ples. The ketoxime derivative of 2-methylpyrrole was prepared from some of the fractions.

The work done thus far does not exclude the possibility of the presence of lower-boiling 1-methylpyrrole or of other 1-substituted pyrroles, as they would not give the same reaction with potassium hydroxide.

Experimental

Preparation of Shale-Oil Naphtha.—Crude shale oil prepared in the N-T-U retorts[3] at the Bureau of Mines Oil-Shale Demonstration Plant at Rifle, Colo., was distilled at an atmospheric pressure of 585 mm. to give 15 gallons of overhead product with a 306° end-point. Shale-oil naphtha with an end-point of 195° was prepared from this material by fractionating in a vacuum-jacketed distilling column 62 cm. tall and 30 mm. inside diameter, packed with stainless-steel helices. The column, which was equipped with an automatic take-off device, had an estimated theoretical-plate value of at least 10. The reflux ratio was maintained at an average of one take-off to four reflux, and the pot temperature never exceeded 230°. Approximately 5 gallons of naphtha was obtained and stored under nitrogen at $-5°$. To remove phenols and carboxylic acids, two 4-liter batches of the naphtha were extracted three times with 2 liters of 10% sodium hydroxide. Extraction was accomplished by vigorous mechanical shaking for 2 hours, with an hour for separation. The extracted naphtha was dried with anhydrous sodium sulfate.

Separation of Pyrroles.—The pyrroles were separated from the naphtha by treating them with solid potassium hydroxide. This was done in two stainless-steel autoclaves equipped with reflux condensers and water traps on the return lines. Each vessel was charged with approximately 3,000 g. of shale-oil naphtha from which tar acids had been extracted. Four hundred grams of solid potassium hydroxide was suspended in the liquid on a Monel-wire screen. The reaction was run at 165° under 400 mm. pressure. Considerable water was evolved and collected. After several days of reaction, excessive gas formation was evident, and the reaction was stopped. The tan-colored cakes of solid residue found in the reaction vessels were washed with pentane and dried in a vacuum desiccator. The potassium salts of the pyrrolic compounds and excess potassium hydroxide were added to water, and the hydrolyzed pyrroles were steam distilled. Approximately 116 ml. of a yellowish oil was obtained. The oil darkened rapidly and developed a reddish color despite being kept at $-5°$ under a nitrogen atmosphere.

Distillation of Pyrroles.—Sixty-eight grams of pyrrolic compounds was subjected to fractional distillation in a micro distilling column packed with stainless-steel helices. The column was vacuum-jacketed, equipped with an automatic take-off device, and had the following dimensions: height 30 cm., diameter 11 mm. Reflux ratio was maintained at 20. Thirteen fractions of approximately 1 ml. each were obtained. The refractive indices of these fractions are shown in Fig. 1.

Identification of Pyrrole.—Fractions 7 and 8 from the distillation reacted with phthalic anhydride according to the method of Ciamician and Dennstedt.[4] Recrystallization yielded yellow-orange needles melting at 239° (literature[4] 240°). Pyrrole phthalate prepared from Eastman Kodak Co. white-label pyrrole melted at 240° and a mixed melting point gave 239°.

Anal. Calcd. for $C_{12}H_8O_2N$: N, 7.11. Found: N, 7.28.

The remainder of fractions 7 and 8 plus 9 was used to form the tetraiodo derivative according to the method of Ciamician and Silber.[5] Flaky yellow crystals were obtained that had no sharp melting point but exhibited a gradual transition between being partly melted and partly decomposed in the temperature range of 140–150°. Similar melting phenomena were noted with tetraiodopyrrole prepared from Eastman Kodak Co. white-label pyrrole. According to the literature, tetraiodopyrrole melts with decomposition in the temperature range 140–150°.

Anal. Calcd. for C_4I_4NH: N, 2.45. Found (from shale oil): N, 2.44. Found (from Eastman pyrrole): N, 2.40.

