Some crystalline δ-lactone was obtained from an early fraction. It showed m.p. 48–49° after sublimation.

B.—The following technique gave both III and IV as crystalline products in reasonable yield. Ten grams of adduct was dissolved in 30 ml. of glacial acetic acid and 1 ml. of concentrated sulfuric acid was added. After standing at room temperature for 96 hours, the honey-colored reaction mixture was neutralized with saturated sodium bicarbonate solution. The neutral product was isolated by ether extraction in the usual manner, and 7 g. (83%) of lactone mixture was obtained. Vacuum distillation separated this mixture into two main fractions, b.p. 70–72° (1.5 mm.) and 79–81° (1.0 mm.), respectively. These products solidified on cooling, the lower boiling cut yielding 2.9 g. of γ-lactone (m.p. 50–51° after recrystallization from petroleum ether) and the higher boiling giving 4.0 g. of δ-lactone (m.p. 48–49° after recrystallization from petroleum ether).

The δ-lactone was resublimed to yield an analytical sample, m.p. 48–49°. It had a single sharp maximum in chloroform at 5.80 μ.

Anal. Calcd. for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 69.91; H, 9.00.

Degradation of III to *m*-Xylene.—One gram (0.006 mole) of III (m.p. 50–51°) was ground to a fine powder and mixed thoroughly with 300 mg. of 10% palladium–charcoal and 3.0 g. of barium oxide. The mixture was placed in a 25-ml. distilling flask and heated gently over a micro-flame. The product, *m*-xylene, came over readily as a colorless liquid. The yield was 0.55 g. (80%). For complete identification of this product, infrared and ultraviolet spectra were taken and a nitro derivative was prepared. Maxima at 13.00, 13.75 and 14.50 μ in the infrared[6] and at 259, 265.4, 268.8 and 272.5 mμ in the ultraviolet,[7] all characteristic of *m*-xylene, were observed. Nitration of 500 mg. of the degradation product using 2 ml. of concentrated sulfuric acid and 2 ml. of fuming nitric acid, and keeping the mixture at 100° for 20 minutes, gave a white precipitate when the reaction mixture was poured onto ice. After recrystallization from 95% ethanol, fine, pale yellow, needles, m.p. 177–180° (lit.[8] 182°), were obtained. A melting point of 177–181° was observed on admixture with an authentic sample of 2,4,-6-trinitro-*m*-xylene.

Degradation of IV to *p*-Xylene.—Five hundred mg. (0.003 mole) of IV (m.p. 48–49°) was degraded in a fashion parallel to that described above. A yield of 300 mg. (88%) of *p*-xylene was obtained. The product was identified by its characteristic infrared (12.58, 13.72, 14.41 μ)[9] and ultraviolet (260.7, 266.1, 269.0, 275.0 mμ)[10] spectra.

Base Hydrolysis of the Diels–Alder Adduct.—Forty grams (0.22 mole) of the Diels–Alder adduct was refluxed with 210 ml. of 5% potassium hydroxide solution for 70 hours. Not all the ester had been hydrolyzed at this point, and 8.5 g. of starting material was recovered by ether extraction. The reaction mixture was then acidified with hydrochloric acid and extracted with five 100-ml. portions of ether. The ether layer was washed with water, dried over anhydrous magnesium sulfate and evaporated. Vacuum distillation of the residual acid gave a main fraction (21.9 g., 82% yield on basis of ester converted), b.p. 104–105° (1.0 mm.). Using a 70-cm. Podbielniak column, no evidence for separation of isomers was obtained. On cooling, however, the acid slowly deposited crystals of V. These crystals were collected and washed with petroleum ether. The crude material, m.p. 60–64°, gave an analytical sample, m.p. 62–64°, on vacuum sublimation.

Anal. Calcd. for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 69.84; H, 8.91.

Degradation of V to *p*-Xylene.—Five hundred mg. (0.003 mole) of V yielded 200 mg. (58%) of colorless distillate when subjected to palladium–charcoal and barium oxide degradation, as described above. The infrared spectrum of the product was indistinguishable from that of authentic *p*-xylene.

