The Pyrolyses of 1,1,4,4,-Tetraphenyl-1,4-butanediol and 1,1,4,4-Tetraphenyl-2-butene-1,4-diol Derivatives. Decomposition Reactions to Form Olefins *via* the Elimination of Two Mole Equivalents of the Hydroxydiphenylmethyl Radical

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The pyrolysis of 1,1,2,4,4-pentaphenyl-1,4-butandiol, *trans*-1,2-bis(hydroxydiphenylmethyl)hexane, *trans*-1,2-bis(hydroxydiphenylmethyl)indan, and *cis-endo*- and *trans*-1,2-bis(hydroxydiphenylmethyl)bicyclo[2.2.1]-heptane gave styrene, cyclohexene, indene, and norbornene respectively, accompanied by benzophenone and benzhydrol. The pyrolysis of *trans*-1,2-bis(hydroxydiphenylmethyl)spiro[2.6]nona-4,6,8-triene afforded indene *via* rearrangement to form *trans*-1,2-bis(hydroxydiphenylmethyl)indan. The pyrolysis of *cis*-1,1,4,4-tetraphenyl-2-butene-1,4-diol afforded 2,2,5,5-tetraphenyl-2,5-dihydrofuran. On the other hand, *trans*-1,1,4,4-tetraphenyl-2-butene-1,4-diol afforded 1,2,4,4-tetraphenyl-3-buten-1-one. The mechanisms of these decomposition reactions are discussed.

Generally, vic-dicarboxylic acids (**1**) can be synthesized by Diels-Alder reactions readily and usually in good yields.[1] The introduction of double bonds to such vic-dicarboxylic acids by the elimination of the two carboxyl groups is a useful reaction for the synthesis of many organic compounds. Several types of such reactions have been developed and used as powerful synthetic methods.[2]

It is known that the pyrolysis of benzopinacol (**5**) gives benzophenone (**3**) and benzhydrol (**4**) *via* a disproportionation reaction of the initially formed hydroxydiphenylmethyl radical (**6**).[3] We investigated the application of this decomposition reaction to the preparation of the olefins from **1** in the expectation that 1,1,4,4-tetraphenyl-1,4-butanediol derivatives (**2**), which can be prepared by the Grignard reaction of **1**, would be pyrolyzed to form the olefins eliminating two mole equivalents of **6**, which in turn disproportionates to **3** and **4**. Various types of **2** were synthesized and pyrolyzed. The pyrolysis of several kinds of 1,1,4,4-tetraphenyl-2-butene-1,4-diol derivatives were also investigated. Here, we wish to report on these results.

Preparations of Glycols

The reaction of a cyclohexane derivative (**7**) with phenyllithium afforded the corresponding diketone (**8**) in a 53% yield; this diketone gave *trans*-1,2-bis(hydroxydiphenylmethyl)hexane (**9**) in a 52% yield in a reaction with phenyllithium. *trans*-1,2-Bis(hydroxydiphenylmethyl)indan (**11**) was prepared in a 62% yield by reaction of phenyllithium with indane derivative (**10**).[4] *cis-endo*- and *trans*-5,6-Bis(hydroxydiphenylmethyl)bicyclo[2.2.1]hept-2-ene (**13a** and **13b**) were synthesized in 71 and 87% yields respectively, by reactions of the corresponding diesters (**12a** and **12b**) with phenyllithium. *cis-endo*- and *trans*-1,2-Bis(hydroxydiphenylmethyl)bicyclo[2.2.1]heptane (**14a** and **14b**) were obtained almost quantitatively by catalytic hydrogenations of **13a** and **13b** respectively. *cis-endo*-8,9-Bis(hydroxydiphenylmethyl)tricyclo[3.2.2.$0^{2,4}$]non-2-ene (**17**) was synthesized in a overall yield of 77% from a corresponding diester (**15**) by reaction with phenyllithium *via* the dicarbonyl compound (**16**). *cis*- and *trans*-1,1,4,4-

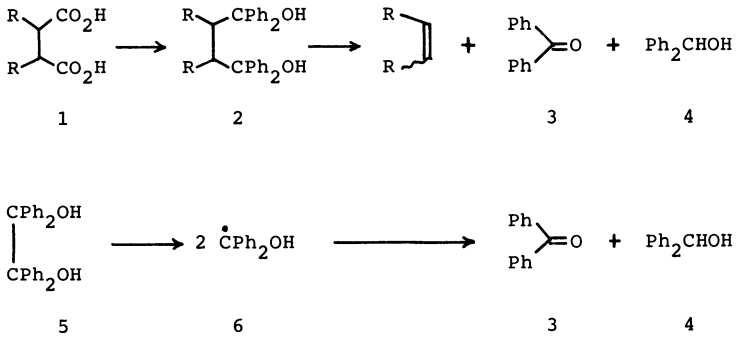


Fig. 1.

