Synthesis of vinyl-substituted oxiranes and their transformation to dihydrofurans

S. V. Popkov,[a] L. V. Kovalenko,[a] V. P. Tashchi,[b] and L. Ya. Bogel'fer [b]*

[a]D. I. Mendeleyev University of Chemical Technology of Russia, 9 Miusskaya pl., 125190 Moscow, Russian Federation. Fax: +7 (095) 200 4204

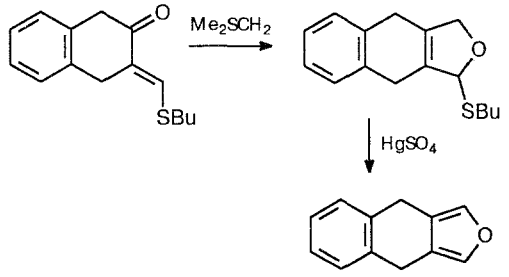
[b]Research Institute of Plant Protecting Chemicals, 33 Ugreshskaya ul., 109088 Moscow, Russian Federation. Fax: +7 (095) 279 3448

The reaction of dimethylsulfonium methylide with the carbonyl function of 2-arylidenecyclohexanones obtained from 2-methylcyclohexanone affords the corresponding spirooxiranes. The application of this reaction to 2,2-dimethyl-6-(5-methylfurfurylidene)cyclohexanone and 2,2-dimethyl-6-(5-chlorofurfurylidene)cyclohexanone leads to substituted 4,4-dimethyl-1-furyl-1,3,4,5,6,7-hexahydroisobenzofurans.

Key words: 2-methylcyclohexanone, aromatic and heterocyclic aldehydes, Claisen—Schmidt reaction, C-methylation, Corey—Chaykovsky reaction, spirooxiranes, substituted hexahydroisobenzofurans.

2,2-Disubstituted oxiranes are precursors of many modern synthetic azole fungicides.[1] The widespread method of synthesis of these compounds is based on the reaction of ketones with dimethylsulfonium or dimethylsulfoxonium methylides according to the Corey—Chaykovsky procedure.[2,3] Reaction of α,β-unsaturated ketones with methylides is also known to afford vinyloxiranes in the case of sulfonium salts, and cyclopropylketones if dimethylsulfoxonium derivatives are used.[2] Previously, oxiranes have been obtained from α-benzylidenecyclohexanones by the Corey—Chaykovsky reaction in rather high yields.[4] In addition, α-(butylthiomethylene)ketones are known to react with dimethylsulfonium methylide to form 3,4-disubstituted 2-butylthio-2,5-dihydrofurans, which can be transformed into 3,4-disubstituted furans by treatment with mercury sulfate.[5] (Scheme 1).

Scheme 1



Labile oxiranes are likely to be the intermediates in this case, too.

Compounds of a similar structure are also formed if 1,3-diphenyl-3-methoxyprop-2-en-1-one is treated with dimethylsulfonium methylide, however, the intermediate 2-methoxy-3,5-diphenyl-2,3-dihydrofuran due to its low stability, eliminates a molecule of methanol to give 2,4-diphenylfuran.[6]

In this work, the reaction of dimethylsulfonium methylide (generated *in situ* by the action of potassium *tert*-butoxide on trimethylsulfonium iodide) with 6-arylidene-2,2-dimethylcyclohexanones (**3a—g**) was studied. The starting substituted ketones **3a—g** were prepared in two steps using a sequence of transformations similar to the one described by Johnson:[7] 1) condensation of aromatic aldehydes (**1a—g**) with 2-methylcyclohexanone in methanol in the presence of 15% KOH; 2) methylation of the resulting ketones (**2a—g**) with methyl iodide in *tert*-butanol in the presence of potassium *tert*-butoxide (Scheme 2).

