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of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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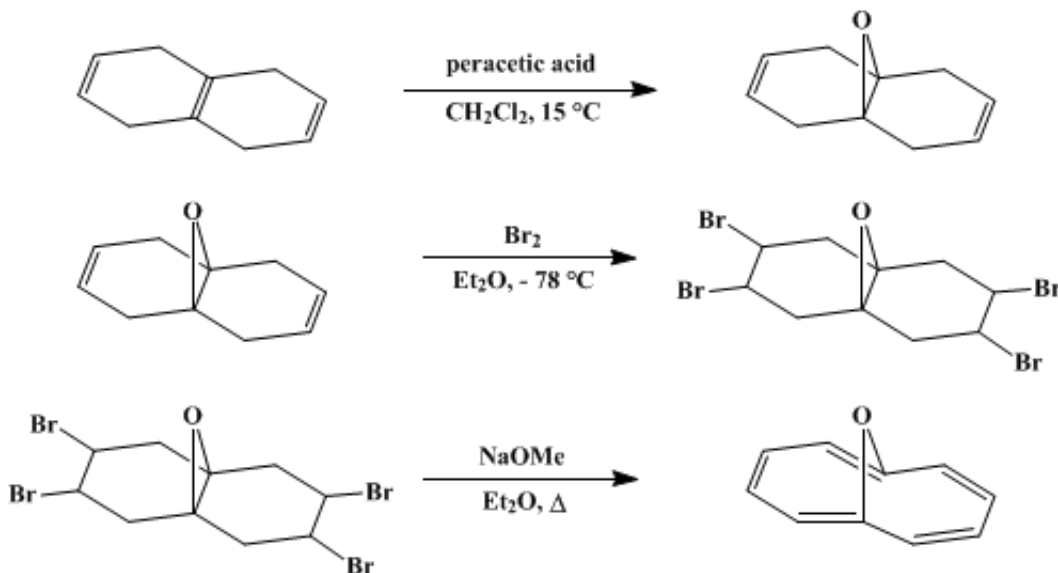
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

1,6-OXIDO[10]ANNULENE

[11-Oxabicyclo[4.4.1]undeca-1,3,5,7,9-pentaene]



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1. Procedure

*Caution! Reactions and subsequent operations involving peracids and peroxy compounds should be run behind a safety shield. Peroxy compounds should be added to the organic material, never the reverse. For relatively fast reactions, the rate of addition of the peroxy compound should be slow enough so that it reacts rapidly and no significant unreacted excess is allowed to build up. The reaction mixture should be stirred efficiently while the peroxy compound is being added, and cooling should generally be provided since many reactions of peroxy compounds are exothermic. New or unfamiliar reactions, particularly those run at elevated temperatures, should be run first on a small scale. Reaction products should never be recovered from the final reaction mixture by distillation until all residual active oxygen compounds (including unreacted peroxy compounds) have been destroyed. Decomposition of active oxygen compounds may be accomplished by the procedure described in Korach, M.; Nielsen, D. R.; Rideout, W. H. *Org. Synth.* 1962, 42, 50 (*Org. Synth.* 1973, Coll. Vol. 5, 414). [Note added January 2011].*

A. 11-Oxatricyclo[4.4.1.0^{1,6}]undeca-3,8-diene. A 1-l., three-necked, round-bottomed flask equipped with a sealed mechanical stirrer, a pressure-equalizing dropping funnel, and a thermometer is charged with 66.1 g. (0.501 mole) of 1,4,5,8-tetrahydronaphthalene [*Org. Synth.*, Coll. Vol. 6, 731 (1988)] and 200 ml. of anhydrous dichloromethane. To the resulting solution is added 75 g. of anhydrous sodium acetate. After the suspension is cooled with an ice bath, 104.5 g. (0.55 mole) of commercial 40% peracetic acid (Note 1) and (Note 2) is added dropwise over a period of 20–30 minutes, while maintaining the temperature at approximately 15° (Note 3) and stirring vigorously. To the reaction mixture is added, without delay, 500 ml. of water, to dissolve the sodium acetate and extract the bulk of the acetic acid. The organic layer is washed successively with two 100-ml. portions of 5% aqueous sodium hydroxide and two 100-ml. portions of water and dried over anhydrous potassium carbonate. The solvent is removed on a rotary evaporator, leaving a solid residue. Two recrystallizations from approximately 50 ml. of petroleum ether (b.p. $40\text{--}60^\circ$), cooling the solution to -40° , yields 58.5–62.0 g.

(79–84%) of [11-oxatricyclo\[4.4.1.0^{1,6}\]undeca-3,8-diene](#) as white needles, m.p. 58–61° ([Note 4](#)).

