Acid-catalyzed Rearrangement of the *exo*-1,2-Dioxetane Derivative from 1-Isopropylidene-4,4-diphenyl-2,5-cyclohexadiene[1)]

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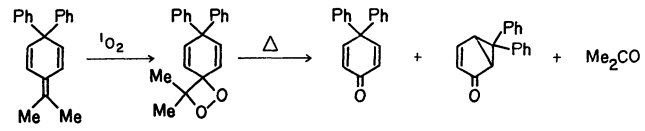
It is shown that acid-catalyzed decomposition of the 1,2-dioxetane derivative, 3,3-dimethyl-7,7-diphenyl-1,2-dioxaspiro[3.5]nona-5,8-diene, obtained from 1-isopropylidene-4,4-diphenyl-2,5-cyclohexadiene, gives 1-methyl-1-(*o*-terphenyl-4′-yl)ethyl hydroperoxide, bis[1-methyl-1-(*o*-terphenyl-4′-yl)ethyl] peroxide, 1-(1-hydroperoxy-1-methylethyl)-4,4-diphenylcyclohexa-2,5-dien-1-ol, and *o*-terphenyl-4′-ol, along with the usual dioxetane-scission product, 4,4-diphenyl-2,5-cyclohexadienone. The distribution and yield of these products depend on acidic agents and/or conditions employed.

Recent work by Zimmerman and coworkers[2)] concerning the thermal decomposition of the 1,2-dioxetane **2** derived from 1-isopropylidene-4,4-diphenyl-2,5-cyclohexadiene (**1**) prompts us to report results concerning the acid-catalyzed decomposition of **2** obtained simultaneously and independently in our laboratory.[1)] Zimmerman and coworkers reported[2)] that the thermal decomposition of **2** produced the rearranging excited state of 4,4-diphenyl-2,5-cyclohexadienone (**3**), which gave 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (**4**),



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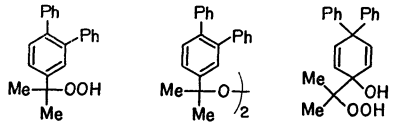
along with **3** and acetone.[3)] In our hands, the acid-catalyzed decomposition of **2** gave the *o*-terphenyl derivatives through a novel rearrangement pathway involving the scission of a carbon-oxygen bond, the migration of a phenyl group, and aromatization, which demonstrates that in the case of a special derivative the new type of cleavage of a dioxetane ring, competing with the usual dioxetane scission, may also occur.[4)]

Results and Discussion

The starting isopropylidenediphenylcyclohexadiene **1** was prepared by the Wittig reaction of the dienone **3** with isopropylidenetriphenylphosphorane.

Photooxidation. Photooxidation of **1** in anhydrous methanol at −78 °C using Rose Bengal as a sensitizer gave, after immediate separation by preparative thin-layer chromatography (TLC) on silica gel below −12 °C, a 60—90% yield of the crystalline dioxetane **2**, mp 57—61 °C (dec). The 1,2-dioxetane structure of **2** was verified by the spectral and chemical properties. A wide range of the yield of **2** depends on the reaction and/or isolation conditions: concentration, irradiation time, temperature, the nature of TLC plate, and so on. In fact, on further purification, **2** appreciably decomposed on a preparative silica gel plate to produce more polar substances (see below).

Decomposition of the 1,2-Dioxetane 2 on Silica Gel. From the observation that the dioxetane **2** is extremely sensitive to the photooxidation and isolation conditions, we have examined the reactivity of **2** to acidic agents. Re-chromatography (preparative TLC on silica gel) of **2** at 0 °C afforded, in addition to the dienone **3** (usually the major product), three crystalline products, the *o*-terphenyl hydroperoxide **5**, mp 125.5—128 °C, the dimeric *o*-terphenyl peroxide **6**, mp 148—150 °C, and the hydroxy hydroperoxide **7**, mp 124—126 °C, respectively. From a number of experiments, it was found that the decomposition of **2** on silica gel was greatly affected not only by temperature for charging and developing but also by the nature of silica gel plates used (probably due to activity, water-content, *etc*). Thus, the yields of these products were not always constant, varying appreciably from run to run; particularly, often compound **7** was not isolated due to its instability (see below).