We studied the reaction of unsaturated ketones (**3a—g**) with dimethylsulfonium methylide and found that in the case of benzylideneketones (**3a—c**) the reaction affords the expected oxiranes (**4a—c**) which are possible to isolate in high yields (81—98 %), and to characterize. Reaction with ketones containing furfurylidene and 5-chlorothienylidene groups (**3d,e**) at C—6 also gives the corresponding oxiranes (**4d,e**), although in lower yields. Attempts to obtain oxiranes from 5-methylfurfurylidene- and 5-chlorofurfurylidene-substituted ketones (**3f,g**) were unsuccessful, since the resulting oxiranes underwent 1,3-sigmatropic rearrangement to

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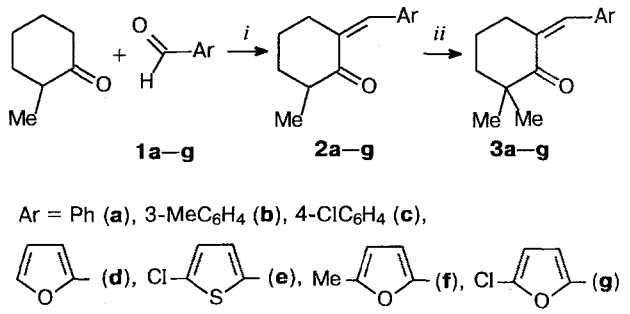
Scheme 2

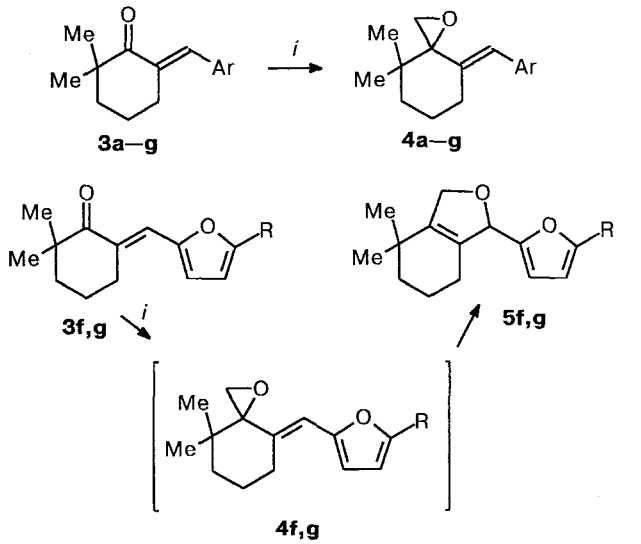


Reagents and conditions: *i.* 15% KOH/MeOH, 20 °C→b.p.; *ii.* 1) *t*-BuOK/*t*-BuOH, 2) CH_3I, 0 °C→b.p.

give substituted dihydrofurans (**5f,g**) in high yield. These compounds were isolated and their structures were established by spectral methods. The formation of the reaction products is described in Scheme 3.

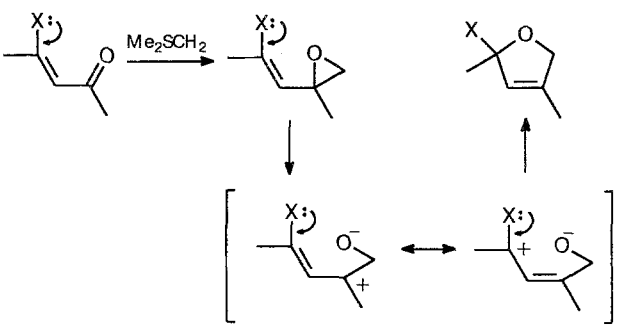
We believe that in the case of 2-benzylidenecyclohexanone derivatives the potential barrier of the transformation of oxirane to the dihydrofuran structure is too high for this type of interaction to take place. In the case of furfurylidene-substituted cyclohexanones, which in addition contain electron-donating substituents (Me, Cl) at C-5 of the furan ring, the mesomeric effect of the furan group stabilizes the intermediate carbocation

Scheme 3



Reagents and conditions: *i.* Me_3SI/DMSO, 0°C; *t*-BuOK/DMSO; then −5 °C, H_2O.

Scheme 4



to such an extent that expansion of the oxirane ring becomes possible.

