[Chem. Pharm. Bull. 33(7)3001—3005(1985)]

Reduction of Vinylogous Thioesters with Lithium Aluminum Hydride. II.[1] Reduction of 2-Methyl-3-phenylthio-5-substituted-2-cyclopentenones[2]

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(Received October 5, 1984)

2,5-Dimethyl-3-phenylthio-2-cyclopentenone (IIb) and 5-*tert*-butyl-2-methyl-3-phenylthio-2-cyclopentenone (IIc) were reduced with an excess of lithium aluminum hydride (LAH) in ether to give quantitatively the corresponding 1,2-addition products, 2,5-dimethyl-3-phenylthio-2-cyclopentenol (IIIb) and 5-*tert*-butyl-2-methyl-3-phenylthio-2-cyclopentenol (IIIc), respectively. Compound IIIb was transformed into the vinylsulfide (IVb) and the enone (Vb) on standing at room temperature, whereas IIIc was transformed into the diene (VII).

5-*tert*-Butyl-2-methyl-3-phenoxy-2-cyclopentenone (IX) gave 3-*tert*-butyl-1-methyl-5-phenoxycyclopentene (XI) in 63.1% yield on reduction with LAH in ether.

Keywords——vinylogous ester; vinylogous thioester; reduction; lithium aluminum hydride; 3-phenylthio-2-cyclopentenone

We previously reported[1] the reduction of 5,5-dimethyl-3-phenylthio-2-cyclohexenone (I) and 2-methyl-3-phenylthio-2-cyclopentenone (IIa) with an excess of lithium aluminum hydride (LAH), and the transformations of these products. The results are shown in Chart 1.

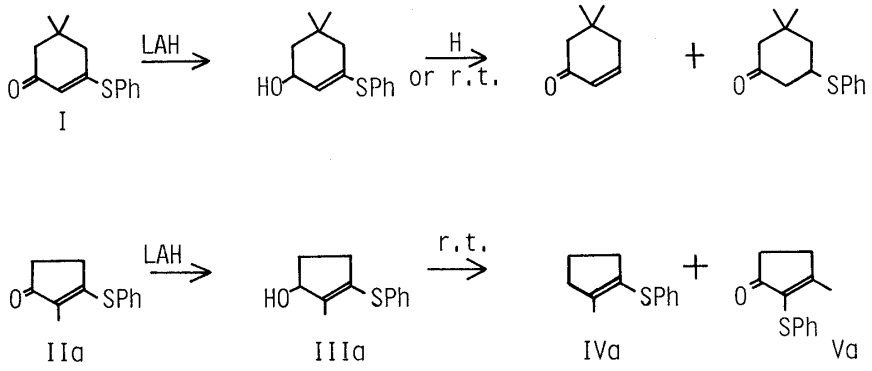

Chart 1

Stimulated by the interesting results obtained with these vinylogous thioesters (VTE), we investigated the reduction of asymmetric five-membered VTE, 2,5-dimethyl-3-phenylthio-2-cyclopentenone (IIb) and 5-*tert*-butyl-2-methyl-3-phenylthio-2-cyclopentenone (IIc). Compound IIb was prepared from 2,4-dimethylcyclopentane-1,3-dione[3] *via* the bromide together with an isomer, 2,4-dimethyl-3-phenylthio-2-cyclopentenone (IIb′). The purification of IIb was performed by silica gel column chromatography. Compound IIb showed a triplet signal ($J=1.5$ Hz, homoallyl coupling[4]) at δ 1.75 ppm due to the C_2-methyl protons in the nuclear magnetic resonance (NMR) spectrum. It was also obtained from IIa by treatment with lithium diisopropylamide (LDA) and methyl iodide.[5] The reduction of IIb with an

