[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY
No. 1381]

The Monoacetylation of 2,4-Diamino-6-nitrotoluene

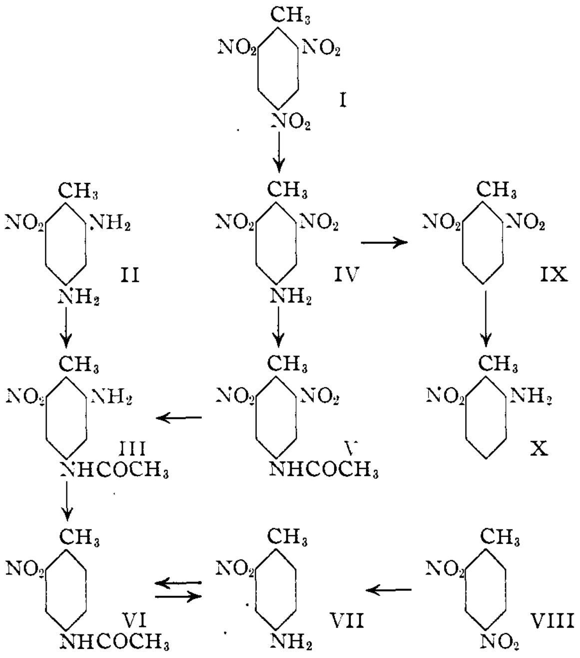
BY ROBERT J. FOSTER, FRED G. ROSICKY AND CARL NIEMANN[1]

When equimolar quantities of acetic anhydride and 2,4-diamino-6-nitrotoluene are allowed to react in dry acetone at room temperature, a monoacetyl derivative is formed in good yield.[2] Parkes and Farthing[2] state that the latter compound can be deaminated via diazotization to give after hydrolysis 2-nitro-4-aminotoluene, thus inferring that the monoacetyl derivative is 2-amino-4-acetamido-6-nitrotoluene. However in the experimental section of their paper[2] it is reported that, when 2,4-diamino-6-nitrotoluene is monoacetylated by three different procedures, including that described above, 2-acetamido-4-amino-6-nitrotoluene is obtained, and that the latter compound can be converted into 2-amino-6-nitrotoluene in the usual manner.

The question as to which of the above conflicting statements is correct has been answered by the demonstration in these laboratories that the monoacetylation of 2,4-diamino-6-nitrotoluene proceeds under the conditions specified by Parkes and Farthing as methods (a) and (c)[2] to form 2-amino-4-acetamido-6-nitrotoluene. This conclusion has been reached by a consideration of the transformations summarized in Table I.

TABLE I

PROOF OF STRUCTURE OF 2-AMINO-4-ACETAMIDO-6-NITROTOLUENE



The authors wish to express their indebtedness to Dr. A. Elek for the microanalyses reported in this communication.

Experimental[3]

2-Amino-4-acetamido-6-nitrotoluene (III).—TNT (I) was converted into 2,4-diamino-6-nitrotoluene (II), m. p. 132.5–134° after recrystallization from water, essentially as described by Ruggli and Zaeslin.[4] Acetylation of II by methods (a) or (c) of Parkes and Farthing[2] gave 2-amino-4-acetamido-6-nitrotoluene (III), m. p. 160–161° after successive recrystallization from 20% aqueous ethanol and toluene followed by drying *in vacuo* at 110°. Parkes and Farthing[2] report a m. p. of 155° for the compound now recognized as III.

Anal. Calcd. for $C_9H_{11}O_3N_3$ (209): C, 51.7; H, 5.3; N, 20.1. Found: C, 51.6; H, 5.4; N, 20.1.

TNT (100 g.) was suspended in 500 ml. of ethanol, 25 ml. of 28% ammonium hydroxide added, the mixture cooled in an ice-bath, and hydrogen sulfide passed through the suspension until the TNT had dissolved. The reaction mixture was then heated on a steam-bath, the hot solution filtered, the filtrate poured into cold water, and the crude 3,5-dinitro-4-methyl-phenylhydroxylamine collected. The latter product was heated with potassium iodide and concd. hydrochloric acid until no more iodine was evolved, water was added to the reaction mixture, the slurry filtered, and the residue extracted with hot dilute hydrochloric acid. The filtrate and extracts were then neutralized with ammonium hydroxide, and the precipitate formed was collected and recrystallized from 40% aqueous acetic acid to give 47.2 g. (55%) of 2,6-dinitro-4-aminotoluene (IV), m. p. 171–172°. Holleman and Böeseken[5] report a m. p. of 171°. Cohn and Dakin,[6] using only a few drops of ammonium hydroxide, obtained a hydroxylamine which upon further reduction with potassium iodide and concd. hydrochloric acid gave 2-amino-4,6-dinitrotoluene, m. p. 212–213°.

