Tetrahedron Vol. 49, No. 39, pp. 8837-8854, 1993
Printed in Great Britain

0040-4020/93 $6.00+.00

1,1,3,3-Tetramethyl-2-methyleneindan Derivatives: Syntheses with Imminent Rearrangement[1]

Rudolf Knorr*, Johannes Freudenreich, Therese von Roman, Johann Mehlstäubl and Petra Böhrer

Institut für Organische Chemie der Universität München, Karlstraße 23, D-80333 München, Germany

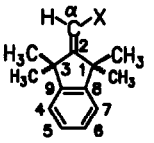
(*Received in Germany* 15 *April* 1993; *accepted* 5 *August* 1993)

Key Words: Alkenes, bromohydrins, enol esters, epoxides, rearrangement

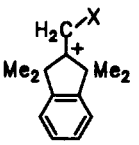
Abstract: The syntheses of 2,2,3,3-tetramethyl-1-indanylidene and of 1,1,3,3-tetramethyl-2-indanylidene derivatives from 1,1,3,3-tetramethyl-2-indanone are reported. Access to the second series is restricted by the ease of methyl migration under carbenium-like conditions, such as electrophilic bromination. The rearrangement products are described and also the methods avoiding their formation. Nucleophilic bromination of the oxirane **19** allows to efficiently prepare the sterically shielded bromoalkene **21** (Section B) or the enol acetate **34** (Section C) and other key compounds for further transformations.

Introduction

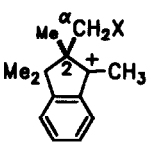
Several properties of 1,1,3,3-tetramethyl-2-methyleneindan derivatives like **1** suggest that this family of compounds might deserve a more frequent application in structural, spectroscopic, mechanistic and computational studies. The 1,1,3,3-tetramethyl-2-indanylidene moiety is rigid, as shown by the crystal structure analyses of three examples[2-4] which differ strongly at the α end of the C-2,C-α double bond. Its geometrical features are therefore transferable and may thus facilitate the quantitative interpretation of data which would otherwise be blurred by conformational ambiguity, for examples substituent-induced chemical shifts[5,6], force-field calculations, or rate constants depending on strain effects[7]. It causes front strain along the C=C bond to a moderate degree so that this double bond and its four ligands remain almost coplanar[2,3]. Transferred to imines (i. e., **1** with N in place of HC-α), this moiety induces energetically well defined accelerations of *syn/anti* stereomutation[8] and excludes nucleophilic attack at the carbon end of the C=N bond[8]. A corresponding steric protection of C-2 in **1** is expected to prevent Michael-type additions of organometallic reagents during the prospective preparations of organolithium derivatives.



1



2

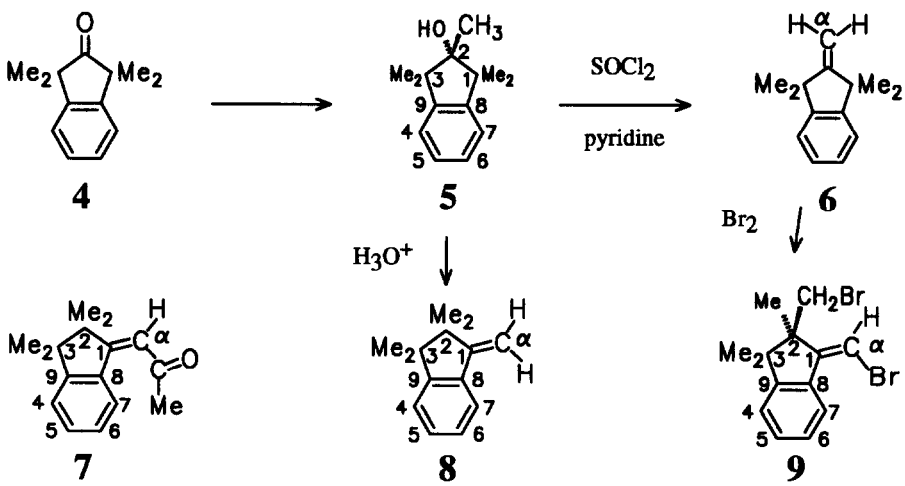


3

However, such beneficial properties are to be paid for by a pronounced inclination to rearrangement during the syntheses of **1**. Although the exocyclic C-α position is still nucleophilic, the usual alkene chemistry with electrophilic reagents becomes very difficult or inapplicable because any opportunity to generate the tertiary carbenium ion **2** implies a possibility for methyl migration[9] to give the tertiary benzyl cation **3**. Formation of **2** is foreseeable by protonation of **1** or by electrophilic addition of X^+ to the terminal olefin (when X = H in **1**). The final stabilization of **3** may occur by deprotonation or by C-2,C-α fission assisted by a donor substituent X (e. g., OH); some of these rearrangements are described here, together with the measures taken to circumvent such preparative obstacles.

A. 1,1,3,3-Tetramethyl-2-methyleneindan (6) and its Rearrangements

The preparation of the alcohol **5** from ketone **4**[10,11] with methyllithium furnished a practically uncontaminated crude product and was thus more expeditive than the addition of methylmagnesium iodide which required boiling xylene as a solvent[12] with subsequent purification. The olefin **6** was best prepared (76%) by dehydration of **5**, whereas the Wittig reaction would be prone to failure[13]; however, we did not try the high-temperature variant[14], and the activated Wittig reagent[15] converted ketone **4** to **6** albeit incompletely.

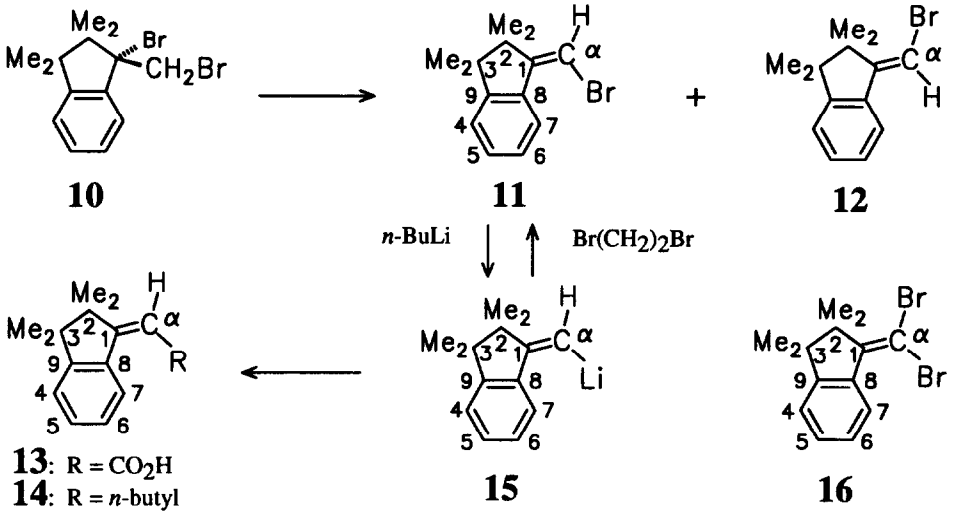


4 **5** **6** **7** **8** **9**

If cooled concd. hydrochloric acid was used in the workup for the alcohol **5**, the equilibrium mixture (14:86) of the olefins **6** and **8** was obtained instead, even though a force-field[16] calculation indicated that **6** might be more stable than **8**. The same product ratio resulted from treatment of the olefin **6** with concd. hydrobromic acid in acetic anhydride, but prolonged interaction furnished the acetylation product **7** as an (*E*)/(*Z*) mixture.

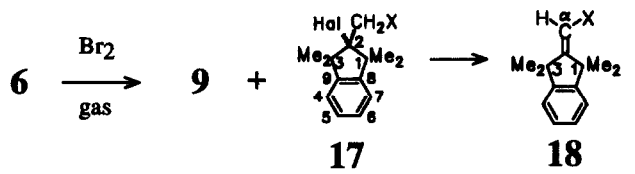
Since **8** is the parent compound of the derivatives **11-16**, its NMR spectra were unequivocally assigned by two-dimensional correlation experiments[17] as follows. In the NOESY ($^1H,^1H$) spectrum the more upfield olefinic absorption showed a correlation with the upfield methyl signal, thus identifying 2-CH_3 and the olefinic proton *cis* to it. The downfield olefinic hydrogen signal was correlated with those of its geminal partner and with 7-H only, the latter with 6-H and this one with 5-H. The 4-H signal was most clearly identified by its relationship to the downfield 3-CH_3 absorption. The resonances of the ^{13}C atoms bonded to these protons were found by HETCOR ($^1H/^{13}C$ with a "window" of 140 Hz). A final COLOCS experiment ($^{13}C/^1H$ with a "window" of 7 Hz) served for confirmations and showed the additional $^3J_{CH}$ relationships C-8/α-H (*trans*), C-9/3-CH_3, C-1/2-CH_3, and C-2/α-H (*trans*).

A corresponding but complete rearrangement was observed on addition of bromine in CCl_4 solution to **6** which afforded the dibromide **9** and a trace of the bromoalkene **11**. The latter was formed via the rearranged olefin **8**, as shown by the treatment of **8** with bromine in CCl_4. The intermediate adduct **10** is very unstable and was found as the transient main product only in situ. Thermolysis of **10** generated **11** and its (*E*) isomer **12** in a 9:1 ratio, whereas a 2:1 mixture resulted from **10** on short contact with potassium *tert*-butoxide. Despite the increased steric repulsion indicated by a downfield ^1H-NMR shift for 7-H, the π system of **11** appeared to remain close to planar as judged from the UV spectrum. The α,α-dibromoalkene **16** formed as a side-product in all brominations was identified by its unusual ^{13}C-α NMR upfield shift and by MS; purer samples of **16** were not obtained by enforced bromination of **11/12**.



Predictable ^{13}C-NMR resonance positions from substituent-induced chemical shifts (SCS)[5] supported the (*Z*) configuration of **11** and could have been confirmed by NOE experiments. However, we preferred chemical evidence with an intention to learn about the vinyllithium derivative **15**. The Br/Li exchange reaction of **11/12** (9:1) with *n*-butyllithium to give **15** and 1-bromobutane was very fast in THF despite (or perhaps due to) the short distance of bromine from 7-H; but these two products coupled rather soon to form **14**. The chemical constitution of **15** (*E*-isomer not detected by NMR) was ascertained by hydrolysis to **8**, and its unchanged configuration by quenching with 1,2-dibromoethane or with bromine which regenerated **11** and **12** in the 9:1 ratio. Therefore, the lithium compound **15** is configurationally stable in THF, save for an improbable coincidence of 9:1 being its equilibrium ratio. The final (*Z*) assignment for **11** and **15** was based on the carboxylation product **13** because no isomeric acid could be found.

The (*Z*) configuration of **13** was proven by the following two-dimensional NMR experiments[17]. NOESY ($^1H,^1H$) correlated α-H → 2-CH_3, 3-CH_3 → 4-H, and 7-H → 6-H → 5-H. With this knowledge, all hydrogen-bearing ^{13}C atoms could be differentiated by HETCOR ($^1H/^{13}C$, "window" 140 Hz), except for C-4 and C-6. The $^3J_{CH}$ relations of the remaining absorptions were established by COLOCS ($^{13}C/^1H$ with "window" 7 Hz) as C-1/2-CH_3, C-2/α-H, C-5/7-H, C-7/5-H, C-8/α-H, C-9/3-CH_3, C-9/5-H, and C-9/7-H, leaving only C-3 and CO_2H. The $^1J_{CH}$ coupling constant of C-7 was found to be increased by ca. 8 Hz over that of the olefin **8**, presumably due to compression of CH-7 by the carboxy function.



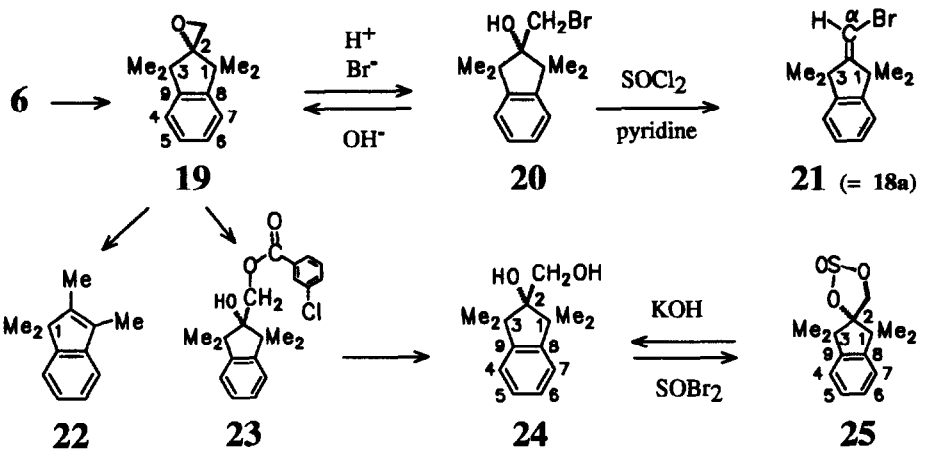
17, 18	Hal	X
a	Br	Br
b	Br, Cl	Cl

It was possible to reduce the described rearrangement by an alternative radical-based bromination of **6** with illumination and high dilution, using gaseous bromine. Inspired by the reported smooth bromination of 1,1-di*tert*-butylethylene[18], we used a similar experimental setup to obtain the unrearranged dibromide **17a** from **6**. The fewest contaminations by the rearranged dibromide **9** were observed when a stream of argon gas containing bromine was swept either onto[18] or into dilute (ca. 1%) solutions of **6**. However, the use of such large volumes of solvent was inconvenient and led to annoying solvent bromination in case of the recommended[18] petroleum ether, with the consequence that purification of **17a** became almost hopeless. Changing to CCl_4 as a solvent, we expected that some chlorine might be introduced at the 2-position of **6** but only bromine at the α-position; this would be unimportant for reasons of the planned elimination to give **18a**. On the contrary, however, chlorine became attached at C-α, leading to **17a** with ca. 28% of **17b**. Thus, although the subsequent production of the bromoalkene **18a** by elimination of HBr with potassium *tert*-butoxide was straightforward, it afforded samples contaminated with the chloroalkene **18b** when the unpurified material from photobromination in CCl_4 was used.