Lactonization of V.—A solution of 2.76 g. (0.018 mole) of V in 10 ml. of glacial acetic acid and 0.25 ml. of concentrated sulfuric acid was allowed to stand at room temperature overnight. The neutral product was isolated in the usual way, and appeared as long needles as soon as the ether was taken off. The yield was 1.9 g. (69%). Recrystallization from 30–60° petroleum ether gave pure white needles, m.p. 48–49°.

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(6) F. D. Rossini, *et al.*, "Infrared Spectral Data," American Petroleum Institute Research Project 44, Carnegie Institute of Technology, Pittsburgh, Pennsylvania, 1955, Serial No. 311.

(7) "Ultraviolet Spectral Data," American Petroleum Institute Research Project 44, Carnegie Institute of Technology, Pittsburgh, Pennsylvania, 1946, Serial No. 56.

(8) I. M. Heilbron, "Dictionary of Organic Compounds," 2nd ed. Vol. IV, Oxford University Press, New York, N. Y., 1953, p. 627.

(9) See reference 6, spectrum Serial No. 312.

(10) See reference 7, spectrum Serial No. 57.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE NATIONAL INSTITUTE OF ARTHRITIS AND METABOLIC DISEASES, NATIONAL INSTITUTES OF HEALTH]

The Synthesis of β-(3-Methoxy-2,6-dinitrophenyl)-D,L-alanine and β-(3-Methoxy-4,6-dinitrophenyl)-D,L-alanine. Proof of the Structures of Two Isomeric Dinitro-*m*-tyrosines

BY ERNEST L. JACKSON

RECEIVED DECEMBER 29, 1956

β-(3-Methoxy-2,6-dinitrophenyl)-D,L-alanine and β-(3-methoxy-4,6-dinitrophenyl)-D,L-alanine have been synthesized from 3-methoxy-2,6-dinitrobenzaldehyde and 3-methoxy-4,6-dinitrobenzaldehyde. These two amino acids have been correlated with two of the β-(3-methoxydinitrophenyl)-D,L-alanines that were obtained by way of the nitration of *m*-tyrosine, thus proving two of the nitration products to be β-(3-hydroxy-2,6-dinitrophenyl)-D,L-alanine and β-(3-hydroxy-4,6-dinitrophenyl)-D,L-alanine.

The nitration of *m*-tyrosine has been shown[1] to produce three crystalline isomers of β-(3-hydroxydinitrophenyl)-D,L-alanine which upon acetylation yielded three isomers of N-acetyl-β-(3-hydroxydinitrophenyl)-D,L-alanine; methylation of two of these compounds afforded two isomers of N-acetyl-β-(3-methoxydinitrophenyl)-D,L-alanine methyl ester. Hydrolysis and deacetylation of these two methyl esters gave the two isomeric β-(3-methoxydinitrophenyl)-D,L-alanines. The present paper describes the third isomer of β-(3-methoxydinitrophenyl)-D,L-alanine and its N-acetyl methyl ester; it also establishes the orientation of the nitro groups for two of the isomers by their comparison with the authentic compounds which have been synthesized from 3-methoxy-2,6-dinitrobenzaldehyde and 3-methoxy-4,6-dinitrobenzaldehyde, the structures of which were proved by Hodgson and Beard[2] and by Tröger and Eicker.[3]

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(1) E. L. Jackson, THIS JOURNAL, **77**, 4860 (1955).

(2) H. H. Hodgson and H. G. Beard, *J. Chem. Soc.*, 2375 (1927).

(3) J. Tröger and C. Eicker, *J. prakt. Chem.*, [2] **116**, 17 (1927).

