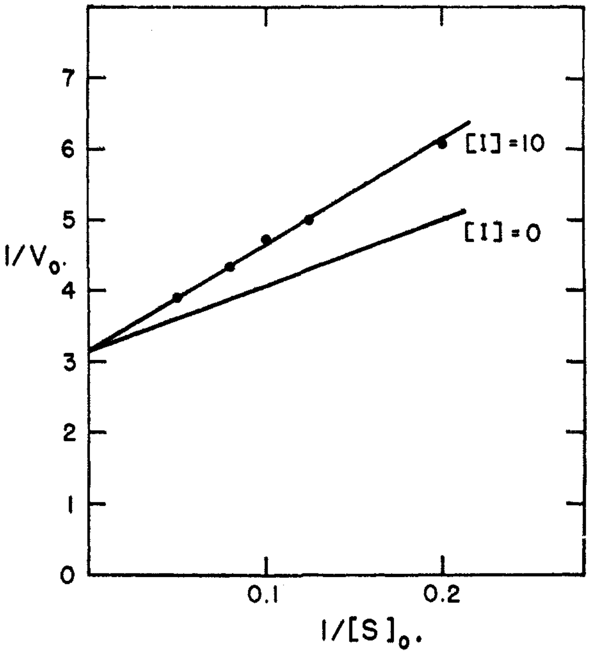

Fig. 1.—Inhibition of the α-chymotrypsin-catalyzed hydrolysis of nicotinyl-L-tryptophanamide by chloramphenicol: $[S]_0$ in moles × $10^{-3}$ per liter, [I] in moles × $10^{-3}$ per liter, $v_0$ (initial velocities) in moles × $10^{-3}$ per liter per min., [E] = 0.208 mg. protein-nitrogen per ml.

under the same conditions, and at an initial substrate concentration of 20 × $10^{-3}$ $M$, gave a mean value for $K_I$ of 13.0 × $10^{-3}$ $M$, with $K_S$ in this instance equal to 30.5 × $10^{-3}$ $M$.[6] With $K_I$ for the system α-chymotrypsin–chloramphenicol of the order of 10 × $10^{-3}$ $M$ it is not surprising that Smith and Worrel[3] could not detect any inhibitory action at chloramphenicol concentrations of 0.69 × $10^{-3}$ $M$ with the methods used in their study.

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Gates and Crellin Laboratories of Chemistry
California Institute of Technology
Pasadena 4, California
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## Preparation of Dibutyl Allylphosphonate

By Gennady M. Kosolapoff

Some time ago Pudovik[1] showed that dialkyl sodiophosphites may add to the double bond of an alkenephosphonate, thus yielding diphosphonates. Such a reaction was observed by him in a number of instances involving the reaction of dialkyl sodiophosphites with aliphatic halides of allyl type. More recently, Rueggeberg and co-workers[2] isolated a tetrabutyl propanediphosphonate from the reaction of allyl bromide and dibutyl sodiophosphite. Since the latter workers failed to state whether or not any of the monosubstitution reaction product was obtained, it was of some interest to look into the possibility of isolation of the allylphosphonate from this reaction. This was done readily, although in disappointing yields, by using the sodiophosphite prepared from the free metal and under conditions in which the free phosphite was present in a slight excess.

**Experimental.** 1.—Dibutyl phosphite (98.0 g.) was allowed to react with 11.5 g. of sodium in 500 ml. of hexane and the resulting solution was treated over 30 minutes with 39 g. of allyl chloride. The mixture was gently refluxed for 30 minutes and was treated with 100 ml. of ice-water, with external cooling. The upper layer was combined with a hexane extract of the lower part of the mixture and the combined hexane solution was washed with three 50-ml. portions of ice-water. Distillation gave 16.5 g. of the crude product, b.p. 151° at 5 mm. The reaction was repeated, with a six-hour refluxing period of the mixture and with an increase of the amount of the original wash water to 500 ml.; the yield of the crude product was 15 g. In both instances the bulk of the distillation residues was the high-boiling diphosphonate reported earlier.[2] Fractionation of the combined products gave 17 g. of dibutyl allylphosphonate, as a colorless liquid, b.p. 110° at 0.4 mm., $n^{25}\text{D}$ 1.4336, $d^{25}_{25}$ 0.9548. Found: P, 13.3; $MR$, 63.7. Calcd. for $(BuO)_2P(O)CH_2CH{:}CH_2$: P, 13.24; $MR$, 63.4.

