by the mixed melting point identical with the material prepared according to procedure (a). A sample of the recrystallized material for analysis was sublimed at 170–180° and 0.005 mm.

*Anal.* Calcd. for $C_6H_{10}O_2N_2$: C, 50.71; H, 7.09; N, 19.70. Found: C, 50.82; H, 7.07; N, 19.66.

### *cis*-3,4-Diamino-2-methyltetrahydrofuran Sulfate (VIII)

(a) **By Drastic Hydrolysis of Hexahydro-2-oxo-4-methyl-1-furo[3,4]imidazole (VII).**—A mixture of 726 mg. of (VII), 9.0 g. of $Ba(OH)_2 \cdot 8H_2O$ and 44 cc. of water was sealed into a pressure tube and the tube was heated to 130–140° for twenty hours. The resulting suspension was removed from the tube, brought to a boil, and carbon dioxide was passed into the hot solution for thirty minutes. The barium carbonate was removed by filtration through filter-cel, the clear filtrate was concentrated to a small volume *in vacuo*, and was acidified to congo red with 2 *N* sulfuric acid. The precipitate of barium sulfate was filtered off, most of the water was removed *in vacuo*, and 823 mg. (75.2% of the theoretical yield) of the crystalline sulfate (VIII) was precipitated from the concentrated solution by the addition of hot methanol. The material was purified by several recrystallizations from dilute methanol, and melted at 270–275° with decomposition.

*Anal.* Calcd. for $C_5H_{14}O_5N_2S$: C, 28.03; H, 6.59; N, 13.07; S, 14.97. Found: C, 27.82; H, 6.38; N, 12.89; S, 15.35.

(b) **By Drastic Hydrolysis of *cis*-3,4-Diaminocarbethoxy-2-methyltetrahydrofuran (IV).**—A mixture of 214 mg. of (IV), 4.2 g. of $Ba(OH)_2 \cdot 8H_2O$ and 22 cc. of water was heated to 140–150° for six hours in a sealed tube, and 33 mg. (18.7% of the theoretical yield) of the sulfate (VIII) was isolated from the reaction mixture by the method outlined above.

The mother liquors from (VIII) were neutralized with 10% sodium bicarbonate and were concentrated to dryness *in vacuo*. Sublimation of the residue at 150–160° and 0.005 mm. gave 73 mg. (62.4% of the theoretical yield) of crystals which melted at 235–238° and were identical with compound (VII).

In another experiment in which 642 mg. of (IV) was hydrolyzed for twenty hours at 140–150° with 12.6 g. of $Ba(OH)_2 \cdot 8H_2O$ and 66 cc. of water, 381 mg. (72.1% of the theoretical yield) of (VIII) was obtained.

## Summary

A procedure for the synthesis of a hexahydro-2-oxo-4-methyl-1-furo[3,4]imidazole isomer has been described. This synthesis involves catalytic hydrogenation of the appropriate furan derivative to the corresponding *cis*-3,4-diaminocarbethoxytetrahydrofuran and cyclization of this compound by treatment with dilute barium hydroxide.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ROCHESTER]

# The Action of Some Benzyl Halides on Salts of Phenylnitromethane and Phenylnitroacetonitrile

BY LEONARD WEISLER[1] AND R. W. HELMKAMP

Treatment of metallic derivatives of primary and secondary nitro compounds with alkyl halides either has failed to produce alkylation or, if alkylation has occurred, has given rise preferentially to nitronic esters rather than C-alkylated products. The nitronic esters frequently have not been isolated in the pure state because of the tendency of a nitronic ester to disproportionate into an oxime and an aldehyde or a ketone.

$$RCH{=}NO_2M + R'CH_2X \longrightarrow RCH{=}NO_2CH_2R' \longrightarrow RCH{=}NOH + R'CHO$$

To further the elucidation of the influence of constitutional and environmental factors on the course of the alkylation of nitronate ions (and of resonating anions in general), it was decided to investigate the action of some benzyl halides, in particular *p*-nitrobenzyl chloride, on salts of phenylnitromethane and phenylnitroacetonitrile. That these nitro compounds might react with *p*-nitrobenzyl chloride to form, at least to some extent, C-benzylated products was suggested by the fact that Posner[2] had been able to separate 2-nitro-1,3-bis-(*o*-nitrophenyl)-propane from the oil produced by the action of *o*-nitrobenzyl chloride on the sodium salt of nitromethane.