excess of LAH in ether, followed by work-up with ammonium chloride–water, gave only a mixture of geometrical isomers of 2,5-dimethyl-3-phenylthio-2-cyclopentenol (IIIb) (*cis*:*trans*=1:3.8). In the NMR spectrum, the signal due to the C_1-proton of the *cis* isomer appeared at δ 4.48 ppm as a doublet (J=6.3 Hz) and that of the *trans* isomer appeared at δ 4.23 ppm as a doublet (J=5.4 Hz). Thus, it was reconfirmed that five-membered VTE give only the 1,2-addition products, in contrast to the five-membered vinylogous ester (VE).[3] Compound IIIb was unstable, like IIIa,[1] and gradually changed on standing at room temperature to yield mainly two compounds, 2,4-dimethyl-1-phenylthiocyclopentene (IVb) and 3,5-dimethyl-2-phenylthio-2-cyclopentenone (Vb). Compound IVb showed a triplet signal (J=2 Hz) at δ 1.90 ppm due to the C_2-methyl protons in the NMR spectrum. This observation ruled out an alternative isomer (IVb′).[4] Compound Vb showed a carbonyl band at 1708 cm^{-1} in the infrared (IR) spectrum and a singlet signal at δ 2.28 ppm due to the C_3-methyl protons in the NMR spectrum. The mass spectrum (MS) revealed that Vb was an isomer of IIb.

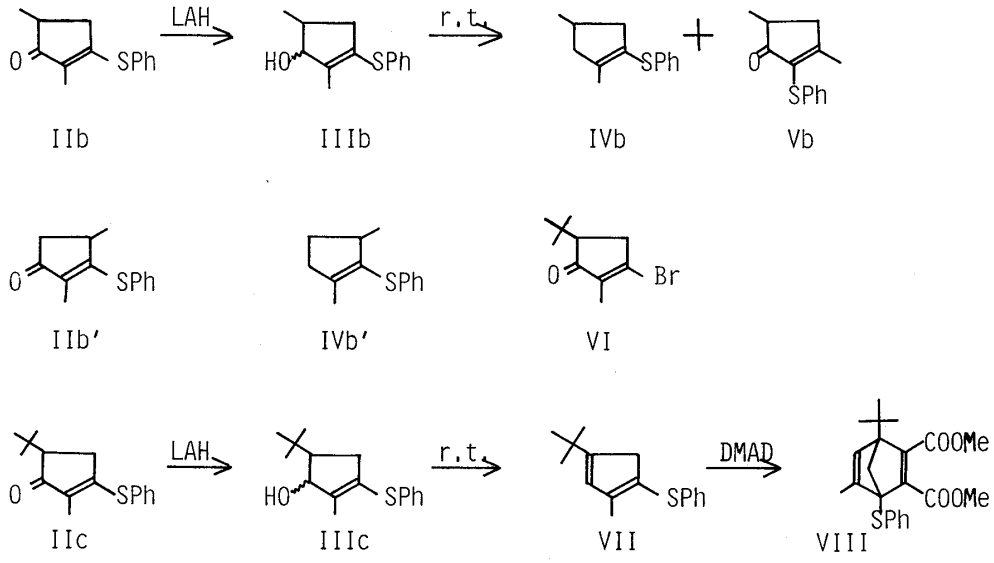

Chart 2

Compound IIc was prepared from the corresponding β-diketone[6] *via* 3-bromo-5-*tert*-butyl-2-methyl-2-cyclopentenone (VI); VI was not accompanied with the corresponding positional isomer. The product (IIc) showed a triplet signal (J=2 Hz) at δ 1.76 ppm due to the vinylic methyl protons. When IIc was reduced with an excess of LAH, it gave an isomeric mixture of 5-*tert*-butyl-2-methyl-3-phenylthio-2-cyclopentenol (IIIc). The ratio of *cis* and *trans* (3:2) was calculated from the integral values of the C_1-proton (*cis*: δ 4.55 ppm, J= 6.0 Hz; *trans*: δ 4.47 ppm, J=3.5 Hz) in the NMR spectrum. The larger ratio of *cis* to *trans* compared with that in IIIc is attributable to the steric hindrance induced by the vicinal *tert*-butyl group in the reduction. Compound IIIc changed gradually at room temperature into 4-*tert*-butyl-2-methyl-1-phenylthio-1,3-cyclopentadiene (VII), which showed a triplet signal (J=2.0 Hz) at δ 2.04 ppm and a singlet signal at δ 6.08 ppm due to the C_2-methyl and C_3-vinylic protons, respectively. Compound VII formed an adduct (VIII) on treatment with dimethyl acetylenedicarboxylate (DMAD). The formula of VIII was confirmed by high-resolution MS. Thus, five-membered VTE (II) examined above showed similar behavior to six-membered VTE (I), in contrast with VE, toward an excess of LAH. Furthermore on standing at room temperature, IIIb underwent a disproportionation reaction, as did IIIa, and IIIc gave the dehydrated product.

