

# Alkoxymercuration of Conjugated Dienes. Regio- and Stereo-selective Synthesis of Unsaturated Diethers

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The alkoxymercuration of a series of conjugated dienes with different substitution patterns and mercury(II) salts is described. 1,2-Alkoxymercuration is found to be in equilibria with the corresponding 1,4-regioisomers which are easily solvolysed owing to the allylic character of the C–Hg bond. The use of mercury(II) oxide–tetrafluoroboric acid as the mercuriating agent allows the regio- and stereo-selective (or specific) synthesis of 1,4- and 1,2-diethers.

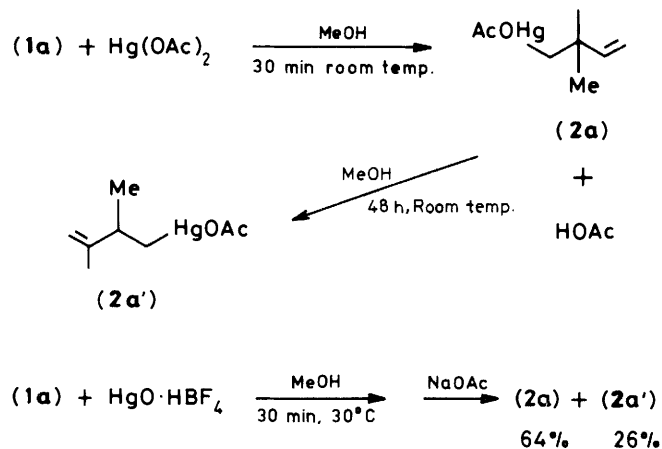
The literature on the oxymercuration of simple alkenes and nonconjugated dienes providing methods of synthetic utility goes back almost a century. However little is known concerning the oxymercuration of conjugated dienes. Most of this work is addressed to the simultaneous oxymercuration of both double bonds in the conjugated system leading to products of 1,2-diaddition.<sup>1,2</sup> Some reports have also appeared on the oxidation of 1,3-dienes under the conditions of the Denigès reaction<sup>3</sup> leading to the formation of mixtures of unsaturated ketones and/or aldehydes and 2,5-dihydrofuran derivatives. More recently Bloodworth<sup>4</sup> reported the oxymercuration of penta-1,3-diene with  $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$  thus providing the first direct evidence that oxymercuration of conjugated dienes can proceed by 1,4-addition. In a previous communication we have shown<sup>5</sup> that conjugated dienes react with aromatic amines and mercury(II) oxide–tetrafluoroboric acid to afford 1,4-cycloamination products. We now report a study of the mono-oxymercuration of a series of representative conjugated dienes with different mercury(II) salts which leads under particular reaction conditions, to the regio- and stereo-selective (or specific) synthesis of unsaturated 1,4- and 1,2-diethers in good yields *via* solvolysis of the corresponding 1,4- and 1,2-alkoxymercuration products.

## Results and Discussion

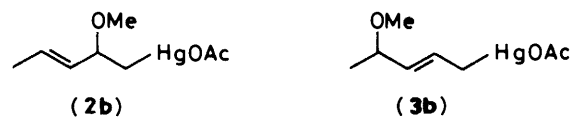
**Alkoxymercuration of Terminal 1,3-Dienes (see Table 1).**—Isoprene (**1a**) and *trans*-penta-1,3-diene (**1b**) were chosen as representative terminal dienes. The oxymercuration of these with different mercury(II) salts in a 1:1 molar ratio with alcohol (methanol or ethanol) as the solvent gives in all instances the corresponding monoaddition adducts. The structure of these adducts depends on the mercury(II) salt, the temperature and reaction time, and also on the substitution pattern of the diene.

The reaction of isoprene (**1a**) with mercury(II) acetate and methanol affords compound (**2a**) under kinetically controlled conditions<sup>6</sup> (30 min, room temp.). When the oxymercuration mixture was set aside for two days at room temperature complete transformation of the adduct (**2a**) into (**2a'**) was accomplished. This transformation takes place much faster when the mercuriation is performed with a strongly dissociated mercury(II) salt such as the tetrafluoroborate (Scheme 1).