B. [3,4,8,9-Tetrabromo-11-oxatricyclo\[4.4.1.0^{1,6}\]undecane](#). A 1-l., three-necked, round-bottomed flask fitted with a sealed mechanical stirrer, a pressure-equalizing dropping funnel, and a calcium chloride drying tube is charged with 59.2 g. (0.400 mole) of [11-oxatricyclo\[4.4.1.0^{1,6}\]undeca-3,8-diene](#) and 500 ml. of anhydrous [diethyl ether](#) ([Note 5](#)). The resulting solution is cooled in an acetone–dry ice bath, and 120 g. (0.75 mole) of [bromine](#) ([Note 6](#)) is added with stirring over a period of 1.5 hours ([Note 7](#)). After the addition is complete, the [ether](#) is removed on a rotary evaporator. The solid residue is dissolved in 800 ml. of hot [chloroform](#). To this solution is added, with gentle stirring, 150 ml. of hot petroleum ether (b.p. 60–90°). The resulting, clear mixture, from which the product begins to crystallize, is allowed to cool to room temperature and then stand in a refrigerator at –40° overnight, completing the crystallization. The yield of white crystalline tetrabromide obtained is 115–125 g. (61–67%), m.p. 151–153° ([Note 8](#)). An additional 18–25 g. of product, m.p. 149–152°, is recovered from the mother liquor by concentration to about one quarter of the volume, giving a total yield of 136–144 g. (73–77%) of material sufficiently pure to be used in the following step.

C. [1,6-Oxido\[10\]annulene](#). A 2-l., three-necked, round-bottomed flask equipped with a sealed mechanical stirrer and a reflux condenser protected by a calcium chloride drying tube is charged with 81 g. (1.5 moles) of [sodium methoxide](#) ([Note 9](#)) and 600 ml. of anhydrous [ether](#). To this slurry is added, with stirring, 117 g. (0.250 mole) of finely powdered [3,4,8,9-tetrabromo-11-oxatricyclo\[4.4.1.0^{1,6}\]undecane](#). The reaction mixture is refluxed with stirring for 10 hours and allowed to stand overnight. Following this, 500 ml. of water is added slowly, dissolving the solids. The [ether](#) layer is separated, and the aqueous layer is extracted with two 100-ml. portions of [ether](#). The combined ethereal solution is washed with 250 ml. of water and dried over anhydrous [potassium carbonate](#). Removal of the [ether](#) on a rotary evaporator affords a brown oil, which when distilled gives 34.4–35.1 g. of yellow [1,6-oxido\[10\]annulene](#), b.p. 77° (0.02 mm.) ([Note 10](#)). This material readily solidifies at room temperature, and two recrystallizations at –40° from 225 ml. of (5:1) [pentane–ether](#) yields 18.3–18.5 g. (51%) of [1,6-oxido\[10\]annulene](#) as pale yellow needles, m.p. 51–52° ([Note 11](#)) and ([Note 12](#)).

2. Notes

1. Satisfactory 40% [peracetic acid](#) is obtainable from Buffalo Electrochemical Corporation, Food Machinery and Chemical Corporation, Buffalo, New York. The specifications given by the manufacturer for its composition are: [peracetic acid](#), 40%; [hydrogen peroxide](#), 5%; [acetic acid](#), 39%; [sulfuric acid](#), 1%; water, 15%. Its density is 1.15 g./ml. The [peracetic acid](#) concentration should be determined by titration. A method for the analysis of peracid solutions is based on the use of [ceric sulfate](#) as a titrant for the [hydrogen peroxide](#) present, followed by an iodometric determination of the peracid present.² The checkers found that [peracetic acid](#) of a lower concentration (27.5%) may also be used without a decrease in yield. The product was found to be sufficiently pure, after only one recrystallization from 60 ml. of petroleum ether (b.p. 40–60°) and cooling overnight to –18°, to be used in the next step.

2. Alternatively [m-chloroperbenzoic acid](#) may be used.³

3. The yields of the desired product decrease substantially if the temperature exceeds 20°.

4. The reported m.p. is 64°.⁴ GC analysis using a 1-m. column containing 20% Reoplex 400 on Diatoport S 6080, operated at 160°, indicates the purity of the product to be ~98%.

5. The rate of bromination of [11-oxatricyclo\[4.4.1.0^{1,6}\]undeca-3,8-diene](#) is markedly higher in [ether](#) than in [dichloromethane](#) or [chloroform](#). The former solvent thus permits the reaction to be carried out at relatively low temperatures.

6. [Bromine](#) was freshly distilled from [phosphorus pentoxide](#).

7. The addition of [bromine](#) should not be started before the solution has cooled to approximately –70°.

8. The tetrabromide apparently consists of a mixture of stereoisomers. After several recrystallizations from [chloroform](#)–petroleum ether (60–90°) the major isomer, m.p. 160–162°, is obtained.

