

tin in boiling acid solution.¹ It was assumed that this coloration was due to the formation of β -(5-pyrrolyl)-isatin or pyrrole blue B. Recently it has been shown,² however, that pyrrole blue B in glacial acetic acid has a maximum absorption at 680–690 $m\mu$ while the maximum absorption in the microreaction was observed in the range for 510–560 $m\mu$. For a more exact comparison the absorption spectrum of the color reaction was determined in a Hilger–Nutting spectrophotometer. The resulting curve A in Fig. 1 is quite different from the spectrum of pyrrole blue B, shown in curve B. The logarithm of specific extinction K is calculated per grams of pyrrole per liter. Thus the compound formed in the color reaction is certainly not pyrrole blue B but seems to be its decomposition product which also forms when solutions of pyrrole blue B are standing for some time. It has been indicated² that the decomposition product has an absorption maximum at 520 $m\mu$.

The author is greatly indebted to the Chemistry Department of the University of Michigan for the permission to use a spectrophotometer and to Dr. F. F. Blicke for the supply of pyrrole.

(1) F. Fromm, *Mikrochemie*, **17**, 141 (1935).

(2) F. Fromm, *THIS JOURNAL*, **66**, 1227 (1944).

COLEGIO DEL SAGRADO CORAZÓN
SANTURCE, PUERTO RICO RECEIVED AUGUST 21, 1945

Benzophenone-ascorbic Acid

By PHILIPPOS E. PAPADAKIS

In view of the known bacteriological action of benzophenone in human tubercle bacilli *in vitro*¹ the following benzophenone derivative of ascorbic acid is reported.²

Procedure.—Equivalent quantities of ascorbic acid and benzophenone chloride in dry toluene were heated under a reflux condenser until no more hydrogen chloride was coming off. The oil-bath temperature was 90°. After filtering, the residue was treated with ice water to dissolve any unreacted ascorbic acid, then with benzene to remove any benzophenone formed and finally it was recrystallized from methyl alcohol; m. p. 207–208°. The substance is insoluble in water, soluble in methyl alcohol and ether. Further work is contemplated for the elucidation of the structure of this substance.

Anal. Calcd. for $C_{15}H_{16}O_6$: C, 67.03, H, 4.73. Found: C, 67.04, H, 4.9.

The microanalyses were done by D. Rigakos of the Rockefeller Institute for Medical Research.

Acknowledgment.—The author wishes to express his appreciation and thanks to Dean Charles M. McConn of Washington Square College, to Professor Arthur C. DeGraff and to Dr. Robert Lehman of the Department of Therapeutics for

(1) B. L. Freedlander, *Am. Rev. Tuberc.*, **49**, 543 (1944).

(2) This work was completed in 1942.

the arrangement which made it possible for him to do this work.

DEPARTMENT OF THERAPEUTICS
NEW YORK UNIVERSITY
COLLEGE OF MEDICINE
NEW YORK 16, N. Y.

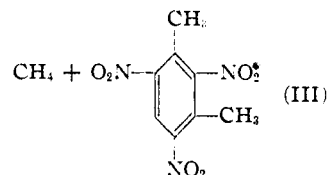
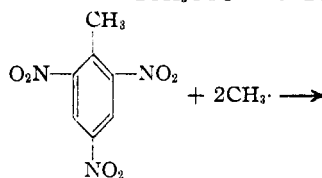
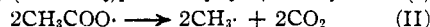
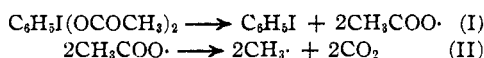
RECEIVED JULY 17, 1945

The Decomposition of Phenyliodoso Acetate¹

By REUBEN B. SANDIN AND WILLIAM B. McCORMACK

Fieser and co-workers² have carried out some very interesting work on the alkylation of α -naphthoquinones and aromatic nitro compounds with tetravalent lead esters, such as lead tetraacetate. By this method, for example, they were able to convert trinitrotoluene in yields as high as 32% into trinitro-*m*-xylene. Because of the similarity between iodoso compounds and certain compounds of lead,³ it occurred to the authors of this paper that phenyliodoso acetate, like lead tetraacetate, might act as a methylating agent. It has already been shown by Criegee and Beucker⁴ that aryliodoso acetates, like lead tetraacetate, can oxidize unsaturated compounds and can bring about the fission of α,β -glycols.

The experimental work described in this paper indicates that phenyliodoso acetate can behave as a methylating agent. By means of phenyliodoso acetate, trinitrotoluene has been converted into trinitro-*m*-xylene to an extent of about 20%. It has also been shown that when phenyliodoso acetate is heated by itself, decomposition occurs above 160°, and some of the reaction products are phenyl iodide, carbon dioxide, ethane and methane. We believe that the following equations represent the sequence of events⁵



Also, the thermal decomposition of some of the phenyliodoso acetate appears to follow reactions I and II. This is followed by the union of methyl

(1) Originally received May 7, 1945.

(2) Fieser and Chang, *THIS JOURNAL*, **64**, 2043 (1942); Fieser, Clapp and Daudt, *ibid.*, **64**, 2052 (1942); Fieser and Oxford, *ibid.*, **64**, 2060 (1942).

(3) Sandin, *Chem. Rev.*, **32**, 258 (1943).

(4) Criegee and Beucker, *Ann.*, **541**, 218 (1939).

(5) The Referee has very kindly suggested this reaction mechanism.

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.

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

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF ALBERTA RECEIVED SEPTEMBER 12, 1945
EDMONTON, ALBERTA, CANADA

Reaction between Amines and Pentachloroethane

BY WALTER H. C. RUEGGEBERG¹ AND MELVIN M. FALKOFF¹

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°.

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

Anal. Calcd. for C₄H₁₂NCl: 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 C₂H₈NCl: 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. C₅H₁₂NCl: 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 C₆H₁₈NCl: Cl, 25.75. Found: Cl, 25.57.

CHEMICAL DIVISION
C. W. S. TECHNICAL COMMAND
EDGEWOOD ARSENAL, MARYLAND

RECEIVED SEPTEMBER 4, 1945

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 Steiner³ in the typical case of the dehydrocyclization of *n*-heptane to toluene, over a catalyst containing 10% Cr₂O₃ 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

(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).