It should be noted that in the above examples of the reactions of dimethylsulfonium methylide with α,β-unsaturated ketones[5,6] the transformation of the intermediate oxirane to the dihydrofuran structure usually proceeds if there is a substituent at the β-position of the starting ketone that can exhibit a positive mesomeric effect (butylmercapto or methoxy group). The mesomeric effect of this substituent assists the heterolytic cleavage of the C—O bond, stabilizing the intermediate mesomeric carbocation, which forms the five-membered ring of 2,5-dihydrofuran after migration of the double bond (Scheme 4).

In the ^1H NMR spectra of all of the oxiranes obtained (**4a—e**) two doublets of the AB spin system of the methylene fragment of the oxirane ring with the characteristic coupling constant (5.4 Hz) at 2.4—3.1 ppm are present. The singlet or triplet at 6.4—6.6 ppm corresponds to the proton of the exocyclic double bond. In the IR spectra of compounds (**4a—e**), the absorption bands of the exocyclic double bond at 1620—1640 cm^{-1} and the characteristic absorption bands of the oxirane cycle at 890 cm^{-1} are present. In the ^1H NMR spectra of the substituted hexahydroisobenzofurans (**5f,g**) formed as a result of isomerization of the intermediate oxiranes (**4f,g**), the complicated AB spin system of the $H_A(3)$ and $H_B(3)$ protons is observed at 4.6—4.8 ppm, which can be considered as a doublet of doublets with J = 11.5 Hz. The doublet of doublets at 5.5 ppm with characteristic J_{1-3A} = 2.3 and J_{1-3B} = 2.2 Hz corresponds to the H(1) proton.

Experimental

The IR spectra (ν/cm^{-1}) were obtained with Specord M-80 and IKS-29 instruments in nujol (for solids) and in liquid films (for liquids). The ^1H NMR spectra (CD_3COCD_3, δ, ppm, J/Hz) were obtained with a Varian XL-400 spectrometer (400 MHz). The courses of the reactions and the purity of the compounds obtained were monitored by TLC on Silufol UV-254 plates.

2-Benzylidene-6-methylcyclohexanone (2a). 15% Aqueous KOH (33 mL) was added dropwise to a solution of 2-methylcyclohexanone (22.4 g, 0.2 mol) and benzaldehyde **1a**