To sum up, the preparation of the unrearranged, pure bromoalkene **18a** by photobromination of **6** is tedious and requires separation from **9** or **17b** or solvent-derived byproducts. Rather than to strive for improvements with other solvents, we have developed the following expeditive syntheses which allow the clean production of **18a** in larger batches.

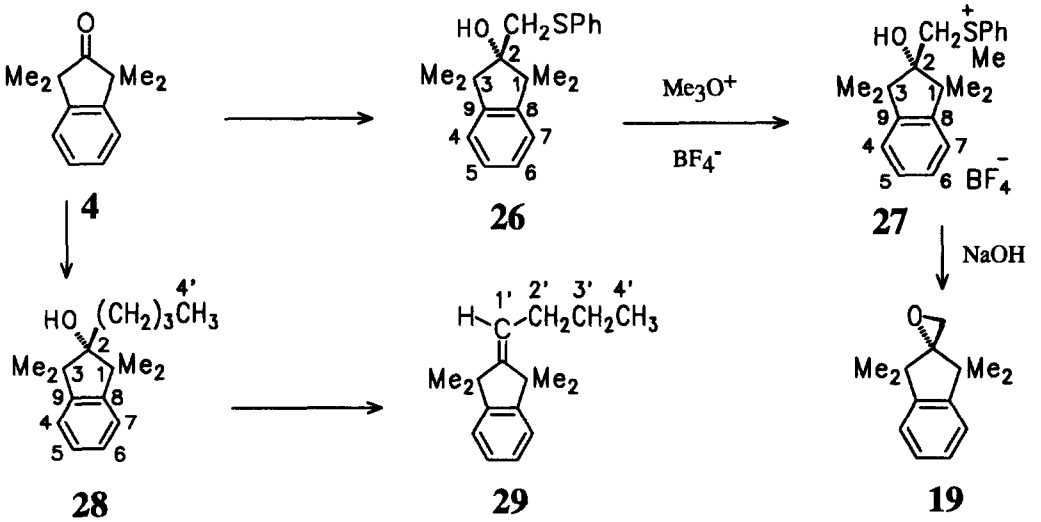
B. The Oxirane Route to 2-Bromomethylene-1,1,3,3-tetramethylindan (21 or 18a)

The results of Section A have demonstrated that electrophilic or radical brominations of 1,1,3,3-tetramethyl-2-methyleneindan (**6**) occur with total or partial rearrangement or other side-reactions. Therefore, a nucleophilic bromination was considered and found to be quite productive. The oxirane **19** was easily generated from **6** by epoxidation with 3-chloroperbenzoic acid in the presence of $NaHCO_3$[19,20]; but it was no less prone to methyl migration by electrophilic reagents like $MgBr_2$ in ether or concd. HBr which formed **22** with loss of (presumably) CH_2O (compare **3** in the introduction). The known[9,21-23] hydrocarbon **22** may also arise with $TiCl_4$ from **4** or its diazo derivative[6]. Nevertheless, trifluoroacetic acid opened the epoxide ring of **19** very cleanly in a warmed chloroform solution saturated with tetraethylammonium bromide; to obtain **20** as the only product, it was essential to avoid basic workup conditions because 2 N NaOH regenerated **19** from **20** within minutes even in a two-phase system (NMR test). The dehydration of **20** furnished only **21** (a key substance to sterically shielded vinylmetallics).



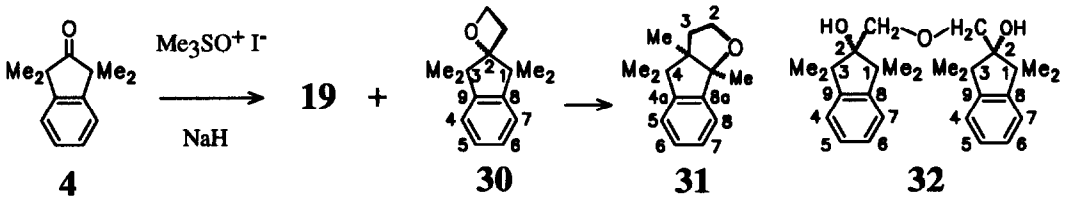
The ester **23** was formed as a byproduct of the oxirane **19** in a more concentrated solution. Saponification of **23** to the diol **24** was performed with the aim of a subsequent bromination by thionyl bromide which, however, produced only the cyclic sulfite **25**. This chiral compound showed diastereotopic CH_2 protons and was hydrolyzed with a base back to **24** for constitutional confirmation.

The oxirane **19** may also be obtained from ketone **4** via the thioether **26** and its sulfonium salt **27** in analogy with a reported[24] procedure. This short route (2-3 steps) involves thioanisole as a malodorous reagent and byproduct which was removed by distillation from the samples of **26** or **19**. For preparation of **26**, a stoichiometric amount of *n*-butyllithium deprotonated solely the methyl group of thioanisole in THF within 15 min at



room temperature as verified by ^1H NMR and deuteration; but THF was also deprotonated in competition (with or without an amine catalyst[25]), leaving some unreacted thioanisole. On the other hand, any excess of *n*-butyllithium would add to the ketone **4**; we prepared the unknown adduct **28** independently and transformed it to the olefin **29** for comparison.

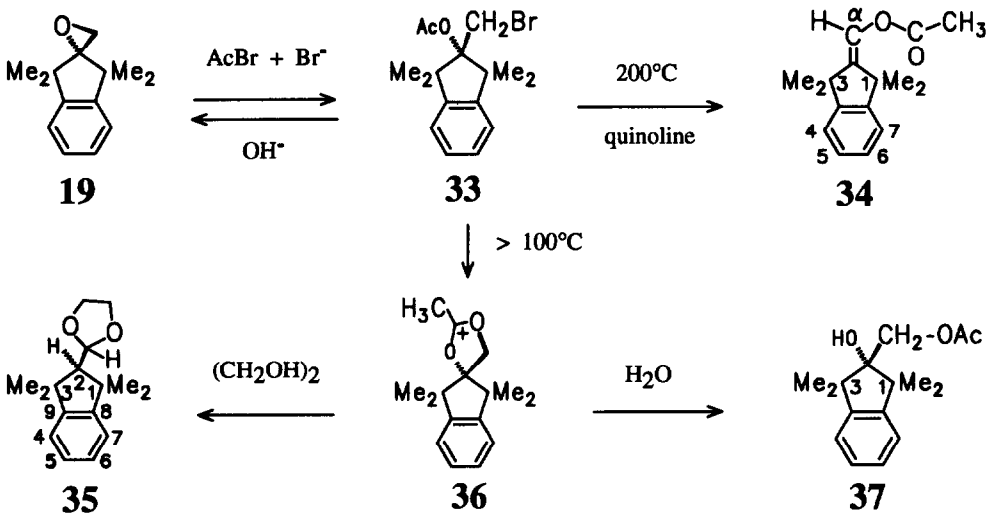
The spectral characterization of the easily purified, chiral sulfonium salt **27** requires a careful choice of conditions because some of its ^{1}H-NMR chemical shifts show an unusual solvent dependence but a practically invariable geminal coupling constant ^2J of the diastereotopic CH_2 protons. Elimination[24] of thioanisole from **27** furnished the oxirane **19** smoothly.



The most obvious and shortest route to **19** proved unrewarding: The addition of ketone **4** to dimethylsulfoxonium methylide[26,27] required sufficiently long reaction periods at elevated temperature so that the product **19** was further methylenated partially or mainly to the oxetane **30**. The side-product **32** was probably formed from **19** by adventitious moisture under such harsh conditions. Imminent methyl migration showed up during chromatography when **30** was rearranged to **31**.

C. Enol Derivatives via the Oxirane 19

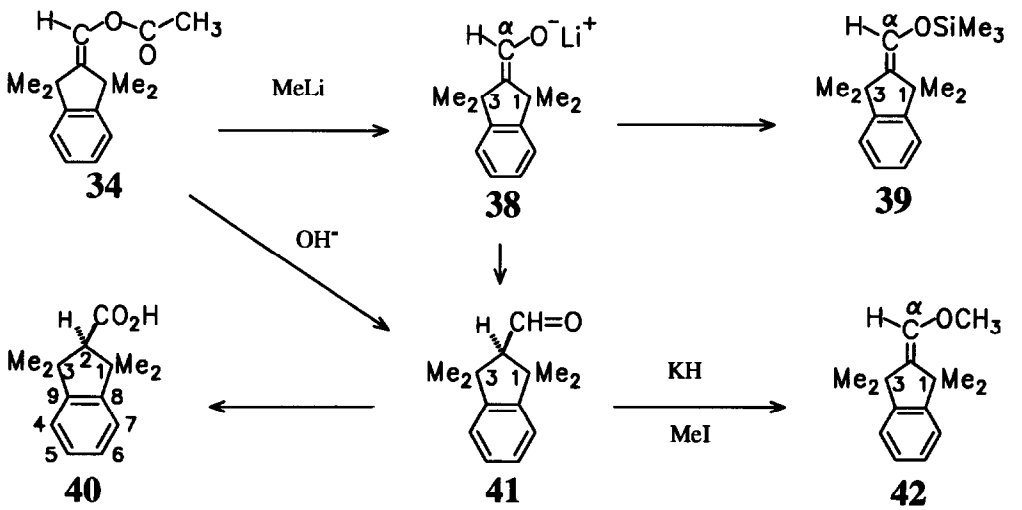
Enol acetates are accessible in one step by treatment of oxiranes with $Et_2O{\cdot}BF_3$. However, the oxirane **19** gave the tetramethylindene **22** under such conditions[27,28] as well as with 4-dimethylaminopyridine[29] in Ac_2O/HOAc. Ring opening of **19** with acetyl bromide was rather slow and at higher temperatures accompanied by decomposition to **22**, unless the nucleophilic bromination was accelerated by 1 equiv. of tetraethylammonium bromide. The resulting tertiary ester **33** crystallized very readily; the alternative constitution as an acetate of the isomeric primary alcohol was excluded by the following two hydrolysis reactions. When **33** was hydrolyzed with a base the oxirane **19** was regenerated quantitatively after 50 h at 100°C. The acidic hydrolysis of **33** was even less efficient with 4 N HCl in aqueous 50% ethanol at 110°C to give the halohydrin **20**.



Furthermore, a useful change of the carbon oxidation numbers was observed in the acetal **35** formed from **33** in hot, acidified aqueous ethylene glycol. This points to an expulsion of bromide by neighboring-group participation via **36** or an equivalent intermediate which might slowly form the acetal **35** by a formal hydride migration under acidic conditions. Accordingly, such a hydride shift was not observed with **33** in hot pyridine when subsequent hydrolysis gave the acetate **37** of diol **24** as expected from an intermediate like **36**. But at higher temperatures in quinoline solvent **33** was cleanly converted into the enol acetate **34** as a key compound for additional derivatives in which atom C-2 may acquire a lower oxidation number (see **35** and **40**).

The original plan to eliminate acetic acid from **33** for direct generation of the bromoalkene **21** thus did not materialize due to the intramolecular substitution of bromide in **36**. The uncatalyzed ester pyrolysis of **33** took place already at 180-200°C within 9 min but did not proceed cleanly under a variety of conditions, including provisions for an in situ distillation of the bromoalkene **21** above 170°C at 12 Torr: Some **21** and acetic acid were formed but accompanied by comparable amounts of unidentified byproducts.

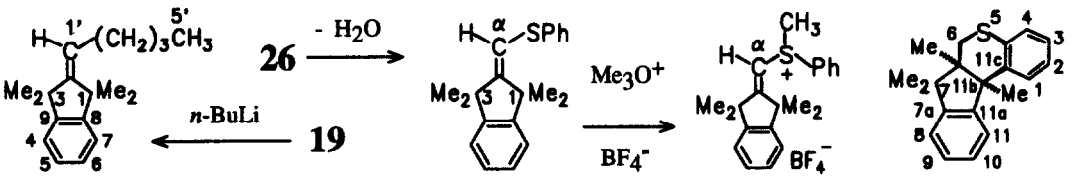
We cleaved the enol acetate **34** with methyllithium, because an attempted fission with $LiAlH_4$ gave complex results. The resultant lithium enolate **38** was stable in diethyl ether solution (^1H NMR) and could not be alkylated with methyl iodide at room temperature, with dimethyl sulfate or with triethyloxonium tetrafluoroborate. It was however quickly converted into the silyl ether **39**. Protonolysis of the enolate **38** or basic hydrolysis of the enol acetate **34** furnished only the aldehyde **41** as an autoxidable liquid which used to precipitate crystals of the corresponding acid **40** unless permanently protected from air. In accord with literature precedence[30] the enol ether **42** became available from the potassium analog of **38** when aldehyde **41** was treated with potassium hydride and methyl iodide to afford 98% of **42**.



n-Butyllithium did not enolize the oxirane **19** to **38** (and thence **41**) but opened the ring very quickly by addition, surprisingly with spontaneous elimination of LiOH to produce 1,1,3,3-tetramethyl-2-pentylideneindan (**43**) directly as the sole product (see Experimental).