In the light of the interesting behavior of IIIc and 5-*tert*-butyl-3-methoxy-2-methyl-2-

cyclopentenone with LAH,[6] the reduction of 5-*tert*-butyl-2-methyl-3-phenoxy-2-cyclopentenone (IX) was examined. The bromide (VI) was treated with phenol in the presence of sodium hydroxide in ethanol to give IX and 5-*tert*-butyl-3-ethoxy-2-methyl-2-cyclopentenone (X) in yields of 48.4 and 37.4%, respectively. When VI was warmed at 50 °C with sodium phenoxide in dimethylsulfoxide (DMSO), it afforded IX in 60.1% yield. Compound IX was reduced with LAH in ether to give mainly 3-*tert*-butyl-1-methyl-5-phenoxycyclopentene (XI) in 63.1% yield. Compound XI showed no carbonyl band in the IR spectrum and exhibited a broad signal due to vinylic methyl protons at δ 1.83 ppm in the NMR spectrum. It was treated with bromine in carbon tetrachloride to give an isomeric mixture of 1,2,3-tribromo-4-*tert*-butyl-2-methylcyclopentane (XII) and 2,4,6-tribromophenol. The structures of XI and XII were confirmed by elemental analyses. In the reduction of IX, 5-*tert*-butyl-2-methylcyclopentanone (XIII), 4-*tert*-butyl-2-methyl-2-cyclopentenone (XIV), 5-*tert*-butyl-2-methyl-2-cyclopentenol (XV), and 3-*tert*-butyl-1-methylcyclopentan-1,2-diol (XVI) were detected as minor product. Compound XIV was transformed to its 2,4-dinitrophenylhydrazone (2,4-DNPH) derivative and the structures of other minor products were suggested by comparison of the gas chromatographic behavior with that of authentic samples obtained previously in our laboratory.[6] The formation of the abnormal reduction product, XI, could be rationalized as shown in Chart 3, but such behavior has not hitherto been observed in alkyl cyclic VE, and further studies are required.