**Action of Benzyl Halides on Salts of Phenylnitromethane.**[3]—No evidence of C-benzylation could be found when equimolecular amounts of benzyl chloride and the sodium salt of phenylnitromethane were refluxed in absolute alcohol solution. That the reaction leads mainly, if not solely, to nitronic ester formation was shown by the isolation of a 76.5% yield of benzaldehyde and an 80% yield of the stereoisomeric benzaldoximes. On the other hand, when *p*-nitrobenzyl chloride was allowed to react under similar conditions, it was possible to separate not only *p*-nitrobenzaldehyde and a mixture of the benzaldoximes but also a 37% yield of a product which by analysis and chemical behavior was shown to be 1-nitro-2-

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(1) Present address: Distillation Products, Incorporated, Rochester, New York.

(2) Posner, *Ber.*, **31**, 657 (1898); *cf.* the formation of 1,2-dinitro-1,2-diphenylethane and 1,2-dinitro-1,2-diphenyleneethane (Nenitzescu and Isacescu, *ibid.*, **63**, 2484 (1930)) and of dinitroparaffins (Hass and Seigle, *J. Org. Chem.*, **5**, 100 (1940)).

(3) Nenitzescu and Isacescu (ref. 2) failed to obtain a reaction on treating the sodium salt of phenylnitromethane with methyl iodide. They found, however, that the action of *t*-butyl bromide yielded the decomposition products of the nitronic ester. The methyl nitronic ester was obtained by Auwers and Otten (*Ber.*, **57**, 456 (1924)) and by Arndt and Rose (*J. Chem. Soc.*, 6 (1935)) through the use of dimethyl sulfate. Brown and Shriner (*J. Org. Chem.*, **2**, 376 (1937)) were unsuccessful in their attempt to bring about a reaction between the sodium salt and diphenylmethyl bromide. The only recorded instance of C-alkylation of phenylnitromethane is that reported by Wieland and Höchtlen (*Ann.*, **506**, 237 (1933)), who isolated triphenylmethylphenylnitromethane in 33% yield from the reaction of triphenylmethyl chloride on the mercury derivative. In a repetition of this work, we obtained a 40% yield.

(*p*-nitrophenyl)-1-phenylethane. It slowly dissolves in an ethanol solution of potassium hydroxide, forming a purple solution, from which it can be recovered on acidification. Unlike nitronic esters, it is stable toward a hot ethanol solution of hydrogen chloride. Oxidation by chromic acid yields benzoic acid and *p*-nitrobenzoic acid. When the compound was heated above its melting point, it underwent decomposition with the evolution of nitrogen oxides to give a viscous oil containing 4-nitrostilbene. The same decomposition product was obtained when the potassium salt of the compound was heated in methanol solution.

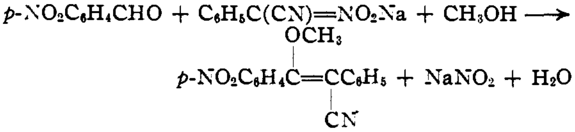
No reaction took place when the mercury derivative of phenylnitromethane was treated with alcohol, ether, and benzene solutions of *p*-nitrobenzyl chloride.

The formation of 1-nitro-2-(*p*-nitrophenyl)-1-phenylethane in fair yield by the action of *p*-nitrobenzyl chloride indicated that 2,4-dinitrobenzyl chloride would be even more likely to produce a C-substituted product. It was found, in fact, that when the latter halide was allowed to react in boiling ethanol solution with the sodium salt of phenylnitromethane, C-benzylation and O-benzylation occurred at nearly the same rate. It was not possible, however, to isolate the benzylated derivatives initially produced. Apparently 2-(2,4-dinitrophenyl)-1-nitro-1-phenylethane readily loses nitrous acid under the conditions of the experiment forming 2,4-dinitrostilbene, while the nitronic ester undergoes the usual dismutation. The yield of the stilbene was 46.6% and that of the benzaldoximes 45.5%.

In contrast to the action of *p*-nitrobenzyl chloride and 2,4-dinitrobenzyl chloride, that of *p*-cyanobenzyl chloride resulted observedly only in O-benzylation. From the reaction mixture, *p*-cyanobenzaldehyde and the benzaldoximes were separated in approximately 80% yields.

