



A Publication  
of Reliable Methods  
for the Preparation  
of Organic Compounds

## Working with Hazardous Chemicals

The procedures in *Organic Syntheses* are intended for use only by persons with proper training in experimental organic chemistry. All hazardous materials should be handled using the standard procedures for work with chemicals described in references such as "Prudent Practices in the Laboratory" (The National Academies Press, Washington, D.C., 2011; the full text can be accessed free of charge at [http://www.nap.edu/catalog.php?record\\_id=12654](http://www.nap.edu/catalog.php?record_id=12654)). All chemical waste should be disposed of in accordance with local regulations. For general guidelines for the management of chemical waste, see Chapter 8 of Prudent Practices.

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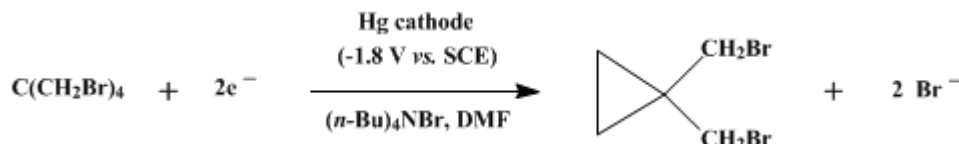
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*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

*Organic Syntheses, Coll. Vol. 6, p.153 (1988); Vol. 52, p.22 (1972).*

## CONTROLLED-POTENTIAL ELECTROLYTIC REDUCTION: 1,1-BIS(BROMOMETHYL)CYCLOPROPANE

[Cyclopropane, 1,1-bis(bromomethyl)-]



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Checked by Edith Feng and Herbert O. House.

### 1. Procedure

*Caution! Since bromine is liberated during the electrolysis, the reaction should be conducted in a hood.*

The electrolysis cell (Note 1) is assembled in a 1000-ml., flat-bottomed Pyrex reaction kettle. The Pyrex cover contains four standard taper outer joints in which are mounted: (1) a 11.5 × 2-cm.-diameter carbon rod (Note 2) surrounded by a 15 × 5.5-cm.-diameter, porous, porcelain cup (Note 3); (2) a 31-cm. × 8-mm.-diameter length of soda-lime glass tubing (Note 4) with a short length of 0.6-mm.-diameter platinum wire fused into the bottom; (3) a tee-tube fitted to hold a thermometer and to allow nitrogen to be passed into the reaction vessel; and (4) a saturated calomel reference electrode fitted with successive salt bridges containing aqueous 1 M sodium nitrate and 1.5 M tetraethylammonium tetrafluoroborate in *N,N*-dimethylformamide (Note 5). The cover is also equipped with a suitable clamp so that it may be fastened to the reaction kettle during the electrolysis.

A sufficient quantity of mercury (about 700 g.) is added to the reaction kettle to form a cathode pool 1-cm. deep, and a Teflon-covered magnetic stirring bar is placed on this mercury pool. A solution of 25.0 g. (0.0651 mole) of pentaerythrityl tetrabromide (Note 6) in 250 ml. of 0.2 M tetra-*n*-butylammonium bromide (Note 7) in *N,N*-dimethylformamide (Note 8) is added to the reaction vessel. An additional 175 ml. (Note 9) of 0.2 M tetra-*n*-butylammonium bromide (Note 7) in *N,N*-dimethylformamide (Note 8) is added to the porous porcelain cup surrounding the carbon-rod anode, and the cover is clamped to the reaction kettle. The glass tubing with a platinum wire contact sealed in the bottom is adjusted so that all of the exposed platinum is below the mercury surface (Note 10). The bottom of the porous porcelain cup should be a sufficient distance above the mercury pool so as not to interfere with the magnetic stirring bar. The salt bridge associated with the calomel reference electrode (Note 5) should be adjusted so that the lower, porous Vycor plug is between 5 and 10 mm. above the surface of the mercury pool. Before the electrolysis is begun a 0.5-ml. aliquot of the reaction solution should be removed from the cathode compartment and analyzed polarographically (Note 11), and the electrical resistances between the cathode and anode and between the cathode and the reference electrode should be measured with a suitable resistance bridge (Note 12). If all electrical connections are satisfactory the cathode-anode resistance should be in the range 20–30 ohms and the cathode-reference resistance should be in the range 5000–15,000 ohms. The electrical leads from the anode and cathode should be connected with a direct current source whose potential may be conveniently adjusted from 0 to 40 volts with a continuous current output of at least 1 amp. A suitable d.c. voltmeter is mounted in parallel with the anode and cathode leads, and a d.c. ammeter, capable of measuring currents of 0 to 3 amps is placed in series in either of the two leads. Finally, a vacuum-tube d.c. voltmeter or some equivalent high-impedance (Note 13) potential measuring device is connected to measure the potential difference between the cathode and the reference electrode. The reaction kettle should be placed in a nonmagnetic bath, to which cooling water may be added if necessary and magnetic stirring started. A very slow stream of nitrogen (1–2 ml. per minute) is passed through the