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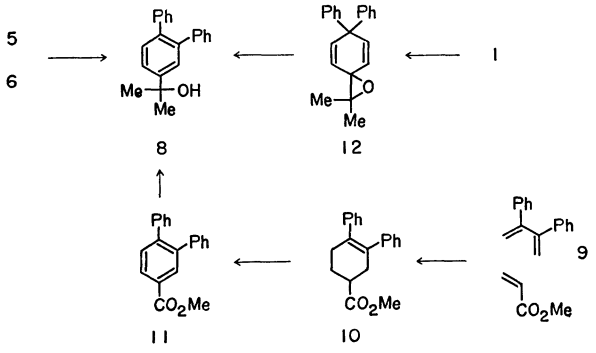
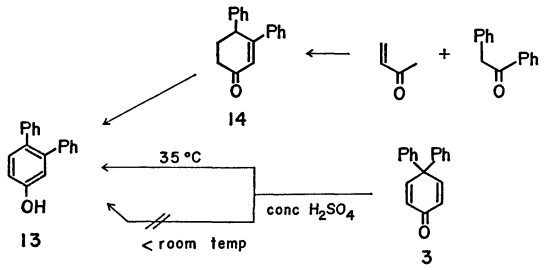
The structure of compound **5** was elucidated on the basis of the following spectral and chemical evidence. Compound **5** revealed the 1,3,4-trisubstituted benzene proton signals in the ^1H NMR and the absorption maxima characteristic of an *o*-terphenyl chromophor in the UV spectrum. Compound **5** showed positive potassium iodide-starch test, and treatment of **5** with various reducing reagents gave quantitatively the hydroxy compound **8**. The authentic sample of **8** was prepared by two alternative ways as shown in Scheme 1. The Diels-Alder reaction of 2,3-diphenyl-1,3-butadiene (**9**) with methyl acrylate provided the adduct **10**. Bromination of **10**, followed by dehydrobromination or direct dehydrogenation of **10** with DDQ afforded methyl *o*-terphenyl-4′-carboxylate (**11**),



Scheme 1.



Scheme 2.

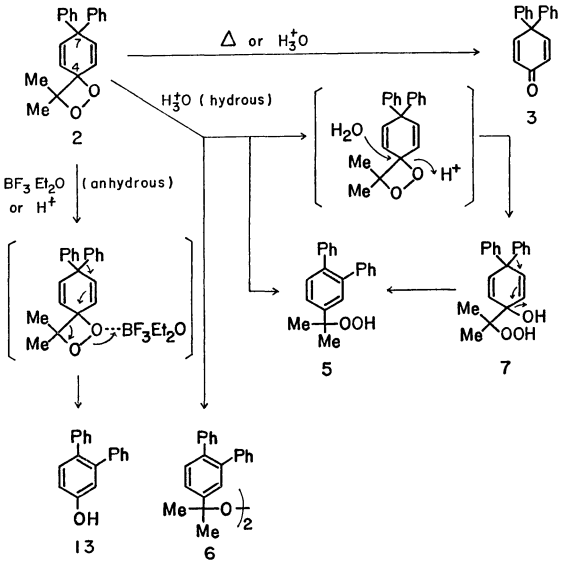
which was then transformed into **8** by the action of excess methylmagnesium iodide. Treatment of **1** with *m*-chloroperbenzoic acid gave the unstable exocyclic epoxide **12**, which was easily converted into **8** by chromatography on silica gel. The sample of **8** thus obtained was identical with that derived from **5**. The latter reaction sequence clearly indicates that the 4,4-diphenyl-2,5-cyclohexadienyl system easily undergoes a phenyl migration and aromatization.

Similarly, the product **6** also gave quantitatively the alcohol **8** on lithium aluminum hydride reduction or catalytic hydrogenation; thus, combining with the close resemblance of the spectral (^{1}H NMR and UV) properties to those of **5** or **8** and with the analytical result, the structure of **6** was assigned to be the dimeric *o*-terphenyl peroxide.

