Organic Syntheses

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of Organic Compounds

Working with Hazardous Chemicals

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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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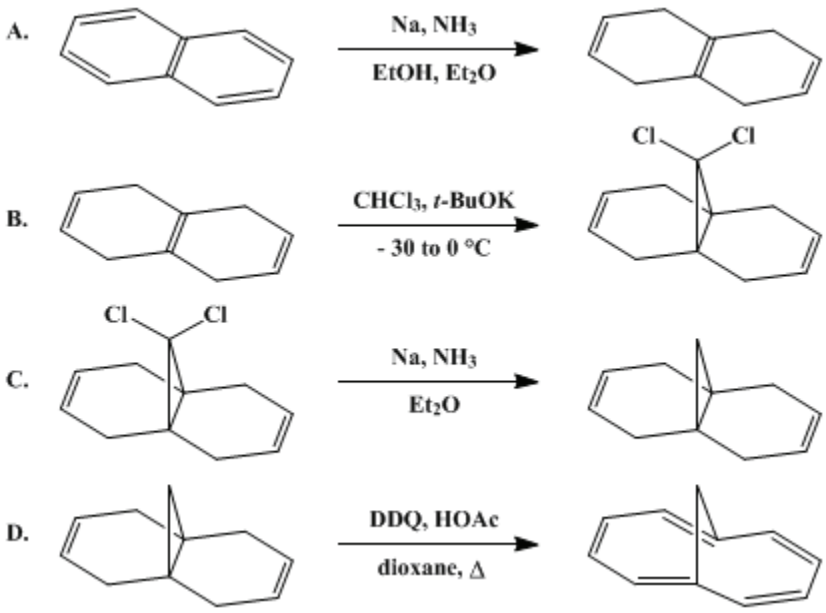
1,6-METHANO[10]ANNULENE

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



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1. Procedure

Caution! This reaction should be carried out in an efficient hood.

A. 1,4,5,8-*Tetrahydronaphthalene* (*isotetralin*). A 12-l. (Note 1),. three-necked, round-bottomed flask is immersed in an acetone–dry ice bath and fitted with a dry ice condenser (Note 2), a tube-sealed stirrer (Note 3), a drying tube (potassium hydroxide), and a gas delivery-tube running to the bottom of the flask. Ammonia (3 l.) is condensed (Note 4) into the flask. The gas delivery-tube is removed, and 192.3 g. (8.361 g.-atoms) of sodium is added in small portions (Note 5), with vigorous stirring, over a period of 1 hour. The flask is then fitted with a dropping funnel, through which a solution of 192.3 g. (1.502 mole) of naphthalene in a mixture of 750 ml. of diethyl ether and 600 ml. of ethanol is added dropwise to the blue solution over 3 hours. After the addition is complete, the reaction mixture is stirred at −78° (Note 6) for another 6 hours. The cooling bath is removed, and the ammonia is allowed to evaporate overnight. The remaining white, solid residue is processed, with ice cooling and stirring under a nitrogen atmosphere, by slow addition of 120 ml. of methanol to destroy unreacted sodium, then 4–5 l. of ice water to dissolve the salts (Note 7). The reaction mixture is extracted with 1 l. of ether. Evaporation of the ether phase at room temperature under reduced pressure gives a coarse, white solid which is collected on a sintered-glass funnel and washed with water. Recrystallization from methanol (about 1.6 l.) using a heated funnel followed by drying of the crystals under reduced pressure (Note 8) gives 148–158 g. (75–80%) of isotetralin, m.p. 52–53° (purity ~98%) (Note 9). Pure 1,4,5,8-tetrahydronaphthalene is reported to have m.p. 58°.[2]

B. 11,11-*Dichlorotricyclo*[4.4.1.$0^{1,6}$]*undeca*-3,8-*diene*. A 3-l., three-necked, round-bottomed flask fitted with a tube-sealed stirrer, a pressure-equalizing dropping funnel, and Claisen-adapter bearing an inlet tube for argon and a low temperature thermometer is charged with a solution of 132.2 g. (1.000 mole) of 1,4,5,8-tetrahydronaphthalene (isotetralin) in 1.3 l. of anhydrous ether (Note 10). To this

solution is added 150 g. (1.33 mole) of potassium *tert*-butoxide (Note 11) under an argon atmosphere, and the resulting suspension is cooled to −30° with an acetone–dry ice bath and stirred efficiently. While these conditions are maintained, a solution of 119.5 g. (1.000 mole) of chloroform in 150 ml. of ether is added dropwise over 90 minutes (Note 12). The mixture is stirred for another 30 minutes at −30° before the temperature is allowed to rise above 0°. Following this, 300–350 ml. of ice water is added to dissolve the salts; the two layers formed are separated (Note 13). The organic layer is washed with two 300-ml. portions of water, while the aqueous layer is extracted with two 200-ml. portions of ether. The ether phases are combined, dried over magnesium sulfate, and filtered. The ether is removed with a rotary evaporator, and the residual liquid (or solid) is distilled under reduced pressure.

