

Some Reactions of 3-Reteneacetic Acid

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3-Reteneacetic acid has been characterized through simple functional derivatives.

β -(3-Retene-ethanol), 1,3-dimethyl-7-isopropylphenanthrene, α -(3-retene)-*o*-nitrocinnamic acid and 3-(*o*-nitrostyryl)-retene have further been prepared by suitable reactions.

3-Reteneacetic acid¹ (I) has been subjected to a series of reactions. The methyl and ethyl-esters and the amide were prepared by conventional methods. Reduction of the ethyl ester(II) by lithium aluminium hydride gave β -(3-retene)-ethanol(III) in good yield. 1,3-Dimethyl-7-isopropylphenanthrene(V), previously prepared by total synthesis², could be prepared in 84 % yield by decarboxylation of I with soda lime.

In connection with other work α -(3-retene)-*o*-aminocinnamic acid was required, wherefore the corresponding nitro compound VI was prepared by condensation of *o*-nitrobenzaldehyde with 3-reteneacetic acid. The Perkin reaction in the Bakunin and Peccerillo modification³ was applied. In this modification the free arylacetic acid is condensed with the substituted benzaldehyde by means of acetic anhydride in the presence of a tertiary amine as catalyst. The yield of VI was 40—45 %.

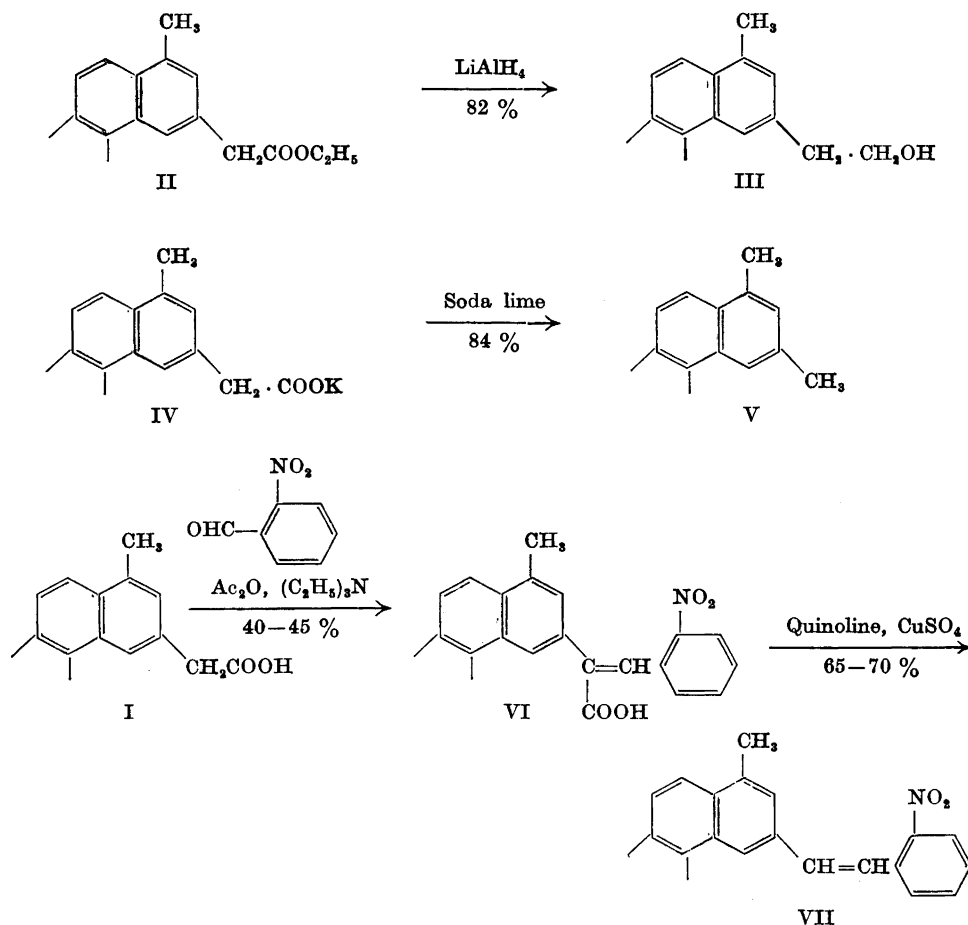
Decarboxylation of VI in quinoline with anhydrous copper sulfate according to a modification⁴ of the method of Galimberti⁵ gave 3-(*o*-nitrostyryl)-retene(VII) in good yield. The substance presumably was contaminated with the geometrical isomer, since the melting point was unsharp; recrystallization gave, however, a pure compound.

EXPERIMENTAL

3-Reteneacetic acid was prepared by the Willgerodt-Kindler reaction as previously reported¹.

Methyl-3-reteneacetate. A mixture of 3-reteneacetic acid (2.9 g, 0.01 mole), methanol (80 ml) and concentrated sulfuric acid (0.4 ml) was refluxed for 3 h. Yield after recrystallization from alcohol 2.7 g; m. p. 118—119.5°. (Found: C 82.2; H 7.27. Calc. for C₂₁H₂₂O₂ (306.4): C 82.3; H 7.24.)

Ethyl-3-reteneacetate. Prepared similarly, refluxing time 7 h. Yield after recrystallization from methanol 2.8 g; m. p. 67—68°. (Found: C 82.4; H 7.51. Calc. for C₂₂H₂₄O₂ (320.4): C 82.5; H 7.55.)