The third component **7** is the most polar compound and shows the simple ^{1}H NMR spectrum including the AB-type signal due to olefinic protons (total 4H) and the broad signal due to two protons exchangeable with deuterium oxide. These data suggests that this compound possesses a symmetrical structure having two hydroxylic functions. Furthermore, **7** is fairly unstable in solutions. The ^{1}H NMR spectrum of **7** in carbon tetrachloride or deuteriochloroform changed gradually on standing, and the final spectrum, after a few hours at 30 °C, was wholly in accord with that of the hydroperoxide **5**. From these facts, the vicinal hydroxy hydroperoxide structure **7** was assigned to this compound, and **7** meets the requirement of an intermediate in the rearrangement of **2** to **5**. The easy transformation of **7** into **5** in chlorinated solvents may be catalyzed by a trace of hydrogen (or deuterium) chloride contaminated.

Decomposition of the 1,2-Dioxetane **2** *by Hydrochloric Acid.* The same decomposition of **2** was also induced by hydrochloric acid, and temperature dependence on product distribution was observed. Thus, treatment of an ethereal solution of **2** with 2—6 M (1 M=1 mol dm^{-3}) hydrochloric acid at room temperature gave **3** (*ca.* 29%), **5** (*ca.* 15%), and **6** (*ca.* 34%), respectively. While below 0 °C **6** was obtained quantitatively. On treating a chloroform solution of **2** with concd hydrochloric acid below −10 °C, **6** also arose as the single product. Further, we found that these compounds **5** and **6** were not interconverted under the conditions examined, and therefore, they would be formed from **2** through different pathways subtly depending upon the environmental conditions.

Decomposition of the 1,2-Dioxetane **2** *under Anhydrous Conditions.* A noteworthy feature of the decomposition of **2** under the anhydrous conditions is the



Scheme 3.

formation of a new product. Treatment of an ethereal solution of **2** with boron trifluoride etherate below −12 °C or with concd sulfuric acid below −10 °C afforded quantitatively *o*-terphenyl-4′-ol (**13**). Compound **13** was identical with a sample, which was prepared through 3,4-diphenyl-2-cyclohexenone (**14**) as shown in Scheme 2, as determined by comparison of the spectra. Since **13** corresponds to the dienone-phenol rearrangement product of the dienone **3**, **3** seems to be the most probable precursor of **13**. It was found, however, that **3** was stable even at room temperature to both of boron trifluoride etherate and concd sulfuric acid in ether. The rearrangement of **3** to **13** ultimately occurred upon prolonged refluxing. Thus, **3** would not be the precursor of **13** from **2** under the decomposition conditions examined. Acid-catalyzed decomposition of the hydroperoxide **5** to **13** corresponds to the synthetic process of phenol from cumene through cumene hydroperoxide, and therefore, the process of **2**→**5**→**13** would be an alternative pathway for the formation of **13**. However, from the fact that compound **5**, as well as compound **6**, was also inert under the decomposition conditions of **2**, this process also appears unlikely. Consequently, **13** would be formed directly from **2** through a novel fragmentation.

When wet ether was used in the decomposition of **2** by boron trifluoride etherate below −20 °C, the peroxide **6** became the sole isolable product (24%).

It is to be noted that the ionic decomposition of **2** was also observed on heating at 60—70 °C in carbon tetrachloride. The reaction was carried out in an NMR tube in the ordinary manner and followed by the ^{1}H NMR spectrum. The temporary production of the hydroxy hydroperoxide **7** could be detected, and the final product was shown to be a 1:2—5:1 mixture of **3** and **5**; there was no indication of the presence of the rearranged bicyclic ketone **4**. Traces of hydrogen chloride and water in carbon tetrachloride may cause the ionic fragmentation. Turning to the photooxidation experiment of **1**, the use of chloroform as a solvent at room temperature led to the formations

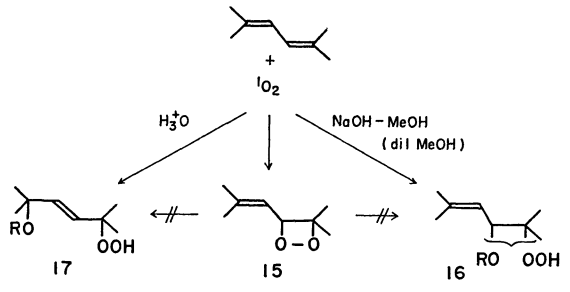
of **3**, **5**, and **6**.

As is clear from the results discussed above the reactivity of the dioxetane **2** is extremely sensitive to acidic agents and environmental conditions, and the product distribution and yield are very diverse. Although the detailed mechanisms for the formation of the products still remained unclarified, because of the low availabilities and/or the high sensitivities of both **2** and products, the results are summarized in Scheme 3.