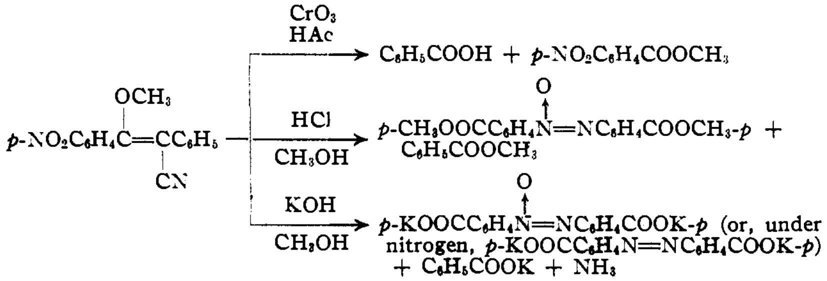
**Action of Benzyl Halides on Salts of Phenylnitroacetonitrile.**[4]—When benzyl chloride and the sodium salt of phenylnitroacetonitrile were heated in methanol solution, O-benzylation occurred practically exclusively as shown by the high yields of the disproportionation products of the nitronic ester which were isolated. Likewise no evidence of C-benzylation was obtained in the similar reaction in which *p*-nitrobenzyl chloride was used. From the reaction mixture it was possible to separate β-methoxy-β-(*p*-nitrophenyl)-α-phenylacrylonitrile, benzoyl cyanide oxime, methyl benzoate, *p*-nitrobenzaldehyde, and methyl nitrobenzoate. The combined yields of the first three of these products accounted for 88% of the sodium salt used. Since the acrylonitrile is formed smoothly and comparatively readily when equimolecular quantities of *p*-nitrobenzaldehyde and the sodium salt of phenylnitroacetonitrile are heated in methanol solution, its formation in the reaction of the sodium salt with *p*-nitrobenzyl chloride is clearly the result of the reaction sequence.

$$C_6H_5C(CN){=}NO_2Na + p\text{-}NO_2C_6H_4CH_2Cl \longrightarrow C_6H_5C(CN){=}NO_2CH_2C_6H_4NO_2 \longrightarrow C_6H_5C(CN){=}NOH + p\text{-}NO_2C_6H_4CHO$$



$$p\text{-}NO_2C_6H_4CHO + C_6H_5C(CN){=}NO_2Na + CH_3OH \longrightarrow p\text{-}NO_2C_6H_4\overset{\overset{\displaystyle OCH_3}{|}}{C}{=}\underset{\underset{\displaystyle CN}{|}}{C}C_6H_5 + NaNO_2 + H_2O$$

The acrylonitrile was found to undergo the following degradation reactions



An attempt to prepare α-nitro-β-(*p*-nitrophenyl)-α-phenylpropionitrile by the action of a benzene solution of *p*-nitrobenzyl bromide on the silver derivative of phenylnitroacetonitrile was unsuccessful. After the reaction mixture had been refluxed for sixteen hours, there were isolated, in addition to some unchanged *p*-nitrobenzyl bromide and a small amount of 1,2-dicyano-1,2-dinitro-1,2-diphenylethane, approximately 80% yields of benzoyl cyanide oxime and *p*-nitrobenzaldehyde.

## Experimental[5]

### Action of Benzyl Halides on Salts of Phenylnitromethane

**Action of Benzyl Chloride.**—A mixture of 25.3 g. (0.20 mole) of benzyl chloride and 31.8 g. (0.20 mole) of the sodium salt of phenylnitromethane in 500 cc. of absolute alcohol was refluxed for four days. After the salt produced in the reaction (11.1 g.) had been removed by filtration, the alcohol was allowed to evaporate, and the residual oil was taken up in chloroform. Extraction of the chloroform solution with a dilute solution of sodium hydroxide removed a mixture of the stereoisomeric benzaldoximes, which were identified by a procedure similar to that described under the action of *p*-nitrobenzyl chloride;

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(4) The action of methyl iodide on the sodium, potassium, and silver derivatives of phenylnitroacetonitrile has been found to give the methyl nitronic ester or its decomposition products (Wislicenus and Enders, *Ber.*, **35**, 1761 (1902); Hantzsch, *ibid.*, **40**, 1541 (1907); Thurston and Shriner, *J. Org. Chem.*, **2**, 191 (1937)). On treatment of the silver compound with diphenylmethyl bromide, Wieland and Höchtlen (ref. 3; *cf.* Shriner and Brown, *ibid.*, **2**, 560 (1938)) obtained yields of 18% of the C-derivative and 50% of the O-derivative. From the reaction mixture of triphenylmethyl chloride and the silver compound, the same investigators isolated triphenylmethyl isocyanate and phenyltriphenylmethyldiazomethane, presumably formed by decomposition of the C-substituted product.

(5) All reported melting points are corrected.

yield, 20.5 g. (85%). Treatment of the alkali-insoluble fraction of the oil with 21.5 g. of phenylhydrazine dissolved in 150 cc. of alcohol gave 30 g. of benzalphenylhydrazone (76.5%), m. p. 157.5–158°.