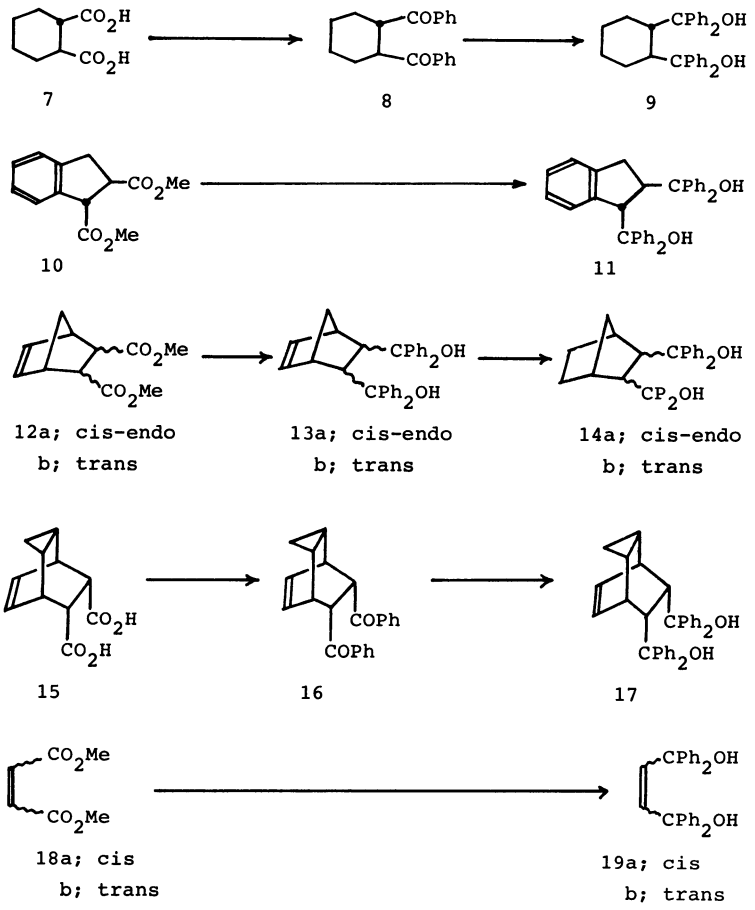


Fig. 2.

Tetraphenyl-2-butene-1,4-diol (**19a** and **19b**) were obtained in 25 and 31% yields respectively by reactions of the corresponding diesters (**18a** and **18b**) with phenyllithium.

1,1,2,4,4-Pentaphenyl-1,4-butandiol (**20**),[5] *trans*-1,2-bis(hydroxydiphenylmethyl)spiro[2.6]nona-4,6,8-triene (**30**),[6] and 1,2-bis(hydroxydiphenylmethyl)benzene (**35**)[7] were synthesized according to the literature.

Pyrolyses

Glycol **20** was pyrolyzed at 250 °C for 2 h to afford styrene (**21**, 40%), together with 1,1,3-triphenyl-1-propane (**22**, 11%), a cyclic ether (**23**, 46%), benzophenone (**3**, 60%), and benzhydrol (**4**, 10%). The pyrolysis of **9** under analogous conditions gave cyclohexene (**24**, 30%) accompanied by a cyclic ether (**25**, 35%), **3** (25%), and **4** (68%). The pyrolysis of **11** gave indene (**26**, 75%), **3** (99%), and **4** (60%). Pyrolysis of *cis-endo*-glycol **14a** afforded norbornene (**27**, 30%), along with a diphenylmethylene derivative (**28**, 37%), a cyclic ether (**29**, 9%), **3** (75%), and **4** (20%); on the other hand, the pyrolysis of *trans*-glycol **14b** gave **27** (27%), **28** (64%), **3** (95%), and **4** (15%). The cyclic ether **29** was not detected. The heating of **30** at 250 °C for 1 h afforded **26** (34%) and **11** (59%),[8] accompanied by **3** (44%) and **4** (26%).

The pyrolysis of *cis-endo*-glycol **13a** yielded cyclopentadiene (**31**, 55%), a cyclic ether **32** (68%), and **19a** (21%); on the other hand, *trans*-glycol **13b** afforded **31** (45%) and a diphenylmethylene derivative (**33**, 44%).[9] The pyrolysis of *cis-endo*-glycol **17** afforded tropylidene (**34**, 80%) and **32** (88%). The pyrolysis of *cis*-glyco **19a** afforded a cyclic ether **32** (53%) and **3** (58%), but *trans*-glycol **19b** gave **33** (45%). The pyrolysis of **35** was carried out at 350 °C in an autoclave, with *t*-butyl alcohol as the solvent, in order to trap benzyne, which was expected to be formed, but resulted in a quantitative formation of a cyclic ether **36**.[7]

Discussion

The mechanism of the formation of the olefins **21**, **24**, **26**, and **27** is considered to be as follows. A bond cleavage of the glycol **2** to form one mole equivalent of **6** gives a radical intermediate **37**, which affords the olefins by eliminating the other mole equivalent of **6**. On the other hand, the dehydration reaction of **2** forms **38**, which gives the diphenylmethylene deriva-

