, Delaware

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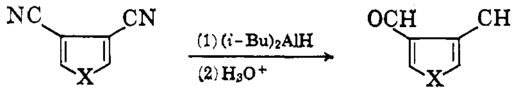
Synthesis of the title compound by cleavage of 3,4-furandicarboxaldehyde with hydroxide ion and related reactions are described. 1,1,2,2-Ethanetetracarboxaldehyde reacts with a variety of transition metal ions to form polymeric chelates and with hydrazine to form 4,4′-bipyrazolyl.

Compounds with two β-dicarbonyl systems capable of chelate formation have been commanding recent interest, mainly in connection with the quest for chelate polymers,[1] but also because of some bearing on the chelate aromaticity problem.[2]

Of particular interest from this point of view is 1,1,2,2-ethanetetracarboxaldehyde, the simplest difunctional β-dicarbonyl chelating agent and one where coplanarity of the two ring systems is most likely to be achieved. Its preparation by the present route[3] and by a different one[4] has been reported recently. Our synthesis of this compound was approached by way of an intermediate containing the desired carbon skeleton that required only modification of functional groups. The unknown 3,4-furandicarboxaldehyde was an attractive choice, since hydrolytic ring opening could convert it to 1,1,2,2-ethanetetracarboxaldehyde.

A number of straightforward approaches to 3,4-furandicarboxaldehyde failed. Thus, Rosenmund reduction of 3,4-furandicarbonyl chloride[5] resulted in decarbonylation and the isolation of 3-furancarboxaldehyde despite the use of quinoline–sulfur poison.[6] Similarly, the McFadyen–Stevens synthesis[7] gave no carbonyl-containing products.

3,4-Furandicarboxaldehyde was synthesized successfully by reducing 3,4-furandicarbonitrile[8] with diisobutylaluminum hydride.[9]



Ia, X = O
b, X = S

IIa, X = O
b, X = S

The success of this reduction prompted a study of this method for general conversion of polynitriles to polyaldehydes. 3,4-Thiophenedicarbonitrile, Ib, was successfully reduced to the corresponding dialdehyde, IIb, although in lower yields than the furan analog; 2,3,4,5-thiophenetetracarbonitrile,[10] on the other hand, could not be converted to the tetraaldehyde.

3,4-Furandicarboxaldehyde is quite stable to acids. Under drastic conditions, it is converted to black, polymeric solids. On the other hand, methanolic potassium hydroxide causes ring opening with such ease that mixing of IIa with a stoichiometric amount of aqueous metal or onium hydroxide at room temperature leads to exothermic formation of the diide III. While no precedent is known for such a facile opening of the furan ring with hydroxide ion,[11] a very plausible mechanism can be written for this reaction. By the same

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[1] (a) J. S. Oh and J. C. Bailar, Jr., *J. Inorg. Nucl. Chem.*, **24**, 1225 (1962); (b) R. G. Charles, *J. Polymer Sci.*, **1**, 267 (1963); (c) V. V. Korshak, E. S. Kronganz, A. M. Sladkov, V. E. Sheina, and L. K. Luneva, *Vysokomolekul. Soedin.*, **1**, 1765 (1959); (d) V. V. Korshak and S. V. Vinogradova, *Dokl. Akad. Nauk SSSR*, **138**, 1353 (1961).

[2] The aromaticity of metal chelates, while intuitively satisfying and easy to accept, has not yet found expression in terms of MO calculations. The chemical reactivity of chelates of a type that could be reconciled with quasiaromaticity is being studied fairly extensively. For a recent review with pertinent references, see J. P. Collman, Advances in Chemistry Series, No. 37, American Chemical Society, Washington, D. C., 1963, p. 78.

[3] S. Trofimenko, *J. Am. Chem. Soc.*, **85**, 1357 (1963).

[4] Z. Arnold, *Collection Czech. Chem. Commun.*, **27**, 2993 (1962).

[5] G. Stork, *J. Am. Chem. Soc.*, **67**, 84 (1945).

[6] E. B. Hershberg and J. Cason, *Org. Syn.*, **21**, 84 (1951); E. Mosettig and R. Mozingo, *Org. Reactions*, **4**, 362 (1948).