A possible short route to the aldehyde **41** was envisaged via the enol thioether **44** which could be prepared by dehydration of the sulfide **26** but was not easily purified owing to the presence of several unidentified

byproducts. One of these was converted into **46** as a result of methyl migration on a chromatographic column, which shows that a sulfur-containing substituent had not saved the 1,1,3,3-tetramethylindan system from imminent rearrangement. Being a ß-protected vinyl sulfide, **44** can be lithiated quite readily as will be published. But all attempts to invent a more expeditive synthesis for the aldehyde **41** by hydrolysis of **44** were thwarted either by the unreactivity of **44** or by its decomposition with rearrangement. Thus the treatment of **44** with $TiCl_4$ yielded the pure starting compound (93%) after 12 h in moist acetonitrile[31] or in refluxing moist acetic acid (7 h), while trifluoroacetic acid[32] (60°C, 3 d) caused slow decomposition.



The ß,ß-di-*tert*-alkyl-substituted vinylsulfonium derivative **45** is sterically protected from nucleophilic attack at the olefinic ß-carbon atom C-2. It was therefore of interest to see if the α-sulfonium substituent in **45** might now serve as a leaving group in competition with demethylation at sulfur. Nucleophilic α-attack was tried with an excess of potassium *tert*-butoxide in THF which could have generated an enol ether from **45**. However, **45** was cleaved within 3 min at room temperature to give the enol thioether **44** by demethylation and equally fast the products of a formal reductive fission, namely thioanisole and the olefin **6**, but no enol ether.

D. Discussion

The reaction conditions studied here may serve as guidelines for applications to other compounds which are similarly prone to rearrangements. Compared with the successful brominations of 1,1,3,3-tetramethyl-2-methylenecyclobutane[33] (which could be prepared by a Wittig reaction) and of di-*tert*-butylethylene[18], the tetramethyl-2-indanylidene derivatives obtained in this and previous work[34] exhibit an increased tendency to rearrange. Our solution of the problem by nucleophilic bromination appears simpler than a related route using silylated oxiranes[28]. Considering further alternatives, a shorter synthesis of bromoalkenes via carbenoids was said to be inapplicable to sterically congested systems[35] in the one variant or to be inefficient[36] in another. It might be noted that the numerous methods of alkene syntheses from alkynes cannot be applied to systems like ours, except for favourable cases[37].

The enol acetate **34**, the aldehyde **41** and its acid **40** are potentially useful for successive synthetic projects. Their preparation is greatly facilitated by favourable properties of their common precursor **33** which crystallizes very well and is perfectly stable. Alternative routes to such compounds were shown to be unrewarding by more conventional procedures, as far as these promote the rearrangement via intermediates in which C-2 acquires some transient carbenium character.

EXPERIMENTAL

IR: Perkin-Elmer 125 or Bruker IFS-45. - UV/Vis: DMR-10 or PRQ 20 (C. Zeiss). - MS: Finnigan MAT 90. - NMR: Varian VXR-400S, XL-100, and HA-60-IL, or Bruker WP-80-CW, WP-80-DS and AC-200; internal standard TMS; ^{13}C-NMR multiplicities were taken from off-resonance or gated-decoupling spectra.

1,1,2,3,3-Pentamethyl-2-indanol (5)

A solution of ketone **4**[10,11] (21.00 g, 111.3 mmol) in anhydrous ether (150 ml) was cooled to -70°C under nitrogen and stirred. Methyllithium (134 mmol) in ether (89.5 ml) was added from a dropping funnel within 17 min. The mixture became dark brown at room temperature overnight; it was cooled in an ice bath during the dropwise addition of 40 ml of distd. water which produced a colourless precipitate and but little gas evolution. After the slow addition of ice-cooled 2 N HCl (100 ml) and shaking with ether (5 x, total 200 ml), the combined ethereal extracts were washed to neutrality and dried with Na_2SO_4. The solvent was evaporated to yield 21.78 g (95%) of practically pure **5** with m.p. 71-73°C. Recrystallization from ligroin gave small colourless flakes with m. p. 79-81.5°C, b. p. ca. 100°C (bath temp.)/12 Torr. - IR (KBr): ν = 3448 cm^{-1} (sharp, O-H), 2982, 2960, 2928, 2868, 1480, 1450, 1383, 1102, 1069, 925, 756. - ^{1}H NMR (CCl_4): δ = 1.10 (s, 1 2-CH_3), 1.19 (s, 2 CH_3), 1.22 (s, 2 CH_3), 7.02 (s, C_6H_4). - ^{13}C NMR ($CDCl_3$): δ = 17.3 (q, ^1J = 126 Hz, 2-CH_3), 23.4 and 29.3 (2 qq, ^1J = 126, ^3J = 4.9 Hz, 2 1-,3-CH_3), 49.6 (unresolved, C-1,-3), 85.7 (m, C-2), 122.9 (dm, ^1J = 156 Hz, C-4,-7), 127.0 (dm, ^1J = 159 Hz, C-5,-6), 148.9 (> sept, ^3J = 3.7 Hz, C-8,-9). - $C_{14}H_{20}O$ (204.3): calcd. C 82.30, H 9.87; found C 82.16, H 9.89.

1,1,3,3-Tetramethyl-2-methyleneindan (6)

The *tertiary* alcohol **5** (37.00 g, 181.1 mmol) was dissolved in 185 ml of distd. pyridine, and the yellow solution was cooled in ice. With magnetic stirring, thionyl chloride (27.0 ml, 369 mmol) was added dropwise within 24 min under argon. The heterogeneous mixture was kept at room temp. overnight and then poured on ice (300 g). The ethereal extracts (4 x, total 200 ml) were combined and shaken with 2 N HCl (5 x 200 ml), washed with 2 N NaOH (3 x) and with water, and dried with Na_2SO_4. The residue (34.76 g, 103%) obtained after solvent evaporation was purified by fractionating distillation, yielding 25.71 g (76%) of colourless **6** with b. p. 90-91°C/12 Torr or 107-108°C/20 Torr, m. p. 25-26°C. - IR (film): ν = 3075 cm^{-1}, 3020, 2960, 2925, 2862, 1655 (C=C), 1483, 1362, 1027, 889, 755, 670. - UV (cyclohexane): λ_{max} (lg ε) = 271 nm (3.142) with fine structure of ca. 940 cm^{-1}. - ^{1}H NMR (CCl_4): δ = 1.35 (s, 4 CH_3), 4.99 (s, =CH_2), 7.04 (s, C_6H_4). - ^{1}H and ^{13}C NMR ($CDCl_3$): See ref.[5] - MS (70 eV): *m/z* (%) = 186 M$^+$ (13), 171 (100), 156 (22), 141 (13). - $C_{14}H_{18}$ (186.3): calcd. C 90.26, H 9.74; found C 90.29, H 9.96.

Equilibration of the Olefins 6 and 8, with Formation of 1-(2,2,3,3-Tetramethyl-1-indanylidene)-2-propanone (7): Acetic anhydride (1.95 ml) and concd. HBr (48%, 0.24 ml) were mixed at +5°C and stirred for 1 h at room temperature. After addition of 200 mg (1.07 mmol) of olefin **6**, the mixture was kept at ambient temp. for at least 1 h and then poured into 100 ml of cold 2 N NaOH. The combined ethereal extracts were washed with distd. water and dried with K_2CO_3 to give 170 mg (85%) of a yellow oil containing only **6** and **8** (14:86). - A large run was worked up as above after a reaction period of 3 d. Its distillation residue contained mainly the ketone **7** which was filtered through basic alumina with CH_2Cl_2 to give a brown, oily mixture of the (*Z*) and (*E*) isomers (77:23) of **7**. - IR (nujol): ν = 1722 cm^{-1} (*E* isomer) and 1690 (*Z*), 1608, 1592. - ^{1}H NMR (CCl_4): δ = 1.04 (s, 2 2-CH_3), 1.09 (s, 2 3-CH_3), 2.21 (s, acetyl CH_3), 6.00 (s, 0.77 H, α-H of *Z* isomer), 6.51 (s, 0.23 H, α-H of *E*), 7.14 (mc, 3 aromat. H and impurities), 8.50 (dm, ^3J = 7 Hz, 7-H). - ^{13}C NMR ($CDCl_3$): δ = 24.5 (q, 2 2-CH_3), 25.0 (q, 2 3-CH_3), 31.7 (q, acetyl CH_3), 47.2 (s, C-3), 49.4 and 51.5 (2 s, C-3,-2 of minor isomer *E*), 52.6 (s, C-2), 117.6 (d, C-α of *E*), 118.6 (d, C-α of *Z*), 122.0 (d, C-4), 126.3 (d, C-6), 128.4 (d, C-7), 130.8 (d, C-5), 135.8 (s, C-8), 156.2 (s, C-9 of *E*), 156.7 (s, C-9), 164.3 (s, C-1 of *E*), 165.7 (s, C-1), 197.9 (s, CO), 198.1 (s, CO of *E*); assignments by comparison with **13** and in accord with SCS[5] by one acyl group.

2,2,3,3-Tetramethyl-1-methyleneindan (8)

After formation of the *tertiary* alcoholate of **5** from 400 mmol of ketone **4**[10,11] with methylmagnesium iodide in boiling xylene (140°C for 20 h), an unapproved workup modification with ice-cold concd. hydrochloric acid led to the rearranged olefin **8** as a 81:19 mixture with **6** (57.1 g, 77%) and some residual **5**. The colourless liquid **8** was distilled at 105-108°C/12 Torr in a Vigreux column. - IR (film): ν = 3070 cm^{-1}, 3020, 2962, 2924, 2863, 1645 (C=C), 1470, 1365, 874, 755. - UV (cyclohexane): λ_{max} (lg ε) = 250 nm (4.030), 271 (3.314), 278 (sh 3.324), 286 (3.414), 294 (3.322). - ^{1}H NMR ($CDCl_3$): δ = 1.05 (s, 2 2-CH_3), 1.09 (s, 2 3-CH_3), 4.92 (s, α-H *cis* to C-2), 5.41 (s, α-H *cis* to C-8), 7.17 (m, 6-H), 7.18 (dm, ^3J = 7 Hz, 4-H), 7.23 (m, 5-H), 7.44 (dm, ^3J = 7 Hz, 7-H); in CCl_4 δ values larger by up to 0.12 ppm. - ^{13}C NMR ($CDCl_3$): δ = 24.1 and 24.7 (2 qq, ^1J = 126, ^3J = 4.8 Hz, 2 2-CH_3 and 2 3-CH_3, resp.), 47.5 (br. m, C-3), 49.5 (m, *J* ca. 4 Hz, C-2), 101.6 (t, ^1J = 157.0 Hz, C-α), 121.0 and 122.5 (2 dd, ^1J = 157, ^3J = 7.5 Hz, C-7 and C-4, resp.),

126.5 and 128.5 (2 dd, ^1J = 159, ^3J = 7.5 Hz, C-6 and C-5, resp.), 138.9 (probably dq, ^3J ca. 10 and 6 Hz, C-8), 153.4 (m, C-9), 158.9 (s, C-1); all assignments by 2D-NMR, see text. - $C_{14}H_{18}$ (186.3): calcd. C 90.26, H 9.74; found C 90.16, H 9.69.

2-Bromomethyl-1-bromomethylene-2,3,3-trimethylindan (9)

Bromine (0.41 ml, 8.0 mmol) in 4 ml of CCl_4 was added from a dropping funnel with stirring under argon to an ice-cooled solution of olefin **6** (747 mg, 4.01 mmol) in 5 ml of CCl_4. After further stirring for 90 min, the orange-brown solution was combined with 10 ml of 2 N NaOH and warmed up. The combined ethereal extracts (5 x 20 ml) were shaken with 2 N NaOH (2 x 20 ml), washed neutral, dried with K_2CO_3, and concentrated to leave 1.58 g (114%) of a yellow oil which fumed from HBr gas. It was separated from traces of **11** by distillation at 105-120°C (bath temp.)/0.03 mbar and by chromatography (on silica gel with light petroleum ether) to afford 942 mg (68%) of **9**. A sample was redistilled and analyzed.

IR (film): ν = 3085 cm^{-1}, 3065, 2965, 2931, 2869, 1623 (w, C=C), 1466, 1456, 1259, 782, 758, 703. - ^{1}H NMR (CCl_4): δ = 1.15 (s, 1 CH_3), 1.26 (s, 2 CH_3), 3.13 and 3.38 (AB system, ^2J = 10.0 Hz, CH_2Br), 6.06 (s, olefinic α-H), 7.13 (mc, 3 aromat. H), 8.15 (mc, 7-H). - ^{13}C NMR ($CDCl_3$): δ = 17.7 and 20.6 (2 q, 2 3-CH_3), 28.7 (q, 2-CH_3), 42.8 (t, CH_2Br), 48.6 (s, C-3), 56.6 (s, C-2), 100.0 (d, C-α), 122.1 (d, C-4), 125.9 (d, C-7), 126.6 and 129.2 (2 d, C-6,-5), 136.4 (s, C-8), 146.8 (s, C-1), 153.5 (s, C-9); assignments by comparison with **11**. - $C_{14}H_{16}Br_2$ (344.1): calcd. C 48.87, H 4.69; found C 48.83, H 4.58.

The bromination of **6** in $CHCl_3$ containing 5 equivalents of tetraethylammonium bromide similarly furnished the rearrangement product **9**. It was contaminated by brominated solvent if the reaction was run in cyclohexane, or by 24% of **11** if conducted in glacial acetic acid.

