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A Novel Synthesis of 3,4-Benzotropolone

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3,4-Benzotropolone has been synthesized with difficulty from tediously-obtainable 2,3-benzosuberone.[1,2] We now wish to develop a method capable of synthesizing simply 3,4-benzotropolone.

There have appeared several examples of the reaction of diazo compounds with quinones. Diazomethane reacts with β-naphthoquinone (I) to afford a resinous product[3] or a dioxole derivative,[4] although it reacts with *p*-benzoquinone to give tropone derivatives in a few cases.[5–7] On the other hand, diazo compounds can react with quinones in the presence of Lewis acid to induce ring enlargement, thus affording troponoids.[8]

We examined the reaction of I with diazomethane in the presence of boron trifluoride etherate. To a methylene chloride solution of I and boron trifluoride etherate, we added an equal volume of an ethereal diazomethane solution. After working up as usual, followed by chromatographic separation, a bright yellow crystalline product (II) was obtained. II exhibited infrared absorption bands (KBr) at 1424, 1398, 1377, and 1329 cm^{-1} assignable to the chelated carbon-oxygen stretching absorption and at 1100 cm^{-1} due to the oxygen-boron stretching absorption.[9] The NMR spectrum ($CDCl_3$) of II showed only aromatic protons at δ 9.0 (1H) assignable to a benzene ring proton *peri* to the carbonyl group of a tropolone ring and at δ 8.0 (6H) for the other benzene and tropolone ring protons. These spectral data, as well as the complete agreement of the results of elemental analysis, indicated II to be a chelate compound of 3,4-benzotropolonoboron difluoride. The structure of II was established unequivocally by the fact that II was again formed in a high yield on the treatment of 3,4-benzotropolone (III) with boron trifluoride etherate.

The ring enlargement of I was examined under various conditions; the results are shown in Table 1. This reaction gave a very low yield in an ethereal solution but a fairly good yield (25.5%) in a 1 : 1 mixture of ether and methylene chloride. The use of an excess amount of boron trifluoride etherate resulted in no increase in the yield.

II was hydrolyzed with dilute sulfuric acid to afford III in an almost quantitative yield, the overall

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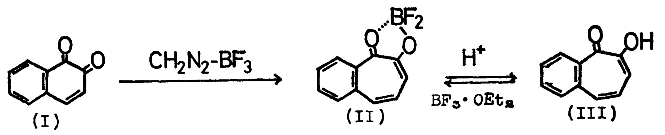

Table 1. The reaction of β-naphthoquinone with diazomethane

Exp. No.	Molar ratio			Solvent	Yied (%)
	Quinone(I)	$BF_3 \cdot OEt_2$	CH_2N_2[b]		
1[a]	1	1	4	Et_2O	2.0
2	1	1	4	CH_2Cl_2	7.1
3	1	1	4	CH_2Cl_2-Et_2O (1:1)	25.5
4	1	1	1.5	CH_2Cl_2-Et_2O (1:1)	18.4
5	1	2	4	CH_2Cl_2-Et_2O (1:1)	22.4

a) The quinone (I) was recovered in 17% yield.
b) Calculated on the basis of *N*-nitrosomethylurea.

yield of III from I amounting to 24%. The present method for the synthesis of III involves a brief sequence starting with the easily-available I; it is markedly superior in its simplicity to another recently-reported method.[2]

Experimental

Reaction of β-Naphthoquinone (I) with Diazomethane in the Presence of Boron Trifluoride Etherate. A distilled ethereal solution (50 m*l*) of diazomethane prepared from nitrosomethylurea (2.1 g, 0.005 mol) was rapidly added to a solution of freshly-prepared I (0.79 g, 0.005 mol) and 47% boron trifluoride etherate (1.5 m*l*, 0.005 mol) in methylene chloride (50 m*l*) under an atmosphere of nitrogen and with cooling in an ice bath. After having been stirred for 30 min, the mixture was poured into water and extracted with methylene chloride. The organic layer was dried over anhydrous sodium sulfate and evaporated under reduced pressure at room temperature. To the residue we then added a small amount of methylene chloride (*ca.* 10 m*l*), and the insoluble crystals were filtered off. The filtrate and the washings were directly charged on a silica-gel column, which was then eluted with methylene chloride. The evaporation of the solvent from the eluate and the recrystallization of the product from benzene gave 3,4-benzotropolonoboron difluoride (II) as yellow crystals; mp 188—195°C. Yield, 0.281 g (25.5%). Found: C, 59.75; H, 3.21%. Calcd for $C_{11}H_7O_2BF_2$: C, 60.05; H, 3.20%.

This reaction was examined under various conditions; the results are given in Table 1.

Hydrolysis of 3,4-Benzotropolonoboron Difluoride (II). A mixture of II (122 mg), 2 N sulfuric acid (15 m*l*), and ether (10 m*l*) was refluxed for 0.5 hr. After the evaporation of the ethanol, the residue was diluted with water and extracted with cyclohexane. The subsequent removal of the solvent from the extract, after drying over anhydrous magnesium sulfate, gave a product (mp 82—85°C) which was sublimed at 130°C/20 mmHg to give pale yellow crystals of III (mp 85—86°C) in 94.3% yield. Admixture with an authentic sample[1] showed no depression of the melting point.

Reaction of 3,4-Benzotropolone (III) with Boron Trifluoride Etherate. To a solution of III (30 mg) in absolute ether (3 m*l*) we added 47% boron trifluoride etherate (0.1 m*l*). The product, precipitated after the mixture had stood for 20 min, was collected by filtration and washed with ether to afford II (35 mg, 90% yield); mp 187—193°C (from benzene). The infrared spectrum of this compound was in complete agreement with that of the sample obtained by the ring enlargement of I.