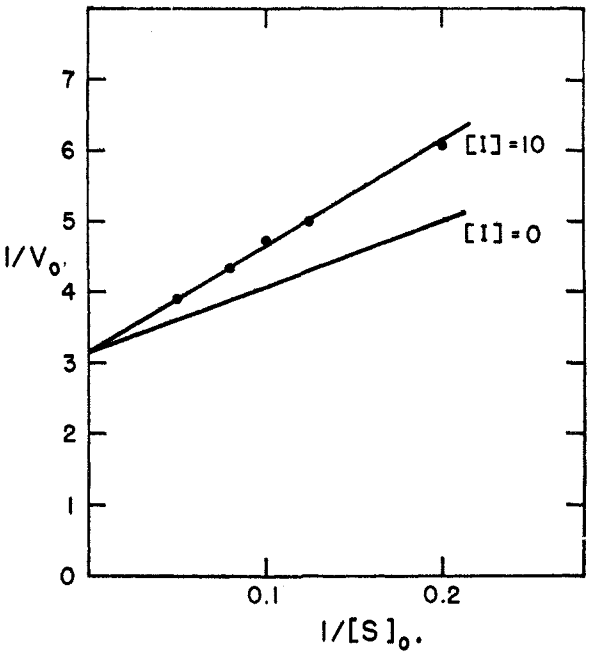

Fig. 1.—Inhibition of the α-chymotrypsin-catalyzed hydrolysis of nicotinyl-L-tryptophanamide by chloramphenicol: $[S]_0$ in moles × 10^{-3} per liter, [I] in moles × 10^{-3} per liter, v_0 (initial velocities) in moles × 10^{-3} per liter per min., [E] = 0.208 mg. protein-nitrogen per ml.

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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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., $n^{25}{}_D$ 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.

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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.