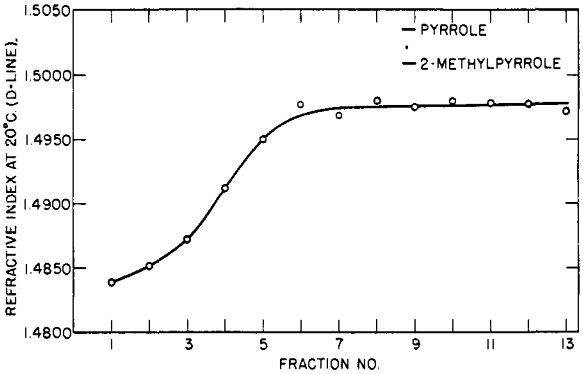

Fig. 1.—Refractive indices of fractions from distillation of pyrroles.

Identification of 2-Methylpyrrole.—Hydroxylamine has been reported[6] to react with pyrroles by opening the pyrrole ring with formation of the ketoxime or aldoxime. Five grams of pyrrolic materials from combination of fractions 2–10 were mixed with 6 g. of hydroxylamine hydrochloride, 4 g. of anhydrous sodium carbonate and 50 g. of 95% ethanol and refluxed for 18 hours. A pale yellow-white crystalline material was found in the reflux condenser, which, after drying, melted at 69°. The value reported by Oddo and Mameli[6] for the ketoxime derivative of 2-methylpyrrole is 69–70°. Molecular weight of the material by the Rast cryoscopic camphor method gave 129.5 (calcd. 130).

Anal. Calcd. for $C_5H_{10}O_2N_2$: N, 21.52. Found: N, 21.54.

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[4] G. Ciamician and M. Dennstedt, *Ber.*, **17**, 2957 (1884).

[5] G. Ciamician and P. Silber, *ibid.*, **18**, 1766 (1885).

(6) G. Ciamician and M. Dennstedt, *ibid.*, **17**, 533 (1884); B. Oddo and R. Mameli, *Gazz. chim. ital.*, **44**, II, 162 (1914).

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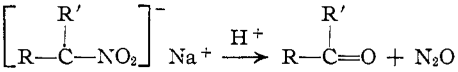
Received March 26, 1951

The Regeneration of Nitroparaffins from Their Salts[1]

By Nathan Kornblum and Galen E. Graham

In 1873 Victor Meyer reported that the salts of aliphatic nitro compounds yield the original nitro compound upon treatment with dilute sulfuric acid.[2] However, some years later Nef[3] showed that the regeneration of aliphatic nitro compounds from their salts is no routine matter. When a cold aqueous solution of the sodium salt of a nitroparaffin is added to cold dilute sulfuric acid (or hydrochloric acid) the nitroparaffin is not obtained. Instead, the reaction which has come to be known by his name occurs.[4]

$$[\mathrm{RCHNO_2}]^-\mathrm{Na}^+ \xrightarrow{\mathrm{H}^+} \mathrm{RCHO} + \mathrm{N_2O}$$



$$\left[\mathrm{R}-\overset{\overset{\mathrm{R'}}{|}}{\mathrm{C}}-\mathrm{NO_2}\right]^- \mathrm{Na}^+ \xrightarrow{\mathrm{H}^+} \mathrm{R}-\overset{\overset{\mathrm{R'}}{|}}{\mathrm{C}}=\mathrm{O} + \mathrm{N_2O}$$

When the order of mixing is reversed, *i.e.*, the acid is added *to* the salt, some nitroparaffin is recovered; but even here the Nef reaction predominates. So readily does it proceed that it is the basis of a general method of synthesizing higher aldoses and ketoses.[5]

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(1) Paper III in the series "The Chemistry of Aliphatic and Alicyclic Nitro Compounds." For paper II see This Journal, **70**, 746 (1948).