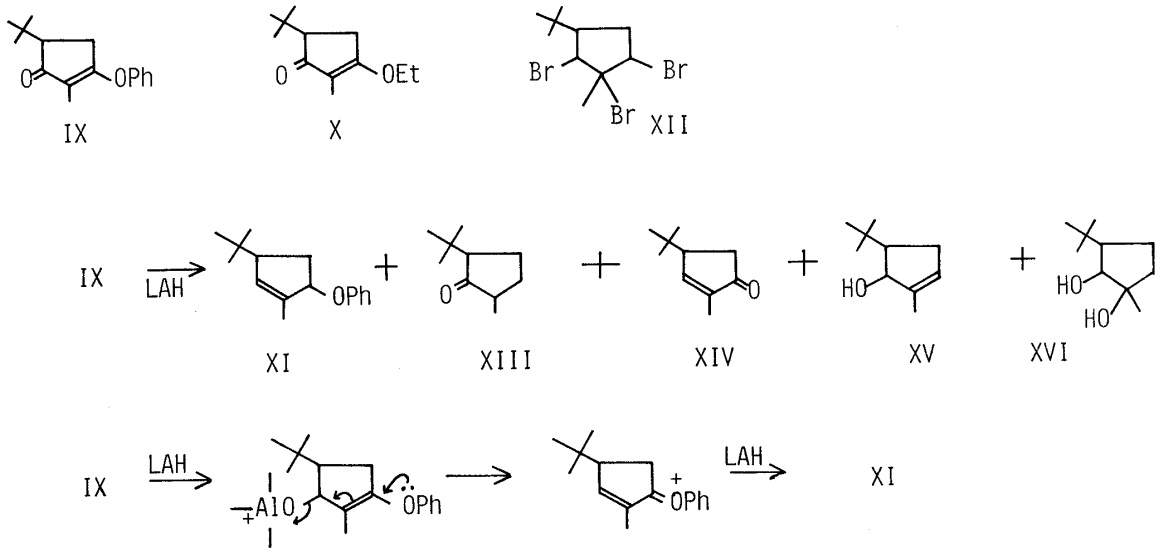

Chart 3

Experimental

All melting points and boiling points are uncorrected. IR spectra were determined by using a JASCO IRA-1 diffraction grating spectrophotometer; absorption data are given in cm^{-1}. Ultraviolet (UV) spectra were obtained in MeOH with a Hitachi 200-01 or 220 spectrophotometer, and absorption maxima are given in nm. Gas chromatography (GC) was carried out on a Shimadzu GC-6AM instrument with a stainless-steel column packed with 5% SE-30. The velocity of N_2 gas flow was 40 ml/min. MS were measured with a JEOL D-200 (70 eV, direct inlet system) spectrometer. GC-MS were taken with a JEOL D-300 instrument. NMR spectra were recorded on JEOL PMX-60 and Varian XL-200 spectrometers with tetramethylsilane (TMS) as an internal standard. The chemical shifts, coupling constants (J), and half-width ($W_{1/2h}$) values are given in δ, Hz, and Hz, respectively. All solvents were removed by evaporation under reduced pressure after drying of the solution over anhyd. Na_2SO_4.

2,5-Dimethyl-3-phenylthio-2-cyclopentenone (IIb)——i) A mixture of PBr_3 (55.0 g, 203 mmol), 2,4-dimethylcyclopentane-1,3-dione[3] (8.51 g, 67.5 mmol) and $CHCl_3$ (40 ml) was refluxed overnight, and then poured into ice-water. The organic layer was washed with 5% NaOH and brine. The residue (6.3 g) obtained after removal of the solvent was distilled to give an isomeric mixture of the bromide. bp < 100 °C (9 mmHg). The bromide (6.3 g,

33.2 mmol) was added to an aq. ethanolic mixture of PhSH (3.8 g, 34.5 mmol) and NaOH (1.76 g, 44 mmol) with stirring under ice-cooling, and the whole was stirred overnight at r.t. The mixture was extracted with Et_2O and the organic layer was washed with brine. The residue obtained after removal of the solvent was fractionated through an SiO_2 column. The benzene eluates afforded IIb and 2,4-dimethyl-3-phenylthio-2-cyclopentenone (IIb′) successively. IIb was recrystallized from hexane. 1.15 g (15.9%). mp 67—78 °C (dec.). IR (Nujol): ν 1690, 1605. NMR (CCl_4): 1.06 (3H, d, $J=6$, C_5-Me), 1.75 (3H, t, $J=1.5$, C_2-Me), 1.8—2.9 (3H, m), 7.2—7.7 (5H, s like). *Anal.* Calcd for $C_{13}H_{14}OS$: C, 71.52; H, 6.46. Found: C, 71.55; H, 6.54. IIb-2,4-DNPH: mp 191—192 °C (recrystallized from EtOH). MS *m/e*: 398 (M^+, base peak). *Anal.* Calcd for $C_{19}H_{18}N_4O_4S \cdot 1/5\,H_2O$: C, 56.76; H, 4.61; N, 13.94. Found: C, 56.87; H, 4.45; N, 14.09. 1 : 1 mixture of IIb and IIb′: 1.42 g (19.6%). bp < 170 °C (2 mmHg). IIb′: NMR (CCl_4): 1.04 (3H, d, $J=6$, C_4-Me), 1.75 (3H, d, $J=1.5$, C_2-Me).

ii)[5] A tetrahydrofuran (THF) soln. of 2-methyl-3-phenylthio-2-cyclopentenone (IIa, 321 mg, 1.57 mmol) was added to an LDA soln. in THF [prepared from diisopropylamine (191 mg, 1.89 mmol) and *n*-BuLi (1.55 M, 1.21 ml, 1.89 mmol)] at −78 °C. MeI (0.24 ml, 3.93 mmol) in THF was added to the mixture at the same temperature. The temperature was allowed to rise to r.t., and water (1 ml) was added to stop the reaction. The residue obtained after concentration was dissolved in $CHCl_3$. The solution was washed with 5% HCl and brine, then evaporated, and the residue was fractionated through an SiO_2 column. IIb eluted with benzene and was recrystallized from Et_2O–hexane. mp 60—64.5 °C. The NMR spectrum was superimposable on that of an authentic sample. 278 mg (81.0%).

