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for the Preparation
of Organic Compounds

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*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

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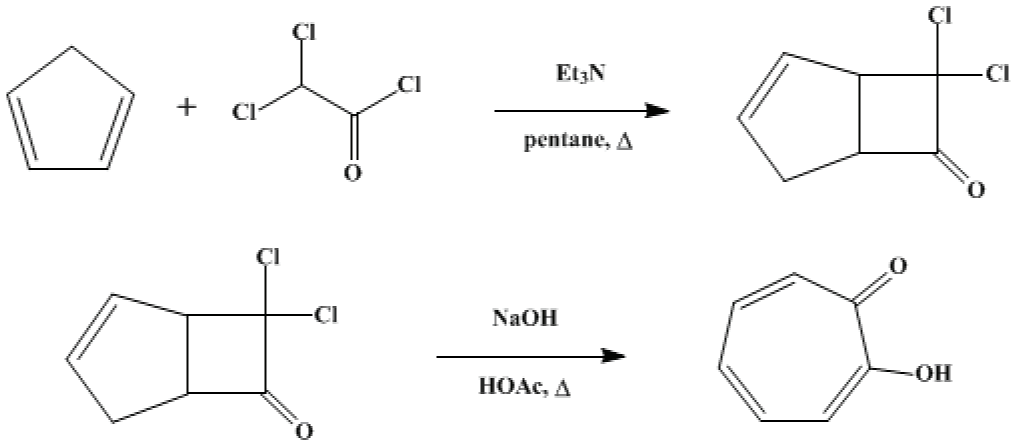
# TROPOLONE

## [2,4,6-Cycloheptatrien-1-one, 2-hydroxy-]



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## 1. Procedure

*Caution! Benzene has been identified as a carcinogen; OSHA has issued emergency standards on its use. All procedures involving benzene should be carried out in a well-ventilated hood, and glove protection is required.*

A. *7,7-Dichlorobicyclo[3.2.0]hept-2-en-6-one*. A 2-l., three-necked, round-bottomed flask fitted with an addition funnel, a reflux condenser, and a mechanical stirrer is charged with 100 g. (0.678 mole) of dichloroacetyl chloride (Note 1), 170 ml. (2 moles) of cyclopentadiene (Note 2), and 700 ml. of pentane (Note 3). The solution is heated to reflux under nitrogen and rapidly stirred while a solution of 70.8 g. (0.701 mole) of triethylamine (Note 4) in 300 ml. of pentane is added over a period of 4 hours (Note 5). After the cream-colored mixture has been refluxed for an additional 2 hours, 250 ml. of distilled water is added, dissolving the triethylamine hydrochloride; the layers are separated in a 2-l. separatory funnel. After extraction of the aqueous layer with two 100-ml. portions of pentane, the combined organic layers are filtered and dried by passage through absorbent cotton. Pentane and excess cyclopentadiene are then removed by rapid distillation. The resulting viscous, orange liquid is fractionally distilled under reduced pressure through a 30-cm. Vigreux column. Heat is supplied from an oil bath held at 105°. During collection of the first fraction, which consists mainly of dicyclopentadiene (Note 6), b.p. 61–62° (9 mm.), the cold finger and take-off tube must be warmed periodically with a heat gun to prevent plugging. The 7,7-dichlorobicyclo[3.2.0]hept-2-en-6-one, 101–102 g. (84–85%), is collected as a colorless liquid, b.p. 66–68° (2 mm.), $n_{D}^{25}$ 1.5129, having a purity >99% as determined by GC analysis (Note 6) and (Note 7).

B. *Tropolone*. A 1-l., three-necked, round-bottomed flask equipped with a mechanical stirrer, addition funnel, and a reflux condenser is charged with 500 ml. of glacial acetic acid and then, *cautiously*, 100 g. of sodium hydroxide pellets. After the pellets have dissolved, 100 g. (0.565 mole) of 7,7-dichlorobicyclo[3.2.0]hept-2-en-6-one is added and the solution is maintained at reflux under nitrogen for 8 hours. Concentrated hydrochloric acid is added until the mixture is about pH 1; approximately 125 ml. of acid is required. After the addition of 1 l. of benzene, the mixture is filtered and the solid sodium chloride is washed with three 100-ml. portions of benzene. The two phases of the filtrate are separated, and the aqueous phase is transferred to a magnetically stirred, 1-l., continuous extractor (Note 8). The combined benzene phase is transferred to a 2-l. pot connected to the extractor, and the aqueous phase is extracted for 13 hours. Following distillation of the benzene, the remaining orange liquid is distilled under reduced pressure through a 30-cm. Vigreux column, removing acetic acid. When tropolone begins to distill into the column, the condenser is replaced with a two-necked flask immersed in ice water. With vacuum applied through one neck of this receiver, tropolone distills at 60° (0.1 mm.) and is collected as a crude yellow solid, 66.4 g. (96%). A solution of the impure product in 150 ml. of dichloromethane is diluted with 600 ml. of pentane, 4 g. of activated carbon is added, and the mixture is heated to boiling. After removal of the carbon by filtration, the solution is maintained at −20° until crystallization is complete. Tropolone, 53 g. (77%) (Note 9), is collected as white needles, m.p. 50–51°, by filtration. Evaporation of the filtrate to dryness, dissolution of the residue in 800 ml. of pentane, treatment with activated carbon, and cooling to −20° yields an additional 8 g. (12%) of tropolone as pale-yellow crystals, m.p. 49.5–51°.