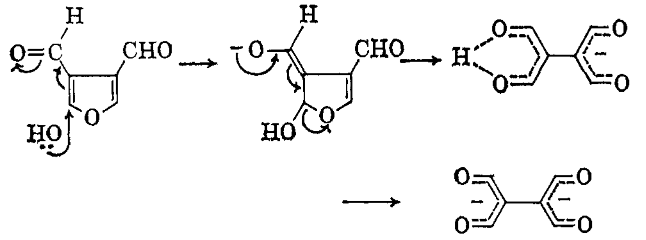
[7] E. Mosettig, *ibid.*, **8**, 232 (1954).

[8] C. D. Weiss, *J. Org. Chem.*, **27**, 3514 (1962).

[9] (a) L. I. Zakharkin and I. M. Khorlina, *Dokl. Akad. Nauk SSSR*, **116**, 422 (1957); (b) A. E. G. Miller, J. W. Biss, and L. H. Schwartzmann, *J. Org. Chem.*, **24**, 627 (1959).

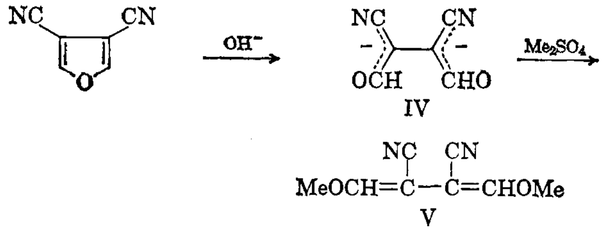
[10] H. E. Simmons, R. D. Vest, D. C. Blomstrom, J. R. Roland, and T. L. Cairns, *J. Am. Chem. Soc.*, **84**, 4746 (1962).

[11] Under drastic conditions 2-phenyl-4-benzoylfuran was reported to be cleaved by KOH: R. C. Fuson, C. L. Fleming and R. Johnson, *ibid.*, **60**, 1994 (1938). On the other hand, diethyl 3,4-furandicarboxylate was rapidly saponified by alcoholic KOH, the furan ring remaining intact: T. Reichstein, A. Grüssner, K. Schindler, and E. Hardmeier, *Helv. Chim. Acta*, **16**, 276 (1933).



III

token, any furan substituted in positions 3 and 4 with electron-delocalizing, yet base-resistant, groups should be similarly cleaved to a diide.



This was confirmed by an analogous cleavage of 3,4-furandicarbonitrile, although this reaction proceeded less cleanly than with IIa. Since in practice the success of the reaction depends on the precipitation of the diide salt, and a cyano group is inferior to the formyl group with respect to chelation, much better results would be anticipated with nonlinear substituents such as nitro, sulfonyl, etc.

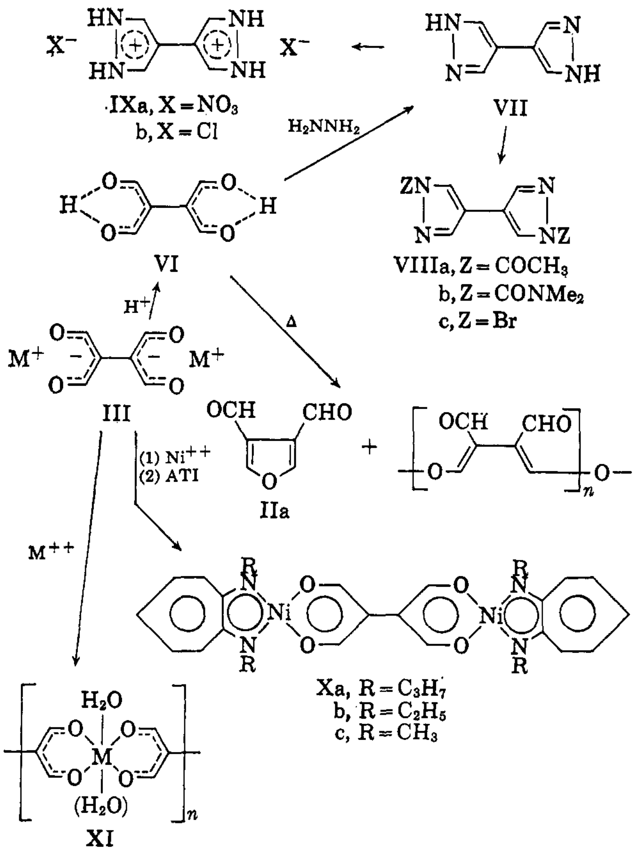
While the diide III could be readily converted to the free acid, VI, the analogous acid from IV could not be isolated. Treatment of IV with methyl sulfate, however, resulted in the formation of a mixture of *cis*- and *trans*-2,3-bis(methoxymethylene)succinonitrile (V), melting over a wide range, from which a pure isomer, m.p. 208°, could be isolated by chromatography.