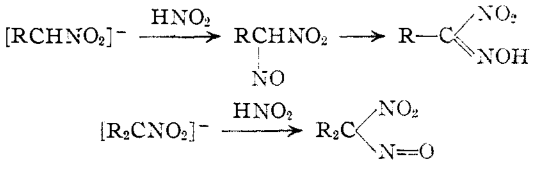
(2) Victor Meyer, *Ber.*, **6**, 1492 (1873).

(3) J. U. Nef, *Ann.*, **280**, 266 (1894).

(4) H. B. Hass and E. Riley, *Chem. Revs.*, **32**, 373 (1943); K. Johnson, Ph.D. Thesis, Purdue University, 1937.

(5) J. C. Sowden and H. O. L. Fischer, This Journal, **67**, 1713 (1945); J. C. Sowden, *ibid.*, **72**, 3325 (1950).

The problem of regenerating nitroparaffins is further complicated by the fact that acidification of solutions of their salts liberates nitrous acid which then proceeds to nitrosate undecomposed nitroparaffin salt.[6] This reaction has recently been patented as a method for preparing nitrolic acids and pseudonitroles.[7]



$$[RCHNO_2]^- \xrightarrow{HNO_2} RCH(NO)NO_2 \longrightarrow R{-}C(NO_2){=}NOH$$

$$[R_2CNO_2]^- \xrightarrow{HNO_2} R_2C(NO_2)N{=}O$$

Recourse to the use of weak acids for regenerating nitroparaffins results in somewhat improved yields, presumably by minimizing the Nef reaction. Salicylic acid,[8] dilute acetic acid,[9] carbon dioxide,[9] boric acid[10] and hydrogen sulfide[10] have all been recommended but without any statement concerning yields. As shown in Table I, dilute acetic acid and carbon dioxide are not always superior to hydrochloric acid.

TABLE I

THE REGENERATION OF NITRO COMPOUNDS FROM THEIR SALTS

Nitro compound[a]	Acid used[b]	n^{20}D of original nitro compound	n^{20}D of regenerated nitro compound	Recovery, %
1-Nitrobutane	$NH_2OH \cdot HCl$	1.4108	1.4111	92[c]
2-Nitrobutane	$NH_2OH \cdot HCl$	1.4040	1.4042	90
2-Nitrobutane	AcOH–Urea	1.4044	1.4042	91
3-Methyl-1-nitrobutane	$NH_2OH \cdot HCl$	1.4171	1.4174	86
1-Nitrohexane	$NH_2OH \cdot HCl$	1.4242	1.4239	89
1-Nitrohexane	AcOH–Urea	1.4245	1.4244	95
1-Nitrohexane	AcOH	1.4245	1.4242	76
1-Nitrohexane	CO_2	1.4245	1.4245	53
1-Nitrohexane	HCl	1.4245	1.4239	34
Nitrocyclohexane	$NH_2OH \cdot HCl$	1.4611	1.4612	89[d]
Nitrocyclohexane	$NH_2OH \cdot HCl$	1.4614	1.4613	90[e]
Nitrocyclohexane	AcOH–Urea	1.4614	1.4612	93
Nitrocyclohexane	AcOH	1.4611	1.4615	74[c]
Nitrocyclohexane	$H_2NCONHNH_2 \cdot HCl$	1.4611	1.4611	88[c]
Nitrocyclohexane	$(N_2H_5)_2SO_4$	1.4611	1.4613	85[c]
Nitrocyclohexane	HCl	1.4611	1.4607	29[c]
Nitrocyclohexane	CO_2	1.4611	1.4613	54[c]
Phenylnitromethane	$NH_2OH \cdot HCl$	1.5331	1.5341	85[c]
Phenylnitromethane	AcOH–Urea	1.5342	1.5338	90
Phenylnitromethane	AcOH	1.5342	1.5335	83
Phenylnitromethane	HCl	1.5339	1.5334	81[c]
Phenylnitromethane	CO_2	1.5342	1.5340	55
1-Nitro-2-phenylethane	$NH_2OH \cdot HCl$	1.5276	1.5276	88

[a] Twenty-gram samples of nitro compound used in all cases. Unless otherwise specified the recoveries are reported for a single run. [b] 20% aqueous acids used in all cases. [c] Average of 2 runs. [d] Average of 6 runs. [e] 100% excess of $NH_2OH \cdot HCl$ employed.