**Action of *p*-Nitrobenzyl Chloride.**—A solution of 42.8 g. (0.25 mole) of *p*-nitrobenzyl chloride in 500 cc. of absolute alcohol was added to 39.8 g. (0.25 mole) of the sodium salt of phenylnitromethane, and the mixture refluxed with stirring. After about an hour salt began to precipitate. The solution turned dark red within the first two hours and gradually changed to a light yellow during the following four hours. At the end of four days the reaction mixture was cooled to room temperature, the alcohol removed by evaporation under an air blast, and the residue taken up in benzene and water. The aqueous solution, after acidification with dilute nitric acid and extraction with ether (which removed about 0.1 g. of a light yellow solid) yielded on evaporation to dryness 14.4 g. of salt, which was converted into 34.8 g. (0.243 mole) of silver chloride.

On evaporation of the solvent, the benzene solution left a red, pasty mass. Trituration of this residue with 200 cc. of ether produced a light yellow crystalline material, which after filtration and washing with ether weighed 21.5 g. An additional 3.5 g. of the same substance was isolated from the ether filtrate by evaporation and cooling in an ice-bath. Recrystallization of the combined crops from alcohol gave 24 g. of light yellow needles, melting at 141–142°. The compound was identified by its analysis and chemical behavior as 1-nitro-2-(*p*-nitrophenyl)-1-phenylethane; yield 36.8%.

*Anal.* Calcd. for $C_{14}H_{12}O_4N_2$: C, 61.76; H, 4.45; N, 10.3; mol. wt., 272. Found: C, 61.85; H, 4.49; N, 10.4; mol. wt., 282.

The oil which remained after evaporation of the ether filtrate was dissolved in benzene, and the solution was extracted with 2 *N* sodium hydroxide solution. Acidification of the alkaline extract by slow addition to dilute hydrochloric acid produced a light brown precipitate, which was taken up in ether. The ether solution, after having been washed with water and dried, was evaporated to dryness. Extraction of the brown semi-solid residue (9.6 g.) with hot water gave a solution from which on cooling 5.5 g. of crude *syn*-benzaldoxime precipitated. Recrystallization from hot water with the use of Norite yielded 4.8 g. of product melting at 125–126°. A mixed melting point of the compound and an authentic sample was undepressed. The material which failed to dissolve in the hot water was taken up in hot benzene. Cooling of the solution resulted in the separation of 1.4 g. of crystals, m. p. 32–34°. No depression of the melting point occurred when the product was mixed with *anti*-benzaldoxime prepared from benzaldehyde and hydroxylamine.

The alkali-insoluble oil (31.2 g.) deposited on standing a small quantity of crystals, which, after recrystallization from water with the use of Norite, melted at 106–107°. They were identified as *p*-nitrobenzaldehyde by the fact that there was no depression of the melting point when the compound was mixed with an authentic sample. Extraction of the oil with hot water removed additional *p*-nitrobenzaldehyde to give a total yield of 10.2 g. When the remaining oil was subjected to steam distillation, a slow decomposition of the nitronic ester presumably present took place, for *p*-nitrobenzaldehyde collected in the condenser and benzaldoximes could be extracted from the residue.

No reaction could be obtained with the mercury salt of phenylnitromethane and *p*-nitrobenzyl chloride in alcohol, ether or benzene.

**Thermal Decomposition of 1-Nitro-2-(*p*-nitrophenyl)-1-phenylethane.**—Three grams of this compound was heated to 180° in a test tube immersed in an oil-bath. The substance melted and then decomposed, evolving oxides of nitrogen. When after thirty minutes the evolution of gas had ceased, the reaction mixture was cooled and dissolved in chloroform. Extraction of the chloroform solution with a solution of alkali gave no evidence of the presence of acidic material. After the solution had been washed with dilute hydrochloric acid and with water, it was dried, and the chloroform allowed to evaporate. The viscous oil which remained was dissolved in hot alcohol, and the solution then cooled in an ice-bath. A small quantity of crystals separated, which, after recrystallization from alcohol, melted at 153–154°. No depression of the melting point occurred when the substance was mixed with a sample of 4-nitrostilbene prepared according to the directions of Pfeiffer and Sergiewskaja.[6]

**Oxidation of 1-Nitro-2-(*p*-nitrophenyl)-1-phenylethane.**—A mixture of 3.0 g. of the nitroethane derivative, 7.0 g. of chromic anhydride and 250 cc. of glacial acetic acid was refluxed for four hours. The acetic acid was then removed by distillation *in vacuo*, and the residue poured into ice water. The precipitate which was formed was identified, after recrystallization from water, as *p*-nitrobenzoic acid, m. p. 237–238°. An ether extract of the aqueous filtrate was found to contain benzoic acid.