It is conceivable that the dienone **3** arises partly from the usual thermal fission and partly from the acid (or impurities)-catalyzed one of the dioxetane ring.

The most important mode of the reaction of **2** under the hydrous conditions is the competitive cleavage of the ring carbon (C4)–oxygen bond of the dioxetane moiety. Such a cleavage of 1,2-dioxetane ring has been observed in the rearrangement of tetramethyl-1,2-dioxetane by boron trifluoride in aprotic solvents, resulted from one-oxygen coordination with boron trifluoride.[4b] In our case, easy and selective cleavage of the C4–O bond in **2** might be due to the allylic nature of C4. The ring opening and the attack of water at C4 gives the hydroxy hydroperoxide **7**. The hydroperoxide **5** is certainly formed by dehydration of **7** as discussed earlier. However, the direct pathway from **2** involving ring opening, migration of a double bond and subsequently of a phenyl group, and deprotonation can not be ruled out. The mechanism for formation of the dimeric peroxide **6** is still obscure. Anyhow, a high migratory aptitude of phenyl group and stabilization by aromatization, in addition to the allylic nature of a dioxetane carbon, should promote the formations of **5** and **6**. Among these factors, a phenyl substituent at C7 plays the most important role in the rearrangement, because the 4,4-dimethyl analogue of **1**, on sensitized photooxidation, underwent exclusively the usual 1,2-dioxetane fission to produce 4,4-dimethyl-2,5-cyclohexadienone in quantitative yield.

In view of the recent findings by Hasty and Kearns,[4a] the vicinal hydroxy hydroperoxide **7** is a unique compound as a product derived from 1,2-dioxetane derivatives. They demonstrated that the mono (epidioxide) **15** derived from 2,5-dimethyl-2,4-hexadiene can not be the intermediate in the formation of the vicinal hydroxy (or methoxy) hydroperoxide **16** which was produced by photooxidation of the above diene in basic nucleophilic solvents, as well as in the formation of the 1,4-hydroxy (or methoxy) hydroperoxide **17** in acidic media.



As described above, the phenol **13** would arise directly from **2**, not through **3** or **5**. An explanation for the process leading to **13** is that the coordination of acidic agents to the dioxetane oxygen atom attached to C4 might initiate the ionic fragmentation, and the simultaneous isomerization and aromatization as in the case of **5** or **6** would produce **13** as shown.

Experimental

Melting points are uncorrected. IR spectra were obtained with a Hitachi EPI-S2 or G2 and UV spectra with a Hitachi EPS-3T spectrophotometer. ^1H NMR spectra were recorded with a JEOL C-60HL (60 MHz), PMX-60 (60 MHz), or PS-100 (100 MHz) instrument with TMS as an internal standard; coupling constants are given in Hz. Mass spectra were taken with a Shimadzu LKB-9000 instrument. Silica gel (Merck GF-254) was used for analytical and preparative thin-layer chromatography (TLC); solvent systems are indicated in parentheses. Almost all of new compounds described in this paper did not give the satisfactory analytical data; the variable percentages (always low) of carbon were observed. This may be due to the thermal instabilities and/or the high contents of aromatic carbon atoms of these compounds.

*1-Isopropylidene-4,4-diphenyl-2,5-cyclohexadiene (**1**).* To a stirred suspension of isopropyltriphenylphosphonium iodide[5] (520 mg, 1.20 mmol) in anhydrous ether (15 ml) was added a solution of butyllithium in hexane (20%, 0.6 ml, 1.30 mmol) dropwise at room temperature under nitrogen. After stirring at room temperature for 15 min, a solution of 4,4-diphenyl-2,5-cyclohexadienone (**3**)[6] (250 mg, 1.00 mmol) in anhydrous ether (6 ml) and DMSO (2.5 ml) was added dropwise, and the reaction mixture was heated under reflux for 2 h. After the removal of insoluble material by filtration, the filtrate was washed with aqueous DMSO (50%, 50 ml). The water layer was extracted with a 2:1 mixture of petroleum ether and ether. The combined organic layers were washed with water and saturated brine, dried, and concentrated. The residual oil (380 mg) was chromatographed on silica gel using petroleum ether as an eluant to afford crystals. Recrystallization from petroleum ether yielded the triene **1** (180 mg, 78%): mp 90 °C (lit,[2] mp 89—91 °C); IR ($CHCl_3$) 1595, 1480, 1440, and 1375 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.89 (6H, s), 5.98 (2H, br. d, J=10.5), 6.67 (2H, d, J=10.5), and 7.42 (10H, s). Found: C, 92.33; H, 7.65%. Calcd for $C_{21}H_{20}$: C, 92.60; H, 7.40%.