Table 1. Spectral properties of 2-arylidene-6-methylcyclohexanones

Compound	^{1}H NMR spectrum, δ, ppm (*J*/Hz)	IR spectrum, ν/cm^{-1}
2a	1.12 (d, 3 H, CH_3, *J* = 6.8), 1.35—1.77 3 (m, 2 H, 2 CH cycl.), 1.85—1.95 (m, 1 H, 1 CH cycl.), 2.05—2.13 (m, 1 H, 1 CH cycl.), 2.38—2.50 m (1 H, 1 CH cycl.), 2.63—2.73 (m, 1 H, 1 CH cycl.), 2.95—3.05 (m, 1 H, 1 CH cycl.), 7.29 (t, 1 H, CH=C exocycl., *J* = 2.2), 7.30—7.45 (m, 5 H, 5 CH aromatic)	1690 (C=O), 1620 (C=C exocycl.)
2b	1.17 (d, 3 H, CH_3, *J* = 6.7), 1.47—1.74 (m, 2 H, 2 CH cycl.), 1.77—1.92 (m, 1 H, 1 CH cycl.), 1.94—2.07 (m, 1 H, 1 CH cycl.), 2.20—2.47 (m, 1 H, 1 CH cycl.), 2.32 (s, 3 H, CH_3Ph), 2.52—2.72 (m, 1 H, 1 CH cycl.), 2.87—3.06 (m, 1 H, 1 CH cycl.), 7.37 (s, 1 H, CH=C exocycl.), 7.03—7.28 (m, 4 H, 4 CH aromatic)	1685 (C=O), 1650 (C=C exocycl.)
2c	1.13 (d, 3 H, CH_3, *J* = 6.7), 1.56—1.78 (m, 2 H, 2 CH cycl.), 1.87—1.95 (m, 1 H, 1 CH cycl.), 2.08—2.14 (m, 1 H, 1 CH cycl.), 2.40—2.50 (m, 1 H, 1 CH cycl.), 2.64—2.74 (m, 1 H, 1 CH cycl.), 2.96—3.04 (m, 1 H, 1 CH cycl.), 7.26 (t, 1 H, CH=C exocycl., *J* = 6.2), 7.48 (s, 4 H, 4 CH aromatic)	1670 (C=O), 1580 (C=C exocycl.)
2d	1.15 (d, 3 H, CH_3, *J* = 7.0), 1.53—1.63 (m, 1 H, 1 CH cycl.), 1.67—1.79 (m, 1 H, 1 CH cycl.), 1.92—2.09 (m, 2 H, 2 CH cycl.), 2.29—2.38 (m, 1 H, 1 CH cycl.), 2.64—2.75 (m, 1 H, 1 CH cycl.), 3.06—3.15 (m, 1 H, 1 CH), 6.50 (q, 1 H, 1 CH fur.*), 6.60 (d, 1 H, 1 CH fur., *J* = 3.4), 7.21 (t, 1 H, CH=C exocycl., *J* = 2.2), 7.56 (d, 1 H, 1 CH fur., *J* = 1.7)	1665 (C=O), 1635 (C=C exocycl.)
2e	1.19 (d, 3 H, CH_3, *J* = 6.9), 1.47—1.67 (m, 1 H, 1 CH cycl.), 1.69—1.86 (m, 1 H, 1 CH cycl.), 1.90—2.11 (m, 2 H, 2 CH cycl.), 2.29—2.47 (m, 1 H, 1 CH cycl.), 2.48—2.67 (m, 1 H, 1 CH cycl.), 2.80—2.98 (m, 1 H, 1 CH), 6.91 (d, 1 H, 1 CH th., *J* = 3.9), 7.06 (d, 1 H, 1 CH th., *J* = 3.9), 7.56 (t, 1 H, CH=C exocycl., *J* = 2.1)	1660 (C=O), 1575 (C=C exocycl.)
2f	1.17 (d, 3 H, CH_3, *J* = 6.9), 1.52—1.62 (m, 1 H, 1 CH cycl.), 1.66—1.78 (m, 1 H, 1 CH cycl.), 1.90—2.08 (m, 2 H, 2 CH cycl.), 2.33 (s, 3 H, CH_3—fur.), 2.35—2.43 (m, 1 H, 1 CH cycl.), 2.65—2.76 (m, 1 H, 1 CH cycl.), 3.01—3.10 (m, 1 H, 1 CH), 6.08 (t, 1 H, 1 CH fur.), 6.49 (t, 1 H, 1 CH fur., *J* = 3.4), 7.27 (s, 1 H, CH=C exocycl.)	1665 (C=O), 1590 (C=C exocycl.)
2g	1.11 (d, 3 H, CH_3, *J* = 6.9), 1.52—1.63 (m, 1 H, 1 CH cycl.), 1.69—1.82 (m, 1 H, 1 CH cycl.), 1.90—2.01 (m, 1 H, 1 CH cycl.), 2.02—2.09 (m, 1 H, 1 CH cycl.), 2.34—2.45 (m, 1 H, 1 CH cycl.), 2.63—2.74 (m, 1 H, 1 CH cycl.), 3.02—3.11 (m, 1 H, 1 CH), 6.52 (d, 1 H, 1 CH fur., *J* = 3.5), 6.83 (d, 1 H, 1 CH fur., *J* = 3.5), 7.10 (t, 1 H, CH=C exocycl., *J* = 2.3)	1700 (C=O), 1620 (C=C exocycl.)

*In Tables 1—4 fur. denotes furyl, th. — thienyl, dihydrofur. — dihydrofuran.