If mercury(II) acetate in methanol is allowed to react with (**1b**) (1 min, room temp.) there is exclusive mercuriation of the terminal double bond to afford (**2b**; X = OAc). In contrast, mercury(II) nitrate yields (1 h of stirring followed by anionic exchange with sodium acetate) a 1:2 mixture of the 1,2- (**2b**) and the 1,4- (**3b**) adducts.<sup>4</sup> In our hands the composition of the reaction mixture was unchanged after a further 2 h at room temperature; the inference of this is that it corresponds to the equilibrium composition. The mercuriation of (**1b**) with  $\text{HgO} \cdot \text{HBF}_4$  in methanol at  $-30^\circ\text{C}$  gives after 30 min the adduct (**2b**).



Scheme 1.



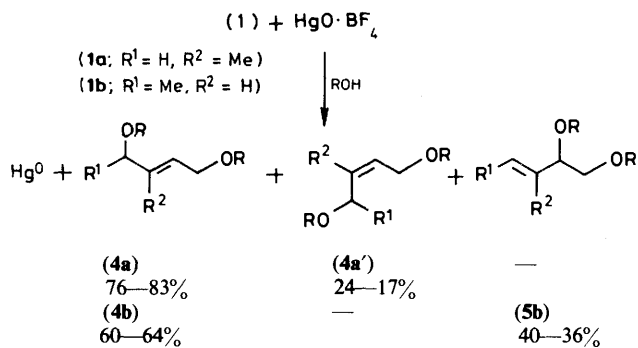
From the above results it is clear that conjugated terminal dienes undergo mercuriation under kinetically controlled conditions to afford 1,2-adducts. The relative reactivity of the two double bonds follows the same trend as that observed in the case of simple olefins or non-conjugated dienes.<sup>2,6</sup>

The alkoxymercuration of the dienes (**1a**) and (**1b**) with  $\text{HgO} \cdot \text{HBF}_4$  at room temperature or higher gives rise to the precipitation of elemental mercury. Consequently, intermediate

Table 1. Alkoxymercuration of conjugated dienes with mercury(II) acetate in MeOH

Conjugated diene	Temp. ( $^\circ\text{C}$ )	Reaction time	Product
( <b>1a</b> ) Isoprene	25	30 min	( <b>2a</b> )
( <b>1a</b> ) Isoprene	25	48 h	( <b>2a'</b> )
( <b>1b</b> ) <i>trans</i> -Penta-1,3-diene	25	1 min	( <b>2b</b> )
( <b>1c</b> ) Hexa-2,4-diene	25	5 min	( <b>2c</b> )
( <b>1d</b> ) Cyclohexa-1,3-diene	0	15 min	( <b>2d</b> )
( <b>1e</b> ) Cyclohepta-1,3-diene	— <sup>a</sup>	— <sup>a</sup>	— <sup>a</sup>
( <b>1f</b> ) Cyclo-octa-1,3-diene	— <sup>a</sup>	— <sup>a</sup>	— <sup>a</sup>
( <b>1g</b> ) $\alpha$ -Terpinene	-10	30 min	( <b>7</b> )

<sup>a</sup> A complex mixture of oxidation products was obtained even at low temperatures. <sup>b</sup>  $\alpha$ -Terpinene = *p*-mentha-1,3-diene.



Scheme 2.

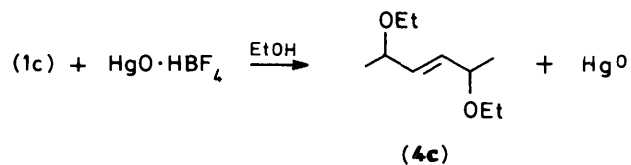
organomercurials could not be detected under these conditions. Spontaneous reduction of the mercury provides a new and convenient method for the synthesis of unsaturated diethers in good yield (Scheme 2). The oxidation of (1a) takes place in a regiospecific fashion and affords compounds (4a) and (4a'). Structural assignments were made on the basis of the upfield absorption of C-4 in (4a') relative to (4a) in the <sup>13</sup>C n.m.r. spectrum which is consistent with the observed trend for *Z-E* stereoisomers.<sup>7</sup> Conversely the oxidation of (1b) shows a low regioselectivity and furnishes a mixture of (4b) and (5b) determined by n.m.r. spectroscopy [for spectral data see the Supplementary publication, SUP No. 23837 (4 pp.)].\*