The distillation is expediently carried out using a 500-ml., round-bottomed flask, an electrically heated 1.5 × 30 cm. column packed with V4A wire spirals (4 mm.) (Note 14), a short, air-cooled condenser (Note 15), and an ice-cooled, three-necked, 250-ml. receiver flask. During the distillation, the liquid is stirred magnetically and heated with an oil bath. The first fraction, b.p. 55–58° (1 mm.), yields *ca.* 50 g. of isotetralin (Note 16), more of which is collected when the column is heated to about 100°. The temperature in the head of the column thereby rises to 90–95°, and it is necessary to change the receiver flask. The second fraction, collected at 95–102° (1 mm.), yields *ca.* 108 g. of 1:1-adducts, which consists of 92% of the desired tricyclo product and 8% of the side-addition product. The residue mainly contains the 2:1-adducts. The fraction containing the 1:1-adducts is recrystallized from methanol (about 500 ml.), giving 87–97 g. (40–45%, based on isotetralin) of 11,11-dichlorotricyclo[4.4.1.$0^{1,6}$]undeca-3,8-diene as long, colorless needles, m.p. 88–89° (Note 17).

C. *Tricyclo*[4.4.1.$0^{1,6}$]*undeca*-3,8-*diene*. Ammonia (800 ml.) is condensed into a 2-l., three-necked round-bottomed flask, immersed in an acetone–dry ice bath and fitted with a dry ice condenser, a tube-sealed stirrer, a drying tube, and a gas delivery tube running to the bottom of the flask. The gas delivery tube is removed, and with vigorous stirring 56 g. (2.4 g.-atoms) of sodium is added in small portions with vigorous stirring over a period of 30 minutes (Note 18). The flask is then fitted with a dropping funnel, through which a solution of 81.4 g. (0.378 mole) of 11,11-dichlorotricyclo[4.4.1.$0^{1,6}$]-undeca-3,8-diene in 500 ml. of anhydrous ether is added over 1 hour, while cooling and stirring are maintained. After addition is complete, the acetone–dry ice bath is removed, and the ammonia is allowed to evaporate overnight. The flask is placed in the acetone–dry ice bath again, and a gentle stream of argon is passed continuously through the system. With stirring, a mixture of 90 ml. of methanol and 90 ml. of ether is added dropwise. The bath temperature is then allowed to rise to 0° and, with continued stirring, 500 ml. of ice water is added slowly. The reaction mixture is transferred to a 2–l. separatory funnel, and the two layers are separated. The organic layer is washed with 200 ml. of water, the aqueous layer is extracted with three 150-ml. portions of pentane (Note 19), and the combined ether–pentane phases are dried over magnesium sulfate. After filtration of the drying agent (Note 20) the solvent is removed by distillation through a 30-cm. Vigreux column. The remaining liquid is transferred to a 250-ml., round-bottomed flask and distilled under reduced pressure through a packed column (Note 21), yielding 46.9–49.7 g. (85–90%) of tricyclo[4.4.1.$0^{1,6}$]undeca-3,8-diene, collected as a colorless liquid at 80–81° (11 mm.), n_D^{20} 1.5180 (Note 22).

D. 1,6-*Methano*[10]*annulene*. A 2-l., three-necked, round-bottomed flask fitted with a tube-sealed stirrer, a reflux condenser protected with a calcium chloride drying tube, and an inlet tube for argon is charged with 900 ml. of anhydrous dioxane (Note 23). To this solvent is added, with stirring, 149 g. (0.656 mole) of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (Note 24). When the DDQ has dissolved, 43.8 g. (0.300 mole) of tricyclo[4.4.1.$0^{1,6}$]undeca-3,8-diene and 10 ml. of glacial acetic acid are added. The system is then flushed with argon, and the stirred mixture is heated under reflux for 5 hours. The reaction starts within a few minutes, as evidenced by effervescing of the solution and massive precipitation of the hydroquinone. At the same time the originally red-brown color of the mixture turns almost black. Following the reflux period, the bulk of the dioxane (600–650 ml.) is removed by distillation through a 15-cm. Vigreux column while stirring is maintained. The resulting pasty mixture is cooled, and 150 ml. of *n*-hexane is added. The solid is suction filtered, washed with 500 ml. of warm *n*-hexane, and dried at 100°, giving *ca.* 144 g. (95%) of pure 2,3-dichloro-5,6-dicyanohydroquinone (Note 25). The filtrate and washings are combined and passed through a 5 × 30 cm. column of neutral alumina (Note 26), which is eluted with *n*-hexane (Note 27). The solvent is removed by distillation through a 30-cm. Vigreux column, and the residual liquid is distilled from a

250-ml., round-bottomed flask through a packed column (Note 28), yielding 36.2–37.0 g.. (85–87%) of faintly yellow 1,6-methano[10]annulene, b.p. 68–72° (1 mm.), which may crystallize in the receiver-flask, m.p. 27–28° (Note 29).