Table 2. Spectral properties of 2-arylidene-6,6-dimethylcyclohexanones

Compound	^{1}H NMR spectrum, δ, ppm (*J*/Hz)	IR spectrum, ν/cm^{-1}
3a	1.12 (s, 6 H, $(CH_3)_2$), 1.70—1.80 (m, 5 H, 5 CH cycl.), 2.80—2.90 (m, 1 H, 1 CH cycl.), 7.25 (t, 1 H, CH=C exocycl., *J* = 2.3), 7.29—7.43 (m, 5 H, 5 CH aromatic)	1680 (C=O), 1615 (C=C exocycl.)
3b	1.12 (d, 6 H, $(CH_3)_2$, *J* = 7.64), 1.70—1.83 (m, 4 H, 4 CH cycl.), 2.24 (s, 3 H, CH_3Ph), 2.60—2.85 (m, 2 H, 2 CH cycl.), 7.15—7.28 (m, 5 H, 4 CH aromatic and CH=C exocycl.)	1695 (C=O), 1650 (C=C exocycl.)
3c	1.11 (s, 6 H, $(CH_3)_2$), 1.76—1.80 (m, 4 H, 4 CH cycl.), 2.78—2.85 (m, 2 H, 2 CH cycl.), 7.19 (t, 1 H, CH=C exocycl., *J* = 2.3), 7.37 (s, 4 H, 4 CH arom)	1685 (C=O), 1625 (C=C exocycl.)
3d	1.09 (s, 6 H, $(CH_3)_2$), 1.73—1.84 (m, 4 H, 4 CH cycl.), 2.84—2.90 (m, 2 H, 2 CH cycl.), 7.16 (t, 1 H, CH=C exocycl., *J* = 2.3), 6.55 (m, 3 H, 3 CH fur.), 6.69 (d.d, 1 H, 1 CH fur., *J* = 3.5 и *J* = 0.6), 7.62 (d, 1 H, 1 CH fur. *J* = 1.8)	1680 (C=O), 1595 (C=C exocycl.)
3e	1.15 (s, 6 H, $(CH_3)_2$), 1.68—1.87 (m, 4 H, 4 CH cycl.), 2.65—2.77 (m, 2 H, 2 CH cycl.), 6.91 (d, 1 H, 1 CH th., *J* = 4.0), 7.05 (d, 1 H, 1 CH fur., *J* = 4.0 Гц), 7.54 (t, 1 H, CH=C exocycl., *J* = 2.1)	1665 (C=O), 1570 (C=C exocycl.)
3f	1.16 (s, 6 H, $(CH_3)_2$), 1.72—1.84 (m, 4 H, 4 CH cycl.), 2.35 (s, 3 H, CH_3 fur.), 2.85—3.00 (m, 2 H, 2 CH cycl.), 6.10 (s, 1 H, 1 CH fur.), 6.50 (s, 1 H, 1 CH fur.), 7.26 (t, 1 H, CH=C exocycl., *J* = 2.2)	1660 (C=O), 1580 (C=C exocycl.)
3g	1.19 (s, 6 H, $(CH_3)_2$), 1.74—1.86 (m, 4 H, 4 CH cycl.), 2.84—2.89 (m, 2 H, 2 CH cycl.), 6.53 (d, 1 H, 1 CH fur., *J* = 3.5), 6.82 (d, 1 H, 1 CH fur., *J* = 3.5), 7.08 (t, 1 H, CH=C exocycl., *J* = 2.3)	1695 (C=O), 1610 (C=C exocycl.)

