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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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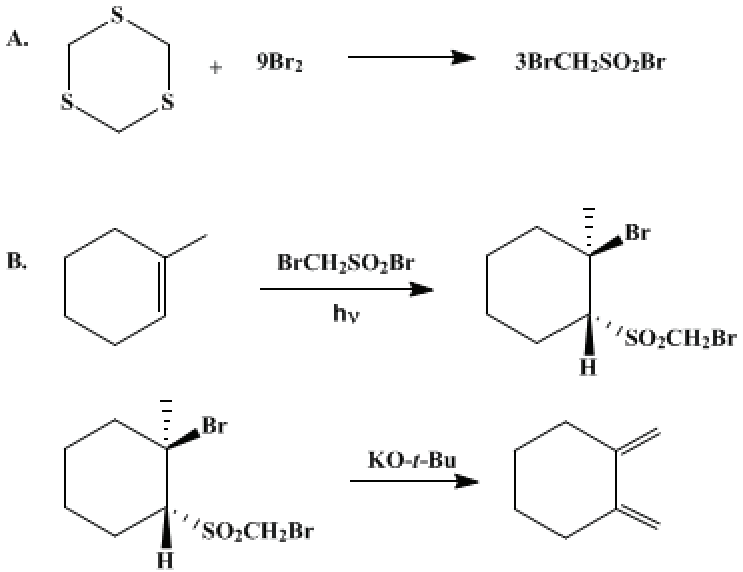
A GENERAL SYNTHETIC METHOD FOR THE PREPARATION OF CONJUGATED DIENES FROM OLEFINS USING BROMOMETHANESULFONYL BROMIDE: 1,2-DIMETHYLENECYCLOHEXANE

[Cyclohexane, 1,2-bis(methylene)-]



Submitted by Eric Block and Mohammad Aslam[1].
Checked by Jeffrey C. Weber and Leo A. Paquette.

1. Procedure

A. *Bromomethanesulfonyl bromide.* A 3-L, three-necked, round-bottomed flask equipped with a mechanical stirrer, a pressure-equalized dropping funnel, and a thermometer is charged with 100 g (0.73 mol) of *sym*-trithiane (Note 1) suspended in 600 mL of water. Bromine (1136 g, 7.1 mol) is added with stirring while keeping the flask temperature around 40°C (Note 2). After the addition of half of the bromine, 600 mL of water is added and bromine addition is continued. After all of the bromine has been added, the reaction mixture is stirred for 0.25 hr. The mixture is transferred to a 4-L separatory funnel, the lower organic layer is separated, and the aqueous layer is extracted with two 200-mL portions of methylene chloride (Note 3). The organic extracts are combined, washed with one 100-mL portion of cold 5% sodium bisulfite solution and with 100 mL of water, dried over anhydrous magnesium sulfate, and concentrated at room temperature with a rotary evaporator to a light-yellow oil. Distillation using a short Vigreux column affords 218–249 g (42–48%) of bromomethanesulfonyl bromide as a light-yellow oil, bp 68–69°C (0.55 mm) (Note 4) and (Note 5).

B. *1-Bromo-1-methyl-2-(bromomethylsulfonyl)cyclohexane.* Four Pyrex test tubes (2.5 × 20 cm) are charged with 1-methylcyclohexene (5.0 g per test tube; total weight 20.0 g, 0.21 mol) (Note 6). Methylene chloride (12 mL) is added to each test tube, which is cooled in ice. An ice-cold solution of bromomethanesulfonyl bromide (13.6 g of bromomethanesulfonyl bromide per test tube; total weight 54.4 g, 0.23 mol) in methylene chloride (12 mL) is added to each test tube with mixing at 0°C (Note 7). The test tubes are attached with the help of several rubber bands to a Pyrex immersion well equipped with a 45-W mercury lamp (Note 8). The immersion well is cooled by circulation of ice water (Note 9) and immersed in a cooling bath maintained at −15°C. The reaction mixture is irradiated for 2 hr. Solid potassium carbonate (1.5 g) is added to each test tube and the contents of the test tubes are filtered through a small column with a glass wool plug into a 250-mL round-bottomed flask. Methylene chloride is removed, first on a rotary evaporator and then with a vacuum pump (1 mm), to give an oil that gradually solidifies (68.3 g, 98%). Recrystallization from 95% ethanol (100 mL) gives white crystals (54.3 g, 78%) (Note 10), mp 59–61°C (Note 11).