## 2. Notes

1. Freshly opened bottles of dichloroacetyl chloride from Aldrich Chemical Company, Inc., were used. The acid chloride can also be prepared by the dropwise addition of 1 volume of dichloroacetic acid to 2.5 volumes of phthaloyl chloride heated to 140°. After the addition is complete, the solution is vigorously heated and dichloroacetyl chloride, b.p. 106–108°, is distilled through a 30-cm. column packed with glass beads; the yield is 85%.
2. Cyclopentadiene was prepared by cracking dicyclopentadiene [*Org. Synth.*, **Coll. Vol. 4**, 475 (1963)] of 95% purity purchased from Aldrich Chemical Company, Inc.
3. Technical grade pentane from Fisher Scientific Company was used.
4. Triethylamine from Eastman Organic Chemicals was used without further purification.
5. Faster addition results in some polymerization of the dichloroketene and darkens the precipitate.
6. Fractions were analyzed by GC (column: 0.3 × 120 cm., 20% SE-52 on Chromosorb P 60/80, 130°, helium flow rate of 60 ml./min.). Retention times of 1.9 minutes for dicyclopentadiene and 4.6 minutes for the 7,7-dichlorobicyclo[3.2.0]hept-2-en-6-one were found.
7. 7,7-Dichlorobicyclo[3.2.0]hept-2-en-6-one has the following spectral characteristics: IR (neat) $cm.^{-1}$: 1806 (C=O), 1608 (C=C); $^1$H NMR ($CCl_4$), δ (multiplicity, number of protons, assignment): 2.70 (m, 2H, $CH_2$), 4.10 (m, 2H, 2C*H*), 5.90 (m, 2H, C*H*=C*H*).
8. A continuous extractor has been described in *Org. Synth.*, **Coll. Vol. 5**, 630 Note 10 (1973).
9. Tropolone has the following spectral characteristics: IR (KBr pellet) $cm.^{-1}$: 3210 (O*H*), 1613 (C=O), 1548 (C=C); $^1$H NMR ($CDCl_3$), δ (multiplicity, number of protons, assignment): 7.33 (m, 5H, 5C*H*), 8.76 (s, 1H, O*H*).

## 3. Discussion

Tropolone has been made from 1,2-cycloheptanedione by bromination and reduction,[2] and by reaction with *N*-bromosuccinimide;[3] from cycloheptanone by bromination, hydrolysis, and reduction;[4] from diethyl pimelate by acyloin condensation and bromination;[5] from cycloheptatriene by permanganate oxidation;[6] from 3,5-dihydroxybenzoic acid by a multistep synthesis;[7] from 2,3-dimethoxybenzoic acid by a multistep synthesis;[8] from tropone by chlorination and hydrolysis,[9] by amination with hydrazine and hydrolysis,[10] or by photoöxidation followed by reduction with thiourea;[11] from cyclopentadiene and tetrafluoroethylene;[12] and from cyclopentadiene and dichloroketene.[13,14]

The present procedure, based on the last method, is relatively simple and uses inexpensive starting materials. Step A exemplifies the 2 + 2 cycloaddition of dichloroketene to an olefin,[15,16,17] and the specific cycloadduct obtained has proved to be a useful intermediate in other syntheses.[18,19,20] Step B has been the subject of several mechanistic studies,[21,22,23,24] and its yield has been greatly improved by the isolation technique described above. This synthesis has also been extended to the preparation of various tropolone derivatives.[14,21,22,25,26,27,28]

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## References and Notes

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## Appendix
## Chemical Abstracts Nomenclature (Collective Index Number);
## (Registry Number)

acyloin

hydrochloric acid (7647-01-0)

acetic acid (64-19-7)

Benzene (71-43-2)

sodium hydroxide (1310-73-2)

sodium chloride (7647-14-5)

nitrogen (7727-37-9)

carbon (7782-42-5)

phthaloyl chloride (88-95-9)

Triethylamine hydrochloride (554-68-7)

Pentane (109-66-0)

dichloromethane (75-09-2)

dichloroacetic acid (79-43-6)

thiourea (62-56-6)

dichloroacetyl chloride (79-36-7)

N-bromosuccinimide (128-08-5)

3,5-Dihydroxybenzoic acid (99-10-5)

Cycloheptanone (502-42-1)

triethylamine (121-44-8)

CYCLOPENTADIENE (542-92-7)

dicyclopentadiene (77-73-6)

cycloheptatriene (544-25-2)

tetrafluoroethylene (9002-84-0)

Tropolone,
2,4,6-Cycloheptatrien-1-one, 2-hydroxy- (533-75-5)

7,7-Dichlorobicyclo[3.2.0]hept-2-en-6-one (5307-99-3)

dichloroketene (4591-28-0)

1,2-cycloheptanedione

diethyl pimelate (2050-20-6)

2,3-dimethoxybenzoic acid (1521-38-6)

Tropone (492-37-5)