1,1,2,2-Ethanetetracarboxaldehyde melts at 194–199° with dehydration to its progenitor and to polymeric products. The saturated solution of VI has a pH of 2.35, making it a considerably stronger acid than 3,4-diacetyl-2,5-hexanedione.[12]

VI reacts readily with hydrazine, forming 4,4′-bipyrazolyl (VII), which was characterized as the dinitrate and the dihydrochloride, and also affords N,N′ derivatives such as diacetyl, bis(dimethylcarbamoyl) and dibromo. (See Chart I).

The dianion III undergoes a two-electron oxidation by bromine, iodine, ferric, and mercurous ions, and forms polymeric chelates upon mixing with solutions of most polyvalent metal ions (*e.g.*, with Mn^{+2}, Fe^{+2}, Co^{+2}, Cu^{+2}, Zn^{+2}, Sn^{+2}, Pb^{+2}, VO^{+2}, Al^{+3}, and Cr^{+3}). All these precipitates are insoluble in water and organic solvents. While thermally stable, they are readily decomposed by dilute acids and give instantaneous ferric chloride and 2,4-DNP tests. Their infrared spectra are characterized by broad bands in the 1500–1600- and 1300–1400-cm.$^{-1}$ regions, along with three small peaks in the 1240–1270-cm.$^{-1}$ region and stronger, broad bands around 810–820 and 740–750 cm.$^{-1}$ (in addition to the bands due to water of hydration). In this respect, the spectra resemble very closely those of the free acid, and the sodium, potassium, or silver salts. One exception is the Cu(II) chelate which has a simpler spectrum with relatively sharp bands at 1620, 1300 (broad), and 910 cm.$^{-1}$. Another is Ni(II) which forms no precipitate at room temperature and does so only on boiling the solution. This product has the same infrared spectrum as the one derived from Cu(II). Both these compounds give ferric chloride and 2,4-DNP tests very sluggishly. That chelation of the Ni(II) ion does take place at room temperature is evidenced by the formation of mixed chelates X, on adding the second ligand to the solution. These monomeric chelates are square planar and diamagnetic in contrast to nickel aminotroponeiminates which, for steric reasons, are tetrahedral and exhibit sizable contact shifts.[13] The polymeric chelates exhibit resistivities in the order of 10^{12}–10^{15} ohm/cm. and display no infrared or ultraviolet photoconductivity.

Chart I



Experimental

The starting material, diethyl 3,4-furandicarboxylate, was prepared in two ways, from diethyl acetylenedicarboxylate[14] or from diethyl succinate.[15] The latter method is preferred for large-scale synthesis. 3,4-Furandicarbonitrile was obtained by the published method.[8]

3,4-Furandicarboxaldehyde (IIa).—3,4-Furandicarbonitrile (6.0 g., 0.051 mole) was stirred under nitrogen in 150 ml. of dry benzene. To the suspension diisobutyl aluminum hydride (21 ml., 0.114 mole) was added slowly. The mixture turned amber, warmed up to about 50°, and the solid dissolved. Toward the end of the addition, the solution became viscous and gelatinous. After being stirred for 2 hr. at room temperature, the complex

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[12] pK_a values of 9.43 and 13.54 (in 50% aqueous dioxane) are reported for the latter: W. C. Fernelius, Wright Air Development Center Technical Report, "Coordination Polymers," WADC-TR-56-202, p. 17.

[13] D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, *J. Chem. Phys.*, **37**, 347 (1962).

[14] O. Diels and K. Alder, *Ann.*, **490**, 243 (1931); O. Alder and H. F. Rickert, *Ber.*, **70**, 1354 (1937).

[15] E. C. Kornfeld and R. G. Jones, *J. Org. Chem.*, **19**, 1674 (1954).

was decomposed by careful addition of methanol (exothermic reaction, gas evolved).