apparatus throughout the electrolysis (Note 14). The potential of the direct current source is adjusted, giving a potential difference of 1.7 to 1.8 volts between the cathode and the reference electrode (Note 15), and the current source is adjusted at 10–15 minute intervals to maintain this potential difference throughout the electrolysis. It is convenient to keep a record of time and the current passing through the cell so that the time when the theoretical amount of electricity (12,500 coulombs or 3.5 amp.-hours) has been passed through the cell can be estimated (Note 16). During the electrolysis the temperature of the catholyte solution is kept below 40° (Note 17) by the use of external cooling if necessary. When approximately the theoretical amount of electricity has been passed through the electrolysis cell (Note 16), typically 4–6 hours), a 0.5-ml. aliquot is removed and analyzed polarographically (Note 11). The electrolysis is continued until the polarographic analysis (Note 11) indicates the consumption of practically all the pentaerythrityl tetrabromide.

The solutions are removed from the cathode and anode (Note 18) compartments and added to 200 ml. of water. The resulting mixture is extracted with four 150-ml. portions of pentane, and the combined pentane extracts are washed with water, dried over anhydrous sodium sulfate, and concentrated by distillation through a short Vigreux column (Note 19). The remaining pentane is removed by distillation and the residual yellow liquid is distilled under reduced pressure, yielding 6.9–8.5 g. (47–58%) of 1,1-bis-(bromomethyl)cyclopropane as a colorless liquid, b.p. 65–67° (5 mm.),  $n_D^{25}$  1.5341–1.5347 (Note 20).

## 2. Notes

1. The electrolysis cell designed by the checkers is shown in Figure 1. The adapters, which hold the reference electrode salt bridge (Note 5), the glass tube with the platinum contact, the tee tube for the nitrogen-inlet, and the thermometer are commercially available from Ace Glass, Inc., Vineland, New Jersey. The adapter which supports the carbon rod anode and the surrounding porous porcelain cup was machined from a Teflon rod; the dimensions of the adapter used by the checkers are indicated in Figure 2. Holes were drilled in the porcelain cup to permit fastening to the Teflon adapter with three stainless-steel machine screws. Electrical contact between the carbon anode and the wire to the external circuitry was achieved by drilling and tapping the end of the carbon rod for a small machine screw. The arrangement used for the remainder of the electrical circuit is indicated in Figure 1.