Reduction of IIb——IIb (0.3 g, 1.38 mmol) in Et_2O was added to a suspension of LAH (311 mg, 8.19 mmol) in Et_2O with stirring at r.t., and the mixture was stirred for 2.5 h at r.t., then refluxed for 2.5 h. NH_4Cl (2.1 g) and water were added, and the reaction mixture was filtered. The filtrate was concentrated to give 2,5-dimethyl-3-phenylthio-2-cyclopentenol (IIIb). 0.26 g. GC (200 °C) t_R: 1.5 min. IR (neat): 1590, 3380 (br). NMR (CCl_4): 1.90 (3H, br s), 4.23 (d, $J=5.4$, *trans* C_1-H), 4.48 (d, $J=6.3$, *cis* C_1-H). MS *m/e* (%): 220 (M^+, 43), 202 ($M^+ - H_2O$, base peak). The crude IIIb was allowed to stand at r.t. for 25 d. The products were fractionated through an SiO_2 column. Elution with benzene and $CHCl_3$ provided 2,4-dimethyl-1-phenylthiocyclopentene (IVb) and 3,5-dimethyl-2-phenylthio-2-cyclopentenone (Vb), respectively. IVb: GC (200 °C) t_R: 1.1 min. IR (neat): 1590. NMR (CCl_4): 1.07 (3H, d, $J=7$, C_4-Me), 1.90 (3H, t, $J=2$, C_2-Me), 1.5—3.0 (5H, m), 7.30 (5H, s). MS *m/e* (%): 204 (M^+, 79), 95 ($M^+ - SPh$, base peak). Vb: GC (200 °C) t_R: 2.5 min. IR (neat): 1708. NMR ($CDCl_3$): 1.26 (3H, d, $J=8$, C_5-Me), 2.28 (3H, s, C_3-Me), 2.37 (1H, dm, $J=20$, C_4-H), 2.58 (1H, qdd, $J=8$, 8, 3, C_5-H), 3.02 (1H, dd, $J=20$, 8, C_4-H). MS *m/e* (%): 218 (M^+, base peak), 203 ($M^+ - Me$, 19). Vb-2,4-DNPH: mp 157—158 °C (recrystallized from EtOH). MS *m/e* (%): 398 (M^+, 93), 289 ($M^+ - SPh$, 61), 216 ($C_{13}H_{14}NS$, base peak). High-resolution MS Calcd for $C_{19}H_{18}N_4O_4S$: 398.1048. Found: 398.1013.

5-*tert*-Butyl-2-methyl-3-phenylthio-2-cyclopentenone (IIc)——3-Bromo-5-*tert*-butyl-2-methyl-2-cyclopentenone (VI) was prepared from 4-*tert*-butyl-2-methylcyclopentane-1,3-dione[6] (2 g, 12.0 mmol) and PBr_3 (10 g, 36.0 mmol) in a manner similar to that used in the case of IIb, in a yield of 62.2%. VI: bp < 130 °C (0.1 mmHg). NMR (CCl_4): 1.00 (9H, s), 1.73 (3H, t, $J=2$, C_2-Me), 2.25 (1H, dd, $J=6.5$, 3, C_4-H), 2.7—3.0 (2H, m, C_4- and C_5-H). *Anal.* Calcd for $C_{10}H_{15}BrO \cdot 1/5\,H_2O$: C, 51.16; H, 6.61. Found: C, 51.25; H, 6.43. An ethanolic soln. of VI (532 mg, 2.3 mmol) was added to an aq. ethanolic mixture of PhSH (300 mg, 2.72 mmol) and NaOH (145 mg, 3.63 mmol) under ice-cooling with stirring. After the mixture had been stirred for 2 h at r.t., water was added to precipitate IIc. IIc obtained by filtration was recrystallized from aq. EtOH. White needles. mp 85—88 °C. The yield was 503 mg (83.8%). IR (Nujol): $\nu_{C=O}$ 1680, $\nu_{C=C}$ 1598. UV λ_{max} (ε): 287 (19300). MS *m/e* (%): 260 (M^+, 7), 204 ($M^+ - CH_2=C(CH_3)_2$, base peak), 110 (58). NMR (CCl_4): 0.88 (9H, s), 1.76 (3H, t, $J=2$, C_2-Me), 2.0—2.2 (2H, m, C_4-H), 2.2—2.5 (1H, m, C_5-H), 7.3—7.7 (5H, m, aromatic H). *Anal.* Calcd for $C_{16}H_{20}OS$: C, 73.80; H, 7.74. Found: C, 73.90; H, 7.85.