1-Bromo-1-bromomethyl-2,2,3,3-tetramethylindan (10)

The equilibrated mixture (see above) of **6** and **8** (14:86, 1.07 mmol) was dissolved in 0.5 ml of CCl_4 in a 5-mm NMR test tube and slowly titrated with bromine until the colour just remained. An immediately taken ^{1}H-NMR spectrum showed **10** as the main product (and some **11**): δ = 1.02, 1.17, 1.34 and 1.43 (4 s, 4 CH_3), 3.86 and 4.26 (AB system, ^2J = 12 Hz, CH_2Br), 7.13 (mc, aromat. H). - After the introduction of 120 mg of potassium *tert*-butoxide and shaking for 5 min, the mixture was worked up with water and ether to give a raw material containing **11** and **12** (2:1).

1-Bromomethylene-2,2,3,3-tetramethylindan (11 and 12)

Solid K_2CO_3 (11.1 g) was added to the olefin **8** (1.50 g, 8.05 mmol) in 15 ml of CCl_4. The suspension was cooled in ice and stirred during the dropwise addition within 10 min of bromine (0.51 ml, 10 mmol) dissolved in 2 ml of CCl_4. After further stirring for only 5 min, the reaction was quenched by addition of 2 N NaOH (10 ml). The combined ethereal extracts (4 x 80 ml) were shaken with 2 N HCl, washed neutral, dried with K_2CO_3, and concentrated. The crude product (2.51 g) contained ca. 70% of **11** and **12** (ratio 9:1) and also traces of **10** and **16**. After twofold fractionating distillation at 79-82°C/0.05 mbar, the almost pure bromoalkene **11** (1.06 g, 50%) was chromatographed on silica gel with light petroleum ether; a middle fraction containing a trace of the (*E*) isomer **12** (δ = 6.51) analyzed correctly. - IR (film): ν = 3075 cm^{-1}, 2964, 2866, 1625 (w, C=C), 1464, 1376, 1366, 781, 757 (s), 699. - UV (cyclohexane): λ_{max} (lg ε) = 258 nm (4.178), 265 (4.140), 286 (3.744), 295 (3.670). - ^{1}H NMR (CCl_4): δ = 1.04 (s, 2 2-CH_3), 1.09 (s, 2 3-CH_3), 5.96 (s, α-H), 7.10 (mc, 3 aromat. H), 8.13 (m, 7-H). - ^{13}C NMR ($CDCl_3$): δ = 24.0 (q, 2 2-CH_3), 24.5 (q, 2 3-CH_3), 47.6 (s, C-3), 53.1 (s, C-2), 96.7 (d, CHBr-α), 122.3 (d, C-4), 125.7 (d, C-7), 126.1 and 129.0 (2 d, C-6,-5), 137.0 (s, C-8), 152.6 (s, C-1), 154.9 (s, C-9); assigned from **8** by SCS[5] for one bromine atom. - $C_{14}H_{17}Br$ (265.2): calcd. C 63.41, H 6.46; found C 63.68, H 6.50.

2-(2,2,3,3-Tetramethyl-1-indanylidene)acetic Acid (13)

A solution of the lithium compound **15** (max. 1.2 mmol) in THF was prepared as described below but kept at -78°C with stirring for 30 min and then poured on solid CO_2 (5 g). The warmed up residue was taken up in 2 N NaOH and purified by extraction with ether. The aqueous layer was acidified and extracted with ether to yield an oily residue which was crystallized from light petroleum ether to afford colourless needles of **13** with m. p. 148.5-150°C (110 mg, min. 40%).

IR (KBr): ν = 3200-2500 cm^{-1} (O-H), 2970, 1689, 1624, 1247, 1232, 762. - ^{1}H NMR ($CDCl_3$ or CCl_4): δ = 1.07 (s, 2 2-CH_3), 1.13 (s, 2 3-CH_3), 5.84 (s, α-H), 7.24 (d, ^3J = 7 Hz, 4-H), 7.26 (tm, ^3J = 7.5 Hz, 6-H), 7.37 (td, ^3J = 7.5, ^4J = 1 Hz, 5-H), 8.53 (dm, ^3J = 7.5 Hz, 7-H), 10.82 (br. s, CO_2H). - ^{13}C NMR ($CDCl_3$): δ = 24.4 and 25.0 (2 qq, ^1J = 126.7, ^3J = 4.6 Hz, 2 2-CH_3 and 2 3-CH_3, resp.), 47.3 (unresolved, C-3), 53.4 (br. m, C-2), 109.5 (d, ^1J = 158.3 Hz, C-α), 122.2 (dd, ^1J = 158.7, ^3J = 8.1 Hz, C-4), 126.4 (dd, ^1J = 160.2, ^3J = 7.2 Hz, C-6), 129.1 (dd, ^1J = 164.8, ^3J = 7.6 Hz, C-7), 130.9 (dd, ^1J = 160.4, ^3J = 8 Hz, C-5), 135.2 (pseudo-q, J = ca. 8 Hz, C-8), 157.1 (br. m, C-9), 170.6 (s, C-1), 172.5 (s, CO_2H); all assignments by 2D-NMR, see text. - $C_{15}H_{18}O_2$ (230.3): calcd. C 78.23, H 7.88; found C 78.50, H 7.90.

2,2,3,3-Tetramethyl-1-pentylideneindan (14)

This *n*-butyl derivative turned up as a side-product formed from the lithium compound **15** and the 1-bromobutane generated by the Br/Li exchange reaction. The hydrolysis product **8** was removed by distillation at 11 Torr from the crude material of two runs. The residue was purified by filtration through basic alumina to give **14** as a pale yellow oil. - ^{1}H NMR (CCl_4): δ = 0.97 (s, 2 CH_3), 1.06 (s, 2 CH_3), 1.03 and 1.40 (2 br. m, *n*-alkyl chain), 2.44 (br. q, ^3J = 7 Hz, 2 H), 5.26 (t, ^3J = 7 Hz, olefinic α-H), 7.07 (m, 3 aromat. H), 7.35 (m, 7-H).

1-Lithiomethylene-2,2,3,3-tetramethylindan (15)

A 5-mm NMR test tube was charged with 82 mg (0.31 mmol) of **11/12** (86:14) in 0.5 ml of anhydrous THF and cooled to -78°C under argon. After the addition of *n*-butyllithium in hexane (0.20 ml, 0.50 mmol) with colouration to green and brown, the mixture was immediately warmed up and analyzed by ^{1}H NMR, showing complete formation of **15** together with some coupling product **14**. - ^{1}H NMR (THF): δ = 0.93 (s, 2-CH_3), 1.05 (s, 3-CH_3), 6.83 (s, α-H), 6.95 (m, 5- and 6-H), 7.03 (dm, ^3J = ca. 7 Hz, 4-H), 7.87 (dd, ^3J = 7, ^4J = 2 Hz, 7-H); no educts **11** and **12** visible.

One half of this solution was withdrawn by syringe, quenched with methanol, and worked up with iced water and ether. The ethereal layers contained mainly **8**, some **14** and hydrocarbon contaminations (^{1}H NMR). - 1,2-Dibromoethane was added to the remaining THF solution which was then worked up in the same way, yielding a contaminated mixture of **11/12** (9:1) and **14**. The same result was obtained by quenching of **15** with elemental bromine at -78°C. - An attempt to prepare **15** with an excess of metallic lithium from **11** in THF (ultrasound irradiation for 30 min at room temp.) furnished only the olefin **8**.

1-Dibromomethylene-2,2,3,3-tetramethylindan (16)

The high-boiling fractions from several runs of **11** were redistilled at 93-104°C (bath temp.)/0.1 mbar with some decomposition. - ^{1}H NMR (CCl_4): δ = 1.09 (s, 2 3-CH_3), 1.21 (s, 2 2-CH_3), 7.10 (mc, 3 aromat. H), 8.23 (m, 7-H). - ^{13}C NMR ($CDCl_3$): δ = 23.1 (q, 2 2-CH_3), 24.6 (q, 2 3-CH_3), 49.2 (s, C-3), 56.1 (s, C-2), 79.4 (s, CBr_2), 122.2 (d, C-4), 126.0 (d, C-6), 126.4 (d, C-7), 129.2 (d, C-5), 138.0 (s, C-8), 150.8 (s, C-1), 154.9 (s, C-9); assigned by SCS[5] for 2 bromine atoms. - MS (70 eV): *m/z* (%) = 346/344/342 M^+ (4/9/5), 265/263 M^+ - Br (10/10), 184 M^+ - Br_2 (100), 169 (17). - $C_{14}H_{16}Br_2$ (344.1): calcd. C 48.87, H 4.69; found C 49.83, H 4.84. - The MS at 175°C showed a Br_3 quadruplet at *m/z* = 610/608/606/604 (total 13%) for traces of $C_{28}H_{31}Br_3^+$.

2-Bromo-2-bromomethyl-1,1,3,3-tetramethylindan (17a)

a) *In high-boiling petroleum ether[18], not diluted:* A Schlenk flask was charged with olefin **6** (290 mg, 1.56 mmol) and K_2CO_3[18] (280 mg, 2 mmol) in 2 ml of the solvent under argon and cooled in ice. A stream of argon carrying bromine vapours was passed onto the surface of the suspension with good stirring and illumination by a 175-W light bulb for 1 h. This Br_2/Ar gas mixture was generated in a 3-necked flask, continuously flushed with argon (20 ml/min), to which a solution of bromine (0.39 ml, 7.6 mmol) in high-boiling petroleum ether (1.5 ml) was added dropwise in such a way that no more than 0.1 ml of liquid ever accumulated at the bottom. - The filtrate of the resulting suspension was evaporated to leave 610 mg of a brown oil which contained **17a** and **9** (86:14) together with brominated saturated hydrocarbons. Fractional crystallization from ethanol yielded 339 mg (62%) of **17a** with m. p. 52-55°C. Small colourless needles were obtained by further recrystallization, m. p. 60-61.5°C (ethanol). - IR (KBr): ν = 2995 cm^{-1}, 2973, 2958, 1482, 1450, 1382, 1369, 1261, 1026, 746 (vs), 672 (C-Br). - ^{1}H NMR (CCl_4): δ = 1.53 and 1.61 (2 s, 2 1-,3-CH_3), 3.92 (s, CH_2Br), 7.00 (mc, C_6H_4). - ^{13}C NMR ($CDCl_3$): δ = 25.6 and 33.4 (2 q, 2 1-,3-CH_3), 37.8 (t, CH_2Br), 51.4 (s, C-1,-3), 88.4 (s, C-2), 121.7 (d, C-4,-7), 127.5 (d, C-5,-6), 147.5 (s, C-8,-9). - $C_{14}H_{18}Br_2$ (346.1): calcd. C 48.58, H 5.24, Br 46.18; found C 48.39, H 5.38, Br 45.31.

b) *In CCl_4, diluted (with formation of 17b):* A 125-W high-pressure lamp (Philips HPK) of the immersion type was used here. The Br_2/Ar gas mixture, generated from 2.00 ml (39 mmol) of bromine in CCl_4 (8 ml) as described under a), was passed for 5 h through an ice-cooled and stirred suspension of K_2CO_3 (7.26 g, 52.5 mmol) and olefin **6** (1.99 g, 10.7 mmol) in 75 ml of CCl_4. The crude product (4.60 g) obtained by filtration and evaporation contained **17a/17b** (65:26) and some side-products including 9% of **9**. It was processed by elimination (see **18b**).

2-Bromomethylene- (18a) and 2-Chloromethylene-1,1,3,3-tetramethylindan (18b) by Elimination

a) **18a**: A sample of **17a** obtained from 5.35 mmol of **6** (1% in petroleum ether) by photobromination as above was purified by chromatography on alumina with light petroleum ether. This raw material (2.13 g) was stirred with potassium *tert*-butoxide (900 mg, 8 mmol) in 6 ml of anhydrous THF for 4 h, refluxed for 20 min, and poured on iced water (30 ml). The combined ethereal extracts (3 x 30 ml) were washed, dried with K_2CO_3, and concentrated to leave 1.52 g of a yellow oil. Distillation at 144°C/11 Torr (710 mg of a green oil) and chromatography (alumina, light petroleum ether) gave 591 mg (42% over two steps) of colourless needles **18a**; compare **21** (= **18a**) for characterization.

b) **18b**: The crude material (4.60 g) of **17a,b** prepared in CCl_4 (see above) was treated with potassium *tert*-butoxide (1.56 g, 13.9 mmol) in 25 ml of THF as described under a). The products **18a** and **b** (3:1) could not be separated by distillation which gave 1.54 g of a colourless oil. - ^{1}H NMR of **18b** (CCl_4): δ = 1.34 (s, 2 3-CH_3), 1.58 (s, 2 1-CH_3), 6.00 (s, α-H), 7.03 (mc, C_6H_4). - MS (70 eV, 20°C): *m/z* (%) = 266/264 $C_{14}H_{17}Br^+$ (6/6), 251/249 $C_{13}H_{14}Br^+$ (100/100), 222/220 $C_{14}H_{17}Cl^+$ (1/3), 207/205 $C_{13}H_{14}Cl^+$ (20/63). - The MS showed also the presence of $C_{14}H_{16}Br_2^+$ (346/344/342, total 11%) and of $C_{14}H_{16}BrCl^+$ (302/300/298, total 6%) with their corresponding fragments.
n-Butyllithium in THF reacted much slower with **18b** than with **18a**.