C. *1,2-Dimethylenecyclohexane.* An oven-dried, 1-L, three-necked, round-bottomed flask equipped with a mechanical stirrer, a pressure-equalized dropping funnel, and a stopper is charged with potassium *tert*-butoxide (59.5 g, 0.53 mol) (Note 12) dissolved in *tert*-butyl alcohol–tetrahydrofuran (9:1, 400 mL total) (Note 13) and cooled in ice. A solution of 1-bromo-1-methyl-2-(bromomethylsulfonyl) cyclohexane (54.0 g, 0.16 mol) in *tert*-butyl alcohol–tetrahydrofuran (9:1, 100 mL) (Note 14) is added dropwise over a 1-hr period. After the addition is complete the reaction mixture is stirred at room temperature for 0.5 hr and then poured into a 2-L separatory funnel containing 500 mL of water. This solution is extracted with two 150-mL portions of pentane. The combined pentane extracts are washed 8 times with water (500 mL) (Note 15), dried over anhydrous magnesium sulfate, and filtered. The pentane is removed by distillation at atmospheric pressure using an efficient Vigreux column and the residue is distilled under reduced pressure to give 11.4 g (65%) of 1,2-dimethylenecyclohexane as a colorless liquid, bp 69–70° (90 mm) (lit.[2] 60–61°C, 90 mm) (Note 16) and (Note 17).

2. Notes

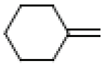
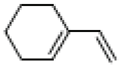
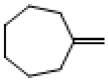
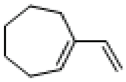
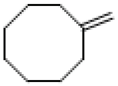
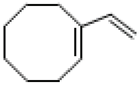
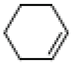
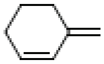
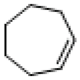
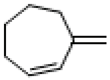
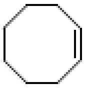
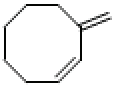
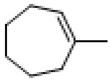
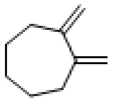
1. *sym*-Trithiane is prepared as described by Bost and Constable[3] and is used without purification. It can be purchased from Aldrich Chemical Company, Inc.
2. This is an exothermic reaction; no outside heating is required. If the temperature goes above 40°C, the flask is cooled by ice–water.
3. In the first of these extractions, the upper phase is the organic one. In the second extraction, the organic layer is at the bottom.
4. The product has refractive index n_{D}^{20} 1.5706 and spectral properties as follows: IR (neat) cm^{-1}: 3040 (vs), 2960 (vs), 1362 (vs), 1205 (s), 1160 (vs), 1105 (m), 830 (s), 680 (s); ^{1}H NMR ($CDCl_3$, 60 MHz) δ: 5.05 (s).
5. The product can be synthesized on a much smaller scale with no loss in yield simply by reducing the quantities as desired.
6. 1-Methylcyclohexene was obtained from the Aldrich Chemical Company, Inc. and was distilled before use.
7. On occasion bromomethanesulfonyl bromide undergoes spontaneous, exothermic addition to olefins. While this problem was not encountered with 1-methylcyclohexene, it is desirable to mix the reagents at low temperature to avoid a possible vigorous spontaneous reaction and to maximize the yield of adduct.
8. The apparatus should be shielded to avoid exposure to ultraviolet light. The immersion well, lamp, and the requisite transformer are available from Hanovia Lamp Division, Canrad-Hanovia Inc., 100 Chestnut Street, Newark, NJ 07105. The test tubes are positioned so as to be as close as possible to the lamp.
9. A "Little Giant" submersible pump (available from Little Giant Pump Co., Oklahoma City, OK) is used to circulate ice water through the immersion well.
10. The first crop (47.0 g) is followed by two other crops (5.2 and 2.1 g) obtained by concentrating and cooling the mother liquor.
11. The spectral properties are as follows: IR (KBr disk) cm^{-1}: 2960 (s), 1450 (m), 1380 (s), 1315 (vs), 1205 (s), 1140 (vs), 1090 (vs), 745 (s); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.56–1.82 (m, 4 H, CH_2), 2.08–2.41 (m, 4 H, CH_2), 2.15 (s, 3 H, CH_3), 3.96 (dd, 1 H, $CHSO_2$), 4.58 (AB quartet, 2 H, $J_{AB} = 11$, CH_2Br); ^{13}C NMR ($CDCl_3$) δ: 22.66, 23.25, 24.27, 29.72, 43.69, 44.39, 65.81, 67.21.
12. Potassium *tert*-butoxide can be obtained from Aldrich Chemical Company, Inc.
13. The *tert*-butyl alcohol and tetrahydrofuran are distilled from calcium hydride prior to use.
14. Warming is required to dissolve the solid in this solvent.
15. The first four washings are done with gentle agitation to avoid emulsion formation.
16. The first cut of the distillate (ca. 1–2 mL) coming below 60°C was discarded.
17. The physical properties of the product are as follows: n_{D}^{20} 1.4722; IR (liquid film) cm^{-1}: 3090 (s), 2940 (s), 2870 (s), 1635 (s), 1440 (s), 895 (vs); ^{13}C NMR ($CDCl_3$) δ: 26.85, 35.37, 107.78, 149.68; GLC analysis (50 m OV-101 fused silica capillary column obtained from Perkin Elmer, Inc.) showed the product to be 90–93% pure. The material has an ^{1}H NMR spectrum corresponding to that reported in the literature:[4] (300 MHz, $CDCl_3$) δ: 1.62–1.66 (m, 4 H, CH_2), 2.24–2.27 (m, 4 H, CH_2), 4.64–4.65 (m, 2 H,