2.—The reaction with allyl bromide gave similar results. Addition of 61 g. of allyl bromide to a refluxing solution of 99 g. of dibutyl phosphite and 11.5 g. of sodium in 400 ml. of xylene in the course of three hours, followed by cooling and washing as above, gave 39 g. of dibutyl allylphosphonate, b.p. 111 at 0.5 mm. Again, the bulk of the distillation residue consisted of the above-mentioned diphosphonate.

Department of Chemistry
Alabama Polytechnic Institute
Auburn, Alabama
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[1] Pudovik, paper presented at the October, 1947, session of the Chemical Section of U. S. S. R. Academy of Science; subsequently published in *Izvestiya Akad. Nauk S. S. S. R., Otdel. khim. nauk*, 522 (1949).

[2] Rueggeberg, Chernack and Rose, This Journal, **72**, 5336 (1950).

## Isolation and Identification of Pyrrole and 2-Methylpyrrole from Shale Oil[1]

By A. G. Janssen, E. R. Schierz, R. Van Meter and John S. Ball

Shale-oil products before treatment generally show excessive color and gum formation. This has been attributed to the presence of pyrrole-type compounds. To investigate this problem further, the particular compounds present should be known. In this research pyrrole and 2-methylpyrrole were isolated and identified from an oil prepared from Colorado oil shale.

Pyrroles, as a class, have been identified in shale oil[2] by the pine-splint test and the isatin test. However, there is no record of previous identifications of individual compounds. This is probably due to the reactivity of the compounds as evidenced in this research by low recoveries from each stage of the separation.

The shale oil studied was produced from Colorado shale of the Green River formation by retorting in an N-T-U retort.[3] Material boiling up to 195° was separated by distillation, and the tar acids were removed by treatment with dilute sodium hydroxide. Pyrroles were then separated as potassium pyrroles by refluxing the naphtha over solid potassium hydroxide. The potassium compounds were washed with pentane and hydrolyzed. The recovered oil was distilled, and derivatives were made from some of the fractions. The phthalic anhydride and tetraiodo derivatives of pyrrole were thus isolated and compared with authentic sam-

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[1] From the Ph.D. Thesis of A. G. Janssen.

[2] R. H. McKee, "Shale Oil," Reinhold Publishing Corp., New York, N. Y., 1925, pp. 116-119; G. E. Mapstone, *Proc. Roy. Soc. N. S. Wales*, **82**, 85 (1949).

[3] U. S. Bur. Mines, Rept. Invest. No. 4457, 1949, pp. 11-17.

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.

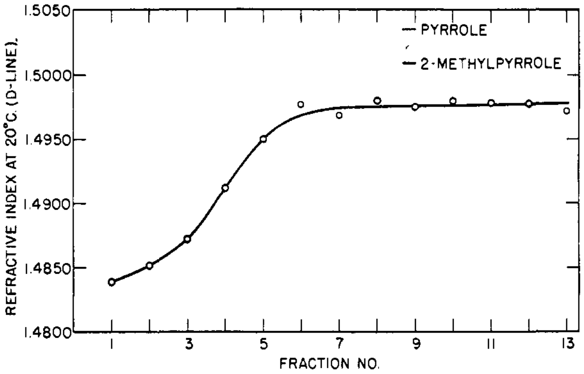

Fig. 1.—Refractive indices of fractions from distillation of pyrroles.

**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.

Petroleum and Oil-Shale Exp. Station
Box 621, Bureau of Mines
Laramie, Wyoming

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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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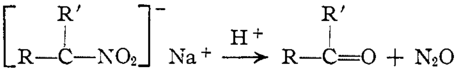
## The Regeneration of Nitroparaffins from Their Salts[1]

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]

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



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

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).