2. Notes

1. It is advisable to use a 10- or 12-l. flask for runs on this scale because the reaction mixture may effervesce if the naphthalene solution is added too quickly.
2. It is necessary to use a dry ice condenser to shorten the time required to condense the ammonia (4 hours compared with 6 hours without the condenser). The ammonia tank was warmed with an air gun during the distillation. The condenser was removed after the ammonia was collected.
3. It is necessary to use a strong stirring motor since the reaction mixture becomes, temporarily, rather viscous.
4. One should not pour the liquified ammonia directly out of the cylinder since particles of iron compounds might be carried along, catalyzing the formation of sodium amide. For the exclusion of moisture it is also necessary to use a drying tower (potassium hydroxide) between the cylinder and the flask.
5. The sodium should be cut into small particles to increase the speed of dissolution and diminish the danger of stirrer blockage.
6. During this period the reaction mixture might turn white. In this case, another portion of sodium must be added until the solution becomes blue again.
7. The white residue should be worked up as soon as possible. On standing the residue gradually turns brown-red due to the formation of decomposition products; isolation of isotetralin then becomes difficult, and the yield may drop sharply. The submitters evaporated any remaining ether from the reaction flask at reduced pressure and filtered the water slurry of isotetralin, obtaining the same yield after crystallization.
8. Isotetralin should not be kept under vacuum longer than necessary since the compound has a relatively high vapor pressure.
9. A second extraction of the aqueous phase with ether yields an additional 1.5 g. of material. A second crop, (29.4 g., m.p. 49–52°) of isotetralin can be obtained from the mother liquors of the recrystallization.
10. All solvents used should be anhydrous.
11. The yield of 11,11-dichlorotricyclo[4.4.1.$0^{1,6}$]undeca-3,8-diene strongly depends on the quality of the potassium *tert*-butoxide used. Commercially available, sublimed potassium *tert*-butoxide was employed. When freshly sublimed potassium *tert*-butoxide is utilized, yields of up to 45% of 11,11-dichlorotricyclo[4.4.1.$0^{1,6}$]undeca-3,8-diene can be obtained. Potassium *tert*-butoxide, prepared by the method of Doering,[3] gave yields comparable to those achieved with the commercial product.
12. The stated reaction temperature should be maintained carefully. Raising the temperature above −30° noticeably reduces the regio-selectivity of the addition of dichlorocarbene, whereas lowering the temperature causes the yield of 1:1-adducts to drop due to partial crystallization of isotetralin.
13. The formation of emulsions may render it difficult to discern the two rather dark layers. In this case it is helpful to acidify with dilute sulfuric acid.
14. The checkers used an electrically heated, 1.5 × 30 cm. Vigreux column and obtained the same results.
15. To prevent isotetralin and the 1:1-adducts from solidifying in the condenser external heating with an IR lamp was applied.
16. The recovered isotetralin can be reused.
17. The product is approximately 99% pure by GC (SE-30 on kieselguhr, 150°). After two or three recrystallizations from methanol, 11,11-dichlorotricyclo[4.4.1.$0^{1,6}$]undeca-3,8-diene shows m.p. 90–91°.
18. For the preparation of the solution of sodium in liquid ammonia, compare part A.
19. If emulsions occur, it is advisable to acidify with dilute sulfuric acid to attain separation of the two layers.
20. The drying agent should be washed well with pentane.
21. The column used for this distillation is described in part B.
22. Tricyclo[4.4.1.$0^{1,6}$]undeca-3,8-diene was shown to be approximately 99% pure by GC (SE-30 on kieselguhr, 150°).
23. The use of anhydrous solvents is necessary to avoid hydrolytic decomposition of 2,3-dichloro-5,6-

dicyano-1,4-benzoquinone.
24. Commercially available 2,3-dichloro-5,6-dicyano-1,4-benzoquinone was employed. 1,6-Methano [10]annulene was obtained in equally good yields, when 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, prepared by the method of Walker and Waugh,[4] was utilized.
25. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone is readily regenerated in good yield from the hydroquinone by oxidation with nitric acid.[4]
26. Brockmann alumina, activity grade II–III, M. Woelm, 344 Eschwege, West Germany.
27. By contrast to the filtrate and washings, which are rather dark, the eluent is yellow due to the color of 1,6-methano[10]annulene.
28. The column used for this distillation is described in part B.
29. The purity of the 1,6-methano[10]annulene was shown by GC (SE-30 on kieselguhr, 150°) to be higher than 99%. Recrystallization of the hydrocarbon from methanol raises its melting point to 28–29°.