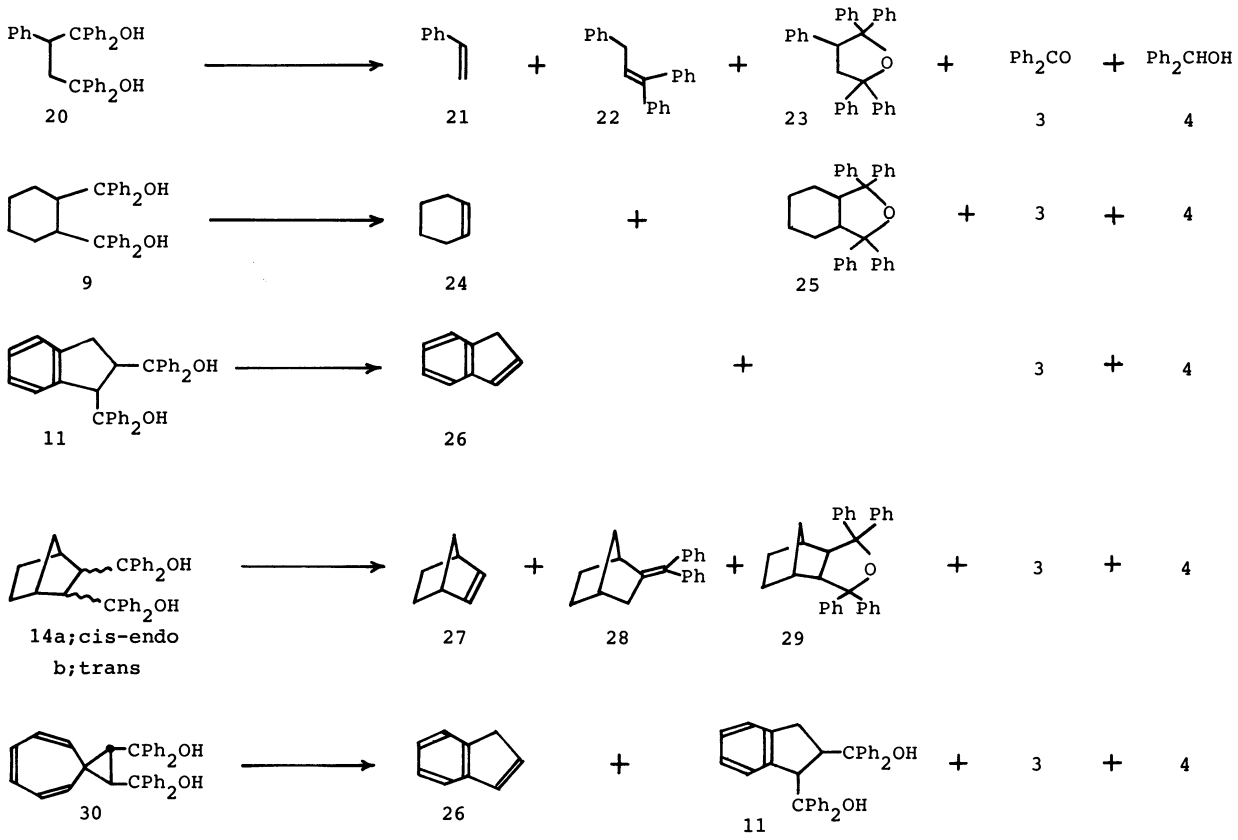


Fig. 3.

tive **39** by eliminating one mole equivalent of **6**.[10]

The formation mechanism of **33** can be considered to be as follows. An O–H bond fission of **19b**, followed by a 1,2-shift of the phenyl group, forms **40**, which gives **33** *via* a dehydration reaction.

The above-mentioned pyrolysis of the 1,2-bis(hydroxydiphenylmethyl) substituted hydrocarbons can be considered to be useful for the synthesis of olefinic compounds, because the desired olefins, styrene (**21**), cyclohexene (**24**), indene (**26**), and norbornene (**27**) are obtained. However, the other desired olefins, spiro[2.6]nonatetraene (**41**),[11] norbornadiene (**42**), and tricyclo[3.2.2.$0^{2,4}$]nonadiene (**43**) could not be obtained from the pyrolysis of **30**, **13**, and **17** respectively.

The spiro compound **30** is considered to have rearranged to **11** before the pyrolysis to afford **41** because of the high temperature.[8] The temperature needed by the pyrolysis seems also to be high enough to cause retro-Diels-Alder reactions in such compounds as **13** and **17**, which have double bonds at positions suitable for retro-Diels-Alder reactions. In order to cause the pyrolysis at lower temperature, pyrolyses of the glycols were also carried out in the presence of several kinds of radical initiators, however, no improvement was observed.

Experimental

All the melting and boiling points are uncorrected. The NMR spectra were measured with a Varian HA-100 or a Hitachi R-20B spectrometer with tetramethylsilane as the internal standard. The mass and IR spectra were recorded with Hitachi M-52 and DS-701G spectrometers respectively. Wako gel C-200 and Wako gel B-5F were used for column and thin-layer chromatography respectively.