3-Methoxy-2,6-dinitrobenzaldehyde in toluene solution yielded, by reduction of the aldehyde group with aluminum isopropoxide, 3-methoxy-2,6-dinitrobenzyl alcohol (m.p. 139.5–140.5°) which reacted with phosphorus pentachloride to produce 3-methoxy-2,6-dinitrobenzyl chloride (m.p. 103.5–104.5°). Ethyl α-acetamido-α-carbethoxy-β-(3-methoxy-2,6-dinitrophenyl)-propionate (m.p. 143°) resulted in 62% yield from the reaction of sodium ethyl acetamidomalonate with 3-methoxy-2,6-dinitrobenzyl chloride in ethanol solution at room temperature. This reaction was unsuccessful in boiling ethanol solution presumably due to the oxidizing[4] action of the nitro groups in the molecule of 3-methoxy-2,6-dinitrobenzyl chloride. β-(3-Methoxy-2,6-dinitrophenyl)-D,L-alanine (m.p. 209° dec.) was produced in 57% yield through reaction of a hot mixture of sulfuric and acetic acids with ethyl α-acetamido-α-carbethoxy-β-(3-methoxy-2,6-dinitrophenyl)-propionate. Acetylation of β-(3-methoxy-2,6-dinitrophenyl)-D,L-alanine in aqueous sodium hydroxide solution by acetic anhydride gave N-acetyl-β-(3-methoxy-2,6-dinitrophenyl)-D,L-alanine (m.p. 252° dec.), methylation of which by either diazomethane or by the methanol–acetyl chloride method of Hanby, Waley and Watson[5] afforded N-acetyl-β-(3-methoxy-2,6-dinitrophenyl)-D,L-alanine methyl ester (m.p. 158–159°).

The isomer of N-acetyl-β-(3-hydroxydinitrophenyl)-D,L-alanine[1] melting at 194–195°, the one previously designated N-acetyl-C, now has been found to react with diazomethane to produce N-acetyl-β-(3-methoxy-2,6-dinitrophenyl)-D,L-alanine methyl ester (m.p. 157–158°). This product was shown by a mixed melting point determination and by comparison of the infrared spectra to be identical with the N-acetyl-β-(3-methoxy-2,6-dinitrophenyl)-D,L-alanine methyl ester that was synthesized from 3-methoxy-2,6-dinitrobenzaldehyde. Hydrolysis and deacetylation of N-acetyl-β-(3-methoxy-2,6-dinitrophenyl)-D,L-alanine methyl ester, derived from N-acetyl-C, by a hot mixture of sulfuric and acetic acids yielded β-(3-methoxy-2,6-dinitrophenyl)-D,L-alanine melting at 208° dec. alone or mixed with the compound which was synthesized from 3-methoxy-2,6-dinitrobenzaldehyde. Isomer C[1] of β-(3-hydroxydinitrophenyl)-D,L-alanine (m.p. 197°, explosively) consequently must be β-(3-hydroxy-2,6-dinitrophenyl)-D,L-alanine.

The synthesis of β-(3-methoxy-4,6-dinitrophenyl)-D,L-alanine from 3-methoxy-4,6-dinitrobenzaldehyde was accomplished by the preparation in successive steps of 3-methoxy-4,6-dinitrobenzyl alcohol (m.p. 135–136°), 3-methoxy-4,6-dinitrobenzyl chloride (m.p. 110–111°) and ethyl α-acetamido-α-carbethoxy-β-(3-methoxy-4,6-dinitrophenyl)-propionate (m.p. 167°) which was converted to β-(3-methoxy-4,6-dinitrophenyl)-D,L-alanine (m.p. 230° dec.) in 68% yield. The purification of the amino acid was facilitated greatly by the use of a Dowex-1 anion exchange resin. A mixed melting point determination and paper chromatography tests, employing both 60% ethanol and *t*-amyl alcohol as solvents, established the identity of this authentic β-(3-methoxy-4,6-dinitrophenyl)-D,L-alanine with the β-(3-methoxydinitrophenyl)-D,L-alanine (m.p. 231–232° dec.) which was prepared[1] from the isomer of N-acetyl-β-(3-methoxydinitrophenyl)-D,L-alanine methyl ester melting at 172–173°. Moreover, this methyl ester was prepared from the authentic β-(3-methoxy-4,6-dinitrophenyl)-D,L-alanine by acetylation to N-acetyl-β-(3-methoxy-4,6-dinitrophenyl)-D,L-alanine (m.p. 212–213°) which reacted with diazomethane to yield N-acetyl-β-(3-methoxy-4,6-dinitrophenyl)-D,L-alanine methyl ester melting at 172–173° alone or mixed with the compound derived from *m*-tyrosine. This proves isomer B[1] of β-(3-hydroxydinitrophenyl)-D,L-alanine (m.p. 235–236° dec.) to be β-(3-hydroxy-4,6-dinitrophenyl)-D,L-alanine.