3-Reteneacetamide. 3-Reteneacetic acid (2.34 g, 0.008 mole) was mixed with phosphorus pentachloride (1.77 g, 10 % excess) and dry benzene (20 ml) was added. After spontaneous initial reaction the mixture was kept at 50–60° for half an hour and a clear solution was obtained. Benzene and phosphorus oxychloride were distilled off at diminished pressure. In order to remove all phosphorus oxychloride some benzene was added to the crystalline residue and evaporated to dryness and this procedure repeated. The crystals were dissolved in hot benzene and after cooling treated with concentrated ammonia water (10 ml). The mixture was left overnight. The precipitate was washed with ammonia water and recrystallized from *n*-propanol. Colourless crystals (2.0 g) m. p. 240–241.5° (subl.). (Found: C 82.5; H 7.25; N 4.82. Calc. for $\text{C}_{20}\text{H}_{21}\text{NO}$ (291.4): C 82.4; H 7.27; N 4.81.)

β -(3-Retene)-ethanol (III). Ethyl-3-reteneacetate (9.6 g, 0.03 mole) dissolved in dry ether (100 ml) was added with stirring in the course of 25 min to a suspension of lithium aluminium hydride (0.7 g) in dry ether (60 ml). The ether refluxed gently during this time and was kept refluxing for further 45 min on a water bath. With external cooling were then added successively water (25 ml) and 4 N sulfuric acid (30 ml). The ether layer was washed with sodium carbonate solution (2 %) and a saturated sodium chloride

solution and dried. After evaporation of the solvent the residue was recrystallized from benzene-hexane; yield 6.8 g (82 %) of colourless crystals with m. p. 117–118.5°. A second recrystallization brought the m. p. to 118–119°. (Found: C 85.9; H 8.00. Calc. for $C_{30}H_{22}O$ (278.4): C 86.3; H 7.97.)

Acetate of III. A mixture of III (0.6 g), acetic anhydride (5 ml) and pyridine (5 ml) was refluxed for 2.5 h and poured in water. The crystalline precipitate was recrystallized from methanol. Yield 0.4 g of white crystals, m. p. 66–67°. (Found: C 82.5; H 7.61; Calc. for $C_{22}H_{24}O_2$ (320.4): C 82.5; H 7.55.)

p-Nitrobenzoate of III. A mixture of III (2.0 g), *p*-nitrobenzoylchloride (1.5 g, 20 % excess), pyridine (10 ml) and dry benzene (20 ml) was heated on a boiling water bath for half an hour, the solution washed with water, hydrochloric acid (2 N) and sodium hydroxide (2 N). After drying the solvent was evaporated and the residue recrystallized twice from *n*-propanol. Yield 1.7 g, light yellow crystals with m. p. 122–123.5°. (Found: C 75.7; H 5.92; N 3.29. Calc. for $C_{27}H_{25}NO_4$ (427.5): C 75.9; H 5.90; N 3.28.)

1,3-Dimethyl-7-isopropylphenanthrene (V). Potassium-3-reteneacetate (IV) was prepared by neutralizing 3-reteneacetic acid(I) in hot *n*-propanol with the calculated amount of alcoholic potassium hydroxide. IV separated on cooling. IV (5 g) was intimately mixed with soda lime (10 g) and heated in a two bulb distilling apparatus with a wide side-arm. The apparatus was evacuated by means of an oil pump. At 0.5 mm pressure and a bath temperature of 325–380° the decarboxylation product distilled and the solid distillate was recrystallized from alcohol. 3.2 g (84 %) of colourless crystals, m. p. 76–77°, were obtained. M. p. reported² 73–76°. (Found: C 91.9; H 8.05. Calc. for $C_{19}H_{26}$ (248.4): C 91.9; H 8.12.) The picrate had m. p. 143.5–144.5°, previously reported² 145–146°.

α -(3-Retene)-o-nitrocinnamic acid (VI). A mixture of 3-reteneacetic acid (14.6 g, 0.05 mole), *o*-nitrobenzaldehyde (8.3 g, 0.055 mole), acetic anhydride (70 ml), and triethylamine (7.0 ml, 0.05 mole) was heated at 95–100° for 21 h. The excess acetic anhydride was decomposed by adding water (40 ml) and heating for further 1.5 h; the reaction mixture was then poured into 5 % hydrochloric acid (500 ml). The yellow product was filtered off, washed with water and dissolved in a hot solution of sodium carbonate. After cooling the rather dark coloured solution was extracted several times with ether and afterwards boiled with charcoal. On acidification of the filtrate a yellow precipitate separated. The product was recrystallized twice from glacial acetic acid. The yield was 9.7 g (45 %), yellow crystals with m. p. 257–258.5°. (Found: Equiv.wt. 422; C 75.8; H 5.40; N 3.27. Calc. for $C_{27}H_{23}NO_4$ (425.5): C 76.2; H 5.45; N 3.29.)

3-(o-Nitrostyryl)-retene (VII). A mixture of VI (0.5 g), anhydrous copper sulfate (0.15 g) and quinoline (12 ml) was heated at 215–220° for 25 min. After cooling the reaction mixture was diluted with benzene and the solution extracted several times with hydrochloric acid (2 N). Some dark coloured material, which had separated in the organic layer, was filtered off and washed with benzene. The filtrate was washed with sodium carbonate (2 %) and dried. After evaporation of the solvent the residue was dissolved in hot *n*-propanol, the solution treated with charcoal and filtered. On cooling yellow crystalline material separated. The yield was 0.3 g (68 %), m. p. 170–176°. The substance was recrystallized from glacial acetic acid, weight 0.23 g, m. p. 177.5–179°. (Found: C 81.4; H 6.10; N 3.63. Calc. for $C_{26}H_{23}O_2N$ (381.5): C 81.9; H 6.08; N 3.67.)

The analyses were performed in this laboratory by miss B. Møller.

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Received December 19, 1958.