All the pyrolysis reactions were carried out under a nitrogen stream without any solvent in a flask connected with three combined traps. The first trap was cooled with an ice–water bath while the second and last ones were cooled with a Dry Ice–acetone bath. Water formed by the dehydration reactions was swept away from the flask by a nitrogen stream and condensed in the first trap. The olefins formed were collected mainly in the second trap.

Preparations of Glycols

Preparation of **9**. A solution of **7** (6.88 g, 40 mmol) in anhydrous tetrahydrofuran (200 ml) was stirred with a solution of phenyllithium (320 mmol) in anhydrous ether (140 ml) at room temperature over a 1 h period. After further stirring at room temperature for 16 h, the reaction mixture was decomposed with water and extracted with ethyl acetate. The organic layer was washed with water and brine, and dried over anhydrous sodium sulfate. After

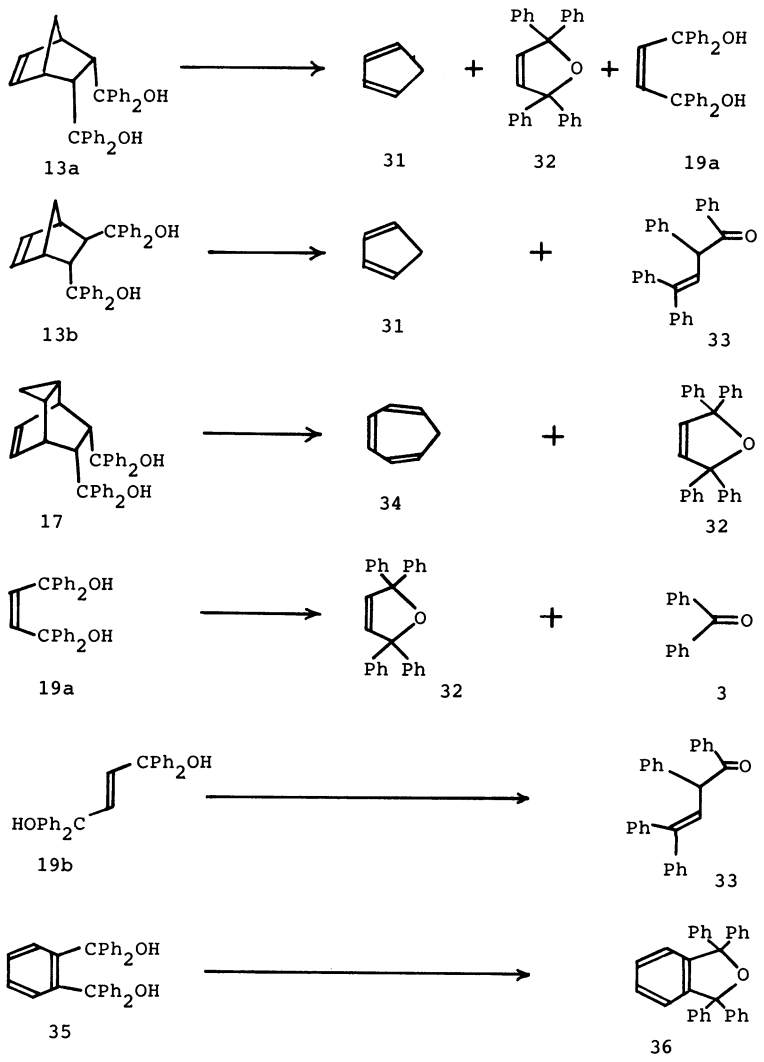

CPh2OH
CPh2OH
13a
31
Ph Ph
O
Ph Ph
32
CPh2OH
CPh2OH
19a
13b
33
17
34
19a
HOPh2C
19b
35
36

Fig. 4.

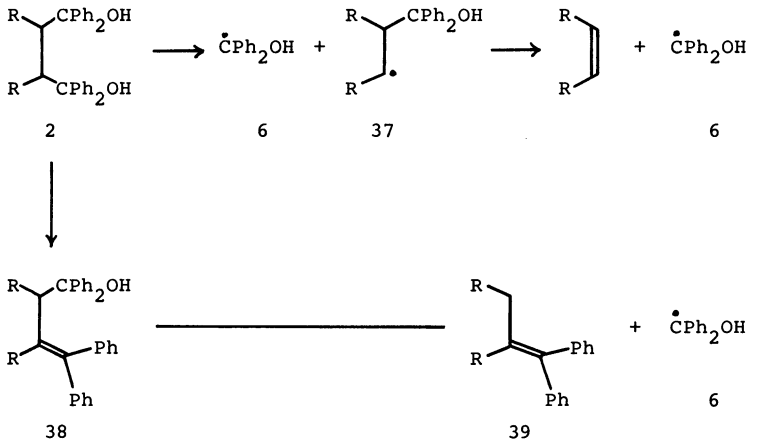
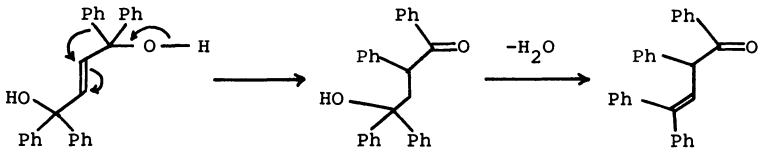
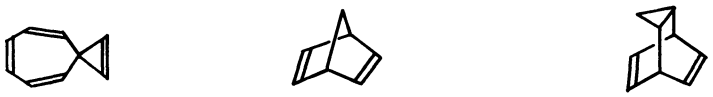

R
CPh2OH
2
6
37
38
39
Ph

Fig. 5.