It has now been found that acids such as hydroxylamine hydrochloride, semicarbazide hydrochloride, dihydrazine sulfate $[(N_2H_4)_2 \cdot H_2SO_4]$ and urea in aqueous acetic acid are very effective agents for regenerating nitroparaffins from their salts. Hydroxylamine hydrochloride and urea in aqueous acetic acid, which were studied most carefully, consistently give 85–95% yields of pure nitroparaffins. Urea in aqueous acetic acid is the least expensive of the various acids studied; since its use involves no inconvenience it is the reagent of choice.

The efficacy of these reagents apparently depends upon two factors: (1) their mild acidity which minimizes the Nef reaction and (2) the rapidity with which they destroy nitrous acid.[11,12,13] In the experiments recorded in Table I a minimal amount of nitrite ion was present since the alkaline solutions were prepared at or below 25° and then acidified immediately. The usefulness of the present procedures will become even more apparent in dealing with solutions of nitroparaffin salts which have stood for some time or which have suffered exposure to elevated temperatures.

That the salts of nitrocyclohexane and 1-nitrohexane give poor yields (29 and 34%, respectively) of the parent nitro compounds upon acidification with hydrochloric acid is not surprising. It is of interest, however, that a number of salts can be acidified with mineral acids and still give an excellent yield of the parent nitro compound. Thus an 81% yield of phenylnitromethane is obtained by treating its salt with hydrochloric acid (Table I); diethyl nitromalonate, $H{-}C{-}NO_2(COOC_2H_5)_2$, is formed in 92% yield from the sodium salt and concentrated hydrochloric acid[14]; trinitromethane is produced in excellent yield by acidifying its potassium salt with sulfuric acid and then steam distilling.[15] Also noteworthy is the preparation of hexanitroethane in 90% yield by treatment of the dipotassium salt of 1,1,2,2-tetranitroethane with a mixture of concentrated sulfuric acid and fuming nitric acid.[16]

It is clear that those salts which are least stabilized by resonance give the poorest yields of nitro compound upon acidification with strong acid. Perhaps of even more significance is the fact that the *aci* forms corresponding to these salts are likewise relatively little stabilized by resonance. To attempt an interpretation of these observations at this time would be premature in view of the complete lack of relevant information on which to base any mechanistic discussion.

Experimental

The following is typical of the procedure used, unless otherwise indicated, in obtaining the data of Table I. In all instances the mole ratios were identical with that described below.

Twenty grams (0.155 mole) of redistilled nitrocyclohexane (b.p. 108–110° (40 mm.); n^{20}D 1.4614) was placed in a 500-ml. flask equipped with a stirrer, a thermometer and a dropping funnel. Stirring was initiated and 62 g. (0.310 mole) of 20% aqueous sodium hydroxide was added drop-

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(6) Presumably the *aci* form of the nitroparaffin also nitrosates rapidly. Also, it is likely that N_2O_3 and not nitrous acid is the actual nitrosating agent. Compare E. D. Hughes, C. K. Ingold and J. H. Ridd, *Nature*, **166**, 642 (1950).

(7) E. M. Nygaard and T. T. Noland, U. S. Patent 2,401,269 (1946); E. M. Nygaard, U. S. Patent 2,401,267 (1946); E. M. Nygaard, J. H. McCracken and T. T. Noland, U. S. Patent 2,370,185 (1945). The origin of the nitrous acid is still an open question.

(8) H. P. den Otter, *Rec. trav. chim.*, **57**, 13 (1937).

(9) T. W. J. Taylor and W. Baker in Sidgwick, "Organic Chemistry of Nitrogen," Oxford University Press, 1945, p. 231.