**Alkoxymercuration of Internal Conjugated Dienes.**—Internal conjugated dienes undergo oxymercuration with two equivalents of mercury(II) acetate to give stable dimercuriated compounds.<sup>2c</sup> In contrast, reaction with 1 equivalent of mercury(II) salt gives monoadducts the stability of which depends on the type of diene and salt employed. Compound (2c; X = OAc) is easily obtained from hexa-2,4-diene (1c) and

The stability of the cyclic 1,2-oxymercurials (2d–f) depends largely on the ring size. Thus, (2d; X = OAc) is readily obtained upon mercuriation of cyclohexa-1,3-diene (1d) with mercury(II) acetate at 0 °C and remains unchanged after 24 h at 0 °C; at room temperature however it starts to decompose after 4 h. In contrast, cyclohepta-1,3-diene (1e) and cyclo-octa-1,3-diene (1f) in alcohol furnish no simple monoadducts when treated with mercury(II) acetate at room temperature; at lower temperatures there is negligible mercuriation.

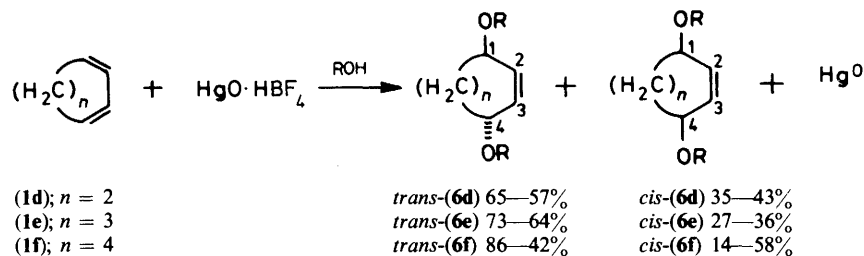
The alkoxymercuration of cyclic and linear disubstituted internal conjugated dienes with HgO–HBF<sub>4</sub> leads in all instances exclusively to the equimolecular mixture of the diastereoisomeric unsaturated 1,4-diethers but the intermediate alkoxymercurial cannot be trapped under our usual experimental conditions.

*cis,trans*-Hexa-2,4-diene (1c) affords in a regio- and stereo-specific process the diethers (4c) with yields up to 75%. The structure of the products was determined in each case on the basis of absorption at ca. 965 cm<sup>-1</sup> characteristic of a *trans*-double bond, and the lack of any peak at 1600 cm<sup>-1</sup> as corresponding to a symmetrical olefin.<sup>8</sup> The presence of regio- and/or *Z-E* stereoisomers could not be detected by <sup>13</sup>C n.m.r. spectroscopy from the crude reaction mixture (Scheme 3).



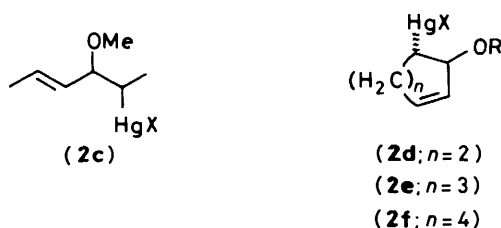
Scheme 3.

Cyclic unsubstituted dienes react very fast with HgO–HBF<sub>4</sub> with precipitation of elemental mercury even at low temperature to afford, in a regiospecific process, the 1,4-



Scheme 4.

mercury(II) acetate in methanol solution at room temperature in less than 5 min and remains unchanged after being stirred for 24 h. Compound (2c; X = OAc) also decomposes when heated in methanol under reflux.



dialkoxycycloalk-2-enes *trans*-(6) and *cis*-(6). The stereoselectivity of the reaction changes with the ring size, reaction temperature, and substitution pattern in the alcohol. The highest degree of stereoselectivity is achieved in the oxidation of (1f), increasing with the ring size and lower temperatures. The structure of the alcohol only modifies the stereoselectivity of the process in runs carried out at 80 °C (Scheme 4, Table 2).