**Figure 1. Cell for controlled-potential electrolytic reduction.**

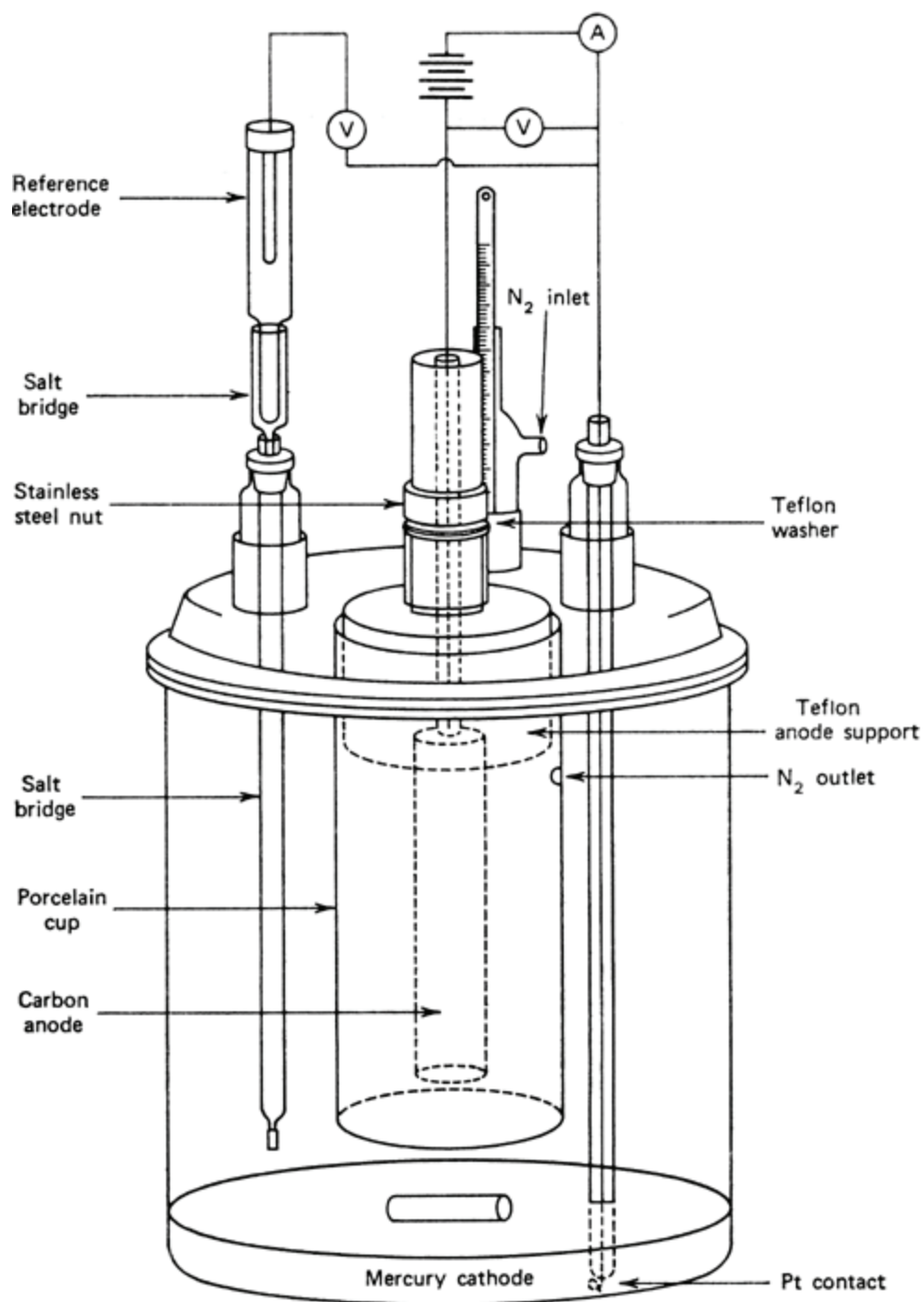
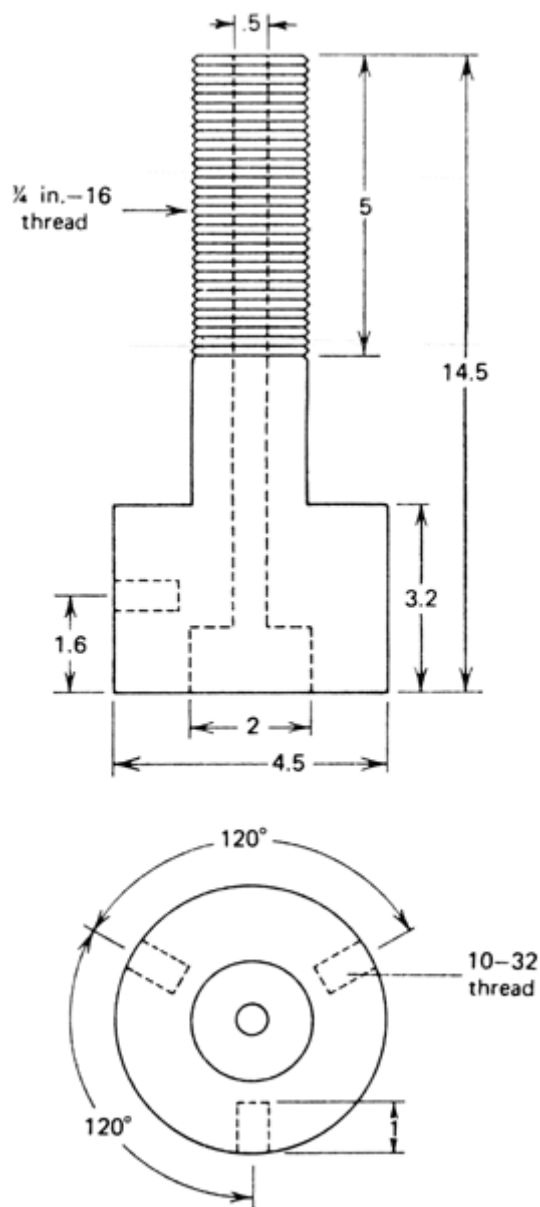