**Treatment of 1-Nitro-2-(*p*-nitrophenyl)-1-phenylethane with Hydrochloric Acid.**—A solution of 1.0 g. of the nitroethane derivative in 80 cc. of alcohol and 20 cc. of 6 *N* hydrochloric acid was refluxed for four hours. From the cooled and concentrated solution 0.95 g. of the original compound was recovered unchanged. The stability of the compound toward hot mineral acid is in marked contrast to that of nitronic esters, which commonly decompose under these conditions.

**Action of Alcoholic Potassium Hydroxide Solution on 1-Nitro-2-(*p*-nitrophenyl)-1-phenylethane.**—One gram of the nitroethane derivative was added to 50 cc. of alcohol containing 0.5 g. of potassium hydroxide. The substance slowly dissolved forming a deep purple solution. No precipitation occurred when the solution was diluted with an equal volume of water. Acidification with hydrochloric acid, however, caused a yellow solid to separate, from which the original compound was isolated on crystallization from alcohol.

A solution of 2 g. of the nitroethane derivative and 0.41 g. of potassium hydroxide in 50 cc. of methyl alcohol was refluxed for twenty-four hours. Concentration and cooling of the solution yielded 0.5 g. of crystals, which were identified after recrystallization from alcohol as 4-nitrostilbene; m. p. 152–154°.

**Action of 2,4-Dinitrobenzyl Chloride.**—A mixture of 15.9 g. (0.10 mole) of the sodium salt of phenylnitromethane, 21.6 g. (0.10 mole) of 2,4-dinitrobenzyl chloride, and 500 cc. of absolute alcohol was refluxed with stirring for forty-eight hours. The solution turned red and then deep brown, and a light brown precipitate gradually formed. The mixture was cooled and filtered, and the solid was washed thoroughly with hot water. Evaporation of the aqueous filtrate yielded 8.0 g. of salt, which was converted into 10.3 g. (0.072 mole) of silver chloride. That the salt consisted in part of sodium nitrite was shown by the evolution of nitrogen oxides when the filtrate was acidified. Crystallization of the water-insoluble residue from glacial acetic acid gave 6.6 g. of yellow crystals melting at 138–139°. They were shown to be 2,4-dinitrostilbene by analysis and the undepressed melting point of a mixture of the substance with a sample prepared according to the directions of Thiele and Escales.[7]

*Anal.* Calcd. for $C_{14}H_{10}O_4N_2$: C, 62.22; H, 3.70. Found: C, 62.35; H, 3.82.

The alcohol filtrate was evaporated under an air blast, the residue taken up in chloroform, and the solution extracted with a dilute solution of sodium hydroxide. From the chloroform solution an additional 6.0 g. of 2,4-dinitrostilbene was obtained, making the total yield of this product 12.6 g. (46.6%). From the alkaline extract 5.5 g. (45.4%) of the stereoisomeric benzaldoximes was isolated according to the procedure previously described.

**Action of *p*-Cyanobenzyl Chloride.**—A mixture of 15.2 g. (0.10 mole) of *p*-cyanobenzyl chloride, 15.9 g. (0.10 mole) of the sodium salt of phenylnitromethane, and 300 cc. of absolute alcohol was refluxed for eight hours. The salt formed in the reaction (5.6 g.) was then removed, and the

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(6) Pfeiffer and Sergiewskaja, *Ber.*, **44**, 1109 (1911).

(7) Thiele and Escales, *ibid.*, **34**, 2843 (1901).

filtrate was concentrated by distillation. The residual, dark red oil was separated into alkali-soluble and alkali-insoluble fractions. From the alkali-insoluble portion, 11.0 g. (0.084 mole) of *p*-cyanobenzaldehyde, m. p. 98–99°, was isolated, while from the alkali-soluble fraction, 9.5 g. (0.079 mole) of the stereoisomeric benzaldoximes was obtained. No evidence of C-alkylation was noted.

### Action of Benzyl Halides on Salts of Phenylnitroacetonitrile

**Action of Benzyl Chloride.**—A mixture of 23.0 g. (0.125 mole) of the sodium salt of phenylnitroacetonitrile, 15.8 g. (0.125 mole) of freshly distilled benzyl chloride, and 400 cc. of methanol was refluxed with stirring for four days. The alcohol was then removed by distillation, and the residue extracted with chloroform. The undissolved salt weighed 7.3 g. Extraction of the chloroform solution with a solution of alkali removed 17.2 g. (0.118 mole) of benzoyl cyanide oxime, m. p. 126–127°. The alkali-insoluble portion on treatment with phenylhydrazine gave 20.0 g. (0.102 mole) of benzalphenylhydrazone, m. p. 157–158°.