Stereoisomeric ratios were determined from the crude reaction mixtures by <sup>1</sup>H and <sup>13</sup>C n.m.r. spectrometry. Different cyclic 1,4-disubstituted alkenes were used as model compounds for comparison with our spectral data to accomplish the stereochemical analysis of compound (6). Our attention was focused on the 1-H, 4-H multiplet which appears separated by up to 0.2 p.p.m. in the mixture of *cis*-(6) and *trans*-(6) isomers. The more shielded protons are assigned to the *cis*-(6) isomer since this trend is observed<sup>9–11</sup> for a series of cycloalk-2-

\* For details of the Supplementary publications scheme, see Instructions for Authors (1984), *J. Chem. Soc., Perkin Trans. I*, 1984, Issue 1.

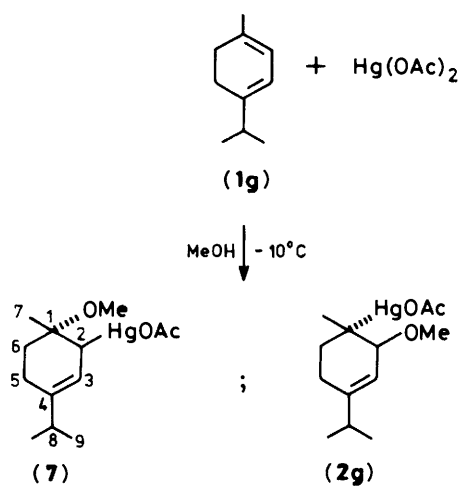
Table 2. Synthesis of unsaturated diethers

Diene	X in HgX <sub>2</sub>	R in ROH	Temp. (°C)	Reaction time (h)	Products <sup>a*</sup>	Ratio	Yield (%) <sup>b</sup>
(1a)	BF <sub>4</sub>	Et	-40	72	(4a)/(4a')	83/17	32
(1a)	BF <sub>4</sub>	Et	80	4	(4a)/(4a')	76/24	24
(1b)	BF <sub>4</sub>	Me	-20	72	(4b)/(5b)	61/39	67
(1b)	BF <sub>4</sub>	Me	80	6	(4b)/(5b)	64/36	54
(1c)	BF <sub>4</sub>	Et	-20	12	(4c)	—	74
(1c)	BF <sub>4</sub>	Et	80	3	(4c)	—	62
(1d)	BF <sub>4</sub>	Et	-20	24	<i>trans</i> -(6d)/ <i>cis</i> -(6d)	57/43	61
(1d)	BF <sub>4</sub>	Et	80	4	<i>trans</i> -(6d)/ <i>cis</i> -(6d)	62/38	82
(1e)	BF <sub>4</sub>	Et	-20	24	<i>trans</i> -(6e)/ <i>cis</i> -(6e)	70/30	57
(1e)	BF <sub>4</sub>	Et	80	4	<i>trans</i> -(6e)/ <i>cis</i> -(6e)	62/38	77
(1f)	BF <sub>4</sub>	Me (A)	80	4	<i>trans</i> -(6fA)/ <i>cis</i> -(6fA)	50/50	92
(1f)	BF <sub>4</sub>	Et (B)	80	4	<i>trans</i> -(6fB)/ <i>cis</i> -(6fB)	70/30	82
(1f)	BF <sub>4</sub>	Pr <sup>i</sup> (C)	80	4	<i>trans</i> -(6fC)/ <i>cis</i> -(6fC)	42/58	71
(1f)	BF <sub>4</sub>	Me	0	4	<i>trans</i> -(6fA)/ <i>cis</i> -(6fA)	85/15	42
(1f)	BF <sub>4</sub>	Et	0	24	<i>trans</i> -(6fB)/ <i>cis</i> -(6fB)	86/14	49
(1f)	BF <sub>4</sub>	Pr <sup>i</sup>	0	24	<i>trans</i> -(6fC)/ <i>cis</i> -(6fC)	86/14	31
(1f)	BF <sub>4</sub>	Bu <sup>i</sup> (D)	0	24	<i>trans</i> -(6fD)/ <i>cis</i> -(6fD)	85/15	35
(1f)	BF <sub>4</sub>	Et	-30	24	<i>trans</i> -(6fB)/ <i>cis</i> -(6fB)	85/15	61
(1f)	BF <sub>4</sub>	Et	-70	12	<i>trans</i> -(6fB)/ <i>cis</i> -(6fB)	85/15	77
(1g)	BF <sub>4</sub>	Me	-40	24	<i>trans</i> -(5g)/ <i>cis</i> -(5g)	50/50	94
(1g)	OAc	Me	25	24	(4g) <sup>c</sup> / <i>trans</i> -(5g)	88/12	45