19b 40 33

Fig. 6.



41 42 43

Fig. 7.

filtering, the solvent was removed on a rotary evaporator. The colorless residue was chromatographed on silica gel to give colorless crystals **8** (6.19 g, 53%) by the use of pet ether–benzene (3:7). Recrystallization from cyclohexane gave pure crystals of **8**.

8: Mp 115—116 °C. Found: C, 82.05; H, 6.86%. Calcd for $C_{20}H_{20}O_2$: C, 82.16; H, 6.89%. IR (KBr): 3100, 2950, 1670, 1600 cm^{-1}. ^1H NMR ($CDCl_3$) δ=1.43 (m, 8H), 3.82 (m, 2H), 7.0—7.5 (m, 10H). Mass *m/z* (rel intensity) 292 (M^+, 6.6), 105 (100), 77 (65).

A solution of **8** (7.70 g, 26 mmol) in anhydrous tetrahydrofuran (180 ml) was added to a solution of phenyllithium (204 mmol) in anhydrous ether (120 ml) at room temperature over a 1 h period and then further stirred for 20 h. The usual workup afforded a colorless tarry material, which was chromatographed on silica gel to give colorless crystals **9** (6.09 g, 52%) by the use of benzene–ether (9:1). Recrystallization from benzene gave pure crystals of **9**.

9: Mp 201—203 °C. Found: C, 84.57; H, 7.25%. Calcd for $C_{32}H_{32}O_2$: H, 85.67; H, 7.18%. IR (KBr): 3400, 3050, 1600 cm^{-1}. ^1H NMR ($CDCl_3$) δ=1.41 (m, 8H), 3.43 (m, 2H), 3.60 (bs, 2H), 7.1—7.5 (m, 20H). MS *m/z* (rel intensity) 430 (M^+, 25), 353 (100), 248 (71).

Preparation of ***11***. A solution of **10** (234 mg, 1 mmol) in anhydrous ether (10 ml) was added to a solution of phenyllithium (8 mmol) in anhydrous ether (10 ml) at room temperature, after which the mixture was stirred for 16 h. The usual workup gave a yellow oil, which was chromatographed on silica gel to give colorless crystals **11** (277 mg, 62%) by the use of benzene–ether (4:1). Recrystallization from ethyl acetate gave pure **11**.

11: Mp 189—190 °C. Found: C, 86.75; H, 6.23%. Calcd for $C_{35}H_{30}O_2$: C, 87.10; H, 6.27%. IR (KBr): 3570, 3070, 1600 cm^{-1}. ^1H NMR ($CDCl_3$) δ=2.05 (bs, 2H, OH), 2.65 (m, 1H), 2.95 (m, 1H), 3.46 (m, 1H), 4.42 (m, 1H), 6.28 (m, 1H), 6.75 (m, 1H), 6.93 (m, 1H), 7.0—7.4 (m, 21H). MS *m/z* (rel intensity) 446 (M^+), 282 (100), 191 (35), 183 (70), 167 (90).

Preparation of ***13a***. A solution of **12a** (420 mg, 2 mmol) in anhydrous ether (50 ml) was added to a solution of phenyllithium (16 mmol) in anhydrous ether (50 ml) at room temperature. After stirring at the boiling temperature for 4 h, the reaction mixture was treated as usual to give colorless crystals **13a** (650 mg, 71%), which were recrystallized from ethyl acetate.

13a: Mp 262—263 °C. Found: C, 86.44; H, 6.59%. Calcd for $C_{33}H_{30}O_2$: C, 86.43; H, 6.59%. IR (KBr): 3470, 3360, 1600 cm^{-1}. ^1H NMR ($CDCl_3$) δ=1.32 (m, 2H), 2.58 (bs, 2H), 4.24 (bs, 2H), 6.49 (m, 2H), 6.8—7.6 (m, 20H). MS *m/z* (rel intensity) 440 (M^+—18, 51), 381 (36), 258 (82), 183 (100), 167 (58).

Preparation of ***13b***. The same procedure as above, but using **12b** (420 mg, 2 mmol) and phenyllithium (16 mmol), gave colorless crystals **13b** (795 mg, 87%), which were then recrystallized from ethyl acetate.

13b: Mp 179—180 °C. Found: C, 86.38; H, 6.68%. Calcd for $C_{33}H_{30}O_2$: C, 86.43; H, 6.59%. IR (KBr): 3470, 3360, 1600 cm^{-1}. ^1H NMR ($CDCl_3$) δ=0.20 (m, 1H), 0.78 (m, 1H), 2.75 (bs, 2H), 3.07 (m, 1H), 3.52 (m, 1H), 3.80 (m, 1H), 5.20 (m, 1H), 6.28 (m, 1H), 6.83 (m, 1H). MS *m/z* (rel intensity) 458 (M^+, 5), 440 (8), 258 (45), 183 (100), 167 (28).