Table 3. Spectral properties of 8-arylidene-4,4-dimethyl-1-oxaspiro[2.5]octanes

Compound	^{1}H NMR spectrum, δ, ppm (*J*/Hz)	IR spectrum, ν/cm^{-1}
4a	0.86 and 0.96 (two s, 6 H, $(CH_3)_2$), 1.56—1.69 (m, 4 H, 4 CH cycl.), 2.10—2.21 (m, 1 H, 1 CH cycl.), 2.82—2.91 (m, 1 H, 1 CH cycl.), 2.46—3.00 (AB system, 2 H, CH_2O, J = 5.4), 6.48 (s, 1 H, CH=C exocycl.), 7.17—7.23 (m, 3 H, 3 CH aromatic), 7.29—7.35 (m, 2 H, 2 CH aromatic, J = 7.4)	1620 (C=C exocycl.) 850 ()
4b	0.91 and 1.03 (two s, 6 H, $(CH_3)_2$), 1.54—1.72 (m, 4 H, 4 CH cycl.), 2.00—2.08 (m, 1 H, 1 CH cycl.), 2.24 (s, 3 H, CH_3Ph), 2.60—2.68 (m, 1 H, 1 CH cycl.), 2.58—3.04 (AB-system, 2 H, CH_2O, J = 5.4), 6.49 (s, 1 H, CH=C exocycl.), 7.04—7.08 (m, 1 H, 1 CH aromatic), 7.12—7.20 (m, 3 H, 3 CH aromatic, J = 1.7, J = 6.4)	1640 (C=C exocycl.) 850 ()
4c	0.85 and 0.95 (two s, 6 H, $(CH_3)_2$), 1.57—1.70 (m, 4 H, 4 CH cycl.), 2.10—2.18 (m, 1 H, 1 CH cycl.), 2.80—2.86 (m, 1 H, 1 CH cycl.), 2.44—2.99 (AB-system, 2 H, CH_2O, J = 25.4), 6.44 (t, 1 H, CH=C exocycl.), 7.21—7.33 (A_2B_2 system, 4 H, 4 CH aromatic J = 8.4)	1590 (C=C exocycl.) 850 ()
4d	0.83 and 0.96 (two s, 6 H, $(CH_3)_2$), 1.53—1.74 (m, 4 H, 4 CH cycl.), 2.10—2.25 (m, 1 H, 1 CH cycl.), 3.31—3.46 (m, 1 H, 1 CH cycl.), 2.41—2.96 (AB-system, 2 H, CH_2O, J = 5.5), 6.26 (t, 1 H, CH=C exocycl.), 6.20 (d, 1 H, 1 CH fur.), 6.34 (d.d, 1 H, 1 CH fur., $^1J = {}^2J$ = 2.1), 7.32 (d, 1 H, 1 CH fur., J = 2.1)	860 ()
4e	0.83 and 0.92 (two s, 6 H, $(CH_3)_2$), 1.60—1.78 (m, 4 H, 4 CH cycl.), 2.16—2.25 (m, 1 H, 1 CH cycl.), 3.00—3.08 (m, 1 H, 1 CH cycl.), 2.39—3.00 (AB-system, 2 H, CH_2O, J = 5.4), 6.46 (t, 1 H, CH=C exocycl.), 6.46 (d, 1 H, 1 CH th., J = 3.9), 6.34 (d, 1 H, 1 CH th., J = 3.9)	1530 (C=C exocycl.) 870 ()

Table 4. Spectral properties of 1,3,4,5,6,7-hexahydroisobenzofurans

Compound	^{1}H NMR spectrum, δ, ppm (*J*/Hz)	IR spectrum, ν/cm^{-1}
5f	1.07 and 1.09 (two s, 6 H, $(CH_3)_2$), 1.48—1.52 (m, 2 H, 2 CH cycl.), 1.66—1.93 (m, 4 H, 4 CH cycl.), 2.66 (d, 3 H, CH fur., J = 1.1), 4.57—4.74 (AB-system, 2 H, CH_2O dihydrofur., J = 11.5), 5.50 (m, 1 H, CH dihydrofur.), 5.88 (m, 1 H, 1 CH fur.), 6.07 (d, 1 H, 1 CH fur., J = 3.1)	1580 (C=C exocycl.) 1240 (C—O)
5g	1.07 and 1.09 (two s, 6 H, $(CH_3)_2$), 1.50 (m, 2 H, 2 CH cycl.), 1.57—1.93 (m, 4 H, 4 CH cycl.), 4.62—4.73 (AB-system, 2 H, 2 CH dihydrofur.), 5.48 (m, 1 H, CH dihydrofur.), 6.09 (d, 1 H, 1 CH fur., J = 3.2), 6.21 (d, 1 H, 1 CH fur., J = 3.2)	1525 (C=C exocycl.) 1230 (C—O)

(25.4 g, 0.24 mol) in MeOH (50 mL) and the mixture was refluxed with stirring on a water bath for 2 h. After cooling, the reaction mixture was extracted with $CHCl_3$, the organic layer was washed with hydrochloric acid and water and dried over $MgSO_4$, and chloroform was removed *in vacuo*. The residue was recrystallized from *i*-PrOH to give ketone **2a** (25.6 g, 64 %), m. p. 62—63 °C, *cf.* Ref. 7: m.p. 61—62 °C.

The other 2-arylidene-6-methylcyclohexanones (**2b—g**) were prepared using similar procedures.