*Photooxidation of **1**. (a) In Methanol at Low Temperature [Isolation of 3,3-Dimethyl-7,7-diphenyl-1,2-dioxaspiro[3.5]nona-5,8-diene (**2**)]*: A solution of **1** (300 mg) and Rose Bengal (5 mg) in anhydrous methanol (40 ml) and petroleum ether (5 ml) was irradiated with three 200 W tungsten lamps at −78 °C for 2.5 h. Finely dispersed stream of dry oxygen was passed through the solution continually during irradiation. The solvent was removed by vacuum distillation at −40 °C. The residue was chromatographed on two thin-layer silica gel plates (20×20 cm, 1:3 ether–petroleum ether) below −12 °C to give 300 mg (90%, the best result) of a pale yellow oil, which crystallized on standing at −12 °C. Recrystallization from petroleum ether at −12 °C gave **2**: mp 57—61 °C (lit,[2] mp 72—74 °C); IR (CCl_4) 1660, 1595, 1485, 1460, 1370, 1210, 1195, 1075, and 695 cm^{-1}; ^1H NMR (CCl_4, 100 MHz) δ 1.43 (6H, s), 6.35 (2H, d, J=10.5), 6.57 (2H, d, J=10.5), and 7.18 (10H, small split s). The dioxetane **2** could be stored as the dilute solutions in anhydrous THF, ether, benzene, and cyclohexane below −20 °C for several months.

(b) In Methanol at Room Temperature: A solution of **1** (130 mg) and Rose Bengal (5 mg) in anhydrous methanol (30 ml) was photooxidized at room temperature. After irradiation for 1.5 h, work-up in the same manner at room

temperature gave 55 mg (47%) of **2** and 50 mg (43%) of **3**, respectively.

(c) In Chloroform at Room Temperature: A solution of **1** (150 mg) and Methylene Blue (5 mg) in $CHCl_3$ (30 ml) was photooxidized at room temperature for 2.5 h and worked up in the same manner to give 40 mg (30%) of **3**, 25 mg (16%) of **5**, and 26 mg (17%) of **6**.

Decomposition of 2 on Silica Gel and the Properties of the Products 5, 6, and 7. The dioxetane **2** was re-chromatographed on thin-layer silica gel (1:3 or 1:4 ether–petroleum ether) at 0 °C to produce four UV detectable bands. Collection of these bands, followed by elution with ether and evaporation of the solvent without applying heat gave, in the order of moving, **6**, **3**, **5**, and **7** (variable yields from run to run), respectively.

1-Methyl-1-(*o*-terphenyl-4′-yl)ethyl hydroperoxide (**5**): mp 125.5—128 °C from methanol; positive KI-starch test; IR (CCl_4) 3600, 3500—3100, 1600, 1480, 1440, and 700 cm^{-1}; UV (EtOH) λ_{max} 235 (ε 31000) and 255 nm (ε 20000);[7] ^1H NMR ($CDCl_3$) δ 1.72 (6H, s), 7.24 (10H, s), around 7.30 (1H, br. s, OOH), 7.43 (1H, dd, J=8.8 and 1.9), 7.58 (1H, d, J=8.8), and 7.58 (1H, d, J=1.9); mass *m/e* 288 (parent peak, M^+-16).

Bis[1-methyl-1-(*o*-terphenyl-4′-yl)ethyl] peroxide (**6**): mp 148—150 °C (not recrystallized); IR (CCl_4) 1600, 1480, 1440, and 700 cm^{-1}; UV (EtOH) λ_{max} 235.5 (ε 60800) and 255 nm (ε 27100); ^1H NMR ($CDCl_3$) δ 1.69 (12H, s), 7.18 (20H, s), 7.41 (2H, d, J=8.5), 7.49 (2H, d, J=2.0), and 7.53 (2H, dd, J=8.5 and 2.0). Found: C, 87.20; H, 6.81%. Calcd for $C_{42}H_{38}O_2$: C, 87.77; H, 6.66%. The molecular weight could not be determined by a mass spectral or vapor pressure osmometric method, being presumably due to easy cleavage of the peroxide linkage.