vinyl CH), 4.92–4.93 (m, 2 H, vinyl CH).

3. Discussion

This procedure illustrates a recently published, simple, general method for the synthesis of conjugated dienes from olefins.[5] The scope of the reaction is shown in Table I.[5] In most of these examples hydrogen bromide elimination can be effected by stirring a solution of the olefin–bromomethanesulfonyl bromide adduct in methylene chloride with 1 equiv of triethylamine at room temperature. Only 2 equiv of the more costly potassium *tert*-butoxide are then needed in the second elimination step; the yields using the two-base procedure are generally superior to that obtained using only potassium *tert*-butoxide.

TABLE I
DIENE SYNTHESIS VIA THE VINYLOGOUS RAMBERG–BÄCKLUND REACTION

	Olefin	Product (Isomer Ratio[a])	Yield, %[b]
1	$C_4H_9CH=CH_2$	$C_3H_7CH=CHCH=CH_2$ (2:1)	38
2	$C_6H_{13}CH=CH_2$	$C_5H_{11}CH=CHCH=CH_2$ (2:1)[c]	61
3	(E)-$C_4H_9CH=CHC_4H_9$	(E)-$C_3H_7CH=CHC(C_4H_9)=CH_2$	68[d]
4	(E)-$C_5H_{11}CH=CHCH_3$	(E)-$C_4H_9CH=CHC(CH_3)=CH_2$ (E)-$C_4H_9CH=CHC(CH_3)=CH_2$ + $CH_2=CHC(C_5H_{11})=CH_2$	52 15
5			53
6			74
7			75
8			41[e]
9			31[e]
10			49[e]
11			43>[e]
12	$PhCH_2CH=CH_2$	$PhCH=CHCH=CH_2$ (1:8)	85
13	$PhOCH_2CH=CH_2$	$PhOCH=CHCH=CH_2$ (9:1)	54
14	$HO(CH_2)_9CH=CH_2$	$HO(CH_2)_8CH=CHCH=CH_2$ (5:1)	86
15	$(CH_3)_3SiCH_2CH=CH_2$	$(CH_3)_3SiCH=CHCH=CH_2$ (1:10)	41
16	$CH_2=CH(CH_2)_6CH=CH_2$	$CH_2=CH(CH_2)_5CH=CHCH=CH_2$	49[f,g,h]
17	$CH_2=CH(CH_2)_6CH=CH_2$	$CH_2=CHCH=CH(CH_2)_4CH=CHCH=CH_2$	40[i,j]
18	$(CH_3)_2Si(CH_2CH=CH_2)_2$	$(CH_3)_2Si(CH=CHCH=CH_2)_2$	38[i]