<sup>a</sup> All new compounds gave satisfactory microanalysis within  $\pm 0.3\%$  of the theoretical values. <sup>b</sup> Based on starting Hg<sup>II</sup> salt. <sup>c</sup> 75/25 Mixture of two diastereoisomers: assignment not made. In the compound key-numbers, A, B, C, and D refer to the R in the alcohol (ROH) from which they are formed.

ene-1, 4-diols and diacetates. \* <sup>1</sup>H N.m.r. spectral data for *cis*-(6) and *trans*-(6) have been recently reported.<sup>13</sup>

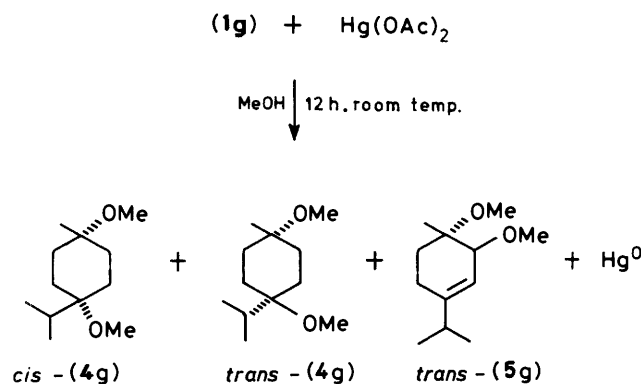
An unusual orientation has been found in the alkoxymercuriation of  $\alpha$ -terpinene (1g) since upon treatment with mercury(II) acetate in methanol solution it affords in a regio- and stereo-specific process the allylic methoxymercuro (7) instead of the expected product (2g). The structure of (7) was unambiguously established by off-resonance <sup>13</sup>C n.m.r. spectroscopy which shows C-1 as a singlet and C-2 as a doublet. The mercuriation takes place at the less hindered double bond. This can be ascertained also by <sup>13</sup>C n.m.r. spectroscopy since the C-5 and C-8 signals remain almost unaffected upon transformation of (1g) into (7) whereas that for C-6 suffers a substantial downfield displacement of *ca.* 5.6 p.p.m. which is consistent<sup>14</sup> with the proposed structure (Scheme 5).



Scheme 5.

\* The <sup>1</sup>H n.m.r. spectra of *cis*- and *trans*-cyclo-oct-2-ene-1,4-diol have been reported by Barrelle and Appar<sup>10</sup> but their stereochemical assignments appear to be erroneous since they attribute the structure *trans*- to the isomer with m.p. 154°C. This m.p. corresponds to the *cis*-isomer, unequivocally synthesized by Horinaka *et al.*<sup>12</sup> by photo-sensitized oxygenation of cyclo-octa-1,3-diene.

When the mercuriation is performed at room temperature and the reaction mixture is set aside for 12 h, compound (7) decomposed to give elemental mercury and a mixture of the diastereoisomeric 1,4-diethers *cis*-(4g) and *trans*-(4g) contaminated only by 12% of one of the 1,2-regioisomers (5g) (Scheme 6).