1,1,3,3-Tetramethylspiro[indan-2,2'-oxirane] (19)

a) *By Epoxidation:* Solid $NaHCO_3$ (2.24 g) was added to a solution of the olefin **6** (3.74 g, 20.1 mmol) in 20 ml of chloroform. With magnetic stirring at room temp., commercial solid 3-chloroperbenzoic acid (5.30 g, at least 21.5 mmol) was added during 25 min such that the internal temperature did not rise above 30°C. (In larger runs with external cooling by ice the peracid may be introduced at once.) The epoxidation was almost complete after 30 min at room temp. (^{1}H-NMR control), but stirring was continued for another 60 min. The suspension was diluted with 30 ml of $CHCl_3$, extracted with 2 N NaOH (3 x 100 ml), washed neutral and dried with Na_2SO_4. The residue obtained after evaporation of $CHCl_3$ may contain some bis(3-chlorobenzoyl) peroxide. It crystallized from light petroleum ether in several crops, yielding 3.59 g (88%) of colourless **19** with m. p. 53-57°C and b. p. 150-151°C/23 Torr or 112-122°C/12 Torr. An analytical sample had m. p. 58-59°C. - IR (KBr): ν = 3026 cm^{-1}, 2980, 2965, 2925, 2866, 1490, 1454, 1365, 1096, 944, 940, 936, 840, 756 (s). - ^{1}H NMR (CCl_4): δ = 1.08 (s, 2 CH_3), 1.25 (s, 2 CH_3), 2.70 (s, OCH_2), 7.04 (s, C_6H_4). - ^{1}H NMR ($CDCl_3$): δ = 1.13, 1.28, 2.82, 7.16. - ^{13}C NMR ($CDCl_3$): δ = 24.3 (qq, ^1J = 127.4, ^3J = 4.8 Hz, 2 CH_3), 29.6 (qq, ^1J = 126.7, ^3J = 4.9 Hz, 2 CH_3), 43.8 (m, 2 C-1,-3), 47.0 (t, ^1J = 172.4 Hz, OCH_2), 74.7 (m, C-2), 122.5 (dm, ^1J = 156.7 Hz, C-4,-7), 127.3 (dm, ^1J = 159.6 Hz, C-5,-6), 148.5 (> sept, ^3J = 3.7 Hz, C-8,-9). - $C_{14}H_{18}O$ (202.3): calcd. C 83.12, H 8.97; found C 83.23, H 8.98. - An attempted epoxidation with magnesium monoperoxyphthalate under the usual conditions[38] led to the recovery of 88% of the pure olefin **6**.

b) *From the sulfonium salt 27:* A solution of **27** (6.50 g, 15.7 mmol) in 60 ml of CH_2Cl_2 was stirred overnight with 2 N NaOH (50 ml) and benzyltriethylammonium chloride (1.60 g, 7.0 mmol). Workup as above yielded quantitatively a mixture of **19** and thioanisole. The oxirane purified by sublimation at 50-70°C (bath temp.)/ca. 0.01 Torr had m. p. 53-54°C.

2-Bromomethyl-1,1,3,3-tetramethyl-2-indanol (20)

Dry tetraethylammonium bromide (20.77 g, 98.9 mmol) and the oxirane **19** (4.00 g, 19.8 mmol) were dissolved in 70 ml of anhydrous chloroform under nitrogen and stirred at room temp., when trifluoroacetic acid (2.94 ml, 38.4 mmol) was added during 2 min. The mixture was heated to vivid reflux at a condensor with a drying tube for 3 h, kept at room temp. overnight, washed neutral with distd. water (no bases!), and dried with Na_2SO_4. After solvent evaporation the brown oil of almost pure **20** was crystallized from pentane with cooling to give colourless rhombohedra (4.74 g, 85%) with m. p. 74-75°C; b. p. 170-171°C/12 Torr. - IR (KBr): ν = 3545 cm^{-1} (sharp, O-H), 2970, 2865, 1481, 1450, 1370, 1072, 759. - ^{1}H NMR (CCl_4): δ = 1.30 (s, 2 CH_3), 1.42 (s, 2 CH_3), 2.14 (br. s, OH), 3.77 (s, CH_2Br), 7.00 and 7.05 (AA'BB' system, C_6H_4). - $C_{14}H_{19}BrO$ (283.2): calcd. C 59.38, H 6.76; found C 59.80, H 6.78.

2-Bromomethylene-1,1,3,3-tetramethylindan (21)

Thionyl chloride (1.00 ml, 13.7 mmol) was added dropwise within 6 min to a solution of the halohydrine **20** (2.00 g, 7.1 mmol) in 5.00 ml (62 mmol) of distd. pyridine stirred in an ice bath. After 1 night at room temp., the brown mixture was poured into 100 ml of 2 N HCl. The combined ethereal extracts (5 x 20 ml) were washed with 2 N HCl (2 x), washed neutral, and dried with Na_2SO_4. The slightly coloured product (1.85 g, 98%) left after solvent evaporation was practically pure (by ^{1}H NMR) and could be used as such. One recrystallization from light petroleum ether gave small colourless rods in 3 crops (1.00 g, 53%) which turned quickly brown with intense daylight; m. p. 58-59°C, b. p. 142-150°C/12 Torr. - IR (KBr): ν = 3075 cm^{-1}, 2965, 2930, 2863, 1630 (C=C), 1588, 1485, 790, 762. - UV (cyclohexane): λ_{max} (lg ε) = 258 nm (2.854), 265 (3.070), 272 (3.149). - ^{1}H NMR (CCl_4): δ = 1.38 (s, 2 3-CH_3), 1.59 (s, 2 1-CH_3), 6.10 (s, α-H), 7.06 (pseudo-s, C_6H_4). - ^{1}H and ^{13}C NMR ($CDCl_3$): See ref.[5]. - $C_{14}H_{17}Br$ (265.2): calcd. C 63.41, H 6.46; found C 63.47, H 6.45.

1,1,2,3-Tetramethylindene (22)

Obtained as the main product by stirring of the oxirane **19** with 1 equivalent of $MgBr_2$ in anhydrous ether for 1 h, or with concd. HBr (48%) for 1 h at room temp., or with acetyl bromide on heating. - B. p. 111-112°C (bath temp.)/16 Torr (ref.[21] 113°C/17 Torr, ref.[23] 104-106°C/15 Torr). - IR (film): ν = 3066 cm^{-1}, 3018, 2961, 2924, 2862, 1637 (w, C=C), 1472, 1452, 1017, 750. - UV (cyclohexane): λ_{max} (lg ε) = 262 nm (4.051), 294 (2.896). - ^{1}H NMR (CCl_4): As in ref.[22,23]

(2-Hydroxy-1,1,3,3-tetramethyl-2-indanyl)methyl 3-Chlorobenzoate (23)

The epoxidation of **6** was performed at +2°C as described for **19** but with doubled concentrations (129 mmol in 70 ml). The crude product (37.47 g) contained 17% of the ester **23**. Oxirane **19** was separated by chromatography on basic alumina with light petroleum ether, and 4.22 g of **23** was then eluted with chloroform. Repeated recrystallization of this material gave colourless needles of pure **23** with m. p. 126.2-127.4°C (methanol). - IR (KBr): ν = 3583 cm^{-1} (sharp, O-H), 2991, 2960, 1712, 1305, 1262, 752. - ^1H NMR (CCl_4): δ = 1.34 (s, 2 CH_3), 1.43 (s, 2 CH_3), 1.89 (br., OH), 4.50 (s, CH_2O), 7.05 (pseudo-s, C_6H_4), 7.33 (m, 2 aromat. H), 7.79 (m, 1 aromat. H), 7.86 (br. s, 1 H). - $C_{21}H_{23}ClO_3$ (358.9): calcd. C 70.29, H 6.46; found C 69.86, H 6.25.

2-Hydroxymethyl-1,1,3,3-tetramethyl-2-indanol (24)

The ester **23** (1.00 g, 2.67 mmol) was heated to reflux for 19 h in CCl_4 (10 ml) with 0.50 g of benzyltriethylammonium chloride in 5 N NaOH (20 ml). After dilution with ether (50 ml) and separation the organic layer was extracted with 2 N NaOH (3 x 20 ml), washed neutral, dried with Na_2SO_4, and the solvent was evaporated. The residue (0.53 g, 90%) of almost pure diol **24** furnished colourless needles with m. p. 119-120°C (cyclohexane). - IR (KBr): ν = 3548 cm^{-1} (w, sharp, O-H), 2988, 2961, 2871, 1481, 1087, 749 (s). - ^1H NMR (CCl_4): δ = 1.24 (s, 2 CH_3), 1.33 (s, 2 CH_3), 2.09 and 2.16 (2 br. s, 2 OH), 3.69 (s, CH_2O), 7.01 (s, C_6H_4); ($CDCl_3$): δ = 1.26, 1.38, 2.23 (s, 2 OH), 3.80, 7.11. - ^{13}C NMR ($CDCl_3$): δ = 24.1 and 28.7 (2 qq, ^1J = 127, ^3J = 5 Hz, 2 1-,3-CH_3), 49.3 (m, C-1,-3), 63.7 (t, ^1J = 142 Hz, CH_2O), 85.9 (m, C-2), 122.5 (dm, ^1J = 157 Hz, C-4,-7), 127.3 (ddd, ^1J = 160 Hz, C-5,-6), 148.8 (m, C-8,-9). - $C_{14}H_{20}O_2$ (220.3): calcd. C 76.33, H 9.15; found C 76.40, H 9.03. - An acid-catalyzed transesterification would perhaps produce **24** faster than this hydrolysis, as observed for **37** (see below).

1',1',3',3'-Tetramethylspiro[1,3,2-dioxathiolane-4,2'-indan]-2-one (25)

Thionyl bromide (0.60 ml, 7.75 mmol) was added dropwise under argon to a stirred solution of the diol **24** (411 mg, 1.87 mmol) in 6 ml of anhydrous pyridine cooled in an ice bath. The mixture was warmed to room temp. within 2 h and poured into 50 ml of ice-cooled 2 N HCl. The ethereal extracts (3 x 20 ml) were washed with 2 N HCl (3 x 10 ml) and water, then dried with K_2CO_3 and concentrated. The residue (690 mg) contained mainly **25** (no **21** or dibromide **17a**) which crystallized as colourless cubes (398 mg, 80%) with m. p. 102-102.5°C (twice from light petroleum ether). - IR (KBr): ν = 2991 cm^{-1}, 2971, 2935, 1484, 1451, 1209 (s), 954 (s), 793, 735, 684. - ^1H NMR ($CDCl_3$): δ = 1.31, 1.34, 1.39 and 1.48 (4 s, 4 CH_3), 4.62 and 4.74 (AB system, ^2J = 10.0 Hz, CH_2O), 7.15 and 7.17 (2 mc, 2 aromat. H), 7.25 (mc, 2 aromat. H). - ^{13}C NMR ($CDCl_3$): δ = 24.4, 25.3, 29.3 and 29.8 (4 CH_3), 47.3 and 49.1 (C-1,-3), 65.9 (CH_2O), 106.7 (C-2), 122.3 and 122.5 (C-4,-7), 127.78 and 127.79 (C-5,-6), 147.3 and 147.5 (C-8,-9). - MS (70 eV, 45°C): *m/z* (%) = 266 M^+ (24), 202 M^+ - SO_2 (9), 187 ($C_{13}H_{15}O^+$, 100). - $C_{14}H_{18}O_3S$ (266.4): calcd. C 63.13, H 6.81, S 12.04; found C 63.32, H 6.88, S 12.06. - The basic hydrolysis of **25** (50 mg) in boiling ethanol (3 h) afforded 42 mg of the diol **24**.

1,1,3,3-Tetramethyl-2-(phenylthio)methyl-2-indanol (26)

A dry 250-ml 3-necked flask was equipped with a magnetic stirring-rod, a pressure-equalizing dropping funnel, a thermometer, and a reflux condensor carrying a nitrogen bubbler. It was charged with thioanisole (11.74 ml, 100 mmol) and 100 ml of anhydrous THF under nitrogen. [15 ml of anhydrous TMEDA[25] (tetramethylethylenediamine) may be added but does not improve the results.] The flask was cooled in a dry-ice bath, and *n*-butyllithium in hexane (50.0 ml, 100 mmol) was added dropwise with stirring at an internal temp. below -55°C. (Addition of ketone **4** after 1 h at -55°C would give the alcohol **28**.) The pale yellow solution was kept at room temp. for 90 min and then recooled. After the dropwise addition of ketone **4**[10,11] (18.0 g, 95.6 mmol) in 50 ml of anhydrous THF below -65°C internal temp., the brown suspension was stirred at room temp. overnight and then poured into ice-cold 2 N HCl (300 ml). The combined ethereal extracts (5 x 100 ml) were shaken with 2 N HCl (3 x 100 ml if TMEDA had been used), washed neutral, and dried with $MgSO_4$. Solvent evaporation left a malodorous solid which contained only **26** together with 15% of thioanisole. Recrystallization from methanol (60 ml) gave 17.1 g (55%) of almost colourless material, but the viscous oil recovered from the mother liquor (9.50 g, ca. 30% after removal of thioanisole in vacuo) may also be used in the next step. The analytical sample had m. p. 70-71°C (4 x from methanol). - IR (KBr): ν = 3504 cm^{-1} (sharp, O-H), 2964, 2870, 1481, 1024, 759, 738. - ^1H NMR (CCl_4): δ = 1.24 and 1.37 (2 s, 2 1-,3-CH_3), 2.37 (s, OH), 3.30 (s, CH_2S), 7.02 (mc, C_6H_4 and 2 H), 7.25 (mc, 3 aromat. H). - ^{13}C NMR ($CDCl_3$): δ = 23.6 and 29.3 (2 qq, ^1J = 126.5, ^3J = 4.8 Hz, 2 1-, 3-CH_3), 40.6 (t, ^1J = 139.6 Hz, CH_2S), 50.4 (unresolved, C-1,-3), 85.0 (unresolved, C-2), 122.4 (dm, ^1J = 156 Hz, C-4,-7), 126.2 (dt, ^1J = 162, ^3J = 7 Hz, *p*-C), 127.1 (dd, ^1J = 159.3, ^3J = 7 Hz, C-5,-6), 128.9 (dd, ^1J = 160.9, ^3J = 7.6 Hz, 2 *m*-C), 129.4 (dt, ^1J = ca. 162, ^3J = 7 Hz, 2 *o*-C), 137.4 (t, ^3J = ca. 8 Hz, *ipso*-C), 148.6 (unresd., C-8,-9). - $C_{20}H_{24}OS$ (312.5): calcd. C 76.88, H 7.74, S 10.26; found C 76.65, H 7.80, S 10.35.