Acetylation of IV by method (c) of Parkes and Farthing[2] gave 66% of 4-acetamido-2,6-dinitrotoluene (V), m. p. 223–225°. An analytical sample of V, m. p. 224.5–225°, was obtained by recrystallization from toluene. Parkes and Farthing report a m. p. of 221.5°.

Anal. Calcd. for $C_9H_9O_5N_3$ (239): C, 45.2; H, 3.8; N, 17.6. Found: C, 45.3; H, 3.9; N, 17.5.

III, m. p. 160–161° after successive recrystallization from 20% aqueous ethanol and toluene, and drying *in vacuo* at 110°, was obtained from V in 60% yield by the same method used for the preparation of II from I. A mixed m. p. of III prepared from II with III prepared from V was 160–161°.

2-Nitro-4-aminotoluene (VII).—III was deaminated to 2-nitro-4-acetamidotoluene (VI), m. p. 145–146° after recrystallization from 50% aqueous ethanol, by treating an ice cold suspension of III in 50% hypophosphorous acid with a concd. aqueous solution of sodium nitrite.[7] Bogert and Kropff[8] report a m. p. of 148° for VI.

Anal. Calcd. for $C_9H_{10}O_3N_2$ (194): C, 55.7; H, 5.2; N, 14.4. Found: C, 55.8; H, 5.1; N, 14.4.

VI was hydrolyzed with 4 *F* hydrochloric acid to give 2-nitro-4-aminotoluene (VII), m. p. 78–79° after recrys-

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[1] To whom inquiries regarding this article should be sent.

[2] G. D. Parkes and A. C. Farthing, *J. Chem. Soc.*, 1275 (1948).

[3] All melting point values are corrected.

[4] P. Ruggli and H. Zaeslin, *Helv. Chim. Acta*, **19**, 434 (1936).

[5] A. Holleman and J. Böeseken, *Rec. trav. chim.*, **16**, 425 (1897).

[6] J. B. Cohn and H. D. Dakin, *J. Chem. Soc.*, **81**, 26 (1902).

[7] N. Kornblum and D. C. Iffland, THIS JOURNAL, **71**, 2137 (1949).

[8] M. T. Bogert and A. H. Kropff, *ibid.*, **31**, 841 (1909).

tallization from water. The yield of VII from III was 40%. Beilstein and Kuhlberg[9] report a m. p. of 77.5° for VII.

Anal. Calcd. for $C_7H_8O_2N_2$ (152): C, 55.3; H, 5.3; N, 18.4. Found: C, 55.2; H, 5.4; N, 18.5.

VII was also prepared from 2,4-dinitrotoluene (VIII). m. p. 70–71°, as described by Beilstein and Kuhlberg,[9] and a mixed m. p. of VII prepared from VI with VII prepared from VIII was 78–79°.

2-Amino-6-nitrotoluene (X).—2,6-Dinitrotoluene (IX), m. p. 65–66°, was obtained in 52% yield from IV using the method described by Kornblum.[10] IX was reduced as described by Bernthsen[11] to give X, m. p. 90–91°, in 80% yield. The m. p. of X is reported[11] to be 90.5°. The m. p. of X was depressed in the presence of VII and *vice versa*.

Summary

2-Amino-4-acetamido-6-nitrotoluene is obtained by the monoacetylation of 2,4-diamino-6-nitrotoluene with acetic anhydride either in acetone solution or in the absence of added solvent.

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[9] F. Beilstein and A. Kuhlberg, *Ann.*, **155**, 1 (1870).

[10] N. Kornblum, "Organic Reactions," **2**, 278 (1944).