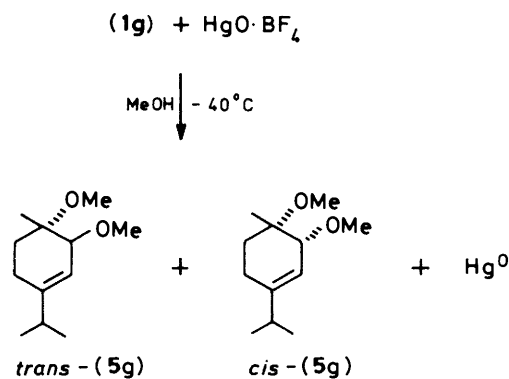
Scheme 6.

Since the nucleophilic displacement of mercury in covalent mercury(II) derivatives, such as acetoxy compounds, appears to involve neighbouring group participation by the  $\beta$ -substituent,<sup>15</sup> we assign tentatively *trans*-stereochemistry to the single 1,2-regioisomer obtained.

The mercuriation of (1g) with HgO-HBF<sub>4</sub> proceeds even at -40°C with precipitation of elemental mercury and regio-specific formation of an equimolecular mixture of diastereoisomeric 1,2-diethers (5g) (Scheme 7).

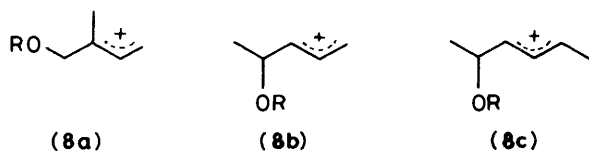
This suggests that the allylic mercury(II) tetrafluoroborate derivative due to the ionic character of the Hg-BF<sub>4</sub> bond undergoes demercuriation to afford the corresponding free allyl cation which is quenched at this low temperature by the solvent at the least hindered side of the unsaturated system.

A number of generalizations can be drawn from the behaviour of 1,3-dienes towards mercury(II) salts in alcoholic solution. Thus reactions with mercury(II) acetate give stable 1,2-adducts, the site of reaction being predictable by the rules operating for simple alkenes.<sup>2</sup> With more ionic salts, such as



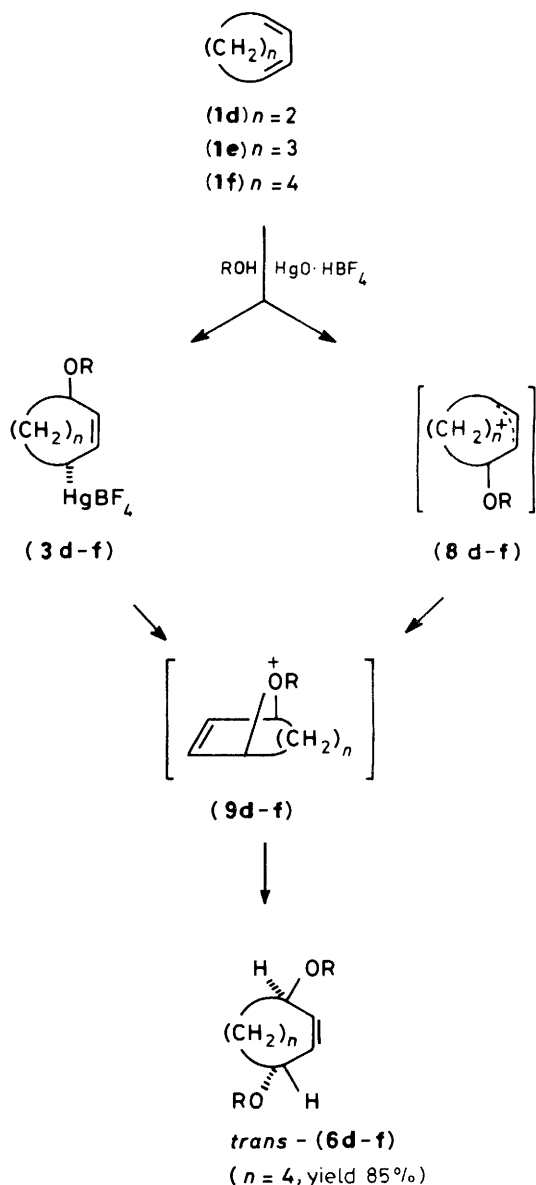
Scheme 7.