**Action of *p*-Nitrobenzyl Chloride.**—No apparent reaction occurred when a methanol solution of equimolar amounts of the sodium salt of phenylnitroacetonitrile and *p*-nitrobenzyl chloride was allowed to stand for five days at room temperature. Likewise there was no evidence of any reaction when the reagents were heated in ether and in benzene at reflux temperatures. However, when a solution of 61.3 g. (0.333 mole) of the sodium salt of phenylnitroacetonitrile and 57.1 g. (0.333 mole) of *p*-nitrobenzyl chloride in 1000 cc. of methanol was refluxed, a slow evolution of nitrogen oxides occurred. When after four days the evolution of gas had practically ceased, the alcohol was removed by evaporation under an air blast. The residue was extracted with benzene, and the undissolved salt was taken up in water. The aqueous solution, after acidification with dilute nitric acid, was extracted with ether. From the ether extract 0.3 g. of a light yellow acidic solid was obtained, which was not identified. Evaporation of the aqueous solution to dryness yielded 19.2 g. of salt, which was transformed into 45.7 g. (0.318 mole) of silver chloride.

The benzene solution on concentration by distillation left a dark red, pasty mass, from which a yellow crystalline material was obtained by trituration with two 250-cc. portions of ether. An additional crop of the same product was isolated from the concentrated and cooled ether solution. Recrystallization of the combined crops from methanol gave 27.7 g. of light yellow crystals, m. p. 176–177°. They were shown by their analysis and chemical behavior to be β-methoxy-β-(*p*-nitrophenyl)-α-phenylacrylonitrile.

*Anal.* Calcd. for $C_{16}H_{12}O_3N_2$: C, 68.57; H, 4.32; N, 10.0; $OCH_3$, 11.08. Found: C, 68.57; H, 4.44; N, 10.3; $OCH_3$, 11.15.

The ether filtrate was thoroughly extracted with 2 *N* sodium hydroxide solution. The aqueous solution was then acidified and extracted with ether. Evaporation of the ether left 25.9 g. of a light brown solid, which after crystallization from water with the use of Norite yielded 23.5 g. (0.159 mole) of benzoyl cyanide oxime, m. p. 126–127°. The melting point of a mixture of the product with a sample of the oxime prepared according to the directions of Thurston and Shriner[8] was undepressed.

The alkali-extracted ether solution was washed with water and dried over calcium chloride, and the ether then evaporated under diminished pressure in a desiccator. The residual, dark brown oil (44.0 g.) was subjected to an exhaustive steam distillation. The first fraction contained a light yellow oil, which, after extraction with ether, yielded on distillation 4.5 g. of a colorless liquid boiling at 192–194° (740 mm.). It was identified as methyl benzoate by its odor and hydrolysis to benzoic acid. During the subsequent steam distillation a light yellow solid collected in the condenser. This product, after recrystallization from water (4.6 g.), was found to be *p*-nitrobenzaldehyde. When the oil which failed to distill with steam was subjected to distillation *in vacuo*, 7.2 g. of a light yellow distillate was obtained, which solidified on cooling. This product, after crystallization from petroleum ether (6.3 g.), melted at 95–95.5° and was shown to be methyl *p*-nitrobenzoate. There remained in the distilling flask 25 g. of a dark, resinous oil, from which no identifiable compound could be isolated. The combined yields of the acrylonitrile derivative, benzoyl cyanide oxime, and methyl benzoate account for 88% of the sodium salt of phenylnitroacetonitrile. No evidence of C-benzylation was obtained.

**Oxidation of β-Methoxy-β-(*p*-nitrophenyl)-α-phenylacrylonitrile.**—A mixture of 3.0 g. of the nitrile, 7.8 g. of chromic anhydride, and 300 cc. of glacial acetic acid was refluxed for three hours, then cooled, and poured into a liter of ice water. On the following day the crystalline precipitate was separated by filtration, washed with water, and dried. Recrystallization from methanol gave 1.1 g. of light yellow needles, m. p. 94.5–95°, which were identified as methyl *p*-nitrobenzoate by their analysis and their undepressed melting point when they were mixed with an authentic sample. The aqueous filtrate was extracted with ether, and the ether extract evaporated to dryness. The residue was redissolved in ether, and the solution extracted with a dilute solution of sodium hydroxide. Acidification of the alkaline extract precipitated 1.0 g. of benzoic acid. From the ether solution an additional 0.2 g. of methyl *p*-nitrobenzoate was isolated.

