

COMMUNICATIONS TO THE EDITOR

A Convenient Method for the Synthesis of 1,3-Bis(diazo)-2-indanone and Its Photochemistry in Methanol at Room Temperature

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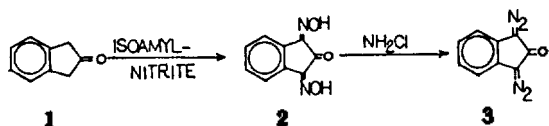
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The diazo function is potentially a more valuable synthetic tool than is presently recognized because of its high reactivity. The most general one involves the synthesis of benzocyclobutene derivatives by the photolysis of α -diazoindanones^{1,2}. But its utility has heretofore been limited by a scarcity of good methods for producing it³. The Wolff-rearrangement has received continuous interests in α -diazocarbonyl compounds^{4,5,6}, since the rearrangement has not only used as the crucial step in the Arndt-Eistert synthesis, but industrially attracted much interests as a photoresist process⁷. In this communication, we report the synthesis of 1,3-bis(diazo)-2-indanone using Foster reaction⁸ and investigation of its photoreaction in methanol.

1,3-Bis(diazo)-2-indanone has been prepared from ninhydrin with tosylhydrazine and aqueous sodium hydroxide⁹. The reaction shows the formation of 1,3-bis(tosylhydrazono)-2-indanone(19%), but the yield of 1,3-bis(diazo)-2-indanone was not recorded in this literature. In an attempt to prepare 1,3-bis(diazo)-2-indanone by this method, we have some difficulty in the separation of reaction mixture to isolate 1,3-bis(diazo)-2-indanone.

Thus we tried Foster reaction for the convenient synthesis of a desired bis(diazo)keto compound. In the experiment of this method, 1,3-bis(diazo)-2-indanone was found to be more easily separated and purified from the reaction mixture. The yield was higher than that of the literature method.



Scheme 1

To a solution of 7 g(0.05 mol) of 2-indanone in 60 ml of ether was added 10 ml of concentrated hydrochloric acid, and the solution was cooled to 0-5 °C, then 17 ml(0.1 mol) of isoamyl nitrite was slowly added dropwise. After 45 min, the external cooling bath was removed, and the resulting solution was allowed to stand for 2 hr at room temperature with stirring.

The reaction mixture was poured into 200 ml of cold water, and the resulting solid was collected, washed well with cold ether and methanol, dried to gives 17.5 g(54%) of 1,3-

bis(oximino)-2-indanone.

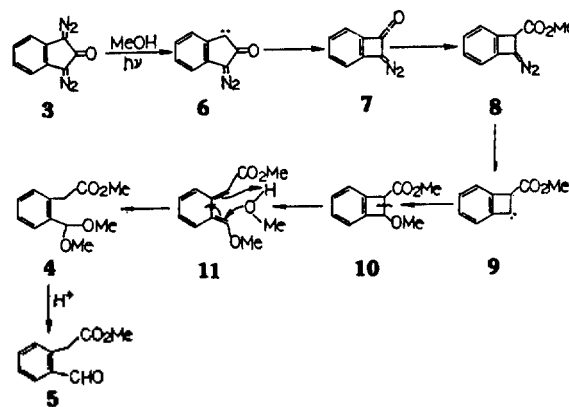
To a solution of a mixture of 10 ml of distilled water, 10 ml of 1 N sodium hydroxide and 10 ml of concentrated ammonium hydroxide was added 0.5 g(2.6×10^{-3} mol) of 1,3-bis(oximino)-2-indanone.

Keeping the reaction mixture between 0 and 5 °C with an external cooling bath, 30 ml of sodium hypochlorite (5% solution) was added dropwise. After stirring for 16 hr in dark place at room temperature the aqueous layer was extracted with two 100 ml portions of chloroform.

The combined extracts were washed well with 200 ml of distilled water and dried over magnesium sulfate. After filtration, the chloroform solution was evaporated under water aspirator at 20 °C to give crude 1,3-bis(diazo)-2-indanone. Purification was accomplished by a very rapid elution through a silicagel column with 1:1 benzene-ether(v/v) solution.

The material in red band was collected and evaporated to dryness to yield 0.3 g(63%) of 1,3-bis(diazo)-2-indanone.