The almost-solid mixture was then transferred to an 800-ml. beaker and decomposed further with ice and dilute sulfuric acid until all the lumps dissolved. The layers were separated and the aqueous layer was extracted four times with 200-ml. portions of ether. The organic layers were combined, dried ($MgSO_4$), stirred with Darco, filtered, and stripped. The residue was recrystallized from carbon tetrachloride. First crop, 2.8 g., had m.p. 77–78°. The mother liquor was evaporated, the residue was sublimed, and the oily sublimate was recrystallized from carbon tetrachloride to yield an additional 0.7 g. of product, m.p. 76–78°, for a total yield of 3.5 g. or 56%.

Anal. Calcd. for $C_6H_4O_3$: C, 58.1; H, 3.25; mol. wt., 124. Found: C, 58.5; H, 3.52; mol. wt. (b.p. in ethylene chloride), 129.

The n.m.r. spectrum consisted of two 1:1 singlets at τ 1.88 (α-hydrogen) and −0.15 (-CHO).

IIa forms a dark red bis-2,4-dinitrophenylhydrazone, m.p. 280–282° (from dimethylformamide).

Anal. Calcd. for $C_{18}H_{12}N_8O_9$: N, 23.2; mol. wt., 484. Found: N, 23.2; mol. wt., 469.

3,4-Thiophenedicarboxaldehyde (IIb).—3,4-Thiophenedicarbonitrile[16] (5.8 g., 0.043 mole) was reduced with diisobutyl aluminum hydride (18 ml., 10% excess) as above. The yield of crude product was 1.36 g. (23%). Sublimation afforded white needles, m.p. 78–80°.

Anal. Calcd. for $C_6H_4O_2S$: C, 51.4; H, 2.88. Found: C, 51.4; H, 2.83.

N.m.r. showed two 1:1 singlets, τ 1.67 and −0.36.

Potassium Salt of 1,1,2,2-Ethanetetracarboxaldehyde (III, M = K).—3,4-Furandicarboxaldehyde (0.73 g.) was stirred at room temperature with a large excess of potassium hydroxide in methanol. An exothermic reaction took place and a white solid separated. It was filtered, washed with methanol, and dried, yielding 1.1 g. (86%). This salt cannot be conveniently recrystallized. It gives instantaneous $FeCl_3$ and 2,4-DNP tests, the former fading rapidly. Infrared (Nujol mull): 6.5 (broad), 7.3 (broad), 7.80, 7.94, 8.06, 12.25 (sh at 12.50), and 13.42 (sh at 13.8) μ. Ultraviolet: λ_{max} 270 mμ (ϵ 39,800).

Tetramethylammonium Salt of 1,1,2,2-Ethanetetracarboxaldehyde (III, M = NMe₄).—3,4-Furandicarboxaldehyde (1.54 g., 0.01235 mole) was stirred at room temperature with 22.4 g. of 10% aqueous tetramethylammonium hydroxide (0.247 mole). The solution was warmed briefly and then evaporated to dryness. The crude salt, obtained in quantitative yield, was recrystallized from isopropyl alcohol and dried at 130° (5 mm.). Tetramethylammonium 1,1,2,2-tetraformylethanediide darkens and decomposes at 216–217° with evolution of trimethylamine. It is very hygroscopic.

Anal. Calcd. for $C_{14}H_{28}N_2O_4$: C, 58.3; H, 9.79; N, 9.71. Found: C, 58.1; H, 9.73; N, 10.1.

Solutions of the **sodium salt of VI** were prepared by stirring known amounts of VI in water, containing a stoichiometric amount of sodium hydroxide.

1,1,2,2-Ethanetetracarboxaldehyde (VI). A.—The potassium salt (III, M = K, 0.47 g.) was dissolved in water and run through a column packed with Amberlite IR-120 ion-exchange resin. The acid eluate was evaporated to dryness, yielding 0.23 g. (74%) of VI, which was purified by sublimation at 170° (5 mm.). It may also be recrystallized from boiling water. The pure material melts with decomposition at 194–199°.

Anal. Calcd. for $C_6H_6O_4$: C, 50.7; H, 4.26. Found: C, 50.8; H, 4.08.

On resublimation of old samples a more volatile sublimate (5%) was also obtained, identified as IIa by mixture melting point and infrared, and a nonvolatile residue remained containing a sharp band at 5.96 μ.

B.—A suspension of IIa (1.24 g.) in 10 ml. of water was stirred with 1.4 g. of potassium hydroxide pellets. An exothermic reaction took place. The dark yellow solution was stirred for 1 hr., then cooled, and acidified with concentrated hydrochloric acid. The precipitate was filtered, washed with water and ethanol, and air dried. The yield of VI was 1.1 g. (78%).