**Action of Potassium Hydroxide on β-Methoxy-β-(*p*-nitrophenyl)-α-phenylacrylonitrile.**—Four grams of the acrylonitrile was added to a solution of 6.3 g. of potassium hydroxide in 100 cc. of methanol, and the mixture was refluxed for thirty hours. Ammonia was slowly evolved. The methanol was then removed by distillation, the residue dissolved in 150 cc. of water, and the solution filtered. Slow addition of the filtrate to dilute hydrochloric acid produced an orange precipitate, which was filtered, washed, and dried. The substance melted at 249–251° with decomposition and was shown, as described below, to be *p*,*p*′-azoxybisbenzoic acid by the analysis of its silver salt and the conversion of the latter into the dimethyl ester. Extraction of the filtrate with ether yielded 2.5 g. of benzoic acid. When the reaction was carried out in an atmosphere of nitrogen, *p*,*p*′-azobisbenzoic acid, m. p. 330° with decomposition, and benzoic acid were produced.

To convert the *p*,*p*′-azoxybisbenzoic acid into its silver salt, the acid was dissolved in dilute sodium hydroxide solution, the excess alkali was carefully neutralized with dilute nitric acid, and then silver nitrate solution was added until precipitation no longer occurred. The precipitate was filtered, washed, and dried *in vacuo*.

*Anal.* Calcd. for $C_{14}H_8O_5N_2Ag_2$: Ag, 43.16. Found: Ag, 43.05.

A mixture of 2.0 g. of the finely pulverized silver salt, 5 g. of methyl iodide, and 50 cc. of benzene was refluxed for three hours. The solution was filtered, the benzene evaporated, and the residue crystallized from methanol. The yield of dimethyl *p*,*p*′-azoxybisbenzoate, m. p. 206–207°, was 1.1 g. (87%). No depression of the melting point occurred when the product was mixed with a sample of the ester prepared according to the directions of Alway and Walker.[9]

**Action of Hydrogen Chloride on β-Methoxy-β-(*p*-nitrophenyl)-α-phenylacrylonitrile.**—A slow stream of hydrogen chloride was passed through a solution of 3.0 g. of the acrylonitrile in 200 cc. of methanol. The solution was gently refluxed for six hours, and the alcohol was then removed by distillation. The pasty, semi-crystalline residue was filtered with suction and washed with ether. It yielded on crystallization from methanol 1.2 g. of dimethyl *p*,*p*′-azoxybisbenzoate, m. p. 206–207°. The ether washings left on evaporation 1 g. of a light brown oil which was identified as methyl benzoate by its odor, boiling point, and hydrolysis to benzoic acid.

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(8) Thurston and Shriner, *J. Org. Chem.*, **2**, 192 (1937).

(9) Alway and Walker, *Ber.*, **36**, 2314 (1903).

**Synthesis of β-Methoxy-β-(*p*-nitrophenyl)-α-phenylacrylonitrile.**—A solution of 10 g. (0.066 mole) of *p*-nitrobenzaldehyde and 12.2 g. (0.066 mole) of the sodium salt of phenylnitroacetonitrile in 200 cc. of methanol was refluxed for fourteen hours. The solution turned red and a copious precipitate formed as the reaction progressed. The mixture was cooled and filtered, and the crystalline mass was washed with cold methanol. Recrystallization from glacial acetic acid gave 13.5 g. (73%) of β-methoxy-β-(*p*-nitrophenyl)-α-phenylacrylonitrile in the form of long yellow needles melting at 176–177°. There was no depression of the melting point when the compound was mixed with the product from the reaction of *p*-nitrobenzyl chloride and the sodium salt of phenylnitroacetonitrile. The nitrile is only slightly soluble in ether, methanol, ethanol, and glacial acetic acid; it is somewhat more soluble in benzene and acetone. When exposed to the light, it turns light brown during the course of a week.

**Action of *p*-Nitrobenzyl Bromide on the Silver Salt of Phenylnitroacetonitrile.**—A mixture of 26.9 g. (0.10 mole) of the silver salt, 21.6 g. (0.10 mole) of *p*-nitrobenzyl bromide, and 80 cc. of dry benzene was refluxed with stirring for sixteen hours. The insoluble salts were then removed by filtration, washed with benzene, and dried *in vacuo*. Their total weight (20.2 g.) showed that complete conversion of the original silver salt into silver bromide had not occurred. The red benzene filtrate was concentrated by distillation, and the residue dissolved in alcohol. The solution deposited on cooling in an ice and salt mixture 0.1 g. of a light brown solid, which, after filtration and crystallization from methanol, melted at 174–175°. The analytical data agreed with the composition of 1,2-dicyano-1,2-dinitro-1,2-diphenylethane.