Preparation of ***14a***. A solution of **13a** (1.50 g, 3.1 mmol) in benzene (150 ml) was hydrogenated over palladium charcoal (10%, 150 mg) to absorb the hydrogen (70 ml, 3.1 mmol). After the subsequent removal of the palladium charcoal by filtration, the solvent was evaporated on a rotary evaporator to give colorless crystals **14a** (1.5 g, *ca.* 100%), which were then recrystallized from ethyl acetate.

14a: Mp 269—270 °C. Found: C, 86.09; H, 6.72%. Calcd for $C_{33}H_{32}O_2$: C, 86.05; H, 7.00%. IR (KBr): 3550, 3250, 1598 cm^{-1}. ^1H NMR ($CDCl_3$) δ=0.8—1.6 (m, 6H), 2.11 (m, 2H), 2.54 (m, 2H), 3.47 (bs, 2H), 7.1—7.5 (m, 20H). MS *m/z* (rel intensity) 442 (M^+—18, 8), 365 (6), 260 (100), 183 (44).

Preparation of ***14b***. A solution of **13b** (3.00 g, 6.2 mmol) in benzene (250 ml) was hydrogenated with palladium charcoal (10%, 200 mg) to absorb the hydrogen (145 ml, 6.2 mmol). The usual work-up afforded colorless crystals **14b** (3.00 g, *ca.* 100%), which were then recrystallized from ethyl acetate.

14b: Mp 191—193 °C. Found: C, 85.81; H, 6.90%. Calcd for $C_{33}H_{32}O_2$: C, 86.05; H, 7.00%. IR (KBr): 3550, 3240, 1600 cm^{-1}. ^1H NMR ($CDCl_3$) δ=0.7—1.5 (m, 6H), 2.32 (m, 3H), 2.59 (m, 1H), 3.22 (bs, 2H), 6.8—7.5 (m, 20H). MS *m/z* (rel intensity) 442 (M^+—18, 10), 424 (22), 365 (36),

260 (100), 183 (61).

Preparation of ***17***. A solution of **15** (6.50 g, 30 mmol) in anhydrous tetrahydrofuran (100 ml) was added to a solution of phenyllithium (240 mmol) in anhydrous ether (70 ml) at room temperature, after which the mixture was stirred for 17 h. The usual workup gave colorless crystals **16** (8.86 g, 90%), which were then recrystallized from benzene.

16: Mp 164—165 °C. Found: C, 83.85; H, 6.14%; M^+, 328. Calcd for $C_{23}H_{20}O_2$: C, 84.12; H, 6.14%; M^+, 328.

A solution of **16** (4.00 g, 12 mmol) in anhydrous tetrahydrofuran (100 ml) was added to a solution of phenyllithium (60 mmol) in anhydrous ether (200 ml) at room temperature, after which the mixture was stirred for 20 h. The usual workup gave colorless crystals **17** (5.00 g, 86%), which were then recrystallized from ethyl acetate.

17: Mp 284—285 °C. Found: C, 87.00; H, 6.66%. Calcd for $C_{35}H_{32}O_2$: C, 86.74; H, 6.66%. IR (KBr): 3470, 3060, 1600 cm^{-1}. ^1H NMR ($CDCl_3$) δ=0.5—1.2 (m, 4H), 2.65 (m, 2H), 3.91 (bs, 2H), 5.18 (bs, 2H), 6.04 (m, 2H), 6.9—7.6 (m, 20H). MS *m/z* (rel intensity) 466 (M^+−18, 38), 375 (16), 284 (64), 183 (100), 167 (47).

Preparation of ***19a***. A solution of **18a** (2.88 g, 20 mmol) in anhydrous ether (150 ml) was added to a solution of phenyllithium (160 mmol) in anhydrous ether (100 ml) at room temperature, after which the mixture was stirred for 19 h. After the usual workup, the brown tarry material was chromatographed on silica gel to yield colorless crystals **19a** (1.96 g, 25%), which were then recrystallized from benzene.

19a: Mp 215—217 °C. Found: C, 85.70; H, 6.10%. Calcd for $C_{28}H_{24}O_2$: C, 85.68; H, 6.16%. IR (KBr): 3550, 3050, 1670 cm^{-1}. ^1H NMR ($CDCl_3$) δ=4.80 (s, 2H), 6.17 (s, 2H), 7.2 (m, 20H). MS *m/z* (rel intensity) 374 (M^+−18, 19), 270 (100), 192 (26).

Preparation of ***19b***. The same procedure as above, but using **18b** (2.88 g, 20 mmol) and phenyllithium (160 mmol), afforded colorless crystals **19b** (2.43 g, 31%), which were then recrystallized from cyclohexane.