2,3-Bis-(methoxymethylene)succinonitrile (V).—3,4-Furandicarbonitrile (5.9 g.) was added all at once to 100 ml. of freshly prepared, saturated methanolic KOH solution stirred at 50°. After 5 min. a sudden precipitation took place, and the flask contents almost solidified. The thick slurry was filtered and pressed dry. The solid was immediately dissolved in a minimum amount of water and treated portionwise with methyl sulfate until the mixture was acidic. It was then saturated with sodium chloride and filtered. Yield of the washed and dried product was 3.5 g. Concentration of the mother liquor yielded 0.9 g. of a second crop, for a total yield of 4.4 g. or 54%.

The material can be distilled *in vacuo*, sublimed, and recrystallized. Despite numerous purifications, however, including chromatography on alumina, the material melted over a wide range, 110–140°.

Anal. Calcd. for $C_8H_8N_2O_2$: C, 58.5; H, 4.91; N, 17.1. Found: C, 58.4; H, 4.95; N, 17.0.

From one of the chromatography fractions a pure isomer, m.p. 208°, was isolated in small yield.

4,4′-Bipyrazolyl.—1.0 g. of VI was added in one portion to 1 g. (excess) of hydrazine hydrate in 20 ml. of water. The solution was stirred overnight. The precipitated 4,4′-bipyrazolyl was filtered, washed with small amounts of water and methanol, and air-dried, yielding 0.90 g. or 95%. The material was purified by sublimation at 250° (1 mm.). It remained unchanged up to 320°. Infrared: 3.20, 7.74, 8.69, 8.81, 9.7, 10.35, 10.95, 11.4, and 12.21 μ.

Anal. Calcd. for $C_6H_6N_4$: C, 53.7; H, 4.51; N, 41.8. Found: C, 54.0; H, 4.45; N, 41.6.

4,4′-Bipyrazolyl Dinitrate (IXa).—Heating of 4,4′-bipyrazolyl in concentrated nitric acid gave, on cooling, a dinitrate, m.p. 249–250°.

Anal. Calcd. for $C_6H_8N_6O_6$: C, 27.7; H, 3.10; N, 32.3. Found: C, 28.0; H, 3.23; N, 32.4.

4,4′-Bipyrazolyl Dihydrochloride (IXb).—Heating of 4,4′-bipyrazolyl in concentrated hydrochloric acid gave, on cooling, a dihydrochloride, m.p. 310°.

Anal. Calcd. for $C_6H_8Cl_2N_4$: C, 34.8; H, 3.86. Found: C, 35.2; H, 4.07.

1,1′-Diacetyl-4,4′-bipyrazolyl (VIIIa).—4,4′-Bipyrazolyl (0.100 g.) was stirred at room temperature with 4 ml. of acetic anhydride and 1 ml. of pyridine. The suspension was refluxed until a solution was obtained; it deposited crystals on cooling. The product was recrystallized from acetic acid, yielding 0.140 g. (87%), m.p. 251–252°.

Anal. Calcd. for $C_{10}H_{10}N_4O_2$: C, 55.0; H, 4.62. Found: C, 55.1; H, 4.83.

1,1′-Bis(dimethylcarbamoyl)-4,4′-bipyrazolyl (VIIIb).—4,4′-Bipyrazolyl (5.0 g.) was refluxed overnight with 10 g. of dimethylcarbamyl chloride in 50 ml. of pyridine. The reaction mixture was evaporated at reduced pressure almost to dryness. The moist residue was stirred with 100 ml. of water and made basic by adding a slight excess of triethylamine. The resulting solid was filtered, washed with water and ethanol, and dried at 120° (5 mm.) overnight, yielding 6.8 g. (63%) of VIIIb. The product was recrystallized from ethyl acetate, m.p. 197–199°.

Anal. Calcd. for $C_{12}H_{16}N_6O_2$: C, 52.2; H, 5.84. Found: C, 52.2; H, 5.91.

