radicals to give ethane, and the abstraction of hydrogen from adjacent organic molecules by methyl radicals to produce methane as shown in reaction III.

Experimental

Phenyliodoso acetate, m. p. 160°, was prepared from iodosobenzene and glacial acetic acid. It was crystallized from acetic acid and its purity was determined by the standard iodine–sodium thiosulfate titration.

A mixture of 1.0 g. of trinitrotoluene, 3.6 g. of phenyliodoso acetate and 10 cc. of acetic acid was heated under reflux for one hour. The solution was dark brown at the end of this period. The reaction mixture afforded 0.2 g. of trinitro-*m*-xylene, m. p. 173–177°. Crystallization from glacial acetic acid raised the m. p. to 180–181°. Mixed with an authentic sample of trinitro-*m*-xylene, the m. p. was 180–182°.

Attempts to bring about the methylation of trinitro-*m*-xylene resulted in the recovery of unchanged starting material. Fieser, *et al.*, have recorded the stability of trinitro-*m*-xylene to lead tetraacetate.

Phenyliodoso acetate was heated in a flask under reflux. Above the melting point a brisk evolution of gas took place. The gas was collected and was shown to be a mixture of carbon dioxide, ethane and methane.[6] The liquid reaction product was heated with aqueous sodium hydroxide under reflux and then steam distilled. Phenyl iodide, in considerable amount, was isolated from the distillate. The alkaline residue was acidified and steam distilled. The distillate afforded a small amount of material which was identified as phenol. It is suggested by the authors that the phenol is probably due to the decomposition of diphenyl iodonium acetate.

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(6) The authors are indebted to James G. Knudsen for the numerous gas analyses which were carried out.

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Reaction between Amines and Pentachloroethane

BY WALTER H. C. RUEGGEBERG[1] AND MELVIN M. FALKOF[1]

In connection with certain chemical warfare problems, we found that aliphatic amines will react smoothly with pentachloroethane at room temperature, or above, to produce amine hydrochlorides in excellent yields.

In general, we found that primary and secondary aliphatic amines react spontaneously with pentachloroethane, generating heat upon contact. Tertiary aliphatic amines, on the other hand, react decidedly more slowly and require heating to effect the formation of the amine hydrochloride. Aromatic amines, as, for example, aniline and pentachloroethane, react only with difficulty even at temperatures above 150°. These differences of reactivity and activation energies are probably related to the basicities of the different amines. After the reaction is complete, the hydrochlorides are filtered off with suction and kept *in vacuo* over concentrated sulfuric acid.

***n*-Butylamine Hydrochloride.**—*n*-Butylamine (3.7 g.) is added dropwise with agitation to a mixture of pentachloroethane (11.0 g.) and dry diethyl ether (14.0); yield 4.5 g.; m. p. 215°.

Anal. Calcd. for $C_4H_{12}NCl$: Cl, 32.35. Found: Cl, 32.34.

Dimethylamine Hydrochloride.—Dimethylamine (2.3 g.) is dissolved in dry benzene (8.8 g.) and this mixture is added dropwise with occasional shaking to pentachloroethane (20.2 g.); yield 3.5 g.; m. p. 170–171°.

Anal. Calcd. for C_2H_8NCl: Cl, 43.48. Found: Cl, 43.17.

Piperidine Hydrochloride.—Piperidine (4.3 g.) is added dropwise to pentachloroethane (11.3 g.) with occasional shaking. After all of the amine has been added, the reaction mixture is cooled to room temperature and dry diethyl ether (14 g.) is added to increase the fluidity of the reaction product, yield 4.4 g.; m. p. 247–248°.

Anal. $C_5H_{12}NCl$: Cl, calcd., 29.16; found, 28.90.

Triethylamine Hydrochloride.—A mixture of triethylamine (5.0 g.) and pentachloroethane (21.4 g.) is heated to 100° over a period of about fifteen minutes; yield 4–5 g.; m. p. 253–255°.

Anal. Calcd. for $C_6H_{16}NCl$: Cl, 25.75. Found: Cl, 25.57.

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(1) Captains, C. W. S., Army of the United States.

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The Catalytic Dehydrocyclization of Paraffins

BY H. STEINER

The catalytic dehydrocyclization of paraffins to aromatic hydrocarbons continues to attract considerable interest. This communication deals with experiments carried out lately by a number of authors on the poisoning of the catalysts used in this reaction and in particular the conclusions drawn from these experiments regarding the mechanism of the catalytic action are discussed.[1,2]

It was shown by Pitkethly and Steiner[3] in the typical case of the dehydrocyclization of *n*-heptane to toluene, over a catalyst containing 10% Cr_2O_3 on alumina, that heptene, which is found always in the products, is an intermediate in this reaction. Thus the over-all reaction consists of two consecutive steps, (1) a dehydrogenation of the paraffin (heptane) to the olefin (heptene), and (2) a subsequent cyclization of the olefin to the aromatic body (toluene). Perhaps the best proof of this mechanism can be found in experiments at small conversions, where, as the contact time approaches zero, the rate of heptene formation remains finite while the rate of toluene formation asymptotically approaches zero. This shows that cyclization starts only after some olefin has formed and suggests strongly that the latter is an intermediate product.[4] The recent experiments of Mattox also show this effect. At longer contact times the concentration of the olefin reaches a maximum and subsequently declines slowly. In this region the stationary state treatment can be applied to a first approximation. Thus, assuming that both dehydrogenation and cyclization

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(1) H. S. Taylor and H. Fehrer, THIS JOURNAL, **63**, 1387 (1941); D. T. Salley, H. Fehrer and H. S. Taylor, *ibid.*, **63**, 1131 (1941).

(2) W. J. Mattox, *ibid.*, **66**, 2059 (1944).

(3) Pitkethly and Steiner, *Trans. Farad. Soc.*, **35**, 979 (1939).

(4) Hoog, *ibid.*, **35**, 1009 (1939).