19b: Mp 219—221 °C. Found: C, 85.98; H, 6.13%. Calcd for $C_{28}H_{24}O_2$: C, 85.68; H, 6.16%. IR (KBr): 3550, 3050, 1670 cm^{-1}. ^1H NMR ($CDCl_3$) δ=4.71 (s, 2H), 6.38 (s, 2H), 7.3 (m, 20H). MS *m/z* (rel intensity) 374 (M^+−18, 13), 270 (100), 192 (24).

Pyrolyses of Glycols

Pyrolysis of ***20***. Glycol **20** (940 mg, 2 mmol) was pyrolyzed at 250 °C for 2 h to give **21** (84 mg, 40%). The residual resinous material was chromatographed on alumina to give a colorless oil (120 mg) and colorless crystals **23** (410 mg, 46%) using pet ether, **3** (210 mg, 60%) using pet ether-benzene (4:1), and **4** (30 mg, 10%) using ether. The colorless oil was distilled under reduced pressure to give a colorless oil **22** (62 mg, 11%).

22: Bp 0.1 Torr (1 Torr=133.322 Pa), 130 °C (bath temperature). Found: C, 92.96; H, 6.98%. Calcd for $C_{21}H_{18}$: C, 93.29; H, 6.71%. IR (neat): 3070, 2920, 1600 cm^{-1}. ^1H NMR ($CDCl_3$) δ=3.46 (d, 2H, J=7 Hz), 6.38 (t, 1H, J=7 Hz), 7.3 (bs, 15H). MS *m/z* (rel intensity) 270 (M^+, 61), 193 (100), 167 (36).

Pyrolysis of ***9***. Glycol **9** (3.00 g, 6.6 mmol) was pyrolyzed at 250 °C for 1.5 h to give **24** (165 mg, 30%). The residue was chromatographed on silica gel to give colorless crystals **25** (1.05 g, 35%), using pet ether-benzene (7:3), **3** (306 mg, 25%) using pet ether-benzene (1:4), and **4** (820 mg, 68%) using ether. The crystals **25** were purified by recrystallization from ethyl acetate.

25: Mp 199—201 °C. Found: C, 89.49; H, 7.09%. Calcd for $C_{32}H_{30}O$: C, 89.26; H, 7.02%. IR (KBr) 3070, 2920, 1600 cm^{-1}. ^1H NMR ($CDCl_3$) δ=1.5 (m, 8H), 3.3 (m, 2H), 7.0—7.4 (m, 20H). MS *m/z* (rel intensity) 353 (M^+−C_6H_5, 10), 246 (100), 168 (32).

Pyrolysis of ***11***. Glycol **11** (482 mg, 1 mmol) was pyrolyzed at 290 °C for 3 h to yield 26 (87 mg, 75%). The residue was chromatographed on alumina to give **3** (180 mg, 99%) using pet ether-benzene (4:1) and **4** (110 mg, 60%) using ether.

Pyrolysis of ***14a***. Glycol **14a** (500 mg, 1.1 mmol) was pyrolyzed at 290 °C for 3 h to yield **27** (32 mg, 30%). The residue was chromatographed on alumina to give colorless crystals **28** (105 mg, 37%) using pet ether, colorless crystals **29** (45 mg, 9%) and **3** (153 mg, 75%) using pet ether-benzene (4:1), and **4** (33 mg, 20%) using ether. The crystals **28** and **29** were recrystallized from benzene and ethanol respectively.

28: Mp 68—69 °C. Found: C, 92.26; H, 7.83%. Calcd for $C_{20}H_{20}$: C, 92.26; H, 7.74%. IR (KBr): 3030, 2960, 1600 cm^{-1}. ^1H NMR ($CDCl_3$) δ=1.3—1.9 (m, 6H), 2.05 (m, 1H), 3.01 (bs, 1H), 7.3 (bs, 10H). MS *m/z* (rel intensity) 260 (M^+, 100), 231 (80), 205 (14), 191 (27), 167 (36).

29: Mp 279—280 °C. Found: C, 89.54; H, 7.00%. Calcd for $C_{33}H_{30}O$: C, 89.55; H, 6.83%. IR (KBr): 3060, 2950, 1600 cm^{-1}. ^1H NMR ($CDCl_3$) δ=0.8—1.7 (m, 6H), 2.44 (bs, 2H), 4.01 (bs, 2H), 6.9—7.4 (m, 20H). MS *m/z* (rel intensity) 442 (M^+, 6), 366 (31), 289 (100), 260 (12), 194 (10).

Pyrolysis of ***14b***. Glycol **14b** (500 mg, 1.1 mmol) was pyrolyzed at 290 °C for 3 h to yield **27** (29 mg, 27%). The same procedure as above gave **28** (183 mg, 64%), **3** (170 mg, 95%), and **4** (20 mg, 15%).

Pyrolysis of ***30***. Glycol **30** (1.00 g, 2.1 mmol) was pyrolyzed at 250 °C for 1 h to yield **26** (80 mg, 34%). The residue was chromatographed on alumina to give **3** (169 mg, 44%), using pet ether-benzene (4:1), colorless crystals of **11** (585 mg, 59%) using benzene-ether (4:1), and **4** (100 mg, 26%) using ether.