3. Discussion

The procedure described for the Birch reduction of naphthalene is a modification of the methods previously developed by Birch,[5] Hückel,[2] and Grob.[6] Apart from this reduction, no other practical approaches to isotetralin are known. The scale employed in the present procedure is not mandatory to achieve optimum yields. Equally good yields were realized when the runs were halved or enlarged up to fourfold. In the latter case, however, the apparatus reaches pilot plant dimensions.

Tricyclo[4.4.1.$0^{1,6}$]undeca-3,8-diene, the strategic intermediate in the synthesis of 1,6-methano[10] annulene from naphthalene, can alternatively be obtained in one step by the reaction of isotetralin with the Simmons–Smith reagent.[7] The two-step preparation of tricyclo[4.4.1.$0^{1,6}$]undeca-3,8-diene utilized here has the following merits: (1) dichlorocarbene adds to the central double bond of isotetralin with exceptionally high regioselectivity (as compared to that of methylene transfer reagents), giving 11,11-dichlorotricyclo[4.4.1.$0^{1,6}$]undeca-3,8-diene as a readily isolable, crystalline compound; and (2) the transformation of the dichloro compound into tricyclo[4.4.1.$0^{1,6}$]undeca-3,8-diene with sodium in liquid ammonia[8] is a simple operation and affords the product in high yield and purity. The dichlorocarbene employed in the two-step cyclopropanation of isotetralin was generated by the original method of Doering and Hoffmann.[3] Other sources of dichlorocarbene, notably the methods of Parham and Schweizer[9] and of Makosza and Wawrzyniewicz,[10] have also been tried, but did not lead to improved yields of adduct.

The rapid conversion of tricylo[4.4.1.$0^{1,6}$]undeca-3,8-diene to 1,6-methano[10]annulene by the high potential quinone, DDQ, is yet another illustration of the usefulness of this agent as a means of dehydrogenation of hydroaromatic compounds.[11] If DDQ is not available, it is recommended that tricyclo[4.4.1.$0^{1,6}$]undeca-3,8-diene be aromatized by a bromination-dehydrobromination sequence similar to that described in the synthesis of 1,6-oxido[10]annulene;[12] both aromatization methods give essentially the same yield of 1,6-methano[10]annulene.

The synthesis of 1,6-methano[10]annulene outlined above is an improved version of the method first suggested by Vogel and Roth.[13] 1,6-Methano[10]annulene represents a Hückel-type aromatic ($4n + 2$) π-system and is similar to benzene or naphthalene in both its physical and chemical properties.[14] The aromatic nature of the hydrocarbon is born out most impressively by its ^{1}H NMR spectrum which exhibits an AA'BB'-system for the vinylic protons at relatively low field (δ 6.8–7.5) and a singlet for the bridge protons at relatively high field (δ 0.5). 1,6-Methano[10]annulene may serve as a starting material for the preparation of other molecules of current interest, such as the bicyclo[5.4.1]dodecapentaenylium ion[14] and benzocyclopropene.[15]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 6, 862

References and Notes

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

alumina

1,6-Oxido[10]annulene

1,4,5,8-Tetrahydronaphthalene (isotetralin)

isotetralin

tricylo[4.4.1.$0^{1,6}$]undeca-3,8-diene

ethanol (64-17-5)

sulfuric acid (7664-93-9)

acetic acid (64-19-7)

ammonia (7664-41-7)

Benzene (71-43-2)

methanol (67-56-1)

ether,
diethyl ether (60-29-7)

chloroform (67-66-3)

iron (7439-89-6)

nitric acid (7697-37-2)

nitrogen (7727-37-9)

sodium (13966-32-0)

Naphthalene (91-20-3)

Pentane (109-66-0)

magnesium sulfate (7487-88-9)

dioxane (123-91-1)

sodium amide (7782-92-5)

n-hexane (110-54-3)

argon (7440-37-1)

2,3-dichloro-5,6-dicyano-1,4-benzoquinone

2,3-dichloro-5,6-dicyanohydroquinone

dichlorocarbene

Benzocyclopropene

1,6-Methano[10]annulene,
Bicyclo[4.4.1]undeca-1,3,5,7,9-pentaene (2443-46-1)

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

11,11-Dichlorotricyclo[4.4.1.$0^{1,6}$]undeca-3,8-diene,
11,11-dichlorotricyclo[4.4.1.$0^{1,6}$]-undeca-3,8-diene (39623-22-8)

Tricyclo[4.4.1.$0^{1,6}$]undeca-3,8-diene (27714-83-6)

potassium tert-butoxide (865-47-4)