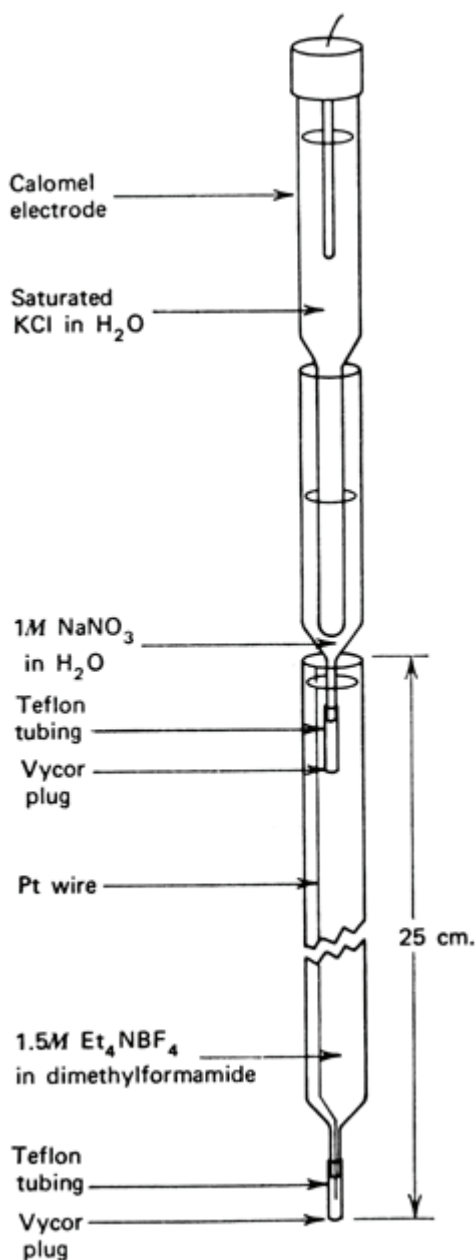
Figure 2. Teflon anode support for the electrolysis cell. Unless otherwise stated, the dimensions are in centimeters.



2. Carbon rods of approximately the dimensions indicated are commercially available from welding supply companies.
3. A suitable porous porcelain cup (Coors 700, unglazed) may be purchased from the Arthur H. Thomas Company.
4. To obtain a satisfactory seal between the platinum and the glass, soda-lime glass rather than Pyrex glass should be employed. Before the platinum wire is sealed into the glass a length of copper wire should be silver soldered to the platinum to provide an accessible electrical lead at the top of the glass tubing.
5. Any commercial saturated calomel electrode of convenient dimensions may be employed. The arrangement of the salt bridges between the calomel electrode and the reaction solution is illustrated in Figure 3. The Teflon tubing is available from Bolab, Inc., 359 Main Street, Reading, Massachusetts 01867, and the porous Vycor plugs are cut from lengths of 1/8-in.-diameter porous Vycor rod ("thirsty" glass or Corning Vycor No. 7930), available from the Electronic Parts Department, Corning Glass Works, Houghton Park, Corning, New York, 14830. The intermediate salt bridge containing aqueous sodium nitrate is used to prevent precipitation of the insoluble potassium tetrafluoroborate at the small fiber in the tip of the calomel electrode.<sup>2</sup> To minimize resistance in the long, lower, nonaqueous salt bridge, a concentrated (1.5 M) solution of tetraethylammonium tetrafluoroborate<sup>3,4</sup> in *N,N*-

dimethylformamide is used with a length of platinum wire inside the tube. Tetraethylammonium tetrafluoroborate was prepared by mixing 5.3 g. (0.025 mole) of tetraethylammonium bromide (Eastman Organic Chemicals) and 3.6 ml. (ca. 0.026 mole) of aqueous 48–50% fluoroboric acid (Allied Chemical Corporation) in 8 ml. of water. The resulting mixture was concentrated under reduced pressure, diluted with ether and filtered, yielding 4.6 g. (85%) of the crude tetrafluoroborate salt, m.p. 375–378° (dec.). Two recrystallizations from methanol-petroleum ether mixtures afforded 3.7 g. (69%) of the pure tetraethylammonium tetrafluoroborate as white needles, m.p. 377–378° (dec.) (after drying).

