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A Convenient Synthesis of 2,3-Benzotropone from α-Tetralone by Ring-expansion

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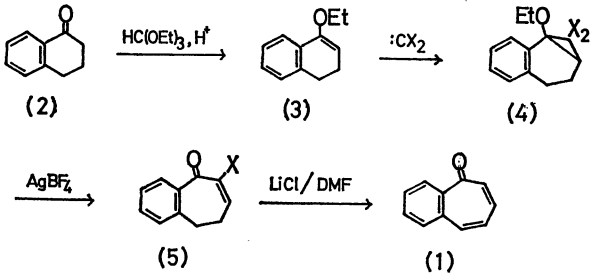
Synopsis. 2,3-Benzotropone (**1**) has conveniently been prepared from easily available α-tetralone (**2**) in good overall yield by the following successive reactions: dihalocarbene addition to enol-ether (**3**) derived from **2**, ring-expansion of the adduct (**4**) to halobenzocycloheptadienone (**5**), and dehydrohalogenation of **5** giving **1**.

2,3-Benzotropone (**1**) is synthesized from 2,3-benzosuberone *via* 7,7-dibromo-2,3-benzosuberone.[1] We now report an alternate method of synthesizing **1** from easily available α-tetralone (**2**) by ring-expansion by modification of Birch and co-workers' synthetic method for monocyclic tropone[2] and nezukone[3] from six-membered ring compounds.

α-Tetralone (**2**) was converted with ethyl orthoformate in the presence of an acid catalyst into 1-ethoxy-3,4-dihydronaphthalene (**3**) in excellent yield [IR(neat), 1636 cm^{-1} for olefinic double bond; NMR (CCl_4), δ 5.33 (t, 1H) for an olefinic proton, 4.32 (q, 2H) and 1.83 (t, 3H) for ethyl protons]. The enol-ether (**3**) reacted with dihalocarbene by Makosza's method[4,5] to give adducts (**4a**, X=Br and **4b**, X=Cl) in good yields (IR and NMR spectra showed the absence of olefinic structure). **4a** was treated with aqueous silver tetrafluoroborate in ethanol at room temperature overnight to give 7-bromo-2,3-benzocyclohepta-2,6-dien-1-one (**5a**)[1] in 79% yield. On the other hand, **4b** did not react at room temperature but reacted with silver tetrafluoroborate under reflux for 45 min in ethanol to give chloro-ketone (**5b**) (31% yield) and **1** (3% yield) along with recovery of the starting material (43%). On Birch and co-workers' synthesis of monocyclic tropones,[2,3] the corresponding seven-membered cyclic dienones were not isolated. The compounds **5a** and **5b** were dehydrohalogenated by the method of Holysz[6] to give **1** in 91 and 86% yields, respectively. Thus, the reaction sequence, **2**—**3**—**4a**—**5a**—**1**, can serve a convenient route for preparing **1** (45% over-all yield).

Reaction of **4a** and **4b** with silver tetrafluoroborate under reflux in ethanol and chromatographic separation of the reaction mixture gave **1** directly in 41 and 35% yields respectively, which also constitutes an additional convenient route to **1**.



a: X=Br, b: X=Cl

Experimental

*1-Ethoxy-3,4-dihydronaphthalene (**3**).* To a solution of α-tetralone (**2**) (20 g, 0.137 mol) and ethyl orthoformate (27.2 ml, 0.164 mol) in anhydrous alcohol (20 ml) was added a few drops of concentrated sulfuric acid. After refluxing for 30 min under nitrogen atmosphere, the solution was allowed to stand for 2 days at room temperature. The reaction mixture was basified with sodium ethoxide, and then evaporated under reduced pressure. The residue was chromatographed on alumina with elution of benzene to give 1-ethoxy-3,4-dihydronaphthalene (**3**) (20.2 g, 84.7%) as a colorless liquid, bp 100—101 °C/2 mmHg. Found: C, 82.86; H, 7.93%. Calcd for $C_{12}H_{14}O$: C, 82.77; H, 8.10%. IR(neat): 1636, 1250 and 1065 cm^{-1}; NMR(CCl_4): δ 1.83 (t, 3H, J=7 Hz), 2.52—2.90 (m, 2H), 3.07—3.33 (m. 2H), 4.32 (q, 2H, J=7 Hz), 5.33 (t, 1H, J=4.5 Hz), 7.40—7.7 (m, 3H) and 7.83—8.05 (m, 1H).

*Dibromocarbene Adduct (**4a**).* To a mixture of **3** (6.87 g, 0.04 mol), bromoform (7.0 ml, 0.08 mol) and triethylbenzylammonium chloride (0.15 g) was added 50% aqueous sodium hydroxide (14 ml) and the solution was stirred at 40 °C for 3 hr. The resulting solution was diluted with water and extracted with dichloromethane. The extract, after washing with water and drying over sodium sulfate, was evaporated and the residual oil was chromatographed on alumina with elution of benzene–hexane (1 : 1). The dibromocarbene adduct (**4a**) was obtained as a nearly colorless oil (10.2 g, 75%), which solidified on standing in a refrigerator. Recrystallization from ethanol gave colorless crystals, mp 61—62 °C. Found: C, 45.26; H, 4.38%. Calcd for $C_{13}H_{14}Br_2O$: C, 45.12; H, 4.08%. IR (KBr): 1053 cm^{-1}; NMR (CCl_4): δ 1.20 (t, 3H, J=7 Hz), 1.86—2.45 (m, 3H), 2.45—2.94 (m, 2H), 3.46 (q, 2H, J=7 Hz), 6.91—7.45 (m, 3H) and 7.52—7.81 (m, 1H).

