butane yielded the 1,4-bis(3,5-dinitro-1,3,5-triaza-cyclohexyl)butane (IIIa); the 1,5-diaminopentane produced an analogous derivative, *i.e.*, 1,5-bis-(3,5-dinitro-1,3,5-triazacyclohexyl)pentane (IIIb). The 1,6-diaminohexane, 1,7-diaminoheptane, and 1,8-diaminoöctane yielded 3-nitro-1,3,5-triazabicyclo[6.3.1]dodecane (IId), 3-nitro-1,3,5-triazabicyclo[7.3.1]tridecane (IIe), and 3-nitro-1,3,5-triazabicyclo[8.3.1]tetradecane (IIf), respectively, although the major reaction was the formation of a rubbery insoluble polymer of the amine and formaldehyde which contained only a few nitramino groups. The 1,9-diaminononane produced solely polymer. The latter derivatives IId, IIe, and IIf, represent ring enlargements of the bicyclic system obtained with ethylenediamine, 1,3-diaminopropane, or 1,3-diaminobutane.

The formation of the derivatives II and III is analogous to the production of the 1,3-dialkyl-5-nitro-1,3,5-triazacyclohexanes[2] and 1-alkyl-3,5-dinitro-1,3,5-triazacyclohexanes,[2] respectively, from primary amines. In no case was there any evidence for the formation of more than one condensation product even when a two-fold excess of amine or I was employed. The cyclic derivatives were slowly soluble in dilute mineral acid with the formation of the dihydrochloride of the amine, and in the case of the two derivatives of III, methylenedinitramine. Warm alkali rapidly degraded the derivatives II or III with the formation of the diamine and formaldehyde; in addition III yielded disodium methylenedinitramine. All of the condensation products slowly decomposed on storage at room temperature; the odor of formaldehyde and the diamine became noticeable after 2–4 weeks.

EXPERIMENTAL[8]

The formation of 3-nitro-1,3,5-triazabicyclo[3.2.1]octane (IIa) is representative of a condensation using the free amine, formalin, and I. To a solution of 4.08 g. (0.0300 mole) of methylenedinitramine[9] (I) (m.p. 100–101°) in 72 ml. (0.86 mole) of 36% formalin maintained at 0°, was added (dropwise) 1.80 g. (0.0300 mole) of ethylenediamine. The mixture was allowed to stand 4 hr. at 0°. The fine needles which had deposited were filtered to yield 5.14 g. (74%) of IIa, m.p. 160° dec.; m.p. 165°, dec., depending on rate of heating (reported 130° by Wright[5]) after recrystallization from acetone. No methylenedinitramine was isolated in several alkaline degradations of IIa; only ethylenediamine (isolated as the diacetyl derivative, m.p. 174–175°, reported 172° by Hofmann[10]) and formaldehyde were recovered. Similar results were obtained with the other derivatives of II. All derivatives of II were soluble in 3N hydrochloric acid; no methylenedinitramine could be isolated from the solutions.

The formation of 1,4-bis(3,5-dinitro-1,3,5-triazacyclohexyl)-butane (IIIa) is typical of a run employing an amine hydro-

chloride and potassium carbonate. To a solution of 4.08 g. of I in 72 ml. of 36% formalin was added 10 ml. of a solution containing 2.64 g. (0.0300 mole) of 1,4-diaminobutane which had been neutralized by 6N hydrochloric acid. To the resulting solution which was maintained at 0°, was added finely powdered potassium carbonate until the reaction mixture was alkaline to nitrazine test paper. The reaction mixture, which contained precipitated IIIa, was allowed to stand 1 hr. at 0° and then filtered to yield 7.30 g. (60%) of crude IIIa, m.p. 120° dec.; m.p. 135° dec. after recrystallization from acetone. Alkaline decomposition of the two derivatives of III produced 1,4-diaminobutane from IIIa (isolated as the diacetyl derivative, m.p. 136°, reported 137° by Haga[11]) and 1,5-diaminopentane from IIIb (isolated as the dibenzoyl derivative, m.p. 134–135°, reported as 132° by Braun[12]) as well as formaldehyde. The alkaline solution was acidified and extracted with ether; evaporation of the ether left methylenedinitramine in 85% yield. Dilute hydrochloric acid, 3N, dissolved III with the formation of formaldehyde, the corresponding diamine dihydrochloride, and methylenedinitramine (I).