**Figure 3. Reference electrode and salt bridges for controlled potential electrolysis.**



6. Crude pentaerythryl tetrabromide, purchased from Columbia Organic Chemicals Company, Inc., was recrystallized from chloroform, yielding the tetrabromide as tan needles, m.p. 158–160°. Alternatively, this material may be obtained by the procedure described in *Org. Synth., Coll. Vol. 4, 753* (1963).

7. Tetra-*n*-butylammonium bromide, obtained from Eastman Organic Chemicals, was recrystallized from chloroform. The white prisms that separated were pulverized and dried under reduced pressure, giving the pure salt, m.p. 116–117.5°.

8. *N,N*-Dimethylformamide, obtained from Allied Chemical Corporation, was purified by distillation

under reduced pressure, b.p. 39–41° (6 mm.).

9. Since the amount of solvent in the anode compartment is slowly depleted as the electrolysis proceeds, it is convenient to begin the electrolysis with the level of solution in the anode compartment about 9 cm. above the level of the solution in the cathode compartment. Alternatively, additional 0.2 M *tetra-n-butylammonium bromide* in *N,N*-dimethylformamide may be added to the anode compartment as the electrolysis proceeds.

10. To avoid competing liberation of *hydrogen* at the cathode, no *platinum* should be exposed to the catholyte solution.

11. The polarographic analysis is obtained at a dropping mercury electrode with any conventional three-electrode polarograph employing a saturated calomel electrode as the reference. The checkers added the 0.5-ml. aliquots of the reaction mixture to 10-ml. portions of 0.2 M *tetra-n-butylammonium bromide* (Note 7) in *N,N*-dimethylformamide (Note 8). The half-wave potentials ( $E_{1/2}$  vs. sce) for the reduction of *pentaerythrityl tetrabromide* and *1,1-bis-(bromomethyl)cyclopropane* are -1.71 ( $\alpha n = 0.44$ ) volts and -2.18 ( $\alpha n = 0.31$ ) volts, respectively.

12. The checkers measured these resistances with a Serfass Conductivity Bridge, Model RCM 15, employing a 1000-Hz. alternating current.

13. Since the resistance in the circuit containing the reference electrode is approximately 10,000 ohms, an accurate measure of the cathode-reference electrode potential can only be obtained by the use of a potential measuring device with an input impedance of at least 100,000 ohms. Although a vacuum-tube voltmeter (VTVM, typical input impedance  $11 \times 10^6$  ohms) is suitable for this purpose, a common multimeter (VOM, typical input impedance 20,000 ohms per volt) is *not a satisfactory alternative*.

14. This slow stream of *nitrogen* passes through the hole about 2.5 cm. from the top of the porous cup surrounding the anode compartment and sweeps the *bromine* formed at the anode out the top of the apparatus through the hole in the center of the Teflon adapter.

15. If the cathode-reference potential is allowed to rise significantly above -1.8 volts, further reduction of the *1,1-bis-(bromomethyl)cyclopropane* will occur. The submitter reports that the dibromide may be reduced to *spiropentane* in 39% yield by employing a cathode-reference potential of -2.0 volts to -2.2 volts.

16. The checkers found that about 1.3 times the theoretical amount of electricity was passed through the cell during the time required to consume the starting material. Presumably the excess electricity is consumed partially in the reduction of impurities (e.g., *oxygen*) and partially in the further reduction of the dibromide to *spiropentane* (Note 15).

17. This temperature limit was selected to avoid the possible loss of solvent and the volatile product in the slow stream of *nitrogen* passed through the cell. Since the rate of the electrolytic reduction is increased with an increase in the reaction temperature, it is advantageous to maintain the temperature of the reaction solution in the range 35–40°.

18. Since some diffusion of the product from the cathode compartment to the anode compartment is probable, both solutions are subjected to the isolation procedure.

19. To avoid the possible loss of the volatile product, the *pentane* solvent should be removed by distillation through a 20–30-cm. Vigreux column rather than by distillation in a rotary evaporator.