(10) A. I. Titov, *J. Gen. Chem.* (*U. S. S. R.*), **18**, 1312 (1948).

(11) F. Wöhler and J. Liebig, *Ann.*, **26**, 261 (1838).

(12) V. Meyer, *ibid.*, **175**, 141 (1875).

(13) E. Francke, *Ber.*, **38**, 4102 (1905).

(14) D. J. Weisblat and D. A. Lyttle, THIS JOURNAL, **71**, 3080 (1949).

(15) E. Schmidt, *Ber.*, **52**, 411 (1919); see also N. S. Marans and R. P. Zelinski, THIS JOURNAL, **72**, 5329 (1950).

(16) W. Will, *Ber.*, **47**, 963 (1914).

wise over a period of 15 minutes; the internal temperature was kept below 25°. Stirring was continued for an additional 30 minutes at which time the mixture contained a small amount of gelled material. This was brought into solution by the addition of 60 ml. of water. The resulting solution was then maintained at 0 to +5° and, while stirring, a solution (precooled to 0 to +3°) of 20.5 g. (0.341 mole) of urea dissolved in 102 g. of 20% aqueous acetic acid (0.341 mole acid) was added dropwise over a period of 20 minutes. The two phase system thus produced was extracted with three 25-ml. portions of petroleum ether (b.p. 35–37°) and the extracts were combined and dried over Drierite. Upon distillation there was obtained 18.6 g. (93% yield) of nitrocyclohexane, b.p. 108–109° (40 mm.), $n^{20}\text{D}$ 1.4612; lit. values,[17] b.p. 109° (40 mm.), $n^{20}\text{D}$ 1.4608.

The influence of acidification temperature was studied in the case of nitrocyclohexane. Hydroxylamine hydrochloride at 25° gave a 77% yield (av. of two runs); this is significantly lower than the 89% yield (av. of six runs) obtained at 0°.

Acknowledgment.—Our sincere thanks go to Mr. Bernard Taub of this Department for furnishing most of the nitroparaffins employed in this study and to Dr. M. Cenker who carried out several preliminary experiments with hydroxylamine hydrochloride.[18] Financial support from the Research Corporation is gratefully acknowledged.

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(17) S. Nametkin, *Ber.*, **42**, 1372 (1909).

(18) M. Cenker, Ph.D. Thesis, Purdue University, 1948.

DEPARTMENT OF CHEMISTRY
PURDUE UNIVERSITY
WEST LAFAYETTE, INDIANA

RECEIVED MARCH 23, 1951

The Friedel–Crafts Synthesis of Germanium and Tin Tetraiodides

BY W. H. NEBERGALL AND ROBERT H. WALSH

In connection with investigations[1] concerning the alkylation and arylation of the halides and hydrides of the Group IV elements the conversion of the tetrachlorides of silicon, germanium and tin to their respective iodides was attempted. It is well known that carbon tetraiodide may be prepared by the interaction of carbon tetrachloride and ethyl iodide in the presence of aluminum chloride[2] as a catalyst.

It was found in the present investigation that tin tetrachloride reacts immediately with ethyl iodide in the presence of aluminum chloride to give a quantitative yield of tin tetraiodide.

$$\mathrm{SnCl_4 + 4C_2H_5I \xrightarrow{AlCl_3} SnI_4 + 4C_2H_5Cl}$$

When aluminum bromide was used as the catalyst the formation of tin tetraiodide was somewhat slower and the crystals were larger; however, the conversion was still quantitative.

Germanium tetrachloride reacted very slowly with ethyl iodide, and after the reaction mixture stood for 48 hours only a 13% yield of germanium tetraiodide was obtained when aluminum chloride was employed as the catalyst. Under similar conditions but with aluminum bromide as the catalyst, a 7% yield of germanium tetraiodide was obtained.