*Anal.* Calcd. for $C_{16}H_{10}O_4N_4$: C, 59.63; H, 3.13. Found: C, 59.89; H, 3.09.

The alcohol was removed by evaporation, the residue taken up in chloroform, and the solution extracted with a solution of sodium hydroxide. From the alkaline extract there was obtained by acidification and crystallization of the resulting precipitate from water 12.4 g. (0.0085 mole) of benzoyl cyanide oxime, while from the chloroform solution it was possible to isolate through the bisulfite addition product 12.2 g. (0.0081 mole) of *p*-nitrobenzaldehyde. The residual oil was found to contain 2.4 g. of unchanged *p*-nitrobenzyl bromide.

## Summary

1. Benzyl chloride and *p*-cyanobenzyl chloride reacted in ethanol with the sodium salt of phenylnitromethane to yield the decomposition products of the nitronic esters formed by O-benzylation. When *p*-nitrobenzyl chloride and 2,4-dinitrobenzoyl chloride were used, C-benzylation likewise occurred, giving 1-nitro-2-(*p*-nitrophenyl)-1-phenylethane (36.8%) and 2,4-dinitrostilbene (46.6%) respectively. No reaction took place between *p*-nitrobenzyl chloride and the mercury derivative.

2. The action of benzyl chloride and of *p*-nitrobenzyl chloride on the sodium salt of phenylnitroacetonitrile in methanol solution and of *p*-nitrobenzyl bromide on a suspension of the silver compound in benzene gave only products resulting from intermediate nitronic ester formation.

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# *cis*-Traumatic Acid and Related Compounds

BY WALTER M. LAUER AND WALTER J. GENSLER*

Traumatic acid, 1-decene-1,10-dicarboxylic acid (I, *n* = 8), has been isolated from string bean pods by English, Bonner and Haagen-Smit and

$$\underset{\text{I}}{HOOCCH{=}CH(CH_2)_nCOOH} \qquad \underset{\text{II}}{HOOC(CH_2)_nCOOH}$$

$$\underset{\text{III}}{HOOCCH_2CH{=}CH(CH_2)_7COOH}$$

has been demonstrated to be active as a plant hormone.[1] In addition, related compounds such as 1,10-decanedicarboxylic acid (II, *n* = 10), sebacic acid (II, *n* = 8),[1a] 1-nonene-1,9-dicarboxylic acid (I, *n* = 7), 1-tridecene-1,13-dicarboxylic acid (I, *n* = 11) and 2-decene-1,10-dicarboxylic acid (III)[2] were shown to possess similar activity but to a lesser degree than traumatic acid. A synthesis of traumatic acid, which led to a product that was identical with the naturally occurring plant wound hormone, was accomplished by these same investigators by condensing the half aldehyde of sebacic acid with malonic acid in the presence of pyridine. The condensation of an aldehyde with malonic acid in the presence of pyridine has been shown to yield *trans* products in the cases of glyoxylic acid,[3a] benzaldehyde[3b] and acetaldehyde.[3c] Consequently, it is presumed that the naturally occurring traumatic acid is the *trans* form.

Biological systems show a high degree of specificity. An example which involves *cis–trans* isomers has been reported by Quackenbush, Platz and Steenbock.[4] These investigators demonstrated that although ethyl linoleate was active in curing acute dermatitis in rats in daily doses of one-half drop, the ethyl ester of elaidinized linoleic acid was inactive at a level of one drop daily.

In view of these considerations, the synthesis of the *cis* form of 1-decene-1,10-dicarboxylic acid

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(1) (a) English, Bonner and Haagen-Smit, THIS JOURNAL, **61**, 3434 (1939); (b) English, Bonner and Haagen-Smit, *Science*, **90**, 329 (1939); English and Bonner, *J. Biol. Chem.*, **121**, 791 (1937); Bonner and English, *Plant Physiol.*, **13**, 331 (1938); English, Bonner and Haagen-Smit, *Proc. Nat. Acad. Sci.*, **25**, 323 (1939); Bonner and English, *Science*, **86**, 352 (1937).

(2) English, THIS JOURNAL, **63**, 941 (1941).

(3) (a) Doebner, *Ber.*, **34**, 53 (1901); (b) Knoevenagel, *ibid.*, **31**, 2602 (1898); Stoermer and Heymann, *ibid.*, **45**, 3099 (1912); (c) von Auwers and Wissenbach, *ibid.*, **56**, 715 (1923); Letch and Linstead, *J. Chem. Soc.*, 455 (1932).

(4) Quackenbush, Platz and Steenbock, *J. Nutrition*, **17**, 115 (1939).