9. As reported by Shani and Sondheimer,^{3,5} the dehydrohalogenation of the tetrabromide with [potassium hydroxide](#) in [ethanol](#) at 50–55° affords a mixture, readily separated by chromatography on alumina, of [1,6-oxido\[10\]annulene](#) and the isomeric [1-benzoxepin](#). The latter compound is also formed during chromatography of [1,6-oxido\[10\]annulene](#) on silica gel.⁶

10. To avoid acid-catalyzed rearrangements of 1,6-oxido[10]annulene it is recommended that the distillation flask be treated with a base before use.

11. The reported m.p. is 52–53°. The purity of the product is greater than 99% as established by TLC, using plates prepared with Silica Gel Si F, obtained from Riedel-De Haen AG, 3016 Seelze, West Germany. If 1,6-oxido[10]annulene is to be used for spectroscopic investigations, care should be taken that its potential contaminants, such as naphthalene, 1-bromonaphthalene, α -naphthol, and 1-benzoxepin, are absent, as checked by TLC. The checkers could not obtain the reported yield of 24.5–25.6 g. (68–71%). Likewise, in experiments where the ether was replaced with tetrahydrofuran or dioxane, the yield given by the submitters could not be obtained.

12. The spectral properties of the product are as follows; ^1H NMR (CDCl_3), δ (multiplicity, assignment): 7.25–7.75 (m, AA'BB', aromatic H); UV (95% $\text{C}_2\text{H}_5\text{OH}$) nm. max. (ϵ): 255 (74,000), 299 (6900), 393 (240) complex band; mass spectrum (250°, 70 eV) m/e (relative intensity > 10%): 144 (M, 43), 116 (40), 115 (100), 89 (15), 63 (15), 51 (10), 39 (11).

3. Discussion

The preparation of 1,6-Oxido[10]Annulene, described simultaneously by Sondheimer and Shani^{3,5} and by Vogel, Biskup, Pretzer, and Böll,⁶ is illustrative of the rather general synthesis of aromatic 1,6-bridged [10]annulenes from 1,4,5,8-tetrahydronaphthalene. In addition to the present compound, the following bridged [10]annulenes have thus far been obtained by this approach: 1,6-methano[10]annulene,^{7,8,9} the 11,11-dihalo-1,6-methano[10]annulenes,^{9,10} and 1,6-imino[10]annulene.¹¹

The epoxidation of 1,4,5,8-tetrahydronaphthalene exemplifies the well-known selectivity of peracids in their reaction with alkenes possessing double bonds that differ in the degree of alkyl substitution.¹² Regarding the method of aromatization employed in the conversion of 11-oxatricyclo[4.4.1.0^{1,6}]undeca-3,8-diene to 1,6-oxido[10]annulene, the two-step bromination–dehydrobromination sequence is given preference to the one-step DDQ-dehydrogenation, which was advantageously applied in the synthesis of 1,6-methano[10]annulene,^{7,9} since it affords the product in higher yield and purity.

1,6-Oxido[10]annulene closely resembles 1,6-methano[10]annulene in many of its spectral properties, particularly in its ^1H NMR, UV, IR, and ESR spectra,¹³ but is chemically less versatile than the hydrocarbon analog due to its relatively high sensitivity toward proton and Lewis acids.

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 6, 731](#)

References and Notes

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

petroleum ether
1,6-Oxido[10]annulene
ethanol (64-17-5)
potassium carbonate (584-08-7)
sulfuric acid (7664-93-9)
acetic acid (64-19-7)
ether,
diethyl ether (60-29-7)
sodium acetate (127-09-3)
sodium hydroxide (1310-73-2)
chloroform (67-66-3)
bromine (7726-95-6)
 α -naphthol (90-15-3)
sodium methoxide (124-41-4)
potassium hydroxide (1310-58-3)
1-bromonaphthalene (90-11-9)
Naphthalene (91-20-3)
hydrogen peroxide (7722-84-1)
Pentane (109-66-0)
dichloromethane (75-09-2)
dioxane (123-91-1)
Tetrahydrofuran (109-99-9)
peracetic acid (79-21-0)
ceric sulfate (13590-82-4)
1,6-Methano[10]annulene (2443-46-1)

1,4,5,8-Tetrahydronaphthalene (493-04-9)

11-Oxabicyclo[4.4.1]undeca-1,3,5,7,9-pentaene (4759-11-9)

11-Oxatricyclo[4.4.1.0^{1,6}]undeca-3,8-diene (16573-72-1)

3,4,8,9-Tetrabromo-11-oxatricyclo[4.4.1.0^{1,6}]undecane (16573-82-3)

1-benzoxepin

phosphorus pentoxide (1314-56-3)

m-Chloroperbenzoic acid (937-14-4)