Silicon tetrachloride failed to react with ethyl iodide in the presence of either aluminum chloride or aluminum bromide.

Experimental

Tin Tetraiodide from Tin Tetrachloride.—A 200-ml. erlenmeyer flask was fitted with a cork stopper containing a calcium chloride drying tube to allow the evolution of ethyl chloride but to protect the reaction mixture from the moisture of the air. Into the flask was weighed 10 g. (0.04 mole) of tin tetrachloride, 40 g. (0.16 mole) of redistilled ethyl iodide and 1.6 g. (0.0076 mole) of aluminum chloride. The flask was quickly closed with the stopper and drying tube. An orange color developed immediately in the reaction mixture, and after 30 to 60 seconds ebullition and effervescence began. After one to two minutes orange crystals of tin tetraiodide started to separate. The contents of the flask were swirled occasionally to keep the reactants well mixed and after five to seven minutes the reaction appeared to be complete. The crystals were transferred to a sintered-glass filtering funnel and washed with ice-cold concentrated hydriodic acid to remove the aluminum chloride. The crystalline tin tetraiodide was air-dried, the yield, 25 g., was essentially quantitative, and a sample of the product which was recrystallized from chloroform melted sharply at 141–142°.

The above procedure was repeated using aluminum bromide in place of aluminum chloride as the catalyst. The reaction was somewhat slower, seven to ten minutes being required for completion, and the crystals of tin tetraiodide were considerably larger. The yield again was essentially quantitative.

Germanium Tetraiodide from Germanium Tetrachloride.—Germanium tetrachloride (0.04 mole), ethyl iodide (0.16 mole) and aluminum chloride (0.0075 mole) were interacted as described above. Coloration was very slow to appear. After one to one and one-half hours the solution was dark red in color, the aluminum chloride had dissolved, and an oil had separated. The reaction mixture was permitted to stand at room temperature for 48 hours and then it was cooled in an acetone–Dry Ice-bath. After 10 minutes, the crystals of germanium tetraiodide which had formed were collected, washed with cold hydriodic acid and air-dried. The yield was 3 g. (13%); m.p. 140–141°.

When the aluminum chloride was replaced by aluminum bromide as the catalyst, the deep red color appeared almost immediately after the addition of the aluminum bromide, which dissolved in about ten minutes. The oil layer was very slow in appearing and it was not observed until after the reaction mixture had stood for about 48 hours. The product was worked up in the usual manner and the yield of crude germanium tetraiodide was 1.5 g. (7%).

Attempted Preparation of Silicon Tetraiodide from Silicon Tetrachloride.—When the procedures outlined above were used in attempts to prepare silicon tetraiodide, there were no indications of any reaction with either aluminum chloride or bromide as the catalyst or with prolonged refluxing. It might be added that when aluminum iodide was employed as the catalyst, the formation of the iodides of carbon, germanium and tin was negligible.

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(1) O. H. Johnson and W. H. Nebergall, THIS JOURNAL, **70**, 1706 (1948); O. H. Johnson and W. H. Nebergall, *ibid.*, **71**, 1720 (1949); W. H. Nebergall and O. H. Johnson, *ibid.*, **71**, 4022 (1949); W. H. Nebergall, *ibid.*, **72**, 4702 (1950).

(2) J. W. Walker, *J. Chem. Soc.*, **85**, 1090 (1904).

DEPARTMENT OF CHEMISTRY
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RECEIVED MARCH 17, 1951

Optically Active Phenylmethylcarbinyl Ethers

BY KURT MISLOW

It was recently pointed out[1] that the usual method of preparation of optically active ethers, by the reaction of an alkyl halide with alkali alcoholate, must, in the case of phenylmethylcarbinyl ethers, have led to partially racemized products. The present work describes successful attempts to convert the carbinol to the ether by means of an alkyl iodide–silver oxide mixture. This method has in the past found extensive application in the alkyla-

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(1) Mislow, THIS JOURNAL, **73**, 3954 (1951).