Reductive Elimination of Bromine from 2,3-Disubstituted 1,4-Dibromo-2-butenes by Iodide Ion: A Convenient Route to 2,3-Bis[iodomethyl]-1,3-butadiene and Related Compounds

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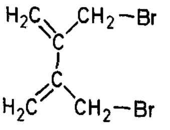
A recent paper has described the preparation and extolled the value of 2,3-bis[bromomethyl]-1,3-butadiene (**1**)[1].



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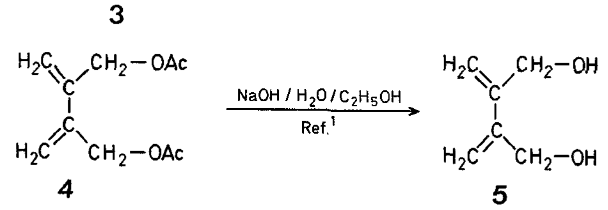
Before the full experimental details for the preparation of this compound were published, we required dienes of this type, in particular the derived[1] 2,3-bis[acetoxymethyl]-1,3-butadiene (**4**) and 2,3-bis[hydroxymethyl]-1,3-butadiene (**5**), for Diels-Alder reactions. From the details then available[2] we were unable to prepare the dibromide **1** in a reproducible manner and therefore an alternative route to such compounds was sought. This paper reports a convenient, high yielding synthesis of the related compound, 2,3-bis[iodomethyl]-1,3-butadiene (**3**), by a novel synthetic procedure, and its conversion to the acetoxy derivative **4** by an alternative method to that described previously. Hydrolysis of the acetoxy derivative **4** gives the diol **5**[1,3]. In this way, both compounds **4** and **5** are obtained in higher overall yield than reported earlier.

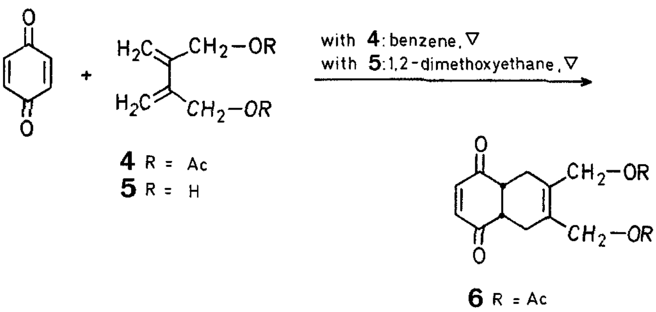
Reductive-elimination of bromine from 2,3-bis[bromomethyl]-1,4-dibromo-2-butene[5] (**2**) by means of excess potassium iodide in acetone was followed by the immediate addition of halogen to the generated diene. However, in the presence of sodium thiosulphate, the halogen was reduced and the diene **3** was then produced in high yield (93%).



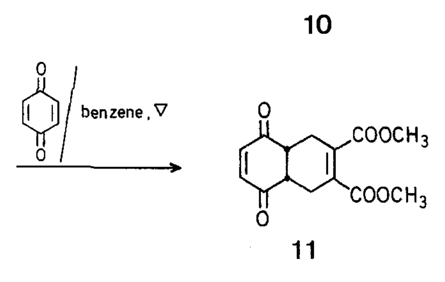
The diene produced initially should be the dibromo compound **1** but in the presence of excess iodide ion this diene was converted entirely to the diiodo-derivative **3**. In the presence of a catalytic amount[6] of iodide ion (10%), the reaction is slower and a mixture of iodo- and bromo-dienes is obtained. Compound **3** (m.p. 95–96°C) is unstable and polymerizes rapidly in the solid state. Solutions of compound **3** in ether (0.1 molar), however, were stable for several months at 0°C.

The attempted acetolysis of the diiodo compound **3**, by means of sodium acetate in acetic acid[1,2], gave only polymer. The diacetate **4** could be prepared, in 86% yield, by the reaction of **3** with silver acetate in acetic acid or, more conveniently, in acetonitrile. The diol **5** was readily obtained by hydrolysis of the diacetate **4**[1].

No conditions[7] have been found which allow the Diels-Alder reaction between the diiodo-diene **3** and benzoquinone. The dienes **4** and **5**, however, do react with benzoquinone to give the adducts **6** and **7**, respectively. These adducts have a marked propensity to enolize to the corresponding hydroquinones and they could be isolated only if precautions were taken to rigorously purify all reagents before use.