tetrafluoroborate or nitrate, the 1,2-adducts are transformed into the 1,4-adducts, only that from *trans*-piperylene (1b) being characterizable at room temperature. Otherwise these adducts undergo fast decomposition to the corresponding 1,4-diethers. Their formation can be envisaged as proceeding by solvolytic cleavage of the allylic C–Hg bond in the 1,4-adducts, probably *via* formation of the corresponding allyl cation.<sup>16</sup> It is noteworthy that oxymethyls derived from simple olefins not having an activated C–Hg bond do not decompose at room temperature after 24 h even in the form of tetrafluoroborate salts.<sup>17</sup> The intermediacy of allyl cations is strongly supported by the *trans*-structure of the resulting 1,4-diethers when derived from linear dienes and also by the relative order of stability shown by the different 1,4-adducts. Thus, the adduct (3b), the solvolysis of which proceeds *via* the monosubstituted allyl cation (8b), is stable at room temperature for several hours as a



nitrate salt or for 1 h as a tetrafluorobate. In contrast, the adducts (3a) and (3c) undergo solvolysis *via* the disubstituted allyl cations (8a) and (8c) respectively and cannot be isolated at room temperature. Thus, the order of stability for the 1,4-adducts appears to be the inverse of that for the corresponding allyl cations.<sup>18</sup> This interpretation also explains well the great reactivity and product distribution found for cyclic dienes. The *Z*-configuration of the olefin in the 1,4-adduct allows the participation of the oxygen lone pair in the displacement of the mercury especially for the cyclo-octa-1,3-diene (1f). For this reason the oxymethyls (3f) are very unstable and when the oxidation of (1f) is carried out at temperatures as low as -60 °C with HgO–HBF<sub>4</sub> the corresponding 1,4-diethers are produced with high stereoselectivity probably *via* the oxonium-type intermediate (9f) to afford the *trans*-isomer (6f) (Scheme 8). In contrast when the ring size is decreased (*n* = 2,3) the possibility of anchimerically assisted displacement of mercury by the oxygen is less important for geometrical reasons, and hence the oxymethyls become more stable and the stereoselectivity in diether formation decreases. For *n* = 2 compounds *trans*-(6d) and *cis*-(6d) should derive mainly from the free allyl cation and a nearly equimolar mixture of both stereoisomers result.

When reactions are carried at 80 °C the stereoselectivity in the oxidation of (1f) is lessened probably because at this temperature the demercuration of (3f) does not require anchimerical assistance and thus takes place *via* the allylic intermediate (8f) instead of (9f).



Scheme 8.

### Conclusions

The monoalkoxymercuration of conjugated dienes proceeds in two steps, the first being the formation of 1,2-adducts in which, with the exception of the mercuration of  $\alpha$ -terpinene, the alkoxy group occupies the allylic position. The 1,2-adducts are stable compounds when derived from mercury(II) acetate but give rise to the formation of 1,4-adducts by the action of strong acids such as nitric or tetrafluoroboric. The 1,4-adducts have an allylic C–HgX bond and this is relatively stable only when the Hg–X bond is little dissociated (e.g. X = OAc) and C is a primary carbon.<sup>19</sup> The reaction of conjugated dienes with HgO–HBF<sub>4</sub> in alcohol as the solvent brings about a new, simple, and convenient method for the 1,4-dialkoxylation of these compounds with good yields.\* The reaction is regio-specific with the exception of that for the *trans*-penta-1,5-diene (1b) in which only regioselectivity is attained. With respect to

\* For other recent approaches to the 1,4-difunctionalization of conjugated dienes useful to introduce OAc, OH, and Cl groups see ref. 13 and previous reports by Bäckvall *et al.* cited therein.

the stereochemistry of the products, most reactions give rise to a reasonably high degree of stereoselectivity, always affording the *trans*-isomer as the major product. For these reasons our method should provide a valuable complement to the oxidation of dienes with singlet oxygen.<sup>20</sup>