1,1′-Dibromo-4,4′-bipyrazolyl (VIIIc).—4,4′-Bipyrazolyl (1.0 g., 0.0075 mole) was stirred in 25 ml. of dry pyridine and bromine (2.4 g., 0.0150 mole) was added slowly. The mixture was stirred until all solids dissolved. The dark brown solution was evaporated on a steam bath at reduced pressure, the residue was stirred with water, and extracted with chloroform. The extracts were dried and concentrated, yielding a solid which was purified by sublimation. Yield of twice-sublimed product was 0.48 g. (22%). The material softened at 190°, and melted at 220–240°. It was sparingly soluble in ethyl acetate and chloroform.

Anal. Calcd. for $C_6H_4Br_2N_4$: C, 24.7; H, 1.37; Br, 54.9; N, 19.2. Found: C, 25.1; H, 1.35; Br, 54.8; N, 19.4.

Mixed Ligand Chelates (X). A. **R = C_3H_7.**—The disodium salt of VI (2.28 g., 0.0122 mole) was stirred in 80 ml. of water with 0.0245 mole of nickel acetate. To the stirred solution was added 5.0 g. of 1-propylamino-7-propylimino-1,3,5-cycloheptatriene (0.0245 mole) followed by about 50 ml. of methanol. The mixture was stirred overnight. The precipitate was filtered, washed with water and methanol, and air dried, yielding 4.66 g. (58%). Recrystallization from cyclohexane afforded bronze colored platelets, m.p. 236–237°. Ultraviolet[17] (chloroform): 296 mμ (ϵ 56,600), 309 (37,400), 238 (33,200), 413 (30,500), around 450 one or two shoulders, 500 (12,000), and a broad band at 659 (600).

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(16) Kindly provided by Dr. C. D. Weis.

(17) The ultraviolet spectra were measured by Dr. L. L. Anderson.

Anal. Calcd. for $C_{32}H_{42}N_4Ni_2O_4$: C, 57.9; H, 6.33; N, 8.44; Ni, 17.6; mol. wt., 663. Found: C, 57.2; H, 6.17; N, 8.35; Ni, 16.9; mol. wt. (b.p. in ethylene chloride), 650.

B. R = C_2H_5.—The ethyl analog was prepared in similar fashion. The crude solid was taken up in chloroform, dried with $MgSO_4$, filtered, and concentrated. Yield of this crystallized material was 21%. It was further purified by recrystallization from chlorobenzene. The pure product decomposed sharply at 285°. Ultraviolet[17] (chloroform): 499 mμ (ε 10,900), 460 (sh) (13,900), 412 (27,600), 338 (sh) (30,300), 318.5 (33,300), 278.5 (50,600), 655.4 (592), 498 (10,700).

Anal. Calcd. for $C_{28}H_{34}N_4Ni_2O_4$: C, 55.5; H, 5.61; N, 9.23. Found: C, 55.7; H, 5.57; N, 9.46.

C. R = CH_3.—The methyl analog was prepared as above. It was obtained in 8% yield as golden platelets (from chlorobenzene) that decompose sharply at 310°. Ultraviolet[17] (chloroform): 660.0 mμ (ε 1,140), 501 (11,400), 463 (12,700), 405 (31,200), 330 (38,200), 306 (38,900), 268 (58,200).

Anal. Calcd. for $C_{24}H_{26}N_4Ni_2O_4$: C, 52.4; H, 4.72; N, 10.2. Found: C, 52.7; H, 4.91; N, 10.1.

Polymeric Chelates of 1,1,2,2-Ethanetetracarboxaldehyde (XI). M = Co (Dihydrate).—A stirred suspension of 0.142 g. of VI in 20 ml. of water was slowly heated until all the solid dissolved. Cobaltous oxide (0.075 g.) was added, and the mixture was heated at 90° and stirred for 3 hr. It was then cooled and the precipitated solid was collected by filtration and washed with water and ethanol. There was obtained 0.167 g. (84% yield) of the cobalt (II) chelate dihydrate of VI as a light pink, microcrystalline solid.

Anal. Calcd. for $C_6H_8CoO_6$: C, 30.6; H, 3.40. Found: C, 30.0; H, 3.51.

The cobalt chelate remained unchanged, except for a slight darkening, when heated up to 310°. It gave instantaneous tests with ferric chloride and 2,4-dinitrophenylhydrazine.