The Diels-Alder reaction of *p*-benzoquinone with dimethyl butadiene-2,3-dicarboxylate (**10**) was also required. The diene **10**[4] was prepared in 85% overall yield by allylic bromination of dimethyl 2,3-dimethylbutenedioate[8] (**8**) with *N*-bromosuccinimide to give (*E*)- and (*Z*)-dimethyl 2,3-bis[bromomethyl]-butenedioate (**9**) followed by debromination of **9** by use of our above described reductive elimination method. Diene **10** underwent the Diels-Alder reaction with *p*-benzoquinone to afford adduct **11** in 72% yield.



2,3-Bis[iodomethyl]-1,3-butadiene (3):

Sodium thiosulphate pentahydrate (25.7 g, 0.15 mol) and potassium iodide (38.5 g, 0.15 mol) are added to a partial solution of 2,3-bis[bromomethyl]-1,4-dibromo-2-butene[5] (**2**; 20.0 g, 0.05 mol) in acetone (200 ml) heated at 45°C. The mixture is vigorously stirred at this temperature for 1 h during which time the colour of the mixture changes from orange to dark red to pale yellow. The suspension is poured onto ice

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(300 g) and extracted with ether (1 x 200 ml, 2 x 100 ml). The combined ether extracts are washed with saturated sodium chloride solution (2 x 50 ml), dried with magnesium sulphate, and evaporated to give **3** as a pale yellow solid; yield: 15.5 g (93%); colourless needles; m.p. 95-96 °C (dec., from acetone/water). This material rapidly darkens on standing (analytical data were not obtained).

I.R. (Nujol): $\nu = 3100$; 1590; 900 cm^{-1}.

^{1}H-N.M.R. (CDCl$_3$/TMS): $\delta = 5.64$ (s, 1 H); 5.50 (s, 1 H); 4.16 ppm (s, 4 H).

This procedure can be scaled up to at least 80 g of the tetrabromide **2**, with similar results.

2,3-Bis[acetoxymethyl]-1,3-butadiene (4):

Silver acetate (15.6 g, 0.093 mol) is added to a solution of the crude diiodo compound **3** (15.5 g, 0.046 mol) in acetonitrile (200 ml) heated at 40 °C. The mixture is stirred in the dark at this temperature for 1 h, then poured onto ice (200 g), filtered, and extracted with ether (2 x 100 ml, 1 x 50 ml). The combined ether extracts are washed with 10% aqueous sodium thiosulphate (50 ml) and saturated aqueous sodium chloride (2 x 50 ml), dried with magnesium sulphate, and evaporated to give **4** as a yellow oil; yield: 8.5 g (92%). Evaporative distillation at 90-95 °C/0.2 torr gives colourless prisms (86%); m.p. 41-43 °C (Ref.[1], m.p. 42-43 °C).

This procedure can be scaled up to at least 50 g of **3**, with similar results.

6,7-Bis[acetoxymethyl]-*cis*-4a,5,8,8a-tetrahydronaphthalene-1,4-dione (6):

A solution of freshly sublimed (120 °C/25 torr) benzoquinone (2.18 g, 0.02 mol) and redistilled diacetate **4** (4.0 g, 0.02 mol) in benzene (25 ml) is heated at reflux under a nitrogen atmosphere in the dark for 18 h. The resulting light yellow solution is evaporated to give a dark yellow oil which is crystallized on trituration with cold (0 °C) ether. The product is filtered and washed with small portions of cold ether to yield **6** as an off-white solid (3.4 g). The combined washings and supernatant are evaporated to give a yellow brown oil which is crystallized from and washed with ether to provide an additional 0.8 g of **6**; total yield: 4.2 g (68%); off-white needles; m.p. 139-141 °C (from benzene/carbon tetrachloride).

$C_{16}H_{18}O_4$	calc.	C 62.74	H 5.92
(306.3)	found	62.52	5.88

M.S.: $m/e = 246$ (M^{+} $-$ CH$_3$COOH).

I.R. (Nujol): $\nu = 1735$; 1690; 1230 cm^{-1}.

^{1}H-N.M.R. (CDCl$_3$/TMS): $\delta = 6.75$ (s, 2 H); 4.75 (poorly resolved ABq, 4 H, $J \approx 12$ Hz); 3.25 (m, 2 H); 2.43 (m, 4 H); 2.10 ppm (s, 6 H).

6,7-Bis[hydroxymethyl]-*cis*-4a,5,8,8a-tetrahydronaphthalene-1,4-dione (7):

A solution of recrystallized diol[1,3] **5** (432 mg, 4.0 mmol) and freshly sublimed benzoquinone (456 mg, 4.0 mmol) in 1,2-dimethoxyethane (8 ml) is heated at reflux under a nitrogen atmosphere in the dark for 8 h. On slowly cooling to room temperature, the pale yellow solution deposits fine off-white needles which are isolated by suction filtration and washed with ether to give an analytically pure sample of **7** (516 mg), m.p. 116-118 °C. Evaporation of the filtrates gives a residue which is washed with ether to give an additional amount of **7**; total yield: 750 mg (84%).