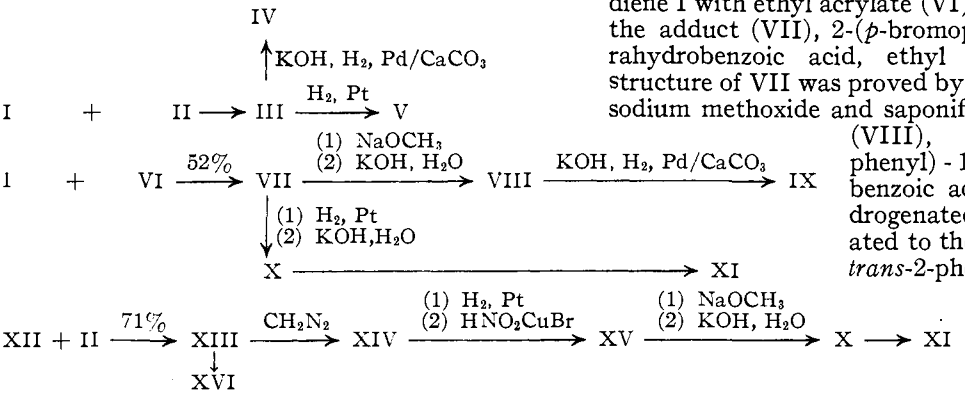
[11] A. Bernthsen, *Ber.*, **15**, 3011 (1882).

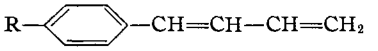
[CONTRIBUTION NO. 76 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TENNESSEE]

Reactions of 1-(*p*-Bromophenyl)-1,3-butadiene[1] and 1-(*p*-Nitrophenyl)-1,3-butadiene with Acrylic Acid and Ethyl Acrylate

BY GUS A. ROPP[2] AND EUGENE C. COYNER[3]

As a continuation of a study[4] of the applicability of the anionoid–cationoid mechanism[5] to Diels–Alder reactions, acrylic acid and ethyl acrylate have now been caused to react with 1-(*p*-bromophenyl)-1,3-butadiene and 1-(*p*-nitrophenyl)-1,3-butadiene, and in all cases *ortho* adducts have been shown to result.





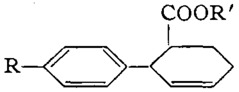
I R = Br

XII R = NO_2

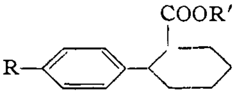
$CH_2 = CHCOOR$

II R = H

VI R = C_2H_5



	R =	R' =
III(*cis*)	Br	H
VII	Br	C_2H_5
VIII(*trans*)	Br	H
XIII	NO_2	H
XIV	NO_2	CH_3



	R =	R' =
IV(*cis*)	H	H
V(*cis*)	Br	H
IX(*trans*)	H	H
X(*trans*)	Br	H
XI(*trans*)	Br	$NH_3CH_2C_6H_5$
XV	Br	CH_3
XVI	OH	H

1-(*p*-Bromophenyl)-1,3-butadiene (I) and acrylic acid (II) formed the adduct (III), *cis*-2-(*p*-bromophenyl)-1,2,5,6-tetrahydrobenzoic acid, for which both the *ortho* structure and the *cis* configuration were shown by hydrogenation and dehalogenation to the known acid (IV), *cis*-2-phenylhexahydrobenzoic acid.[4,6] The adduct III was also hydrogenated to the acid (V), *cis*-2-(*p*-bromophenyl)-hexahydrobenzoic acid. The diene I with ethyl acrylate (VI) gave in 52% yield the adduct (VII), 2-(*p*-bromophenyl)-1,2,5,6-tetrahydrobenzoic acid, ethyl ester. The *ortho* structure of VII was proved by isomerization with sodium methoxide and saponification to the acid (VIII), *trans*-2-(*p*-bromophenyl)-1,2,5,6-tetrahydrobenzoic acid which was hydrogenated and dehalogenated to the known acid (IX), *trans*-2-phenylhexahydrobenzoic acid.[7] The adduct VII was also hydrogenated and saponified to form (X), *trans*-2-(*p*-bromophenyl)-hexahydrobenzoic acid, which was converted to its benzylamine salt (XI).

1-(*p*-Nitrophenyl)-1,3-butadiene (XII) and acrylic acid yielded 71% of the adduct (XIII), 2-(*p*-nitrophenyl)-1,2,5,6-tetrahydrobenzoic acid.

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[1] Presented in part at the 114th National Meeting of the American Chemical Society, St. Louis, Mo., September, 1948.

[2] Oak Ridge National Laboratory, Oak Ridge, Tennessee (Research Corporation Fellow 1946–1948).

[3] Mallinckrodt Chemical Works, St. Louis, Mo.

[4] Ropp and Coyner, THIS JOURNAL, **71**, 1832 (1949).

[5] Meek and Ragsdale, *ibid.*, **70**, 2502 (1948).

[6] Gutsche, *ibid.*, **70**, 4150 (1948).

[7] Fujise, *Ber.*, **71B**, 2461 (1938).