Isomer A[1] of β-(3-hydroxydinitrophenyl)-D,L-alanine (m.p. 234° dec.) would be expected from orientation rules to be β-(3-hydroxy-2,4-dinitrophenyl)-D,L-alanine.

Experimental

Except where otherwise stated, melting points are corrected and, in the case of the amino acids, their N-acetyl derivatives and N-acetyl methyl esters the melting points were determined with the bath of the Hershberg apparatus preheated to 15–30° below the melting point.

3-Methoxy-2,6-dinitrobenzyl Alcohol and 3-Methoxy-4,6-dinitrobenzyl Alcohol.—To a solution of 2.5 g. of pure 3-methoxy-2,6-dinitrobenzaldehyde[2,3] in 40 ml. of anhydrous toluene was added 3.7 ml. of approximately 1.4 *M* solution of aluminum isopropoxide in anhydrous 2-propanol. After the solution had been refluxed for 3 hr., 10 ml. of anhydrous 2-propanol was added. The mixture was heated for 2 hr. on the steam-bath in an apparatus[6] that allowed slow distillation of the solvent and the acetone formed, 2-propanol being replenished as needed. The solvent was evaporated *in vacuo* and the solid residue was mixed thoroughly with 60 ml. of 5% hydrochloric acid. The crude 3-methoxy-2,6-dinitrobenzyl alcohol was collected, washed with water and recrystallized from ethanol as light-brown prismatic needles, yield 2 g. or 80%, m.p. 139.5–140.5°.

Anal. Calcd. for $C_8H_8N_2O_6$: C, 42.11; H, 3.53; N, 12.28. Found: C, 42.39; H, 3.46; N, 12.06.

Pure 3-methoxy-4,6-dinitrobenzaldehyde[2,3] (2.42 g.) in 38 ml. of anhydrous toluene was reduced by aluminum isopropoxide (3.6 ml. of 1.4 *M* solution in anhydrous 2-propanol) as described for the reduction of 3-methoxy-2,6-dinitrobenzaldehyde. Purified from ethanol and dried in an evacuated desiccator over calcium chloride, the light-brown crystals of 3-methoxy-4,6-dinitrobenzyl alcohol melted at 135–136°, yield 1.7 g. or 70%. Found: C, 42.27; H, 3.72; N, 12.20.

3-Methoxy-2,6-dinitrobenzyl Chloride and 3-Methoxy-4,6-dinitrobenzyl Chloride.—A mixture of 1.74 g. of 3-methoxy-2,6-dinitrobenzyl alcohol and 26 ml. of chloroform, which had been washed with water and dried over calcium chloride, was boiled for a few minutes, then cooled to 0–5° and treated with 1.91 g. of phosphorus pentachloride. The cold mixture was shaken until all solid dissolved. The solution was kept at room temperature for 2 hr., 16 ml. of *n*-hexane was added and a little amorphous solid was removed by filtration. The solution was washed once with water, four times with 5% sodium bicarbonate solution and finally with water. After the solution had been dried over calcium chloride and filtered, the solvent was evaporated *in vacuo* and the residue was recrystallized from a mixture of benzene and *n*-hexane; yield 1.6 g. or 84%, m.p. 103.5–104.5°.

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(4) *Cf.* M. Harnik and E. Margoliash, *J. Org. Chem.*, **20**, 1650 (1955).

(5) W. R. Hanby, S. G. Waley and J. Watson, *J. Chem. Soc.*, 3239 (1950).

(6) A. L. Wilds in R. Adams, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 178.

Anal. Calcd. for $C_8H_7ClN_2O_5$: C, 38.96; H, 2.86; Cl, 14.38; N, 11.36. Found: C, 39.31; H, 2.77; Cl, 14.89; N, 11.29.

3-Methoxy-4,6-dinitrobenzyl alcohol (1.25 g.) in 25 ml. of absolute chloroform was treated with phosphorus pentachloride (1.37 g.) as described for the similar reaction with 3-methoxy-2,6-dinitrobenzyl alcohol. The crude product was recrystallized as yellow prisms from absolute ethanol and dried in an evacuated desiccator over calcium chloride; yield 1.1 g. or 81%, m.p. 110–111°. Found: C, 39.30; H, 2.91; Cl, 14.17; N, 11.27.