RESEARCH DEPARTMENT, CHEMISTRY DIVISION,
   ORGANIC CHEMISTRY BRANCH
U. S. NAVAL ORDNANCE TEST STATION
CHINA LAKE, CALIF.

(11) T. Haga and R. Majima, *Ber.*, **36**, 338 (1903).
(12) J. Braun and S. W. Pirkernelle, *Ber.*, **67**, 1056 (1934).

An Ivanov Reaction with the Use of α-Phenylpropionic Acid

HAROLD E. ZAUGG AND ROBERT W. DENET

The renewed interest in the Ivanov reaction lately exhibited in several laboratories[1-3] prompts us to report the results of an Ivanov reaction of α-phenylpropionic acid with formaldehyde. When a procedure, adapted from that reported by Blicke, Raffelson, and Barna[4] for the preparation of tropic acid in 80% yield from phenylacetic acid and formaldehyde, was applied to α-phenylpropionic acid, α-methyltropic acid (I) was obtained in only trace amounts. Also isolated in poor yield was a somewhat larger quantity of *sym.* dimethyldiphenylsuccinic anhydride (II), m.p. 157–159°,

$$C_6H_5C(CH_3)COOH$$
$$|$$
$$CH_2OH$$

I

II
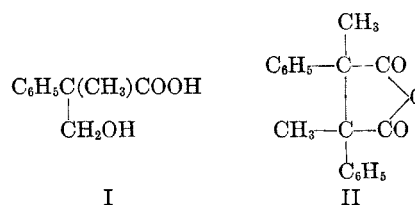
(1) F. F. Blicke and H. Zinnes, *J. Am. Chem. Soc.*, **77**, 5399, 6051, 6247 (1955) and previous papers.
(2) H. E. Zimmerman and M. D. Traxler, *J. Am. Chem. Soc.*, **79**, 1920 (1957).
(3) A. W. Weston and R. W. DeNet, *J. Am. Chem. Soc.*, **73**, 4221 (1951).
(4) F. F. Blicke, H. Raffelson, and B. Barna, *J. Am. Chem. Soc.*, **74**, 253 (1952).

(8) All melting points are corrected. The combustion analyses were performed by Mr. Everett Bens of this laboratory.
(9) R. C. Brian and A. H. Lamberton, *J. Chem. Soc.*, 1633 (1949).
(10) A. W. Hofmann, *Ber.*, **21**, 2332 (1888).

formed by oxidative coupling of two molecules of the Ivanov reagent.[5] McKenzie and Ritchie[6] prepared the succinic acid corresponding to II by treatment of α-chloro-α-phenylpropionic acid with either metallic copper or ethylmagnesium bromide. They assigned the racemic configuration to this acid, which split off water at the melting point to give the anhydride II, m.p. 159–160°. In the present work, the low yields of characterized products do not preclude the possibility that some of the meso-form of *sym.* dimethyldiphenylsuccinic acid, which does not form the corresponding anhydride at its melting point,[6] was formed also. However, it is felt that if an appreciable amount had been present, it would have interfered considerably with the purification of the minute amount of α-methyltropic acid formed in the reaction. If one can assume that the racemic form of the succinic acid is indeed formed to the near exclusion of the meso-form, a transition state involving minimum phenylphenyl interaction similar to the one proposed by Zimmerman and Traxler[2] for the Ivanov reaction of phenylacetic acid with benzaldehyde may also be involved in the oxidative coupling reaction. However, any extension of these stereochemical mechanisms to the coupling reactions of the α-chloro derivatives studied by McKenzie and Ritchie[6] must account for their observation that the use of metallic silver led to the meso-form of *sym.* dimethyldiphenylsuccinic acid in contrast to the production of the racemic form when metallic copper was used.

It should be noted that the purpose of this work was to prepare α-methyltropic acid by a reasonably unequivocal method. Foster and Ing[7] reported the preparation of this acid by the action of nitrous acid on ethyl β-amino-α-methyl-α-phenylpropionate followed by hydrolysis of the hydroxy ester, but later found[8] that their hydroxy acid was actually the isomeric rearranged product, α-benzyllactic acid, m.p. 98°. The α-methyltropic acid obtained in the present work melted at 86–87°.