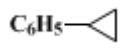
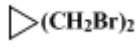

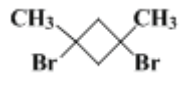

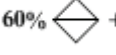
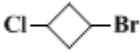



20. On a GC column, packed with Apiezon M suspended on Chromosorb P and heated to 70°, the product exhibits a single peak with a retention time of 23.2 minutes. The sample exhibits IR absorption ( $\text{CCl}_4$ ) at 3100, 3030, 2985, 1440, 1340, and 1235  $\text{cm}^{-1}$  with  $^1\text{H}$  NMR ( $\text{CCl}_4$ ) singlets at  $\delta$  3.45 ( $\text{CH}_2\text{Br}$ ) and 0.90 (cyclopropyl  $\text{CH}_2$ ). The mass spectrum of the sample has abundant fragment peaks at  $m/e$  149, 147, 67, 41, and 39.

### 3. Discussion

*1,1-Bis-(bromomethyl)cyclopropane* has been obtained as one component in a mixture of isomeric bromides by reaction of *methylenecyclobutane* with *bromine*<sup>5</sup> and by reaction of *cyclopropane-1,1-dimethanol* with *phosphorus tribromide*.<sup>6,7,8</sup> The present method illustrates a general procedure for the preparation of cyclopropane and cyclobutane derivatives by the electrolytic reduction of 1,3- and 1,4-dihalides.<sup>9,13,10,15,14,16,11,12</sup> In at least some cases, this method is clearly superior to the reductive cyclizations of dihalides effected with metals or with chromium(II) salts. Examples of this reductive ring closure are provided in Table I. The reaction appears to give the best results when dibromides rather than dichlorides are used as starting materials and when an aprotic solvent such as *N,N*-dimethylformamide or *acetonitrile* is used. These electrolytic ring closures proceed by way of a stepwise

reaction mechanism.<sup>14</sup>

TABLE I  
ELECTROLYTIC REDUCTIVE RING CLOSURE OF DIHALIDES

Dihalide	Product(s)	Yield, %	Ref.
$\text{Br}(\text{CH}_2)_3\text{Br}$	 (only product)	60–80	13,14
$\text{Br}(\text{CH}_2)_4\text{Br}$	(only product) 25%  + 75% $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$	—	13
$\text{Br}(\text{CH}_2)_5\text{CH}_3$	+ 75% $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$ $\text{CH}_3(\text{CH}_2)_3\text{CH}_3$ (only product)	80	13
$\text{C}_6\text{H}_5\text{CH}(\text{Br})\text{CH}_2\text{CH}_2\text{Br}$		70	15
		39	14
	$\text{CH}_3$ —  — $\text{CH}_3$	55–94	13
	60%  +		
	+		
	20%  +	—	13
	+		
	10% 		
$\text{CH}_3\text{CH}(\text{Br})\text{CH}_2\text{CH}(\text{Br})\text{CH}_3$ (either meso or racemic isomer)	$\text{H}_3\text{C}$ —  — $\text{CH}_3$ + (both <i>cis</i> and <i>trans</i> isomers) $n\text{-C}_5\text{H}_{12}$ + isomeric pentenes	—	16
(either meso or racemic isomer)	(both <i>cis</i> and <i>trans</i> isomers) $n\text{-C}_5\text{H}_{12}$ + isomeric pentenes		

## References and Notes

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

petroleum ether

methanol (67-56-1)

ether (60-29-7)

hydrogen (1333-74-0)

acetonitrile (75-05-8)

chloroform (67-66-3)

bromine (7726-95-6)

sodium sulfate (7757-82-6)

oxygen (7782-44-7)

phosphorus tribromide (7789-60-8)

nitrogen (7727-37-9)

mercury (7439-97-6)

platinum (7440-06-4)

Pentane (109-66-0)

sodium nitrate

silver (7440-22-4)

Pentaerythrityl tetrabromide (3229-00-3)

N,N-dimethylformamide (68-12-2)

fluoroboric acid (16872-11-0)

spiropentane (157-40-4)

1,1-Bis(bromomethyl)cyclopropane,  
Cyclopropane, 1,1-bis(bromomethyl)-,  
1,1-bis-(bromomethyl)cyclopropane (29086-41-7)

tetraethylammonium tetrafluoroborate (429-06-1)

potassium tetrafluoroborate (14075-53-7)

tetraethylammonium bromide (71-91-0)

Tetra-n-butylammonium bromide (1643-19-2)

methylenecyclobutane (1120-56-5)

cyclopropane-1,1-dimethanol