$C_{12}H_{14}O_4$	calc.	C 64.85	H 6.35
(222.2)	found	64.51	6.20

M.S.: $m/e = 222$ (M^{+}).

I.R. (Nujol): $\nu = 3340$; 1680 cm^{-1}.

^{1}H-N.M.R. [CDCl$_3$/CD$_3$OD (2/1)/TMS]: $\delta = 6.67$ (s, 2 H); 4.23 (s, 2 H); 4.03 (poorly resolved ABq, 4 H, $J \approx 12$ Hz); 3.35 (m, 2 H); 2.43 ppm (m, 4 H).

(*E*)- and (*Z*)-Dimethyl 2,3-Bis[bromomethyl]-butenedioate (9):

A mixture of (*Z*)-dimethyl 2,3-dimethylbutenedioate[8] (**8**; 2.58 g, 15.0 mmol), *N*-bromosuccinimide (5.87 g, 33.0 mmol), and azobisisobutyronitrile (~3 mg) in carbon tetrachloride (50 ml) is heated at reflux under a 100 W light and a nitrogen atmosphere for 1.8 h. The hot suspension is filtered and evaporated to give **9** as a pale yellow oil; yield: 5.11 g (~100% yield of crude product). The crude bromoester obtained is of satisfactory purity for use in the next step.

I.R. (neat): $\nu = 1735$; 1640; 1270 cm^{-1}.

^{1}H-N.M.R. (CCl$_4$/TMS): $\delta = 4.40$ (s), 4.16 (s, 4 H); 3.83 (s), 3.75 ppm (s, 6 H).

A portion (350 mg) of the product was purified by flash chromatography[9] on silica gel with ethyl acetate/petroleum ether (b.p. 65-68 °C) (7/93) as eluent. Further purification of both isomers can be achieved by evaporative distillation at 100 °C/0.05 torr.

E-isomer (first to elute): liquid, 170 mg.

M.S.: $m/e = 332$, 330, 328 (M^{+}).

I.R. (neat): $\nu = 1740$; 1635; 1270 cm^{-1}.

^{1}H-N.M.R. (CCl$_4$/TMS): $\delta = 4.40$ (s, 4 H); 3.83 ppm (s, 6 H).

Z-isomer, liquid, 170 mg.

$C_8H_{10}Br_2O_4$	calc.	C 29.12	H 3.05
(330.0)	found	28.92	3.03

M.S.: $m/e = 332$, 330, 328 (M^{+}).

I.R. (neat): $\nu = 1735$; 1640; 1270 cm^{-1}.

^{1}H-N.M.R. (CCl$_4$): $\delta = 4.16$ (s, 4 H); 3.75 ppm (s, 6 H).

Dimethyl 1,3-Butadiene-2,3-dicarboxylate (10):

To a solution of the crude bromoesters **9** (4.80 g, 14.5 mmol) in acetone (50 ml) are added sodium thiosulphate pentahydrate (11.18 g, 45.1 mmol) and potassium iodide (7.49 g, 45.1 mmol). The mixture is stirred for 1 h at 45 °C, then poured onto ice (75 g), and extracted with ether (3 x 25 ml). The combined ether extracts are washed with saturated aqueous sodium chloride (10 ml), dried with magnesium sulphate, and evaporated. The residue is evaporatively distilled at 75-80 °C/0.5 torr to give **10** as a colourless liquid; yield: 2.1 g (85%). Spectral data for this compound are in agreement with those reported[4].

Dimethyl 1,4-Dioxo-*cis*-4a,5,8,8a-tetrahydronaphthalene-6,7-dicarboxylate (11):

A solution of freshly sublimed benzoquinone (2.48 g, 0.023 mol) and distilled diester **10** (3.91 g, 0.023 mol) in benzene (30 ml) is heated at reflux under a nitrogen atmosphere in the dark for 32 h. The solvent is evaporated and the residue is washed with cold (0 °C) ether to give **11** as an off-white solid; yield: 4.6 g (72%); off-white flakes; m.p. 133-135 °C (from dichloromethane/hexane).

$C_{14}H_{14}O_6$	calc.	C 60.43	H 5.07
(278.3)	found	59.86	5.21

M.S.: $m/e = 278$ (M^{+}).

I.R. (Nujol): $\nu = 1740$; 1730; 1690; 1650; 1600; 1260 cm^{-1}.

^{1}H-N.M.R. (CDCl$_3$/TMS): $\delta = 6.83$ (s, 2 H); 3.83 (s, 6 H); 3.38 (m, 2 H); 2.73 ppm (m, 4 H).

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