(2-Hydroxy-1,1,3,3-tetramethyl-2-indanyl)methyl-(methyl)phenylsulfonium Tetrafluoroborate (27)

A solution of the ß-hydroxy sulfide **26** (12.9 g, 41.3 mmol) in anhydrous CH_2Cl_2 (24 ml) was added dropwise within 30 min to a stirred suspension of trimethyloxonium tetrafluoroborate (8.19 g, 55.4 mmol) in 20 ml of the same solvent. After further stirring for 10 min, 0.5 N NaOH (100 ml) was added dropwise during 15 min (gas evolution) and the two-phase system was stirred overnight in an attempt to produce the oxirane **19** directly according to literature[24] analogy. However, CH_2Cl_2 (4 x 75 ml) extracted **19** together with a large amount of unreacted salt **27**. The combined extracts were washed with distd. water (2 x 150 ml) and dried with $MgSO_4$. After solvent evaporation, the oxirane **19** was removed from the crystalline residue by elution with CCl_4 to leave the salt **27** (6.95 g, 41%). A sample was washed repeatedly with CCl_4 by suction until analytically pure. The colourless powder **27** with m. p. 183-183.5°C was insoluble in chloroform and water but soluble in 2 N HCl, CH_2Cl_2, acetone or DMSO. - IR (KBr): ν = 3481 cm^{-1} (O-H), 2965, 1485, 1447, 1084 (vs, BF_4). - ^1H NMR ([D_6]acetone): δ = 1.35, 1.38, 1.52 and 1.54 (4 s, 2 1-,3-CH_3), 3.62 (s, SCH_3), 4.18 and 4.56 (AB system, ^2J = 14 Hz, CH_2S), 7.17 (pseudo-s, C_6H_4), 7.74 (mc, *m*- and *p*-H), 8.22 (mc, *o*-H); ([D_6]DMSO): δ = 1.24, 1.24, 1.39 and 1.39, 3.39, 3.90 and 4.32, 7.18, 7.70, 8.12; (CH_2Cl_2): δ = 1.28, 1.32, 1.48 and 1.51, 3.44, 3.75 and 4.41, 7.15, 7.66, 8.01. - ^{13}C NMR ([D_6]DMSO): δ = 23.0, 24.0, 29.5 and 29.8 (4 qm, ^1J = ca. 127 Hz, 2 1-,3-CH_3), 30.5 (q, ^1J = 145.5 Hz, SCH_3), 50.2 and 50.7 (unresolved, C-1,-3), 51.5 (tm, ^1J = 141 Hz, CH_2S), 85.1 (unresd., C-2), 122.5 (dm, ^1J = 157 Hz, C-4,-7), 127.1 (unresd., *ipso*-C), 127.1 and 127.3 (2 dm, ^1J = 159 Hz, C-5,-6), 130.4 and 130.6 (2 dm, 2 *m*-,*o*-C), 133.8 (dt, ^1J = 163, ^3J = 7 Hz, *p*-C), 147.5 and 147.6 (unresd., C-8,-9); ([D_6]acetone): δ = 23.4, 24.6, ca. 30.3 and ca. 30.5, ca. 31, 51.5 and 52.0, 53.2, 87.0, 123.6, 128.6 (*ipso*-C and C-5,-6), 131.5 and 131.9, 135.2 (*p*-C), 148.4 and 148.5. - $C_{21}H_{27}BF_4OS$ (414.3): calcd. C 60.88, H 6.57; found C 60.82, H 6.55.

2-Butyl-1,1,3,3-tetramethyl-2-indanol (28)

The slow addition of 5 mmol of *n*-butyllithium in hexane (3.9 ml) to a benzene or THF solution (5 ml) of ketone **4**[10,11] (915 mg, 4.86 mmol) furnished almost pure **28** quantitatively after workup with 2 N HCl and ether. Colourless prisms of **28** (0.40 g, 31%) with m. p. 80-81°C crystallized from light petroleum ether. - IR (KBr): ν = 3533 and 3446 cm^{-1} (2 sharp O-H), 2992, 2955 (s), 2868, 1478, 1470, 1384, 1078, 766. - ^1H NMR (CCl_4): δ = 0.97 (mc, CH_3 and OH?), 1.21 and 1.27 (2 s, 2 1-,3-CH_3), ca. 1.5 (br. m, 2 CH_2), 1.57 (m, CH_2), 6.98 (s, C_6H_4). - ^{13}C NMR ($CDCl_3$): δ = 14.2 (qm, ^1J = 125 Hz, C-4'), 23.9 and 29.5 (2 qq, ^1J = 125, ^3J = 5 Hz, 2 1-,3-CH_3), 24.0, 26.0 and 32.5 (3 tm, ^1J = ca. 125 Hz, C-3', -2' and -1', resp.), 50.4 (s, C-1,-3), 86.5 (unresd., C-2), 122.8 (dm, ^1J = 157 Hz, C-4,-7), 127.1 (dm, ^1J = 159 Hz, C-5,-6), 149.3 (> sept, ^3J = 3.7 Hz, C-8,-9). - $C_{17}H_{26}O$ (246.4): calcd. C 82.87, H 10.64; found C 82.76, H 10.56.

2-(1-Butylidene)-1,1,3,3-tetramethylindan (29)

A small sample of the alcohol **28** was dehydrated as described for **6** to give the propyl-substituted olefin **29** as a colourless oil with b. p. 150-165°C (bath temp.)/12 Torr, forming clear crystals with m. p. 25-28°C. - IR (film): ν = 3019 cm^{-1}, 2959, 2928, 2862, 1483, 1458, 1361, 754. - ^1H NMR (CCl_4): δ = 0.95 (t, ^3J = 7 Hz, 4'-H_3), ca. 1.1 (obscured, 3'-H_2), 1.27 (s, 2 3-CH_3), 1.42 (s, 2 1-CH_3), 2.25 (q, ^3J = 7 Hz, 2'-H_2), 5.26 (t, ^3J = 7.5 Hz, 1'-H), 7.05 (s, C_6H_4). - ^1H and ^{13}C NMR ($CDCl_3$): Ref.[5] - $C_{17}H_{24}$ (228.4): calcd. C 89.41, H 10.59; found C 89.19, H 10.13.

1,1,3,3-Tetramethylspiro[indan-2,2'-oxetane] (30)

A solution of dimethylsulfoxonium methylide in anhydrous DMSO (50 ml) was prepared[26,27] from trimethylsulfoxonium iodide (7.50 g, 34 mmol) with sodium hydride. The ketone **4**[10,11] (5.64 g, 30.0 mmol) was added in batches, and the mixture was heated under argon to 100-120°C for 21 h because very little conversion had occurred at 65°C during 3 h. The cooled solution was poured into iced water and this mixture was extracted with hexane (5 x). The combined extracts were washed neutral, dried with $MgSO_4$, and concentrated. The residue (4.70 g) contained ca. 30% of the starting compound **4** together with the oxirane **19**, the oxetane **30** and the 1,5-diol **32** (ratio dependent on the reaction conditions). After a partial separation from **19** by distillation at 0.014 Torr the oxetane was purified by sublimation at 67°C (bath temp.)/11 Torr to obtain colourless needles with m. p. 59-60°C. - IR (KBr): ν = 2981 cm^{-1}, 2956, 2929, 2875, 1480, 1446, 1376, 1365, 1247, 1027, 991, 971 (s), 952, 765 (s). - ^1H NMR (CCl_4): δ = 1.19 and 1.44 (2 s, 2 1-,3-CH_3), 2.61 (t, ^3J = 8 Hz, CH_2), 4.29 (t, ^3J = 8 Hz, OCH_2), 7.03 (s, C_6H_4); ($CDCl_3$): δ = 1.22 and 1.50, 2.62, 4.32, 7.07. - ^{13}C NMR ($CDCl_3$): δ = 22.5 (tt, ^1J = 135.5, ^2J ca. 2 Hz, CH_2), 22.9 and 28.4 (2 qq, ^1J = 127, ^3J = 4.9 Hz, 2 1-,3-CH_3), 48.7 (m, C-1,-3), 64.9 (tt, ^1J = 148.9, ^2J = 3.7 Hz, OCH_2), 101.5 (m, C-2), 122.6 (dm, ^1J = 156 Hz, C-4,-7), 127.1 (dm, ^1J = 159 Hz, C-5,-6), 148.1 (> sept, ^3J = ca. 3.5 Hz, C-8,-9). - $C_{15}H_{20}O$ (216.3): calcd. C 83.28, H 9.32; found C 82.98, H 9.13.

An attempt to isolate **30** by chromatography afforded the rearranged product **31**.

3,3a,4,8b-Tetrahydro-3a,4,4,8b-tetramethyl-2H-indeno[1,2-b]furan (31)

Chromatography of the crude oxetane **30** with chloroform on silica gel gave **31** as a spectroscopically almost pure oil which needed no further processing. - IR (film): ν = 2978 cm^{-1}, 2933, 2868, 1478, 1374, 1108, 1042, 757. - ^1H NMR (CCl_4): δ = 1.10 (s, 2 CH_3), 1.28 (s, CH_3), 1.37 (s, CH_3), 1.70 and 3.60 (2 br. m, ABKL system of CH_2CH_2O), 7.07 (mc, C_6H_4); ($CDCl_3$): similar but 4 methyl signals (δ = 1.10, 1.11, 1.28, 1.44). - ^{13}C NMR ($CDCl_3$): δ = 15.4, 22.9, 23.9 and 28.5 (qt, qq, q and qq, all ^1J = 126 Hz, all ^3J = ca. 5 Hz; 3a-, 4-, 8b- and 4-CH_3, resp.), 39.3 (br. t, ^1J = 131 Hz, C-3), 46.0 and 56.2 (2 br. s, C-3a and -4), 65.8 (ddd, average ^1J = 145 Hz, OCH_2), 91.9 (br. s, C-8b), 122.6 and 123.6 (2 dm, ^1J = 157 Hz, C-5,-8), 127.0 and 128.1 (2 dm, ^1J = 159 Hz, C-6,-7), 146.9 and 149.1 (2 m, C-4a,-8a). - $C_{15}H_{20}O$ (216.3); MS (70 eV, 85°C): *m/z* (%) = 216 M^+ (20), 201 (100), 183 (17).

2,2'-[Oxybis(methylene)]bis(1,1,3,3-tetramethyl-2-indanol) (32)

This 1,5-diol **32** could be isolated from the higher-boiling fractions or the distillation residue of the oxetane **30** and also by chromatography. The colourless crystals were thorougly washed with CCl_4 (somewhat soluble) until analytically pure with m. p. 169-170°C. - IR (KBr): ν = 3590 and 3566 cm^{-1} (2 sharp O-H), 2980, 2956, 2930, 2868, 1486, 1450, 1378, 1095, 1070, 983, 953, 759. - ^1H NMR ($CDCl_3$): δ = 1.30 and 1.41 (2 s, 4 1-,3-CH_3), 2.32 (variable s, 2 OH), 3.78 (s, 2 OCH_2), 7.12 (narrow m, 2 C_6H_4). - ^{13}C NMR ($CDCl_3$): δ = 24.1 and 28.8 (2 qq, ^1J = 127, ^3J = 4.9 Hz, 4 1-,3-CH_3), 49.4 (s, 2 C-1,-3), 74.1 (t, ^1J = 141 Hz, 2 OCH_2), 85.0 (m, 2 C-2), 122.3 (dm, ^1J = 157 Hz, 2 C-4,-7), 127.2 (dm, ^1J = 159 Hz, 2 C-5,-6), 148.8 (> sept, ^3J = ca. 3.7 Hz, 2 C-8,-9). - $C_{28}H_{38}O_3$ (422.6): calcd. C 79.58, H 9.06; found C 79.38, H 8.88.