*Dichlorocarbene Adduct (**4b**).* A mixture of **3** (3.5 g, 0.02 mol), chloroform (2.4 ml, 0.03 mol), 50% aqueous sodium hydroxide (3.8 ml) and triethylbenzylammonium chloride (170 mg) was stirred for 4 hr at 45 °C. The mixture was diluted with water, extracted with dichloromethane, the extract was dried over sodium sulfate, and evaporated. The residual oil was chromatographed on alumina to give the adduct (**4b**) (4.03 g, 78%) as a nearly colorless liquid, bp 118 °C/3.5 mmHg. IR (neat): 1061 and 895 cm^{-1}; NMR (CCl_4): δ 1.17 (t, 3H, J=7 Hz), 1.90—2.50 (m, 3H), 2.50—2.87 (m, 2H), 3.42 (q, 2H, J=7 Hz), 6.90—7.40 (m, 3H) and 7.50—7.70 (m, 1H). Found: C, 60.94; H, 5.46%. Calcd for $C_{13}H_{14}Cl_2O$: C, 60.72; H, 5.49%.

*Treatment of **4a** with Silver Tetrafluoroborate.* To a solution of silver tetrafluoroborate prepared from silver oxide (5.0 g, 0.022 mol), 42% fluoroboric acid (40 ml) and ethanol (80 ml) was added the dibromocarbene adduct (**4a**) (7.0 g, 0.020 mol), and the mixture was stirred at room temperature for 16 hr. The reaction mixture was poured into saturated aqueous sodium chloride to give a precipitate which was filtered and washed with dichloromethane thoroughly. The filtrate and the washings were combined and extracted with

dichloromethane. The extract was washed with aqueous sodium bicarbonate and with water, then dried over sodium sulfate, and evaporated. The residue was chromatographed on silica gel to give the starting substance (0.22 g, 3.1%), 7-bromo-2,3-benzocyclohepta-2,6-dien-1-one[1] (**5a**) (3.80 g, 79.4%), and an unknown oil A (0.52 g, ν_{CO} 1679 cm^{-1}). **5a** solidified on standing in refrigerator and recrystallized from ethanol to give pale yellow crystals, mp 39—40 °C.

When the same reaction was performed under refluxing for 2 hr, there resulted **5a** (0.19 g, 4%), **1** (1.28 g, 41%), an unknown oil B (0.50 g, ν_{CO} 1677 and 1713 cm^{-1}) and an unknown oil C (0.28 g, ν_{CO} 1728 cm^{-1}).

*Treatment of **4b** with Silver Tetrafluoroborate.* A solution of **3b** (1.80 g, 7 mmol) in ethanol (15 ml) was added to a solution of silver tetrafluoroborate prepared from silver oxide (1.85 g, 8 mmol) and 42% fluoroboric acid (15 ml), and the mixture was gently refluxed on a water bath for 45 min. After the same work-up as described in **4a**, the starting material (0.78 g, 43%), the chloro ketone (**5b**) (0.43 g, 31%) and **1** (0.05 g, 3%) were obtained. **5b** was a pale yellow oil. Found: C, 68.77; H, 4.60%. Calcd for $C_{11}H_9ClO$: C, 68.58;, H, 4.70%. IR (neat): 1661 (vs), 1613 and 1600 cm^{-1}. NMR (CCl_4): δ 2.47—2.80 (m, 2H), 2.90—3.18 (m, 2H), 7.0—7.5 (m, 4H) and 7.5—7.8 (m, 1H).

The 4 hr's refluxing of the solution of **4b** (1.56 g, 6 mmol), silver oxide (2.1 g, 9 mmol), 42% fluoroboric acid (16 ml) and ethanol (16 ml) gave **1** (0.33 g, 35%) and an unknown oil C (0.13 g).

*Dehydrobromination of **5a**.* A solution of **5a** (805 mg, 3.4 mmol), lithium chloride (4.2 g) in dimethylformamide (50 ml) and benzene (15 ml) was heated under nitrogen atmosphere. After the benzene was removed azeotropically (30 min), the solution was refluxed for one hr. It was poured into water and extracted with benzene. The extract was washed with water, dried over sodium sulfate, and evaporated. The residual oil was chromatographed on silica gel with benzene–ether eluent to give **1** (480 mg, 91%).

*Dehydrochlorination of **5b**.* Refluxing of a solution of **5b** (0.38 g, 2 mmol) and lithium chloride (2.5 g, 0.06 mol) in dimethylformamide (30 ml) for 2 hr under similar conditions followed by the same work-up as above gave **1** (0.27 g, 86%).

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