1-(1-Hydroperoxy-1-methylethyl)-4,4-diphenylcyclohexa-2,5-dien-1-ol (**7**): mp 124—126 °C (not recrystallized); IR (CCl_4) 3600, 3650—3100, 1595, 1490, 1175, 865, and 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.18 (6H, s), 2.24 (2H, br. s, OH and OOH), 6.07 (2H, d, J=10.5), 6.32 (2H, d, J=10.5), and 7.28 (10H, s).

Decomposition of 2 by Hydrochloric Acid. (a): A stock solution of **2** in ether (*ca.* 41 mg, 2.1 ml) was diluted with anhydrous ether (2 ml) at −20 °C, and then 2 M HCl (1 drop) was added to this solution. The resulting mixture was vigorously stirred at room temperature for 15 min. The mixture was washed with dilute $NaHCO_3$ solution, water, and saturated brine, dried, and evaporated. The residue was chromatographed on preparative TLC (1:3 ether–petroleum ether) to afford **3** (*ca.* 29%), **5** (*ca.* 15%), and **6** (*ca.* 34%).

(b): The reaction mixture (the same amount as above) was stirred at −18——8 °C. After the reaction was completed (4 d), the mixture was worked up in the same manner, except the use of 1:6 ethyl acetate–petroleum ether as a developing solvent in this case, to give **6** (*ca.* 90%).

(c): A stock solution of **2** in THF (*ca.* 30 mg, 3 ml) was diluted with anhydrous ether (2 ml) at −20 °C, and then 6 M HCl (0.4 ml) was added. The reaction mixture was vigorously stirred at 0 °C for 50 min. Work-up in the same manner yielded **6** (*ca.* 100%).

(d): A stock solution of **2** in cyclohexane (*ca.* 65 mg, 6.5 ml) was diluted with $CHCl_3$ (5 ml) at −10 °C, and then concd HCl (a catalytic amount) was added. The reaction mixture was vigorously stirred below 10 °C for 10 min and worked up in the same manner to give **6** (*ca.* 97%).

Decomposition of 2 under the Anhydrous Conditions and the Product 13. (a): By Boron Trifluoride Etherate. A stock solution of **2** in THF (*ca.* 50 mg, 3 ml) was diluted with anhydrous ether (10 ml) at −70 °C under nitrogen, and then boron trifluoride etherate (1 drop) was added. The reaction mixture was stirred at −18——12 °C for 2.5 h. Then, the mixture was passed through a short column of silica gel with the aid of ether and evaporated. The residue was chromatographed on preparative TLC (1:7 ethyl acetate–petroleum ether) to give 40 mg (*ca.* 100%) of very viscous oily *o*-terphenyl-4′-ol (**13**): yellow ferric chloride test; IR ($CHCl_3$) 3570, 3550—3100, 3040, 3010, 1600, 1470, 1300, 1210, 890, and 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.60 (1H, br.s, OH), 6.73 (1H, dd, J=9.1 and 2.8), 6.77 (1H, d, J=2.8), 7.05 (10H, m), and 7.15 (1H, d, J=9.1). This compound was identical with the synthetic sample (IR, ^1H NMR, see below).

When ether saturated with water was used for dilution and the reaction was conducted below −20 °C for 15 h, only **6** (*ca.* 24%) was obtained.

(b) By Concd H_2SO_4: A stock solution of **2** in ether (*ca.* 40 mg, 2 ml) was diluted with anhydrous ether (2 ml) at −70 °C, and then concd H_2SO_4 (1 drop) was added. The reaction mixture was stirred below −10 °C for 1 h under nitrogen. Work-up in the usual manner (washing, evaporation, and chromatography) gave 30 mg (*ca.* 100%) of **13**.