EXPERIMENTAL

To a stirred solution of isopropylmagnesium bromide in ether (prepared from 87 g. of isopropyl bromide and 16 g. of magnesium) was added, with cooling, a solution of α-phenylpropionic acid (35 g., 0.23 mole) in 500 ml. of dry toluene. The mixture was then stirred and refluxed overnight. After removal of the ether by distillation, gaseous formaldehyde (generated from 23 g. of trioxane) was introduced into the stirred refluxing mixture over a 4-hr. period by means of a stream of dry nitrogen. The mixture was then stirred overnight at room temperature, cooled in an ice bath and treated with excess aqueous ammonium chloride

(5) D. Ivanov and A. Spassov, *Bull. soc. chim. France* [5] 2, 76 (1935), reported the formation of *sym.* diphenylsuccinic acid by oxidation of the Ivanov reagent of phenylacetic acid with either oxygen (8% yield) or bromine (22% yield).
(6) A. McKenzie and A. Ritchie, *Ber.*, 71, 643 (1938).
(7) R. Foster and H. R. Ing, *J. Chem. Soc.*, 938 (1956).
(8) R. Foster and H. R. Ing, *J. Chem. Soc.*, 925 (1957).

followed by dilute sulfuric acid. The layers were separated and the toluene layer was extracted with excess 10% sodium carbonate solution. Acidification of the carbonate extract gave an oil which was taken up in ether and dried over anhydrous magnesium sulfate. Filtration and removal of the ether by distillation followed by vacuum (0.5 mm.) distillation of the residue gave three fractions, b.p. 90–135° (7.9 g., n_D^{25} 1.5268), b.p. 135–150° (4.5 g., n_D^{25} 1.5510), and b.p. 150–215° (5.8 g., n_D^{25} 1.5569). The first fraction was largely unreacted α-phenylpropionic acid. The other two fractions were treated separately with saturated sodium bicarbonate solution. Insoluble neutral material (a larger amount from the third fraction) crystallized from the second and third fractions and was filtered. Recrystallization from a benzene-cyclohexane mixture gave colorless *sym.* dimethyldiphenylsuccinic anhydride, m.p. 157–159° (lit.,[6] m.p. 159–160°).

Anal. Calcd. for $C_{18}H_{16}O_3$: C, 77.12; H, 5.75; O, 17.12. Found: C, 77.08; H, 5.98; O, 16.97.

The infrared spectrum of this product indicated the presence of a phenyl, a C-methyl, a five-membered anhydride ring, and the absence of hydroxyl.

The filtered bicarbonate extract of the middle fraction was acidified with dilute hydrochloric acid. The precipitated oil was taken up in ether and dried over anhydrous magnesium sulfate. Filtration, removal of the ether by distillation and trituration of the residue with pentane gave a small amount of a solid acid. Recrystallization from an ethylene dichloride–pentane mixture gave α-methyltropic acid, m.p. 86–87°.

Anal. Calcd. for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71; O, 26.65. Found: C, 66.37; H, 6.89; O, 26.82.

The infrared spectrum was entirely consistent with the assigned structure.

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ORGANIC RESEARCH DEPARTMENT
ABBOTT LABORATORIES
NORTH CHICAGO, ILL.

Monochloro-p-dioxane and Trichloro-p-dioxanes

R. K. SUMMERBELL AND HANS E. LUNK

Among the characterized chlorination products of *p*-dioxane, the dichloro and tetrachloro derivatives predominate.[1] In the chlorination of *p*-dioxane at 90°, the second chlorine atom is introduced more readily than the first as indicated by the failures to isolate a monosubstituted product.[2] However, it appears that the ease of introduction decreases for the third chlorine atom as evidenced by the very high yields of 2,3-dichloro-*p*-dioxane.

(1) R. C. Elderfield, *Heterocyclic Compounds*, John Wiley and Sons, Inc., New York, 1957, Volume 6, p. 11.
(2) Ref. (1), p. 10.