Pyrolysis of ***13a***. Glycol **13a** (500 mg, 1.1 mmol) was pyrolyzed at 270 °C for 2 h to give **31** (40 mg, 55%). The residue was chromatographed on alumina to give colorless crystals **32** (284 mg, 68%) using pet ether and **19a** (88 mg, 21%) using benzene-ether (1:1). The crystals **32** were recrystallized from ethyl acetate.

32: Mp 184—185 °C. Found: C, 89.85; H, 5.83%. Calcd for $C_{28}H_{22}O$: C, 89.80; H, 5.92%. IR (KBr): 3050, 1590 cm^{-1}. ^1H NMR ($CDCl_3$) δ=6.42 (s, 2H), 7.2 (bs, 20H). MS *m/z* (rel intensity) 374 (M^+, 46), 297 (100), 269 (82), 220 (59).

Pyrolysis of ***13b***. Glycol **13b** was pyrolyzed at 250 °C for 2 h to give **31** (65 mg, 45%). The residue was submitted to thin-layer chromatography on silica gel, using pet ether-benzene (1:1) as the developing solvent to give colorless crystals **33** (370 mg, 44%, R_f=0.45). The structure of **33** was determined by comparison of its physical properties with the literature.[9]

Pyrolysis of ***17***. Glycol **17** (500 mg, 1 mmol) was pyrolyzed at 290 °C for 3 h to give **34** (75 mg, 80%). The residue was chromatographed on alumina to give **32** (322 mg, 83%) using pet ether.

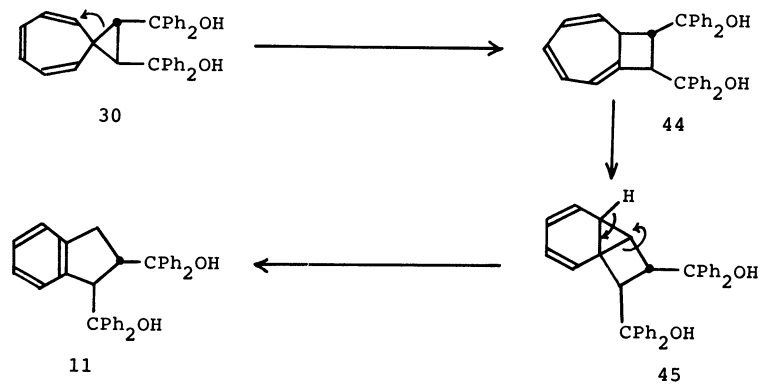


Fig. 8.

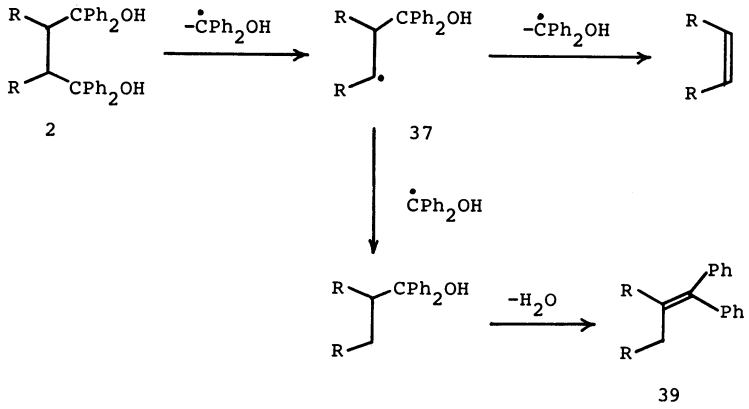


Fig. 9.

Pyrolysis of 19a. Glycol **19a** (1.00 g, 2.6 mmol) was pyrolyzed at 250 °C for 2 h. The residue was chromatographed on silica gel to yield colorless crystals **32** (506 mg, 53%) using pet ether and **3** (272 mg, 58%) using pet ether–benzene (4:1).

Pyrolysis of 19b. Glycol **19b** (1.00 g, 2.6 mmol) was pyrolyzed at 250 °C for 2 h. The residue was submitted to thin-layer chromatography on silica gel, using pet ether–benzene (1:1) as the developing solvent to give colorless crystals **33** (382 mg, 40%, R_f=0.45).

Pyrolysis of 35 A solution of **35** (1.00 g, 2.3 mmol) in *t*-butyl alcohol (40 ml) was heated at 330 °C for 5 h in an autoclave. The subsequent evaporation of the solvent gave colorless crystals **36** (950 mg, *ca.* 100%, mp 174—175 °C, lit,[7] 174—175 °C).

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8) The formation mechanism of the indane derivative (**11**) from the spiro compound (**30**) is considered to be as follows: a 1,7-shift of the carbon atom of the three-membered ring of **30** gives the bicyclo[5.2.0]nona-1,3,5-triene derivative (**44**), which then tautomerizes to the tricyclo[3.3.0.$0^{1,4}$]nonadiene (**45**). A cleavage of the three-membered ring of **45** followed by a hydrogen shift, affords **11**.[12]

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10) A referee has suggested the possibility of a step-by-step decomposition as is shown in Fig. 9. We are indebted to the referee.

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