1-Methyl-1-(o-terphenyl-4′-yl)ethanol (8). (a) From 5: To a solution of **5** (26 mg) in anhydrous THF (5 ml) was added lithium aluminum hydride (12 mg), and the reaction mixture was heated at 50 °C for 1 h. The cooled mixture was poured into ice–water and thoroughly extracted with ether. The combined extracts were washed with water and saturated brine, and dried. Removal of the solvent under reduced pressure gave 23 mg (94%) of **8**: mp 144.5—145.5 °C from methanol–petroleum ether; IR (CCl_4) 3500, 3400 (br.), 1600, 1480, 1395, 1360, and 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.70 (6H, s), 7.24 (10H, s), 7.43 (1H, dd, J=8.8 and 1.9), 7.58 (1H, d, J=8.8), and 7.58 (1H, d, J=1.9); mass *m/e* 288 (M^+). This compound was identical with the synthetic sample (see below) as determined by the mixed melting point determination and by comparison of the spectra.

Reduction of **5** with other reagents (triethyl phosphite–toluene, KI–isopropyl alcohol, dimethyl sulfide–benzene) also gave **8** in good yield.

(b) From 6: To a solution of **6** (25 mg) in anhydrous ether (8 ml) was added lithium aluminum hydride (5 mg) with ice-cooling under nitrogen. After being stirred for 30 min, the mixture was poured into ice–water, and the water layer was extracted with ether three times. The combined extracts were washed with water and saturated brine. Evaporation of the solvent under reduced pressure left 26 mg (100%) of **8**.

Catalytic hydrogenation of **6** over Pd–C in ethanol also gave quantitatively **8**.

(c) From 1: To the well-stirred mixture of a solution of **1** (250 mg, 0.92 mmol) in CH_2Cl_2 (20 ml) and 0.5 M $NaHCO_3$ solution (6 ml) was added portionwise *m*-chloroperbenzoic acid (85%, 224 mg, 1.10 mmol) at 0 °C,[8] and the reaction mixture was stirred at 0 °C for 2 h. The organic layer was separated, washed with dilute NaOH solution and saturated brine, dried, and evaporated. The ^1H NMR spectrum indicated that the crude product was a 2:1 mixture of the epoxide **12** and **8**. Preparative TLC (1:2 ether–petroleum ether) of the crude mixture showed a single UV detectable band. Collection of this band, followed by elution with ether and evaporation provided 260 mg (98%) of **8**.

(d) Synthesis: 2,3-Diphenyl-1,3-butadiene (**9**), bp 150—170 °C (bath)/10 Torr (1 Torr=133.322 Pa), mp 46—47 °C, was prepared by dehydration of 2,3-diphenylbutane-

2,3-diol with $KHSO_4$.[9]

A mixture of **9** (1.4 g, 6.5 mmol), methyl acrylate (3.3 g, 38 mmol), and hydroquinone (20 mg) was heated in a sealed tube at 140 °C (bath temperature) for 15 h. The excess acrylate was removed by distillation under reduced pressure. The residual yellow solid was dissolved in 1:6 ether–petroleum ether and passed through a short column of silica gel to afford 1.74 g (88%) of methyl 3,4-diphenyl-3-cyclohexenecarboxylate (**10**), which gradually crystallized on standing: mp 181 °C; IR (neat, before crystallized) 1735, 1595, 1485, 1430, 1170, and 700 cm^{-1}; ^1H NMR (CCl_4) δ 1.70—2.20 (2H, m), 2.20—2.80 (5H, m), 3.59 (3H, s), and 6.92 (10H, s).

A solution of **10** (584 mg, 2.0 mmol) and DDQ (1.36 g, 6.0 mmol) in toluene (10 ml) was heated under reflux for 26 h under nitrogen. The solvent was removed by distillation under reduced pressure. The brown residue was chromatographed on silica gel (30 g) using 1:1 ether–petroleum ether as an eluant to give 535 mg (92%) of methyl *o*-terphenyl-4′-carboxylate (**11**): IR ($CHCl_3$) 1715, 1600, 1435, 1120, and 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.93 (3H, s), 7.20 (10H, s), 7.53 (1H, d, J=9.0), and 8.00—8.21 (2H, m).

A solution of **10** (292 mg, 1.0 mmol), NBS (373 mg, 2.1 mmol), and dibenzoyl peroxide (8 mg) in CCl_4 (4 ml) was heated under reflux for 80 min under nitrogen. After removal of the insoluble precipitate by filtration, the solvent was expelled by distillation under reduced pressure. The residue was dissolved in pyridine (5 ml), and the resulting solution was heated under reflux for 1 h. The reaction mixture was poured into water and extracted with ether three times. The combined extracts were washed with water, dilute $CuSO_4$ solution, water, and saturated brine, and dried. Evaporation of the solvent left 280 mg (97%) of **11**.