Ethyl α-Acetamido-α-carbethoxy-β-(3-methoxy-2,6-dinitrophenyl)-propionate and Ethyl α-Acetamido-α-carbethoxy-β-(3-methoxy-4,6-dinitrophenyl)-propionate.—Ethyl acetamidomalonate (1.54 g.) was dissolved in a solution of 0.187 g. of sodium in 60 ml. of absolute ethanol. 3-Methoxy-2,6-dinitrobenzyl chloride (1.59 g.) was shaken with this solution at room temperature and nearly all of the crystals soon dissolved. It was kept at room temperature for 43 hr., some crystals of sodium chloride were removed and, after the solution had been made slightly acid with acetic acid, the solvent was evaporated at 25° *in vacuo*. The crystalline residue was taken up in hot absolute ethanol, some insoluble solid was filtered off and the filtrate was concentrated to deposit at 25° a dense mass of crystals of ethyl α-acetamido-α-carbethoxy-β-(3-methoxy-2,6-dinitrophenyl)-propionate, which was dried in an evacuated desiccator over calcium chloride; yield 1.7 g. or 62%, m.p. 143°.

Anal. Calcd. for $C_{17}H_{21}N_3O_{10}$: C, 47,77; H, 4.95; N, 9.83. Found: C, 47.63; H, 4.89; N, 9.86.

Ethyl acetamidomalonate (1.0 g.) was dissolved in a solution of 0.12 g. of sodium in 40 ml. of absolute ethanol. 3-Methoxy-4,6-dinitrobenzyl chloride (1.03 g.) was shaken mechanically with this solution at room temperature for 47 hr. The suspended crystals were collected, washed with absolute ethanol, dried and then stirred with 15 ml. of cold water. The undissolved crystals (1.0 g. melting at 159–163°) were purified by recrystallization first from absolute ethanol and then from ethyl acetate to give 0.75 g. of pure ethyl α-acetamido-α-carbethoxy-β-(3-methoxy-4,6-dinitrophenyl)-propionate melting at 167°. Found: C, 47.99; H, 4.81; N, 9.60.

β-(3-Methoxy-2,6-dinitrophenyl)-D,L-alanine and β-(3-Methoxy-4,6-dinitrophenyl)-D,L-alanine.—To a solution of 1.58 g. of ethyl α-acetamido-α-carbethoxy-β-(3-methoxy-2,6-dinitrophenyl)-propionate in 47 ml. of glacial acetic acid was added 63 ml. of 6.258 *N* sulfuric acid. After the solution had been refluxed for 8 hr., it was diluted with 60 ml. of water and concentrated *in vacuo* (bath 65°) to 20 ml., some sirup having separated. It was diluted with 50 ml. of water, the mixture was concentrated *in vacuo* to *ca.* 30 ml., then diluted with 70 ml. of water and heated on the steam-bath for a few minutes. After being cooled to room temperature, the mixture of solution and sirup was extracted six times with ethyl acetate. The hot aqueous solution was treated with sufficient barium hydroxide solution to remove sulfate ions exactly. The solution upon concentration *in vacuo* yielded in two crops 0.5 g. of crystalline β-(3-methoxy-2,6-dinitrophenyl)-D,L-alanine, most of which melted at 208°. The ethyl acetate extract was concentrated *in vacuo* to deposit a thick, brown sirup which was dissolved in 250 ml. of hot water. The filtered aqueous solution was extracted with benzene and then evaporated *in vacuo* to deposit solid material which, after further purification from water, increased the yield of β-(3-methoxy-2,6-dinitrophenyl)-D,L-alanine to 0.6 g. or 57%. The analytical sample was recrystallized from water as almost colorless needles and dried for 24 hr. in the air at room temperature. These crystals, which melted at 209° (uncor., dec.), lost 5.3% in weight at 100° *in vacuo*.

Anal. Calcd. for $C_{10}H_{11}N_3O_7$: C, 42.11; H, 3.89; N, 14.74; OCH_3, 10.88. Found (dried at 100° *in vacuo*): C, 41.91; H, 3.83; N, 14.51; OCH_3, 10.77.