Reduction of IIc——An ethereal soln. of IIc (228 mg, 0.88 mmol) was added to a suspension of LAH (240 mg, 6.3 mmol) at r.t., and the mixture was stirred for 1 h. After being refluxed for 1 h, the mixture was worked up as usual to give 5-*tert*-butyl-2-methyl-3-phenylthio-2-cyclopentenol (IIIc) as a mixture of *cis* and *trans* isomers (3 : 2). 226 mg (quantitative). IR ($CHCl_3$): ν_{OH} 3430 (br), 3600 (sharp), $\nu_{C=C}$ 1580. NMR ($CDCl_3$): 0.86 and 1.00 (9H, each s, *tert*-Bu), 1.85 (3H, br s, vinyl Me), 4.47 (d, $J=3.5$, *trans* C_1-H), 4.55 (d, $J=6.0$, *cis* C_1-H). MS *m/e* (%): 262 (M^+, 19), 244 ($M - H_2O$, 27), 229 (*m/e* 244 − Me, 35), 204 ($M^+ - C_4H_{10}$, base peak). High-resolution MS Calcd for $C_{16}H_{21}OS$ ($M^+ - 1$): 261.1312. Found: 261.1445. IIIc changed gradually to 4-*tert*-butyl-2-methyl-1-phenylthio-1,3-cyclopentadiene (VII) during 3 d at r.t. bp < 150 °C (0.5 mmHg). NMR (CCl_4): 1.12 (9H, s, *tert*-Bu), 2.04 (3H, t, $J=2.0$), 3.0—3.2 (2H, m, $>CH_2$), 6.08 (1H, br s, vinylic H), 7.07 (5H, br s, aromatic H). MS *m/e* (%): 244 (M^+, 73), 229 ($M^+ - Me$, 68), 188 ($M^+ - C_4H_8$, 42), 119 (*m/e* 229 − PhSH, base peak). A benzene soln. of VII (184 mg, 0.75 mmol) and DMAD (128 mg, 0.9 mmol) was refluxed for 3 h. GC (200 °C) t_R: 1.3 min (VII), 7.2 (DMAD adduct, VIII). VIII: NMR ($CDCl_3$): 1.37 (9H, s, *tert*-Bu), 2.14 (3H, s, vinylic Me), 3.80 and 3.83 (each 3H, s, OMe), 7.37 (5H, br s, aromatic H). MS *m/e* (%): 386 (M^+, 92.4), 329 ($M^+ - C_4H_9$, 92.4), 316 ($C_6H_2(CH_3)(SPh)(COOMe)_2$, base peak), 285 (*m/e* 316 − OMe, 77.2). High-resolution MS Calcd. for $C_{22}H_{26}O_4S$: 386.1552. Found: 386.1594.

Reaction of VI and Phenol——i) An ethanolic soln. of VI (1.69 g, 7.3 mmol) was added to an aq. mixture of phenol (0.76 g, 8.0 mmol) and NaOH (0.46 g, 11.5 mmol). After being refluxed for 3.5 h, the mixture was poured into ice-water and extracted with Et_2O. The organic layer was washed with brine and dried. The residue (1.45 g) obtained after removal of the solvent was crystallized and recrystallized from *n*-hexane to give 5-*tert*-butyl-3-ethoxy-2-methyl-

2-cyclopentenone (X, 102 mg). The mother liquid was fractionated by SiO_2 column chromatography. 5-*tert*-Butyl-2-methyl-3-phenoxy-2-cyclopentenone (IX, 866 mg) and X (433 mg) were eluted successively with benzene. IX was distilled and then crystallized. IX: bp135—145 °C (1.3—1.4 mmHg). mp 42—46 °C. GC (170 °C) t_R: 3.4 min. IR (Nujol): $\nu_{C=O}$ 1645, $\nu_{C=C}$ 1590. NMR ($CDCl_3$): 0.94 (9H, s, *tert*-Bu), 1.57 (3H, t, J=2.0, vinylic Me), 1.9—2.8 (3H, m), 6.7—7.7 (5H, m, aromatic H). *Anal.* Calcd for $C_{16}H_{20}O_2 \cdot 1/20\,H_2O$: C, 78.36; H, 8.26. Found: C, 78.24; H, 8.24. X: mp 79—81 °C. GC (170 °C) t_R: 1.2 min. IR (Nujol): ν 1620. NMR ($CDCl_3$): 1.01 (9H, s, *tert*-Bu), 1.37 (3H, t, J=6.5, $-CH_2\underline{CH_3}$), 1.54 (3H, t, J=2.0, vinylic Me), 1.9—2.6 (3H, m), 4.20 (2H, q, J=6.5, OCH_2). *Anal.* Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.69; H, 10.24.