2-Bromomethyl-1,1,3,3-tetramethyl-2-indanyl Acetate (33)

Acetyl bromide (2.37 ml, 32 mmol) was added dropwise to a stirred solution of dry tetraethylammonium bromide (5.71 g, 27.2 mmol) and the oxirane **19** (5.00 g, 24.7 mmol) in 26 ml of anhydrous chloroform. The mixture was warmed at 47°C for 17 h at a good reflux condensor carrying a drying tube. The brown solution was poured into a mixture of 2 N NaOH (50 ml) and ethanol (50 ml), which was then extracted with ether or chloroform (3 x 30 ml). The combined extracts were shaken with 2 N NaOH (100 ml), 2 N HCl (2 x 100 ml), washed neutral, and dried with Na_2SO_4. Solvent evaporation left 7.83 g (97%) of a yellow powder containing only **33**. One recrystallization from ethanol gave 6.81 g (85%) of pure **33** as colourless needles with m. p. 164-165°C. - IR (KBr): ν = 3000 cm^{-1}, 2982, 2962, 2930, 2870, 1740 (C=O), 1250, 1238, 1191, 1025, 761. - UV (cyclohexane): λ_{max} (lg ε) = 271 nm (3.089, sharp band with down-progression ca. 980 cm^{-1}), 306 (1.410, br.). - ^1H NMR (CCl_4): δ = 1.39 and 1.45 (2 s, 2 1-,3-CH_3), 1.97 (s, acetyl CH_3), 4.31 (br. s, CH_2Br), 6.97 and 7.07 (AA'BB' system, C_6H_4). - $C_{16}H_{21}BrO_2$ (325.2): calcd. C 59.09, H 6.51; found C 59.39, H 6.57.

(1,1,3,3-Tetramethyl-2-indanylidene)methyl Acetate (Enolester 34)

A dry, thin-walled reagent test tube was charged with the bromo acetate **33** (2.00 g, 6.15 mmol) in 1.45 ml of distd. quinoline and lowered into an oil bath preheated to 195°C. The temperature was kept at 210°C (±20°) during the reaction period of 6-10 min, but gas evolution was not observed. After quick cooling the tube was rinsed with ether which was repeatedly shaken with 2 N HCl (total 50 ml), washed neutral, and dried with Na_2SO_4. The crude material (1.57 g) was slightly contaminated; pure **34** crystallized from light petroleum ether as colourless flakes (911 mg, 61%), with m. p. 80-81°C after one further crystallization.

IR (KBr): ν = 2963 cm^{-1}, 2925, 2864, 1753 (C=O), 1682 (w, C=C), 1483, 1455, 1380, 1368, 1240 (s), 1224 (s), 1095, 760. - ^1H NMR (CCl_4): δ = 1.40 (s, 2 3-CH_3), 1.49 (s, 2 1-CH_3), 2.12 (s, acetoxy), 7.04 (s, C_6H_4), 7.13 (s, α-H); (diethyl ether): δ = 1.38, 1.51, 2.09, 7.07, 7.22; ($CDCl_3$): δ = 1.41 (s, 2 3-CH_3), 1.52 (s, 2 1-CH_3), 2.20 (s, acetoxy), 7.16 (mc, 5-,6-H), 7.23 (mc, 4-,7-H), 7.26 (s, α-H). - ^{13}C NMR ($CDCl_3$): Ref.[5] - $C_{16}H_{20}O_2$ (244.3): calcd. C 78.65, H 8.25; found C 79.01, H 8.24.

2-(1,1,3,3-Tetramethyl-2-indanyl)-1,3-dioxolane (35)

A solution of the bromo acetate **33** (500 mg, 1.54 mmol) in 13 ml of ethyleneglycol/water/concd. HCl (8:3:2) was heated to 130°C for 15 h. After cooling and extraction with ether (4 x 50 ml) the combined extracts were washed neutral and dried with Na_2SO_4. Their solid evaporation residue (540 mg) consisted mainly of crude **35** which was difficult to purify by repeated crystallization from ethanol; colourless platelets, m. p. 142-143°C. The constitution was proven by the formation of **35** (m. p., ^1H NMR) from the aldehyde **41** in acidic ethyleneglycol (18 h at 100°C).

IR (KBr): ν = 2964 cm^{-1}, 2893 (s), 1484, 1361, 1045 (s), 1024, 949, 777. - ^1H NMR (CCl_4): δ = 1.23 and 1.38 (2 s, 2 1-,3-CH_3), 1.82 (d, ^3J = 8.6 Hz, 2-H of indanyl), 3.80 and 3.92 (AA'BB' system, OCH_2CH_2O), 4.95 (d, ^3J = 8.6 Hz, 2-H of dioxolane), 6.98 (s, C_6H_4); the AB system (δ = 1.82/4.95) was confirmed by decoupling. - ^{13}C NMR ($CDCl_3$): δ = 26.5 and 30.5 (2 qquint, ^1J = 126, ^3J = 5 Hz, 2 1-,3-CH_3), 44.8 (unresolved, C-1,-3), 61.2 (dm, ^1J = 128 Hz, C-2 of indanyl), 64.3 (t, ^1J = 149 Hz, OCH_2CH_2O), 105.3 (dm, ^1J = 165 Hz, C-2 of dioxolane), 122.3 (dd, ^1J = 158, ^3J = 5 Hz, C-4,-7), 126.9 (dm, ^1J = 160 Hz, C-5,-6), 150.7 (m, C-8,-9). - $C_{16}H_{22}O_2$ (246.3): calcd. C 78.01, H 9.00; found C 78.41, H 8.90.

(2-Hydroxy-1,1,3,3-tetramethyl-2-indanyl)methyl Acetate (37)

The bromo acetate **33** (400 mg, 1.23 mmol) in 15 ml of dry pyridine was heated at 110°C until completely converted into **37** after 19 h. The mixture was diluted with ether (40 ml) and shaken 5x with 2 N HCl (total 150 ml). The organic layer was washed neutral, dried with Na_2SO_4, and evaporated. The slightly contaminated oil **37** (390 mg, 121%) gave 141 mg (52%) of the pure diol **24** (m. p., NMR) by trans-esterification on attempted crystallization from methanol; it was therefore not further purified. - ^{1}H NMR (CCl_4): δ = 1.26 and 1.36 (2 s, 2 1-,3-CH_3), 2.09 (s, acetyl CH_3), 4.25 (s, CH_2O), 7.03 (mc, C_6H_4).

Lithium (1,1,3,3-Tetramethyl-2-indanylidene)methoxide (Enolate 38)

A 5-mm NMR test tube charged with enol ester **34** (77 mg, 0.31 mmol) in 0.40 ml of anhydrous ether was cooled to -78°C under argon. After addition of methyllithium in ether (0.33 ml, 0.48 mmol) the spectrum of **38** was recorded at room temp. - ^{1}H NMR (ether): δ = 1.34 (s, 3-CH_3), 1.59 (s, 1-CH_3), 6.87 (s, α-H), 7.01 (s, C_6H_4); no change was observed after the addition of methyl iodide (2 equiv.).

(1,1,3,3-Tetramethyl-2-indanylidene)methyl Trimethylsilyl Ether (39)

Methyllithium in ether (1.25 ml, 1.81 mmol) was added to a solution of the enol ester **34** (200 mg, 0.82 mmol) in 4 ml of anhydrous ether under argon at -78°C. After stirring for 1 h, chlorotrimethylsilane (0.260 ml, 2.06 mmol) was added by syringe and the mixture was warmed up. On addition of 30 ml of distd. water the separated aqueous layer was acidic. It was extracted with ether (3 x 10 ml), and the combined extracts were washed neutral and dried with Na_2SO_4. After solvent evaporation, the residue (227 mg, 101%) contained only **39** which distilled at 56°C (bath temp.)/0.013 mbar as a colourless oil (181 mg, 81%). - IR (film): ν = 3019 cm^{-1}, 2958, 2921, 2861, 1673 (s, C=C), 1482, 1254, 1217, 1147, 1109, 871, 848, 755. - ^{1}H NMR ($CDCl_3$): δ = 0.22 (s, $OSiMe_3$), 1.36 (s, 2 3-CH_3), 1.50 (s, 2 1-CH_3), 6.32 (s, α-H), ca. 7.13, 7.16, 7.19 and 7.21 (4 mc, 4 aromat. H); (CCl_4): δ = 0.22, 1.33, 1.45, 6.18, 7.02 (s, C_6H_4). - ^{13}C NMR ($CDCl_3$): Ref.[5]. - $C_{17}H_{26}OSi$ (274.5): calcd. C 74.39, H 9.55; found C 74.55, H 9.68.

1,1,3,3-Tetramethylindan-2-carboxylic Acid (40)

The acid **40** was formed quantitatively from pure samples of the aldehyde **41** within a few days under air. Recrystallization from light petroleum ether gave colourless needles with m. p. 189-190.5°C. - IR (KBr): ν = 3400-2700 cm^{-1} (br., O-H), 2968, 2933, 2870 (C-H), 2730, 2632, 2560 (O-H), 1698 (s, C=O), 1482, 1258, 766, 756. - ^{1}H NMR ($CDCl_3$): δ = 1.41 and 1.52 (2 s, 2 1-,3-CH_3), 2.91 (s, 2-H), 7.16 and 7.24 (AA'BB' system, C_6H_4), ca. 11.2 (br., CO_2H); (CCl_4): δ = 1.40, 1.53, 2.84, 7.05, 11.9. - ^{13}C NMR ($CDCl_3$): δ = 27.4 and 30.2 (2 1-,3-CH_3), 45.6 (C-1,-3), 64.8 (C-2), 122.3 (C-4,-7), 127.3 (C-5,-6), 149.4 (C-8,-9), 178.3 (CO_2H). - $C_{14}H_{18}O_2$ (218.3): calcd. C 77.03, H 8.31; found C 77.07, H 8.26.

1,1,3,3-Tetramethylindan-2-carbaldehyde (41)

a) As described for **38**, a solution of the enolate was prepared from the enol ester **34** (97 mg, 0.40 mmol) in 4 ml of anhydrous ether with 0.60 ml (0.90 mmol) of methyllithium in ether. (This solution did not react with triethyloxonium tetrafluoroborate in 20 min at room temp.) The mixture was treated with 20 ml of distd. water, then with 30 ml of 2 N NaOH, and the separated aqueous phase was shaken with ether (3 x 20 ml). The combined ethereal layers were washed neutral, dried with Na_2SO_4, and the solvent was evaporated to leave 97 mg of crude **41** as the only product. Bulb-to-bulb distillation in a microtube at 64-96°C (bath temp.)/0.018 mbar gave pure **41** as a colourless, partially solidifying oil which had to be stored at -20°C under argon but was stable in dilute solutions. - IR (film): ν = 3067 cm^{-1}, 3018, 2961, 2930, 2868, 2760, 1707 (vs), 1483, 1449, 1368, 763, 756. - ^{1}H NMR (CCl_4): δ = 1.40 and 1.44 (2 s, 2 1-,3-CH_3), 2.43 (d, ^3J = 3.5 Hz, 2-H), 7.05 (mc, C_6H_4), 9.90 (d, ^3J = 3.5 Hz, CH=O); ($CDCl_3$): δ = 1.43 (s, 2 1-,3-CH_3), 2.51 (d, ^3J = 4.0 Hz, 2-H), 7.14 (mc, C_6H_4), 9.95 (d, ^3J = 4.0 Hz, CH=O). - $C_{14}H_{18}O$ (202.3): calcd. C 83.12, H 8.97; found C 83.15, H 9.15.

b) Alternatively, 73% of **41** was obtained from the enol ester **34** with refluxing methanol/2 N NaOH (2:1) within 3 h under air without formation of the acid **40**. Similarly, hydrolysis in refluxing methanol/2 N HCl (1:1) yielded only **41** and its dimethyl acetal.

Methyl [(1,1,3,3-Tetramethyl-2-indanylidene)methyl] Ether (42)

The crude aldehyde **41**, prepared from 1.133 g (4.64 mmol) of the enol ester **34**, was dissolved in anhydrous THF (10 ml) and added dropwise to a slurry of potassium hydride in the same solvent under argon. After 2 h at room temp. the mixture was cooled in a water bath and treated with an excess of methyl iodide for 1 h. Workup with ether and water afforded the almost pure solid **42** (988 mg, 98%) which was recrystallized from methanol in fractions to give colourless flakes with m. p. 41-43°C. - IR (KBr): ν = 2956 cm^{-1}, 2925, 2859, 2834, 1680 (C=C), 1482, 1455, 1226, 1135, 1101 (s), 757. - ^{1}H NMR ($CDCl_3$): δ = 1.36 (s, 2 3-CH_3), 1.48 (s, 2 1-CH_3), 3.60 (s, OCH_3), 6.00 (s, α-H), 7.15 and 7.20 (2 mc, C_6H_4); (CCl_4): δ = 1.32, 1.42, 3.54, 5.84, 6.97.

- ^{13}C NMR ($CDCl_3$): δ = 28.7 and 33.0 (2 qq, ^1J = 127, ^3J = 4.5 Hz, 2 1-CH_3 and 2 3-CH_3, resp.), 44.8 (m, C-3), 46.4 (m, C-1), 59.7 (qd, ^1J = 142.5, ^3J = 5.5 Hz, OCH_3), 122.2 and 122.4 (2 dm, ^1J = ca. 156 Hz, C-7,-4), 126.8 and 127.0 (2 dd, ^1J = 159, ^3J = 7 Hz, C-5,-6), 137.3 (m, C-2), 142.3 (dq, ^1J = 172.8, ^3J = 5.5 Hz, α-C), 149.6 (m, C-9), 150.6 (m, C-8). - $C_{15}H_{20}O$ (216.3): calcd. C 83.28, H 9.32; found C 83.65, H 9.46.