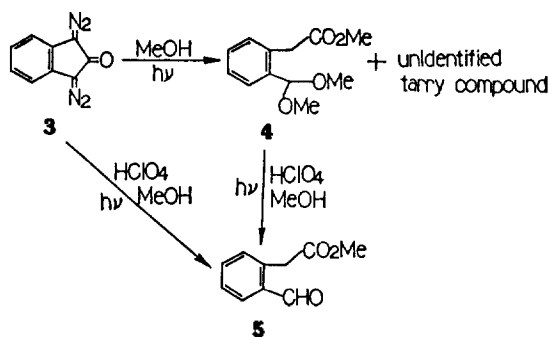
Photoirradiation of 0.8 g(4.3×10^{-3} mol) of 1,3-bis(diazo)-2-indanone in methanol for 13 hr gave 0.33 g(35%) of *o*-(dimethoxymethyl) methyl phenyl acetate(4). All irradiations were conducted using a 400 W high pressure mercury lamp with a water-cooled jacket until the nitrogen bubble stopped. Compound 4 was separated by preparative TLC (Kieselgel 60 GF 254, $R_f = 0.87$, 50% ether in hexane) and was identified by ¹H NMR spectrum and GC-MS spectrum.



Scheme 2

In the formation of compound 4, it seems likely that the first diazo group of compound 3 is photolyzed to carbene(6) followed by ring contraction, *i.e.* Wolff rearrangement, to give diazoketene(7). Compound 8 arises by addition of methanol to the Wolff rearranged product 7. And then compound 10 is formed from the elimination of the second diazo group remained in compound 8 by attacking of methanol.

It is generally accepted that singlet carbene generated by photolysis of diazo compounds in alcohol inserts into O-H bond rather than the C-H bond of alcohol¹⁰. Continuous irradiation of compound 10 in methanol gives to ring opened compound 4. Photolysis of compound 3 in the presence of perchloric acid (10 mol% of compound 3) for 5 hr gave *o*-(formyl) methyl phenyl acetate (16%) ($R_f = 0.44$, 50 % ether in hexane).



Scheme 3

Conversion of compound 4 into compound 5 was carried out under the same condition for 2 hr. We have obtained compound 5 (53%) as a major product by the TLC.

The formation of compound 5 was probably due to acid hydrolysis of compound 4. The 2,4-dinitrophenylhydrazone of compound 5 was formed as red crystals, which melted at 232-234 °C (decomp).

We think that both photolytic reactions of compound 3

proceed in same pathways.

References

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11. Spectroscopic data (¹H-NMR, IR, GC-MS) were obtained for the compounds: 1,3-bis(oximino)-2-indanone(2); mp 225-226 °C; IR(KBr) 3000-3400, 1740, 1420, 1005, 840 cm⁻¹; 1,3-bis(diazo)-2-indanone(3); mp. 126-127 °C; ¹H-NMR (60 MHz, CCl₄) δ 7.2(s, 4H); IR(KBr) 2100, 1650, 1360, 1180 cm⁻¹; *o*-(dimethoxy methyl)methyl phenyl acetate(4); ¹H-NMR (60 MHz, CCl₄) δ 7.1-7.5(m, 4H, Ar-H), 5.4(s, 1H, CH), 3.68(s, 2H, CH₂) 3.62(s, 3H, CO₂CH₃), 3.2(s, 6H, 2OCH₃); IR(NaCl) 1740, 1430, 1340, 1150, 1050 cm⁻¹; GC-MS *m/e* 224(M⁺) 161(B): *o*-(formyl) methyl phenyl acetate(5); ¹H-NMR (60 MHz, CCl₄) δ 10(s, 1H, CHO), 7.1-7.8(m, 4H, Ar-H), 3.9(s, 2H, CH₂), 3.5(s, 3H, CO₂CH₃); IR(NaCl) 1740, 1705, 1250, 1160 cm⁻¹.

Photochemistry of 1,3-Bis(diazo)-2-indanone in Argon Matrix at Low Temperature

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Ring contraction of bis(diazo)keto compounds represents a general method for the preparation of highly strained ring compounds¹. Attempts to generate cycloheptyne², cyclohexyne³ and cyclopentyne⁴ have been successful with corresponding diazo compounds. But the synthesis of the more

strained cyclic alkyne, such as cyclobutyne has been unsuccessful. The mechanism of the photochemical Wolff rearrangement adds special interest to the ring contraction of bis(diazo)keto compounds⁵. Stereochemical⁶ and CIDNP⁷ evidence is consistent, in most cases of Wolff rearrange-