ii) A mixture of VI (3.57 g, 15.4 mmol) and PhONa (2.14 g, 18.4 mmol) in DMSO was warmed at 50 °C for 5.5 h. The mixture was diluted with water and then extracted with Et_2O. The organic layer was washed with 5% HCl and water. The residue (3.38 g) obtained after removal of the dried solvent was fractionated through an SiO_2 column. VI (357 mg, 10.0%) and IX (2.27 g, 60.1%) were eluted with *n*-hexane–Et_2O (97 : 3) and benzene, respectively.

Reduction of IX——IX (646 mg, 2.6 mmol) was added to a suspension of LAH (600 mg, 15.8 mmol) in Et_2O at r.t. during 10 min and the mixture was stirred at r.t. for 2 h. After being refluxed for 2 h, the mixture was worked up as usual to give an oily residue (533 mg). GC-MS (the temperature was allowed to raise from 100 °C to 270 °C) t_R (min): 0.8 (PhOH), 1.5 (5-*tert*-butyl-2-methylcyclopentanone, XIII), 1.6 (5-*tert*-butyl-2-methyl-2-cyclopentenol, XV), 2.3 (4-*tert*-butyl-2-methyl-2-cyclopentenone, XIV), 3.0 (3-*tert*-butyl-1-methylcyclopentan-1,2-diol, XVI), and 7.4 (3-*tert*-butyl-1-methyl-5-phenoxycyclopentene, XI). The structures were determined by GC, by co-injection with authentic samples.[6] The product was micro-distilled. XI: 385 mg (63.1%). bp < 130 °C (3 mmHg). NMR ($CDCl_3$): 0.76 and 0.80 (9H, each s, *tert*-Bu), 1.73 (3H, br s, vinylic Me), 4.86—5.04 (1H, m, OCH<), 5.50—5.70 (1H, m, vinylic H), 6.8—7.0 and 7.1—7.4 (5H, m, aromatic H). *Anal.* Calcd for $C_{16}H_{22}O \cdot 1/5\,H_2O$: C, 82.14; H, 9.65. Found: C, 82.29; H, 9.56. XIV-2,4-DNPH: mp 181—183 °C (red prisms by repeated recrystallization from EtOH). MS *m/e* (%): 332 (M^+, 19), 275 ($M^+ - tert$-Bu, 43), 57 (*tert*-Bu, base peak). *Anal.* Calcd for $C_{16}H_{20}N_4O_4$: C, 57.82; H, 6.07; N, 16.86. Found: C, 57.71; H, 6.30; N, 16.74. XI was brominated with a small excess of Br_2 in CCl_4. The residue obtained after removal of the solvent was purified through an SiO_2 column to give 1,2,3-tribromo-4-*tert*-butyl-2-methylcyclopentane (XII) and 2,4,6-tribromophenol from the hexane and benzene fractions, respectively, in good yields. XII: GC (70 °C) t_R: 2.2 min. NMR ($CDCl_3$): 1.01 and 1.06 (each s, *tert*-Bu), 2.01, 2.09, and 2.13 (each s, CH_3), 2.0—3.2 (m), 3.9—4.2, 4.5—4.7, and 4.8—5.0 (each m, >CH–Br). *Anal.* Calcd for $C_{10}H_{17}Br_3$: C, 31.86; H, 4.55. Found: C, 32.17; H, 4.51.

References and Notes

1) Part I: K. Matoba, M. Tokizawa, T. Morita, and T. Yamazaki, *Chem. Pharm. Bull.*, **33**, 368 (1985).
2) A part of this work was presented at the 62nd Meeting of the Hokuriku Branch of the Pharmaceutical Society of Japan, Toyama, June 1984.
3) K. Matoba, N. Miyabayashi, and T. Yamazaki, *Yakugaku Zasshi*, **93**, 1401 (1973).
4) C. M. Cimarusti and J. Wolinsky, *J. Org. Chem.*, **31**, 4118 (1966).
5) M. Koreeda, Y. Liang, and H. Akagi, *J. Chem. Soc., Chem. Commun.*, **1979**, 449.
6) K. Matoba and T. Yamazaki, *Yakugaku Zasshi*, **93**, 1406 (1973).