2-(1-Pentylidene)-1,1,3,3-tetramethylindan (43)

n-Butyllithium (1.0 equivalent) in THF opened the oxirane ring of **19** at room temp. with a half-conversion time $t_{1/2}$ = ca. 2 min which was increased to ca. 3 min in the presence of 1 equiv. of lithium 2,2,6,6-tetramethylpiperidide (LiTMP). 2 equiv. of LiTMP alone did not react in THF within 1 h at room temp. with **19** (92 % recovered). In pentane solvent no reaction of **19** with *n*-butyllithium was observed within 21 h at room temp.; but **19** was opened with $t_{1/2}$ << 2 min when 1 equiv. of TMEDA was subsequently added to this solution. A second futile attempt to enforce deprotonation instead of ring-opening of **19** with *n*-butyllithium and 1 equiv. of LiTMP in pentane changed only $t_{1/2}$ to ca. 2 h. All conversions gave **43** quantitatively (in situ ^1H NMR), but it was deemed unnecessary to purify **43** further because its NMR spectra were almost identical with those of the 1-butylidene analogue **29**. - ^1H NMR (CCl_4): δ = 0.94 (m, 5'-H_3), 1.29 (s, 2 3-CH_3), ca. 1.37 (obscured, 3'- and 4'-H_2), 1.45 (s, 2 1-CH_3), 2.27 (m, 2'-H_2), 5.27 (t, ^3J = 7.5 Hz, 1'-H), 7.03 (s, C_6H_4). - ^{13}C NMR ($CDCl_3$): δ = 14.1 (qt, ^1J = 124 Hz, C-5'), 22.5 (tm, ^1J = ca. 123 Hz, C-4'), 28.1 (tm, ^1J = 125 Hz, C-3'), 30.0 (qq, ^1J = 127 Hz, 1-CH_3), 32.6 (qq, ^1J = 127 Hz, 3-CH_3), 32.7 (tm, ^1J = ca. 124 Hz, C-2'), 46.4 (m, C-1), 47.0 (m, C-3), 122.4 and 122.6 (2 dm, ^1J = ca. 157 Hz, C-7 and C-4), 122.9 (dm, ^1J = ca. 145 Hz, C-1'), 126.8 and 126.9 (2 dm, ^1J = ca. 159 Hz, C-5 and C-6), 149.4 (m, C-9), 150.9 (m, C-8), 157.9 (m, C-2).

Phenyl [(1,1,3,3-Tetramethyl-2-indanylidene)methyl] Thioether (44)

The ß-hydroxy sulfide **26** (19.0 g, 60.8 mmol) was dissolved in distd. pyridine (40 ml, 495 mmol) in a 3-necked flask (250 ml) fitted with a pressure-equalizing dropping funnel, magnetic stirring rod, internal thermometer and a reflux condensor carrying a drying tube. With external cooling in ice, thionyl chloride (8.90 ml, 122 mmol) was slowly added from the funnel. The turbid mixture was stirred overnight at room temp. and then poured into ice-cooled 2 N HCl (200 ml). A voluminous yellow precipitate containing side-products did not dissolve on extraction with ether (4 x 50 ml) and was discarded. The combined extracts were washed with 2 N HCl (2 x 20 ml), washed neutral with water, and dried with $MgSO_4$. The oily residue (only 7.52 g) contained **44** and a trace of the olefin **6** together with ca. 30% of unidentified side-products; this result was not improved by a shorter reaction period or by refluxing before workup. Therefore, fractional crystallization was difficult and could be best achieved with methanol to give typically 5.10 g (28%) of **44**: Colourless needles with m. p. 89-90°C (5 x from methanol). Alternatively, the crude product may be purified by chromatography to afford 36% of **44**. - IR (KBr): ν = 2959 cm^{-1}, 2923, 2858, 1582, 1476, 1362, 1023, 757, 740, 690. - ^1H NMR (CCl_4): δ = 1.41 (s, 2 3-CH_3), 1.59 (s, 2 1-CH_3), 6.10 (s, α-H), 7.07 (pseudo-s, C_6H_4), 7.19 (mc, 5 aromat. H). - ^1H and ^{13}C NMR ($CDCl_3$): Ref.[5]. - $C_{20}H_{22}S$ (294.5): calcd. C 81.58, H 7.53, S 10.89; found C 81.81, H 7.68, S 10.86.

Methyl(phenyl)[(1,1,3,3-tetramethyl-2-indanylidene)methyl]sulfonium Tetrafluoroborate (45)

A solution of the enol thioether **44** (1.17 g, 3.97 mmol) in anhydrous chloroform (18 ml) was added dropwise to a stirred suspension of trimethyloxonium tetrafluoroborate (1.40 g, 9.47 mmol) in 10 ml of the same solvent under argon. Since conversion remained incomplete at room temp., the flask was equipped with a reflux condensor carrying a drying tube to heat the mixture to 80°C for 16 h. With cooling in ice the addition of water (40 ml) caused a vivid gas evolution. The chloroform was separated and the aqueous layer extracted with CH_2Cl_2 (3 x 20 ml). The combined organic layers were washed neutral, dried with Na_2SO_4, and concentrated. The crude residue (1.64 g) was washed with CCl_4 to leave 1.10 g (70%) of the salt **45** which recrystallized as colourless plates with m. p. 232-233°C (2 x from methanol). - IR (KBr): ν = 2965 cm^{-1}, 2926, 2864, 1484, 1447, 1084 (vs, BF_4), 755. - ^1H and ^{13}C NMR ($CDCl_3$): Ref.[5]. - $C_{21}H_{25}BF_4S$ (396.3); calcd. C 63.65, H 6.36; found C 63.79, H 6.36.

C/S Fission of 45: The sulfonium salt **45** (210 mg, 0.53 mmol) was added to a cooled solution of potassium *tert*-butoxide (250 mg, 2.23 mmol) in 5 ml of anhydrous THF. After less than 2 h of stirring at room temp. the mixture was treated with distd. water (15 ml), and worked up with ether to yield 100 mg of a yellow oil containing the enol thioether **44**, the olefin **6** and thioanisole in a molar ratio 37:32:31 (^1H NMR). The latter two compounds were removed by evaporation to leave only **44** with m. p. 82-84°C.

6,6a,7,11b-Tetrahydro-6a,7,7,11b-tetramethylindeno[2,1-c][1]benzothiopyran (46)

The raw material containing **44** (see above) was chromatographed on silica gel with light petroleum ether. A forerun of olefin **6** and traces of **8**, then the remained enol thioether **44** was eluted and immediately following the tetracycle **46** (2.83 g, 16%). After repeated sublimation at 88°C (bath temp.)/12 Torr the colourless powder **46** had m. p. 91-92°C. - IR (KBr): ν = 2970 cm^{-1}, 2933, 2871, 1482, 1462, 1455, 1436, 1373,

769 (vs), 742. - ^{1}H NMR (CCl_4): δ = 0.84, 1.16, 1.25 and 1.60 (4 s, 4 CH_3), 2.45 and 3.06 (AB system, ^3J = 13.0 Hz, CH_2S), 7.06 (br. m, 2 C_6H_4). - ^{13}C NMR ($CDCl_3$): δ = 21.0 (qt, ^1J = 127 Hz, 6a-CH_3), 26.1 (q, ^1J = 128.0 Hz, 11b-CH_3), 25.7 and 29.3 (2 qq, ^1J = 126 Hz, 2 7-CH_3), 38.1 (tm, ^1J = ca. 140 Hz, C-6), 48.6 (m, C-6a), 54.7 and 54.8 (2 m, C-7 and -11b), 122.0, 125.3, 125.6, 125.8, 126.4, 126.6, 127.3 and 129.6 (8 dm, 8 aromat. CH), 136.1 (m, C-4a), 146.3 and 147.3 (2 m, C-7a and -11a), 151.3 (m, C-11c). - MS (70 eV, 50°C): *m/z* (%) = 294 M^+ (56), 279 (100), 237 (12), 185 M^+ - SPh (17), 175 (19). - $C_{20}H_{22}S$ (294.5): calcd. C 81.58, H 7.53; found C 81.91, H 7.65.

Acknowledgement: We thank Dr. D. S. Stephenson for 2D-NMR spectra (compounds **8** and **13**) as well as the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for their generous support.

REFERENCES

1. Sterically Congested Molecules, 9; Part 8, see ref.[5]; Part 7, see ref.[17].
2. Knorr, R.; von Roman, T.; Nöth, H.; Böck, S. *J. Chem. Soc., Perkin Trans. 2* **1992**, 127-130.
3. Polborn, K.; Knorr, R.; Böhrer, P. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1992**, *C48*, 490-492.
4. Knorr, R.; Hoang, T. P.; Nöth, H.; Linti, G. *Organometallics* **1992**, *11*, 2669-2673.
5. Knorr, R.; von Roman, T.; Freudenreich, J.; Hoang, T. P.; Mehlstäubl, J.; Böhrer, P.; Stephenson, D. S.; Huber, H.; Schubert, B. *Magn. Reson. Chem.* **1993**, *31*, 557-565.
6. Knorr, R.; Ferchland, K.; Mehlstäubl, J.; Böhrer, P.; Hoang, T.-P.; Stephenson, D. S. *Chem. Ber.* **1992**, *125*, 2033-2040.
7. Takeuchi, K.; Ohga, Y.; Kitagawa, T. *J. Org. Chem.* **1991**, *56*, 5007-5008.
8. Knorr, R.; Ferchland, K.; Mehlstäubl, J.; Hoang, T. P.; Böhrer, P.; Lüdemann, H.-D.; Lang, E. *Chem. Ber.* **1992**, *125*, 2041-2049.
9. Compare Horn, D. E.; Krapcho, A. P.; Grenon, B. J. *J. Org. Chem.* **1979**, *44*, 454-456.
10. Klages, C.-P.; Voß, J. *Chem. Ber.* **1980**, *113*, 2255-2277.
11. Knorr, R.; Mehlstäubl, J.; Böhrer, P. *Chem. Ber.* **1989**, *122*, 1791-1793, and references cited therein.
12. Mehlstäubl, J. *Doctoral Dissertation*, Univ. of Munich, **1985**.
13. Compare Olah, G. A.; Wu, A. H.; Farooq, O. *J. Org. Chem.* **1989**, *54*, 1375-1378.
14. a) Fitjer, L.; Scheuermann, H.-J.; Klages, U.; Wehle, D.; Stephenson, D. S.; Binsch, G. *Chem. Ber.* **1986**, *119*, 1144-1161. - b) Fitjer, L.; Quabeck, U. *Synth. Commun.* **1985**, 855-864.
15. Corey, E. J.; Kang, J. *J. Am. Chem. Soc.* **1982**, *104*, 4724-4725.
16. MM2: Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127-8134. - Allinger, N. L.; Yuh, Y. H. *Pure Appl. Chem.* **1983**, *55*, 191-197.
17. The 2D-NMR setup was described by Knorr, R.; Stephenson, D. S.; Böhrer, P.; Hoang, T.-P. *Magn. Reson. Chem.* **1993**, *31*, 388-393.
18. Bolze, R.; Eierdanz, H.; Schlüter, K.; Massa, W.; Grahn, W.; Berndt, A. *Angew. Chem.* **1982**, *94*, 927-927; *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 924; *Angew. Chem. Suppl.* **1982**, 2039-2049.
19. Korach, M.; Nielsen, D. R.; Rideout, W. H. *J. Am. Chem. Soc.* **1960**, *82*, 4328-4330.
20. Paquette, L. A.; Lin, H.-S.; Gallucci, J. C. *Tetrahedron Lett.* **1987**, *28*, 1363-1366.
21. Cologne, J.; Pichat, L. *Bull. Soc. Chim. Fr.* **1949**, *16*, 177-185, p 181.
22. Skattebøl, L.; Boulette, B. *J. Org. Chem.* **1966**, *31*, 81-85.
23. Buddrus, J. *Chem. Ber.* **1968**, *101*, 4152-4162.
24. Shanklin, J. R.; Johnson, C. R.; Ollinger, J.; Coates, R. M. *J. Am. Chem. Soc.* **1973**, *95*, 3429-3431.
25. Compare Corey, E. J.; Seebach, D. *J. Org. Chem.* **1966**, *31*, 4097-4099, and cited references.
26. Corey, E. J.; Chaykovsky, M. *J. Am. Chem. Soc.* **1965**, *87*, 1353-1364.
27. Farcasiu, D. *Synthesis* **1972**, 615-616.
28. Hudrlik, P. F.; Hudrlik, A. M.; Rona, R. J.; Misra, R. N.; Withers, G. P. *J. Am. Chem. Soc.* **1977**, *99*, 1993-1996.
29. Höfle, G.; Steglich, W.; Vorbrüggen, H. *Angew. Chem.* **1978**, *90*, 602-615; *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 569. - Scriven, E. F. V. *Chem. Soc. Rev.* **1983**, *12*, 129-161.
30. Lenoir, D.; Seikaly, H. R.; Tidwell, T. T. *Tetrahedron Lett.* **1982**, *23*, 4987-4990.
31. Mukaiyama, T.; Kamio, K.; Kobayashi, S.; Takei, H. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 3723-3723.
32. Cookson, R. C.; Parsons, P. J. *J. Chem. Soc., Chem. Commun.* **1976**, 990-990.
33. Samuel, S. P.; Niu, T.; Erickson, K. L. *J. Am. Chem. Soc.* **1989**, *111*, 1429-1436.
34. Knorr, R.; Lattke, E.; Räpple, E. *Liebigs Ann. Chem.* **1980**, 1207-1215.
35. Entmayr, P.; Köbrich, G. *Chem. Ber.* **1976**, *109*, 2175-2184.
36. Williams, D. R.; Nishitani, K.; Bennett, W.; Sit, S. Y. *Tetrahedron Lett.* **1981**, *22*, 3745-3748.
37. A special solution for similar systems was just described by Reddy, G. B.; Hanamoto, T.; Hiyama, T. *Tetrahedron Lett.* **1991**, *32*, 521-524.
38. Brougham, P.; Cooper, M. S.; Cummerson, D. A.; Heaney, H.; Thompson, N. *Synthesis* **1987**, 1015-1017.