β-(3-Methoxy-2,6-dinitrophenyl)-D,L-alanine was prepared also from N-acetyl-β-(3-methoxy-2,6-dinitrophenyl)-D,L-alanine methyl ester, which was obtained as described below by the reaction of diazomethane with one of the isomers of N-acetyl-β-(3-hydroxydinitrophenyl)-D,L-alanine[1] (N-acetyl-C, m.p. 194–195°). A solution of 75 mg. of this N-acetyl-β-(3-methoxy-2,6-dinitrophenyl)-D,L-alanine methyl ester (somewhat impure; m.p. 145–147°) in a mixture of 2 ml. of acetic acid and 2.3 ml. of 5.76 *N* sulfuric acid was kept at 100° under reflux for 5 hr. The product (47 mg.) was isolated as previously described[1] and purified by several recrystallizations from water as almost colorless needles. The air-dried crystals melted at 208° (uncor., dec.) and lost 5.8% in weight at 100° *in vacuo*. A mixed melting point determination with crystals of β-(3-methoxy-2,6-dinitrophenyl)-D,L-alanine prepared from ethyl α-acetamido-α-carbethoxy-β-(3-methoxy-2,6-dinitrophenyl)-propionate showed no depression. Found (dried at 100° *in vacuo*): C, 42.52; H, 4.09.

For the preparation of β-(3-methoxy-4,6-dinitrophenyl)-D,L-alanine, a solution of 0.542 g. of ethyl α-acetamido-α-carbethoxy-β-(3-methoxy-4,6-dinitrophenyl)-propionate in a mixture of 16 ml. of glacial acetic acid and 21.7 ml. of 6.258 *N* sulfuric acid was refluxed for 6 hr. The solution was diluted with 150 ml. of water and left overnight at 25° to deposit 26 mg. of crystalline ethyl α-acetamido-α-carbethoxy-β-(3-methoxy-4,6-dinitrophenyl)-propionate melting at 163–164°. The solution was concentrated *in vacuo* to a small volume, then diluted with water, and the concentration *in vacuo* was repeated. The solution was diluted with water and extracted twice with ethyl acetate. After treatment with barium hydroxide for exact removal of sulfate ions, the aqueous solution was evaporated *in vacuo* to dryness. The crystalline residue was taken up in water and the solution was evaporated again *in vacuo;* this operation was repeated until the distillate was free of acetic acid. The crystals were dissolved in 75 ml. of hot water, the yellow solution was filtered, cooled and passed through a column (13 × 1.7 cm.) of Dowex 1-X2, 200–400 mesh in the acetate form; the column was then washed with some water. The small residue left by evaporation of the solution, which had passed through the column, was found by paper chromatography to be free of β-(3-methoxy-4,6-dinitrophenyl)-D,L-alanine. The column was eluted with 200 ml. of *N* acetic acid, and the eluate was evaporated *in vacuo* to dryness. The crystalline residue was dissolved in hot water and the solution was evaporated *in vacuo;* this operation was repeated until the distillate was free of acetic acid. Recrystallization of the compound from water as slightly yellow needles gave in two crops 246 mg. (68%) of β-(3-methoxy-4,6-dinitrophenyl)-D,L-alanine, most of it melting at 228° dec. After another recrystallization from water and drying in the air at room temperature, the crystals melted at 230° (uncor., dec.) and lost 3.0% in weight at 100° *in vacuo*. Found (dried at 100° *in vacuo*): C, 42.45; H, 4.10; N, 14.96.

The melting point of a mixture of the above described crystals of authentic β-(3-methoxy-4,6-dinitrophenyl)-D,L-alanine with crystals of the previously reported[1] β-(3-methoxydinitrophenyl)-D,L-alanine (m.p. 231–232° dec.), which was prepared from the isomer of N-acetyl-β-(3-methoxydinitrophenyl)-D,L-alanine methyl ester melting at 172–173°, showed no depression. The melting point was depressed when crystals of the authentic compound were mixed with crystals of β-(3-methoxydinitrophenyl)-D,L-alanine[1] of m.p. 234–235° dec. which was prepared from the isomer of N-acetyl-β-(3-methoxydinitrophenyl)-D,L-alanine methyl ester melting at 128–129°. In paper chromatography tests, with the use of both water–ethanol (2:3) and *t*-amyl alcohol saturated with water, the authentic β-(3-methoxy-4,6-dinitrophenyl)-D,L-alanine showed R_f values in agreement with the values for the compound that was derived from N-acetyl-β-(3-methoxydinitrophenyl)-D,L-alanine methyl ester melting at 172–173°. The R_f value for the compound in water–ethanol (2:3) was 0.66, and in *t*-amyl alcohol the R_f was 0.32. For the isomer melting at 234–235° dec. the R_f value in water–ethanol (2:3) was 0.76, and *t*-amyl alcohol the R_f was 0.47.