### Experimental

<sup>1</sup>H and <sup>13</sup>C N.m.r. spectra were recorded in a Varian FT-80A n.m.r. spectrometer. Double resonance experiments were performed with a Varian EM390 spectrometer. Chemical-shift values are in p.p.m. relative to internal SiMe<sub>4</sub>. I.r. spectra were recorded in a Pye Unicam SP 1025 i.r. spectrophotometer. All reagents were used as supplied without further purification. Mercury(II) oxide-tetrafluoroboric acid was prepared as previously reported.<sup>21</sup>

*Reaction of Conjugated Dienes with Mercury(II) Acetate and Methanol (Table 1): Typical Experimental Procedure.*—Mixtures of conjugated diene (10 mmol) and mercury(II) acetate (3.2 g, 10 mmol) in methanol (30 ml) were stirred for the reaction times and at the temperatures recorded in Table 1. The excess of alcohol was evaporated at room temperature under reduced pressure and the oily residue analysed by <sup>1</sup>H and <sup>13</sup>C n.m.r. spectroscopy. Products were identified in all instances as the corresponding 1,2-adducts. For spectral data see the Supplementary Publication—details on p. 630.

*Reaction of trans-Penta-1,3-diene (1b) with Mercury(II) Nitrate and Methanol.*—Mercury(II) nitrate monohydrate (3.2 g, 10 mmol) was added to (1b) (1.4 g, 20 mmol) in methanol (30 ml) and the mixture was shaken at room temperature. After 10 min the clear solution gave a negative test (NaOH) for Hg<sup>II</sup> and potassium acetate (4.0 g) was added. The solvent was evaporated under reduced pressure, THF added, and the white solid residue filtered off. The THF solution was evaporated and the n.m.r. spectra of the resulting oil recorded. The product was identified as a mixture of (2b) and (3b) in a 0.33/0.67 molar ratio.

*Reaction of (1b) with Mercury(II) Nitrate and Methanol.*—Mercury(II) nitrate monohydrate (3.2 g, 10 mmol) was added to (1b) (1.4 g, 20 mmol) in methanol (30 ml) and the mixture stirred at room temperature for 3 h. The work-up procedure was analogous to that described above and the n.m.r. spectra of the oily residue showed this to be a mixture of (2b) and (3b) in a 0.27/0.73 molar ratio.

*Reaction of (1b) with Mercury(II) Tetrafluoroborate and Methanol.*—Mercury(II) tetrafluoroborate (1.9 g, 5 mmol) was added to (1b) (0.7 g, 10 mmol) in methanol (15 ml) and the mixture was stirred at -30 °C for 30 min. The reaction was worked up in the manner described above, and the n.m.r. spectra of the oily residue showed this to be (2b).

*Reaction of Conjugated Dienes with Mercury(II) Oxide-Tetrafluoroboric Acid and Alcohols: Solvolysis of the Alkoxymercurials (Table 2): Typical Experimental Procedure.*—Mercury(II) tetrafluoroborate (1.9 g, 5 mmol) was added to the conjugated dienes (10 mmol) in alcohol (15 ml) and the mixtures

stirred for the reaction times and at the temperatures recorded in Table 2. Mercury(0) was precipitated quantitatively and filtered off. The solution was extracted with ether, and the extract dried (Na<sub>2</sub>SO<sub>4</sub>) and evaporated. The n.m.r. spectra of the residue showed this to be the corresponding 1,4- and/or 1,2-diethers as summarized in Table 2. The products were purified by the usual methods, i.e. distillation and/or column chromatography (silica; ether).

*Reaction of  $\alpha$ -Terpinene with Mercury(II) Acetate and Methanol: Solvolysis of the Methoxymercurial (Table 2).*—A solution of (1g) (0.7 g, 10 mmol) and mercury(II) acetate (1.6 g, 5 mmol) in methanol (15 ml) was allowed to stand at room temperature for 12 h. Mercury(0) precipitated quantitatively and was filtered off. The solution was worked up as above and a liquid residue (0.45 g, 45%) obtained. The product was identified as a mixture of (4g) and *trans*-(5g) in a 0.88/0.12 molar ratio. The diastereoisomers (4g) appeared as a 3:1 mixture but structural assignments proved impossible.

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