2-(3-Methylbenzylidene)-6-methylcyclohexanone (2b), yield 43 %, b.p. 127—132 °C (0.2 Torr), n_D^{20} = 1.5754. Found (%): C, 83.91; H, 8.59. $C_{15}H_{18}O$. Calculated (%): C, 84.07; H, 8.47.

2-(4-Chlorobenzylidene)-6-methylcyclohexanone (2c), yield 65 %, b.p. 144—150 °C (0.01 Torr), m.p. 63—64 °C (*i*-PrOH). Found (%): C, 71.56; H, 6.50. $C_{14}H_{15}ClO$. Calculated (%): C, 71.64; H, 6.44.

2-Furfurylidene-6-methylcyclohexanone (2d), yield 64.6 %, b.p. 95—97 °C (0.01 Torr), n_D^{20} = 1.5930, m.p. 51—52 °C, *cf.* Ref. 8: m.p. 51 °C.

2-(5-Chlorothenylidene)-6-methylcyclohexanone (2e), yield 51 %, m.p. 105—107 °C (*i*-PrOH). Found (%): C, 60.24; H, 5.43; Cl, 14.74; S, 13.25. $C_{12}H_{13}ClOS$. Calculated (%): C, 59.87; H, 5.43; Cl, 14.73; S, 13.32.

2-(5-Methylfurfurylidene)-6-methylcyclohexanone (2f), yield 89.6 %, b.p. 128—130 °C (0.1 Torr), m.p. 41—42 °C. Found (%): C, 75.94; H, 8.05. $C_{13}H_{16}O_2$. Calculated (%): C, 76.44; H, 7.90.

2-(5-Chlorofurfurylidene)-6-methylcyclohexanone (2g), yield 34 %, b.p. 118—121 °C (0.05 Torr), m.p. 63—64 °C. Found (%): C, 64.01; H, 5.91. $C_{12}H_{13}ClO_2$. Calculated (%): C, 64.15; H, 5.83.

6-Benzylidene-2,2-dimethylcyclohexanone (3a). Ketone **2a** (18.5 g, 92.5 mmol) was added to a solution of *t*-BuOK (31.3

g, 279 mmol) in *t*-BuOH (280 mL) under an inert atmosphere (Ar). The mixture was stirred for 15 min and then cooled in an ice bath, MeI (50.8 g, 358 mmol) was added dropwise and the mixture was refluxed for 1.5 h. After removal of the solvent *in vacuo*, water was added to the residue, the precipitate was filtered off, dried, and recrystallized from *i*-PrOH to give ketone **3a** (14.7 g, 74 %), m.p. 82—83 °C, *cf.* Ref. 7: m.p. 82—83 °C.

The other 2,2-dimethyl-6-arylidenecyclohexanones (**3b—g**) were obtained using similar procedures.

6-(3-Methylbenzylidene)-2,2-dimethylcyclohexanone (3b), yield 34 %, m.p. 63—64 °C. Found (%): C, 83.69; H, 9.14. $C_{16}H_{20}O$. Calculated (%): C, 84.16; H, 8.83.

6-(3-Chlorobenzylidene)-2,2-dimethylcyclohexanone (3c), yield 95 %, m.p. 95—96 °C (*i*-PrOH). Found (%): C, 71.93; H, 6.78. $C_{15}H_{17}ClO$. Calculated (%): C, 72.43; H, 6.89.

6-Furfurylidene-2,2-dimethylcyclohexanone (3d), yield 73.5 %, b.p. 106—108 °C (0.06 Torr), n_D^{20} = 1.5754. Found (%): C, 76.12; H, 7.82. $C_{13}H_{16}O_2$. Calculated (%): C, 76.34; H, 7.89.

6-(5-Chlorothenylidene)-2,2-dimethylcyclohexanone (3e), yield 82 %, m.p. 68—69 °C (*i*-PrOH). Found (%): C, 61.15; H, 6.01; Cl, 13.93; S, 12.27. $C_{13}H_{15}ClOS$. Calculated (%): C, 61.29; H, 5.94; Cl, 13.92; S, 12.58.