[a] (*Z*):(*E*) ratio.

[b] Overall yield of distilled product.

[c] (*Z*):(*E*) ratios 5:1 and 1:16 from (*E*)- and (*Z*)-1-octenylbromomethyl sulfones, respectively (59–61% overall distilled yields).[2]

[d] Analysis by GLC indicated < 1% (*Z*)-isomer.

[e] Et_3N step omitted.

[f] Isomers not resolved by GLC.

[g] Two equivalents of diene used.

[h] Includes ∼5% of 1,3,9,11-dodecatetraene.

[i] Two molar equivalents of 1 used.

[j] ∼80% (*Z*,*Z*).

1,2-Dimethylenecyclohexane, a useful diene for Diels–Alder reactions,[6,7,8] has previously been synthesized in 11–77% yield in multistep procedures from *cis*-1,2-cyclohexanedicarboxylic anhydride[6] or acid,[7] from diethyl phthalate,[2] or from cyclohexanone.[4]

References and Notes

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

$C_4H_9CH{=}CH_2$

$C_3H_7CH{=}CHCH{=}CH_2$

$C_6H_{13}CH{=}CH_2$

$(E)\text{-}C_4H_9CH{=}CHC_4H_9$

$(E)\text{-}C_3H_7CH{=}CHC(C_4H_9){=}CH_2$

$(E)-C_5H_{11}CH=CHCH_3$

$(E)-C_4H_9CH=CHC(CH_3)=CH_2$

$CH_2=CHC(C_5H_{11})=CH_2$

$PhCH_2CH=CH_2$

$PhCH=CHCH=CH_2$

$PhOCH_2CH=CH_2$

$PhOCH=CHCH=CH_2$

$HO(CH_2)_9CH=CH_2$

$HO(CH_2)_8CH=CHCH=CH_2$

$(CH_3)_3SiCH_2CH=CH_2$

$(CH_3)_3SiCH=CHCH=CH_2$

$CH_2=CH(CH_2)_6CH=CH_2$

$CH_2=CH(CH_2)_5CH=CHCH=CH_2$

$CH_2=CHCH=CH(CH_2)_4CH=CHCH=CH_2$

$(CH_3)_2Si(CH_2CH=CH_2)_2$

$(CH_3)_2Si(CH=CHCH=CH_2)_2$

ethanol (64-17-5)

potassium carbonate (584-08-7)

Cyclohexanone (108-94-1)

hydrogen bromide (10035-10-6)

bromine (7726-95-6)

sodium bisulfite (7631-90-5)

Pentane (109-66-0)

methylene chloride (75-09-2)

magnesium sulfate (7487-88-9)

Tetrahydrofuran (109-99-9)

diethyl phthalate (84-66-2)

1-methylcyclohexene

triethylamine (121-44-8)

tert-butyl alcohol (75-65-0)

calcium hydride (7789-78-8)

tert-BUTYL (1605-73-8)

Bromomethanesulfonyl bromide (54730-18-6)

1,2-Dimethylenecyclohexane,
Cyclohexane, 1,2-bis(methylene)- (2819-48-9)

1-Bromo-1-methyl-2-(bromomethylsulfonyl)cyclohexane (120696-44-8)

1,3,9,11-dodecatetraene

potassium tert-butoxide (865-47-4)

sym-Trithiane (291-21-4)

cis-1,2-cyclohexanedicarboxylic anhydride