N-Acetyl-β-(3-methoxy-2,6-dinitrophenyl)-D,L-alanine and N-Acetyl-β-(3-methoxy-4,6-dinitrophenyl)-D,L-alanine.—A solution of 0.15 g. of β-(3-methoxy-2,6-dinitrophenyl)-D,L-alanine, derived from 3-methoxy-2,6-dinitrobenzaldehyde, in 0.4 ml. of water and 0.42 ml. of 1.92 *N* sodium hydroxide was kept in ice-water during the alternate addition of six 0.36-ml. portions of 1.92 *N* sodium hydroxide and six 0.06-ml. portions of acetic anhydride. After 4 hr. at room temperature the mixture of solution and solid was treated with 0.9 ml. of 6.258 *N* sulfuric acid. The somewhat impure crystals of N-acetyl-β-(3-methoxy-2,6-dinitrophenyl)-D,L-alanine (0.15 g.) were collected, washed with water and purified by recrystallization from aqueous ethanol (1:1) or from ethyl acetate. After being dried in an evacuated desiccator over calcium chloride, the pure light-yellow crystals melted at 252° dec.

Anal. Calcd. for $C_{12}H_{13}N_3O_8$: C, 44.04; H, 4.00; N, 12.84. Found (dried at 100° *in vacuo*): C, 44.25; H, 4.14; N, 12.65.

β-(3-Methoxy-4,6-dinitrophenyl)-D,L-alanine (50 mg.), derived from 3-methoxy-4,6-dinitrobenzaldehyde, was acetylated as described for β-(3-methoxy-2,6-dinitrophenyl)-D,L-alanine using one-third the quantities of sodium hydroxide, acetic anhydride and sulfuric acid. The crude product (50 mg., m.p. 205°) was purified from absolute ethanol; m.p. 212–213°. Found (dried at 79° *in vacuo*): C, 43.83; H, 3.98; N, 12.70.

N-Acetyl-β-(3-methoxy-2,6-dinitrophenyl)-D,L-alanine Methyl Ester and N-Acetyl-β-(3-methoxy-4,6-dinitrophenyl)-D,L-alanine Methyl Ester.—A solution of 50 mg. of N-acetyl-β-(3-methoxy-2,6-dinitrophenyl)-D,L-alanine in 2.5 ml. of pure dioxane was mixed with a dry ether solution of diazomethane, prepared[7] from 0.4 g. of N-nitrosomethylurea and 4 ml. of ether. After the solution had been kept at 26–27° for 16 hr., the solvent was evaporated to deposit a sirup which crystallized upon being stirred with ether. Purified by recrystallization as slightly yellow needles from aqueous methanol and dried in an evacuated desiccator over calcium chloride, the compound melted at 158–159°, yield 35 mg.

Anal. Calcd. for $C_{13}H_{15}N_3O_8$: C, 45.75; H, 4.43; N, 12.32. Found: C, 45.55; H, 4.54; N, 12.31.

The compound was prepared also by esterification of N-acetyl-β-(3-methoxy-2,6-dinitrophenyl)-D,L-alanine with the use of methanol and acetyl chloride.[5] To a solution prepared by adding 0.5 ml. of acetyl chloride to 5 ml. of methanol was added at 0° 43 mg. of N-acetyl-β-(3-methoxy-2,6-dinitrophenyl)-D,L-alanine. The solution was kept at 25° for 23 hr., and the solvent then was evaporated at 30° *in vacuo;* the sirup was taken up in methanol, the solvent was evaporated and the operation was repeated. The sirup was crystallized as needles from methanol and purification was completed by recrystallization from benzene; m.p. 157–158°, not depressed when the substance was mixed with crystals of the methyl ester prepared with the use of diazomethane.