To a solution of methylmagnesium iodide, prepared from magnesium (1.34 g) and methyl iodide (9.9 g) in anhydrous ether (25 ml), was added dropwise a solution of **11** (5.29 g, 18.3 mmol) in anhydrous ether–benzene (2:1, 50 ml) over a period of 15 min at room temperature under nitrogen, and the reaction mixture was stirred for 100 min. Saturated NH_4Cl solution was added, and the water layer was extracted with each 40 ml portions of ether three times. The combined extracts were washed with 2 M HCl, water, and saturated brine. Evaporation of the solvent left a dark brown oil (5.5 g). Chromatography of this oil on silica gel (160 g) using 1:1 ether–petroleum ether as an eluant afforded 5.17 g (98%) of **8**.

*o-Terphenyl-4′-ol (**13**).* *(a) From **3***: To a solution of **3** (50 mg) in anhydrous ether (3 ml) was added concd H_2SO_4 (1 drop), and the reaction mixture was heated under reflux for 48 h. When the mixture was stirred at room temperature, no reaction was observed after 12 h. The cooled mixture was diluted with more ether and washed with dilute $NaHCO_3$ solution and saturated brine, and the solvent was removed by distillation. The residue was chromatographed on preparative TLC (1:5 ethyl acetate–petroleum ether) to yield 35 mg (70%) of **13**.

The reaction of **3** (50 mg) by boron trifluoride etherate (2 drops) in boiling anhydrous ether (4 ml) proceeded extremely slowly. Even after 3.5 d, almost starting material remained unchanged.

(b) Synthesis: To a solution of deoxybenzoin (19.7 g, 0.1 mol) in anhydrous ether (300 ml) was added methyl vinyl ketone (freshly distilled, 7.1 g, 0.1 mol) at 0 °C. Then, to this solution was added dropwise a solution of KOH (1.7 g) in ethanol (15 ml) over a period of 30 min at 0 °C under nitrogen, and the resulting mixture was stirred at 0 °C for 70 min; white precipitate gradually separated. This slurry was poured into a mixture of ice (200 g) and 1 M HCl (35 ml), and the precipitate was collected by filtration, washed with water, and dried *in vacuo* over concd H_2SO_4. The organic layer of the filtrate was separated, washed with water and saturated brine, and evaporated to dryness to yield a solid material. The precipitate and the solid residue were combined and suspended in ethanol (95%, 300 ml). To this slurry was added concd HCl (20 ml), and the resulting mixture was heated under reflux. After 20 min, the mixture became a homogeneous solution, and the refluxing was continued for 2 h. The reaction mixture was poured into cold water (500 ml) and extracted with ether three times. The combined extracts were washed with water and saturated brine, and dried. Evaporation of the solvent and recrystallization of the solid residue from aqueous methanol gave 17 g (69% overall) of 3,4-diphenyl-2-cyclohexenone (**14**): mp 96—97.5 °C; IR (CCl_4) 1670, 1600, 1490, 1442, 1328, 1250, 1170, 885, and 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.00—2.80 (4H, m), 4.35 (1H, m), 6.75 (1H, s), and 7.30 (10H, split s). Found: C, 86.75; H, 6.54%. Calcd for $C_{18}H_{16}O$: C, 87.06; H, 6.50%.

A solution of **14** (124 mg, 0.5 mmol), DDQ (139 mg, 0.6 mmol), and fused *p*-toluenesulfonic acid (19 mg) in anhydrous benzene (12 ml) was heated under reflux for 4 h under nitrogen. The reaction mixture was poured into ice–water and extracted with ether. The combined extracts were washed with water and saturated brine, and evaporated. The residue was chromatographed on preparative TLC (1:4 ethyl acetate–petroleum ether) and distilled at 90—140 °C (bath)/0.3—0.5 Torr to afford 108 mg (88%) of viscous oily **13**, which gradually crystallized on standing: mp 48—51 °C (still adhesive, being unable to recrystallize). Found: C, 87.48; H, 5.96%. Calcd for $C_{18}H_{14}O$: C, 87.77; H, 5.73%.

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