6-(5-Methylfurfurylidene)-2,2-dimethylcyclohexanone (3f), yield 68.1 %, m.p. 45—46 °C. Found (%): C, 76.88; H, 8.23. $C_{14}H_{18}O_2$. Calculated (%): C, 77.03; H, 8.31.

6-(5-Chlorofurfurylidene)-2,2-dimethylcyclohexanone (3g), yield 87 %, m.p. 71—72 °C. Found (%): C, 64.95; H, 6.17. $C_{13}H_{15}ClO_2$. Calculated (%): C, 65.41; H, 6.33.

8-Benzylidene-4,4-dimethyl-1-oxaspiro[2.5]octane (4a). A solution of *t*-BuOK (9.4 g, 84 mmol) in DMSO (41 mL) was added dropwise to a mixture of ketone **3a** (14.3 g, 67 mmole) and Me_3SI (19.2 g, 94 mmol) in DMSO (41 mL) for 30 min while the reaction mixture was cooled on an ice bath. After stirring for 15 min, the mixture was cooled in an ice—salt bath and then water (200 mL) was added dropwise for 30 min. The mixture was extracted with Et_2O, and the organic layer was washed with water and dried over $MgSO_4$. After removal of the solvent the residue was recrystallized from isooctane to give oxirane **4a** (14.9 g, 97 %), m.p. 51—52 °C. Found (%): C, 84.33; H, 8.89. $C_{16}H_{20}O$. Calculated (%): C, 84.17; H, 8.83.

The other 8-arylidene-4,4-dimethyl-1-oxaspiro[2.5]octanes (**4b—e**) were prepared using similar procedures.

8-(3-Methylbenzylidene)-4,4-dimethyl-1-oxaspiro[2.5]-octane (4b), quantitative yield, m.p. 45—47 °C; Found (%): C, 84.51; H, 9.18. $C_{17}H_{22}O$. Calculated (%): C, 84.25; H, 9.15.

8-(3-Chlorobenzylidene)-4,4-dimethyl-1-oxaspiro[2.5]-octane (4c) yield 81 %, m.p. 66—67 °C. Found (%): C, 72.83; H, 7.05. $C_{16}H_{19}ClO$. Calculated (%): C, 73.13; H, 7.29.

8-Furfurylidene-4,4-dimethyl-1-oxaspiro[2.5]octane (4d), yield 72 %, b.p. 90—93 °C (0.05 Torr) n_D^{20} = 1.5462. Found (%): C, 77.21; H, 8.27. $C_{14}H_{18}O_2$. Calculated (%): C, 77.03; H, 8.31.

8-(5-Chlorothenylidene)-4,4-dimethyl-1-oxaspiro[2.5]-octane (4e) was purified by chromatography on silica gel L (100/250 μm). Ratio of sorbent to substance 60 : 1, eluent: ethyl acetate : hexane, 1 : 25. Yield 68 %, oil, n_D^{25} = 1.5457. Found (%): C, 62.37; H, 6.31. $C_{14}H_{17}ClOS$. Calculated (%): C, 62.56; H, 6.38.

1-Furyl-4,4-dimethyl-1,3,4,5,6,7-hexahydroisobenzofurans (5f, g) were formed from 2,2-dimethyl-6-furfurylidene-cyclohexanones (**3f, g**) under conditions of the synthesis of 8-benzylidene-4,4-dimethyl-1-oxaspiro[2.5]octane (**4a**).

1-(5-Methylfuryl)-4,4-dimethyl-1,3,4,5,6,7-hexahydro-isobenzofuran (5f), yield 76 %, b.p. 95—96 °C (0.08 Torr), n_D^{25} = 1.5119. Found (%): C, 76.97; H, 8.63. $C_{15}H_{20}O_2$. Calculated (%): C, 77.55; H, 8.68.

1-(5-Chlorofuryl)-4,4-dimethyl-1,3,4,5,6,7-hexahydro-isobenzofuran (5g), yield 56 %, b.p. 92—93 °C (0.08 Torr), n_D^{25} = 1.5145. Found (%): C, 65.86; H, 6.42. $C_{14}H_{17}ClO_2$. Calculated (%): C, 66.53; H, 6.78.

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