M = Mn (Dihydrate).—To a solution of 0.01 mole of manganous acetate in 60 ml. of water was added a solution prepared by dissolving 1 g. of the sodium salt of VI (about 90% pure), in 50 ml. of water and acidifying with excess acetic acid,[18] the latter being added to destroy carbonate impurities present in the sample. After a few minutes a precipitate started separating; the mixture was stirred and boiled for 15 min. and then allowed to cool slowly to room temperature. After 6 hr., the precipitate was filtered, washed with water and methanol, and air-dried. There was obtained 1.39 g. (72% yield) of the white manganese (II) chelate dihydrate.

Anal. Calcd. for $C_6H_8MnO_6$: C, 31.1; H, 3.46; Mn, 23.8. Found: C, 31.8; H, 2.81; Mn, 23.9.

M = Cd (Dihydrate).—This material was prepared in 90% yield by the above method. It turns yellow at 240° and slowly darkens up to 320°.

Anal. Calcd. for $C_6H_8CdO_6$: C, 25.0; H, 2.78. Found: C, 24.6; H, 2.91.

M = Zn (Monohydrate).—Zinc oxide (0.0814 g., 0.001 mole) was stirred in 25 ml. of water with 0.142 g. (0.001 mole) of VI. After stirring for 30 min., the undissolved zinc oxide was removed by filtration. A white precipitate (0.066 g.) of the zinc (II) chelate monohydrate separated from the filtrate on standing.

Anal. Calcd. for $C_6H_6O_5Zn$: C, 32.2; H, 2.69; Zn, 29.3. Found: C, 31.1; H, 2.80; Zn, 29.2.

On heating, this material darkened slightly from 250° on but did not decompose up to 300°.

The chelates of Fe^{+2}, Cu^{+2}, Pb^{+2}, VO^{+2}, Al^{+3}, and Cr^{+3} were prepared by metathesis at room temperature, except for Ni^{+2}, which required boiling of the solution for 30 min. Their intractability precluded obtained good analyses although in qualitative respects (infrared spectra, carbonyl, and enol tests) they resembled the above compounds. The chelates of Cu^{+2} and Ni^{+2} had similar infrared spectra which were different from those of the other compounds, and the chelates were more stable toward hydrolysis.

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[18] 1,1,2,2-Ethanetetracarboxaldehyde salts are not affected by acetic acid. This is in contrast to the analogous salts of 3,4-diacetyl-2,5-hexanedione from which the weaker acid is immediately liberated.

Aziridines from Diazomethane and Fluorine-Substituted Imines

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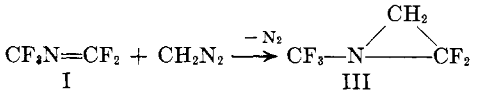
Diazomethane reacted with fluorine-substituted imines to give aziridines directly. However, when 2-(2,4-dinitrophenyl)-2H-azirine (IX) was used, no nitrogen evolution was observed and 1-(3-azido-2-methylpropenyl)-2,4-dinitrobenzene (X) was formed. The energy of activation and the frequency factor for the inversion of nitrogen in 2,2-difluoro-1-trifluoromethylazirine (IV) were found to be 5.5 ± 0.5 kcal. and 5 × 10^8 sec.$^{-1}$, respectively, by means of F^{19} n.m.r. spectroscopy.

The addition of diazomethane to various Schiff bases forms 1,2,3-triazolines.[1] Attempts to obtain aziridines by pyrolysis or photolysis of the above triazolines have failed, degradation products being obtained instead.[2] Aziridines, that were hydrolytically unstable, have been obtained by the addition of dichlorocarbene to anils,[3] and more recently, aziridinium perchlorates were prepared by the addition of diazomethane to iminium perchlorates.[4]

In this paper, the facile reaction of diazomethane with negatively substituted imines to give the corresponding aziridines is reported. The imines used were perfluoro-2-azapropene[5] (I), (1-chloro-2,2,2-trifluoroethylideneamino)pentafluorosulfur[6] (IIa), and (1-azido-2,2,2-trifluoroethylideneamino)pentafluorosulfur (IIb) prepared from IIa by treatment with sodium azide in nitrobenzene or acetonitrile.

The reaction of diazomethane with perfluoro-2-azapropene (I) in xylene at 0° evolved 1 molar equiv. of nitrogen and gave the aziridine III. The higher boiling



I III

xylene was used as a solvent instead of ethyl ether, because the volatile product could be distilled out of the mixture. In the case of the imines IIa and IIb, the reaction was run in ethyl ether and there were obtained the aziridines IVa and IVb, Va, and Vb, respectively.

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