employing decane as an internal standard, indicated that a 43% vield of 2 was formed after 1 hr at 25°.2

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Registry No.-1, 6651-36-1; 2, 6126-52-9; 2 DNPH, 23260-65-3; 3, 10468-40-3; 4, 13377-10-1; 5, 7106-07-2; methyllithium, 917-54-4; propylene oxide, 75-56-9; methyl bromide, 74-83-9; ethyl bromide, 74-96-4; oxetane, 503-30-0.

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# An Efficient Synthesis of 4,5-Benzotropone from o-Xylylene Dibromide

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Our study of the chemical properties of benzazocine<sup>1</sup> and homobenzazocine systems<sup>2</sup> necessitated inter alia the availability of a ready, inexpensive, and plentiful source of 4,5benzotropone (2). The original procedure of Thiele and Wertz<sup>3,4</sup> involves condensation of o-phthaldialdehyde (1) with dimethyl acetonedicarboxylate and subsequent hydrolysis and decarboxylation (eq 1). For large-scale synthesis, however, the cost of 1 becomes prohibitive and the requirements of an autoclave and 200° in the final stage is an unattractive feature. Srivastava and Dev<sup>5</sup> have examined selenium dioxide oxidation of benzocycloheptatriene (3) as a route to 2. Although 4,5-benzotropone is indeed formed (27%), the 2.3 isomer (4, 13% yield) contaminates the product (eq 2). Also, hydrocarbon 3 is not readily available. Bat-



tiste's recently discovered multistep route from the benzyne-furan adduct 5 to  $2,^6$  while novel and elegant in concept, has in our hands not proven amenable to convenient scale-up (eq 3).



In the present approach, we have focused on the fact that 2 is a bisdehydro derivative of 4,5-benzocycloheptenone (8), and have gained simple access to 8 in 51% overall yield by bisalkylation of the readily available o-xylylene dibromide  $(6)^7$  with lithic tert-butyl acetate<sup>8</sup> and subsequent Dieckmann cyclization<sup>9</sup> (eq 4). Addition of 6 to a cold



 $(-78^{\circ})$  solution of the lithium enolate in anhydrous tetrahydrofuran followed by gradual warming to room temperature during 3 hr routinely afforded >90% yield of di-tertbutyl ester 7 of purity adequate for direct cyclization. A comparable attempt to employ lithio ethyl acetate<sup>10</sup> was unsuccessful. Bromination of 8 with molecular bromine in carbon tetrachloride solution can be conveniently arrested at the  $\alpha, \alpha'$ -dibromo ketone stage, since this dibromide precipitates from solution when formed. Direct dehydrobromination of this solid with lithium chloride in dimethylformamide solvent<sup>11</sup> provides 2 in 85% isolated yield. Benzylic bromination with N-bromosuccinimide is not equally successful because the ready elimination of hydrogen bromide which ensues has an appreciable deleterious effect. Acid scavengers are seemingly of little value.

In summary, the scheme illustrated by eq 4 has proven to be an especially reliable route to quantities of the title ketone.

## **Experimental Section**

4.5-Benzocycloheptenone (8). To a cold  $(-78^{\circ})$  solution of 206.4 g (1.10 mol) of N-isopropylcyclohexylamine in 700 ml of dry tetrahydrofuran was added 1 mol of n-butyllithium in hexane (Alfa Inorganics) via cannula. After being stirred for 20 min at this temperature, the solution was treated dropwise with 127.8 g (1.1 mol) of tert-butyl acetate<sup>12</sup> at such a rate that the temperature did not exceed  $-68^{\circ}$ . Some solid which had precipitated earlier was now totally redissolved. After an additional 20 min at  $-78^{\circ}$ , a solution of 110.0 g (0.416 mol) of  $6^7$  in 500 ml of the same solvent was added below  $-68^{\circ}$ . When all had been introduced, the mixture was allowed to warm to  $-23^{\circ}$  and stirred for 2.5 hr at this temperature. The cooling bath was removed and when 25° was attained, 1 l. of cold hydrochloric acid (100 ml of concentrated HCl diluted to volume) was added and the mixture was poured into 1 l. of brine. The organic layer was separated and combined with the ethereal extracts (3  $\times$  500 ml) of the aqueous phase before washing with 1 Mhydrochloric acid, drying, and evaporation. There was obtained 130 g (93.5%) of 7 as a light orange oil which was utilized directly;  ${}^{1}H$  NMR (CDCl<sub>3</sub>)  $\delta$  7.13 (s, 4), 2.75-3.15 (m, 4), 2.3-2.7 (m, 4), and 1.43 (s, 18).

A 5-l., three-necked Morton flask was fitted with a mechanical stirrer, high-dilution adapter to which a condenser was attached,<sup>13</sup> constant addition funnel, and nitrogen inlet tube. Sodium hydride (48.0 g of 50% mineral oil dispersion freed of oil by washing with toluene, 1 mol) was introduced, followed by 1.4 l. of dry toluene and 5 ml of dry tert-butyl alcohol. After being blanketed by nitrogen, this slurry was brought to reflux with rapid stirring. A solution of the unpurified 7 in 1.5 l. of dry toluene was added slowly during 3-4 days; subsequently, heating was maintained for an additional 3-4 hr. After cooling, glacial acetic acid (90.0 g, 1.5 mol) was introduced dropwise (some thickening occurs), followed by

rapid addition of 1 l. of ice water. The layers were separated and the organic phase was washed with brine, dried, and evaporated.

To the residue was added 400 ml of methanol and 200 ml of 6 Nhydrochloric acid and this mixture was refluxed for 3 hr, poured onto ice, and extracted with ether. After washing with saturated sodium bicarbonate solution, the organic phase was dried and evaporated. Distillation of the residue afforded 34 g (51% overall from 6) of 4,5-benzocycloheptenone, bp 88° (0.3 mm), mp 41-42° (lit.<sup>14,15</sup> mp 41-42°, 42-43°).

4,5-Benzotropone (2). A magnetically stirred solution of 8 (17.3 g, 0.108 mol) in 325 ml of carbon tetrachloride was treated dropwise with 34.5 g (0.216 mol) of bromine dissolved in 195 ml of the same solvent. Upon completion of the addition, the mixture was brought briefly to reflux. The solvent was removed in vacuo and the off-white solid residue was added to 975 ml of dry dimethylformamide containing 13.05 g (0.308 mol) of lithium chloride. After 1 hr at the reflux temperature under nitrogen, the dimethylformamide was removed in vacuo and the residue was partitioned between ether (400 ml) and water (200 ml). The organic layer was washed with water  $(3 \times 250 \text{ ml})$ , dried, and evaporated. Trituration of the residue with boiling pentane afforded 14.3 g (85%) of 4,5-benzotropone as yellow flakes, mp 68-69° (lit.<sup>3,4,6</sup> mp 66-67°, 67.5-68.5°, 69°).

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Registry No.-2, 4443-91-8; 6, 91-13-4; 8, 37949-03-4; N-isopropylcyclohexylamine, 1195-42-2; tert-butyl acetate, 540-88-5.

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# **Reactions of Glycyrrhetic Acid Derivatives with** Trifluoromethyl Hypofluorite. Preparation of a New Triterpenoid System

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Trifluoromethyl hypofluorite, CF<sub>3</sub>OF, is known to give with some types of double bonds addition products which, after a brief treatment with bases, produce monofluoro compounds.<sup>1</sup> We have investigated the reaction of this reagent with a conjugated enone and with an enol acetate derived from glycyrrhetic acid (1). This is the first attempt to

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