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A Novel One-Step Conversion of 3,3,3-Triphenylpropionic acid to 10-cyano-10-phenyl-9-anthrone.

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***Abstract*:** 3,3,3-Triphenylpropionic acid transformed to 10-cyano-10-phenyl-9-anthrone when it was treated in connsecutive order with trifluoroacetic anhydride and sodium nitrite in trifluoroacetic acid.
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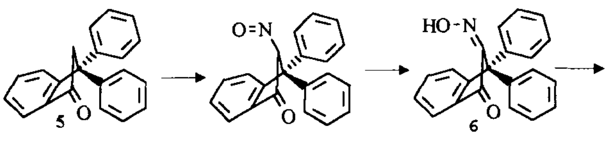
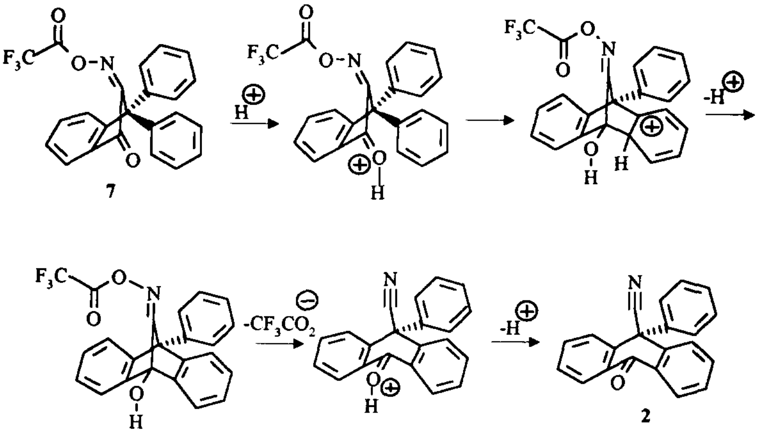
Earlier [1] we reported a new procedure for shortening a carbon chain by one carbon atom with the concomitant conversion of carboxylic acids to nitriles. The reaction has been used to contract the carbon chain of natural bile acids[2]. The reaction took unexpectedly a different path when 3,3,3-triphenylpropionic acid **1** was used as substrate and did not result in the formation of triphenylacetic acid nitril but in 10-cyano-10-phenyl-9-anthrone **2**. The chemical structure of **2** was estabilished using mass spectral data, IR ,^{13}C NMR spectroscopies and microanalysis. The mass spectrum of **3** showed peaks at m/e 295, 294, 218, 190 which are attributable to parent peak, [M-H], [M-H-Ph], [M-H-Ph-CO]. The ir spectrum of the compound **3** revealed presence of the C≡N (2240 cm^{-1}) and C=O (1675 cm^{-1}) group. For comparison[3] the C=O absorption of 10-cyano-9-anthrone is at 1675 cm^{-1}. In ^{13}C nmr were found the signals of all types of carbon atom: one signal of carbonyl carbon [182 ppm], one signal of carbon C≡N group [120.7 ppm], seven signals of tertiary atoms [130.3, 129.9, 128.6, 128.5, 128.4, 127.2, 126.9 ppm], four signals of quaternary atoms [148.4, 135.2, 133.5, 49.6 ppm], the latter peaks assigned to the carbon atom connected with the C≡ N group. We propose a mechanism which includes the following steps: the formation of the anhydride **3** and subsequently the acyl cation **4**, intermolecular acylation by Friedel-Crafts to give 3,3-diphenylindanone **5**, C-nitrosation of the later, oxime **6** formation, its trifluoroacetylation to give compound **7**, intermolecular electrophilic addition of the carbonyl group **7** to one of the phenyl groups and, lastly, second order Beckmann rearrangement of the producing anthrone **2**.

$$\underset{\mathbf{1}}{Ph_3CCH_2CO_2H} \xrightarrow{(CF_3CO)_2O} \underset{\mathbf{3}}{Ph_3CCH_2COOCOCF_3} \xrightarrow{-CF_3CO_2^{\ominus}} \underset{\mathbf{4}}{Ph_3CCH_2\overset{\oplus}{C}O} \longrightarrow$$



5 6



Further investigation provided us with data in agreement with proposed mechanism. When treated with trifluoroacetic anhydride and trifluoroacetic acid in the absence of sodium nitrite, 3,3,3-triphenylpropionic acid was shown to produce 3,3-diphenylindanone **5**. This result supports Friedel-Crafts intramolecular acylation. It was also demonstrated that 3,3-diphenylindanone **5** is converted to 10-cyano-10-phenyl-9-anthrone **2** under the reaction conditions. In addition, 1-indanone is not converted to o-carboxyphenylacetonitrile under the reaction conditions but produces the 2-hydroxyimino-1-indanone. Therefore, the phenyl substituents at the position 3 of the indanone **5** are indispensable in assisting the second order Beckmann rearrangement.

10-cyano-10-phenyl-9-anthrone :

To a cooled (0 °C) and stirred solution of 3,3,3-triphenylpropionic acid (3.02 g, 10 mmol) in trifluoroacetic anhydride (4.2 ml, 30 mmol) and trifluoroacetic acid (5 ml) under stirring was added in parts within 1 hr 30 min. sodium nitrite, taking care that temperature would not rise over 5 °C. After all the sodium nitrite was added we allowed temperature to rise to room temperature and left the reaction mixture for 12 hours. Then it was poured into solution of potassium carbonate (12 g) in water (50 ml). The reaction mixture was extracted with ethyl acetate (30 ml x 3). Evaporation of the solvent gave 10-cyano-10-phenyl-9-anthrone (2.21 g, yield 75 %, m.p. 161-163 °C (acetic acid).

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