The reaction of diazomethane with the isomer of N-acetyl-β-(3-hydroxydinitrophenyl)-D,L-alanine melting at 194–195° (N-acetyl-C)[1] gave N-acetyl-β-(3-methoxy-2,6-dinitrophenyl)-D,L-alanine methyl ester identical with the authentic compound obtained by the esterification of N-acetyl-β-(3-methoxy-2,6-dinitrophenyl)-D,L-alanine. A solution of 40 mg. of pure N-acetyl-β-(3-hydroxydinitrophenyl)-D,L-alanine (m.p. 194–195°) in 2 ml. of pure dioxane was treated with diazomethane as described for N-acetyl-β-(3-methoxy-2,6-dinitrophenyl)-D,L-alanine; yield 28 mg., m.p. 157–158°. A mixed melting point with crystals of the methyl ester prepared from N-acetyl-β-(3-methoxy-2,6-dinitrophenyl)-D,L-alanine showed no depression and the infrared spectra (solid potassium bromide disk method) of the compound from the two sources were identical. Found: C, 46.23; H, 4.43.

The reaction of diazomethane with N-acetyl-β-(3-methoxy-4,6-dinitrophenyl)-D,L-alanine (38 mg.) was carried out as described for the similar reaction with N-acetyl-β-(3-methoxy-2,6-dinitrophenyl)-D,L-alanine, using 0.3 g. of N-nitrosomethylurea, 3 ml. of ether and 2 ml. of dioxane. The product, after purification from methanol and drying in an evacuated desiccator over calcium chloride, melted at 172–173°, not depressed when mixed with crystals of the previously reported[1] isomer of N-acetyl-β-(3-methoxydinitrophenyl)-D,L-alanine methyl ester melting at 172–173°. Found: C, 45.78; H, 4.39.

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[7] W. E. Bachmann and W. S. Struve, in R. Adams, "Organic Reactions," Vol. I, John Wiley & Sons, Inc., New York, N. Y., 1942, p. 50.

[CONTRIBUTION FROM THE GENERAL LABORATORIES, U. S. RUBBER CO.]

Chain Scission in the Oxidation of Hevea. IV. Low Molecular Weight Products from Dry Rubber

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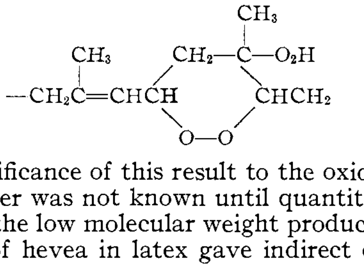
Estimates of yields of volatile products from the scission by oxygen of hevea rubber in latex[2] have been supplemented with measurements on dry rubber at 140°. The results make it possible to outline a mechanism for the scission reaction which accounts quantitatively for known products.

Some time ago Bolland and Hughes[1] deduced a structure (I) for the primary oxidation product of 1,5-dimethyl-1,5-dienes from the results of functional group analyses of partially oxidized squalene, oxidized under conditions of high chain length so that the primary product was obtained in high yield.


I

The significance of this result to the oxidation of hevea rubber was not known until quantitative estimates of the low molecular weight products of the oxidation of hevea in latex gave indirect evidence that a closely related structure must be formed in order to account for the observed products of the scission reaction.[2]

In latex the observed end-products, acetic acid, formic acid and carbon dioxide, are produced in stoichiometric ratios of 1:1:3. The yields relative to the production of new molecules by breaking the hydrocarbon chain show that six chain atoms appear as low molecular weight products at each scission.[3] A reasonable process involving six chain atoms in the scission reaction can be visualized readily by making use of a simple modification of the reaction mechanism postulated by Bolland and Hughes to account for I as a primary product. The important features of this mechanism are the ready addition of a peroxide radical to a double

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[1] J. L. Bolland and H. Hughes, *J. Chem. Soc.*, 492 (1949).

[2] E. M. Bevilacqua, THIS JOURNAL, **77**, 5394, 5396 (1955).

[3] E. M. Bevilacqua, *Rubber Age*, **80**, 271 (1956).