offered for ozone insertion in glycosides, where it was found that α glycosides are inert to ozone while β glycosides reacted by C–H bond cleavage,[8] and for specificity of heterolytic C–O bond cleavage in the base-catalyzed hydrolysis of esters.[9,10] Alternatively, the low reactivity of the trans isomer may derive from a small concentration of the less stable conformation. Hence, the rate ratio must be considered a lower limit for the relative reactivity of axial and equatorial hydrogens.

A further contribution to the enhanced reactivity of the cis isomer may be made by the fact that the cis isomer is less stable than the trans isomer. This energy difference has been found to be 0.34–0.73 kcal/mol depending on the solvent.[4,11] However, since the transition states leading to the common radical 4 are different for the two isomers, it is difficult to estimate the importance of this effect.

Irradiation of the individual isomers of 1 also showed that the initial hydrogen abstraction is irreversible and that the intermediate radical 4 rearranges or loses methyl radical instead of picking up a hydrogen atom from the system, since none of the alternative isomer was found during the irradiations. The reaction step leading to the loss of methyl is presumably irreversible and we are presently looking into the reversibility of the ring opening step in a different model system.

This work adds another chapter to the unfolding story of the many ways in which the oxygens attached to the "anomeric" carbon in carbohydrates and model systems can influence the chemistry of such systems. These effects have been collectively called "the anomeric effect" even though several theoretical interpretations for the various effects have been offered.[12]

## Experimental Section

Irradiations were carried out in a Rayonet photochemical reactor using 16 RPR 3000 lamps. Sample solutions which were 0.039 M in *trans*-**1**, 0.034 M in *cis*-**1**, and 0.079 M in benzophenone dissolved in benzene were degassed by at least three freeze–pump–thaw cycles and sealed in Pyrex under vacuum. Samples were removed after 2–15 h of irradiation, acetophenone was added as internal standard, and solutions were analyzed by gas chromatography on 10% Carbowax 20M on Chromosorb W or 3% OV-17 on Chromosorb Q.

Products were identified by comparison of gas chromatographic retention times on three different columns and by infrared spectra of samples collected off the GC column with those of authentic material prepared by literature methods.[13]

Starting acetal 1 was prepared as a mixture of cis and trans isomers by the method of Eliel and Giza.[5] The individual isomers could be separated to 99% purity by two passes through a 5 ft × 0.25 in. gas chromatographic column of 5% SE-30 on 60–70 mesh Anakrom ABS. The trans isomer eluted first, the assignment being made on the basis of the NMR signal for the "anomeric" hydrogen.

**Registry No.**—*cis*-**1**, 7429-27-8; *trans*-**1**, 7429-28-9.

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# Addition of Tetrachloro-*o*-quinone to 2-Butenes

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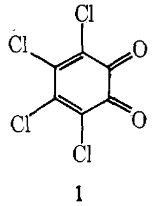
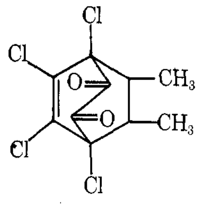
Tetrachloro-*o*-quinone (**1**, TCQ) is known to add to various conjugated and reactive olefins by thermal or photolytic initiation[1,2] to give 1,4-dioxenes and bicyclic α diketones. It has been reported[2] that thermal addition of TCQ to *cis*- and *trans*-stilbenes is stereospecific giving *cis*- and *trans*-dioxenes (**4** and **5** in which $CH_3 = C_6H_5$), respectively, indicating that the thermal reaction is concerted and follows the Woodward–Hoffmann rules, i.e., the reaction is governed by the $[4_s + 2_s]$ electrocyclization process.[3] On the other hand, photoaddition of the same system is a nonconcerted process but, interestingly, retains a high degree of stereoselectivity. As our previous report on the allied reaction indicates,[4] the stereochemical course of such cycloaddition reactions is best demonstrated with a simple olefin instead of using stilbenes, since a conjugated olefin has a low triplet state energy (e.g., $E_t = 50$ kcal/mol for stilbene)[5] and a lower energy barrier of isomerization. We wish to report the results on thermally and photolytically initiated addition reaction of TCQ to *cis*- and *trans*-2-butenes.

## Results and Discussion

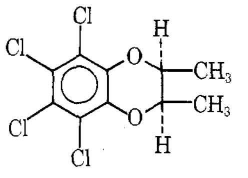
A benzene solution of TCQ and *cis*-2-butene was heated at 130 °C in a sealed tube from which a Diels–Alder adduct **2** (60%) and *cis*-dioxene **4** were isolated. The yellow crystals of **2** were readily recrystallized to a homogeneous compound which exhibited typical α-diketone absorption at 1758 cm$^{-1}$. The NMR signal for the methyl and methine protons at $\tau$ 8.90 (doublet) and 8.30 indicated that the methyl groups had the cis configuration; the syn- or anti relation of the methyl group with respect to the carbonyl groups could not be determined. A similar thermal addition to *trans*-2-butene gave a more complex mixture from which an impure fraction of Diels–Alder type adduct **3**, an unknown compound having the molecular formula of $C_{10}H_9O_2Cl_3$, and *trans*-dioxene **5** were isolated after silicic acid chromatography. In spite of repeated recrystallization and further chromatography, the first ketone fraction could not be obtained in the pure state owing prob-



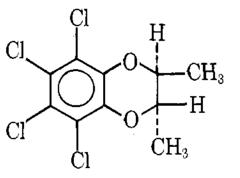
**1**



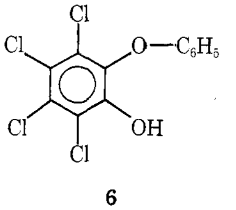
**2** or **3**



**4**



**5**



**6**

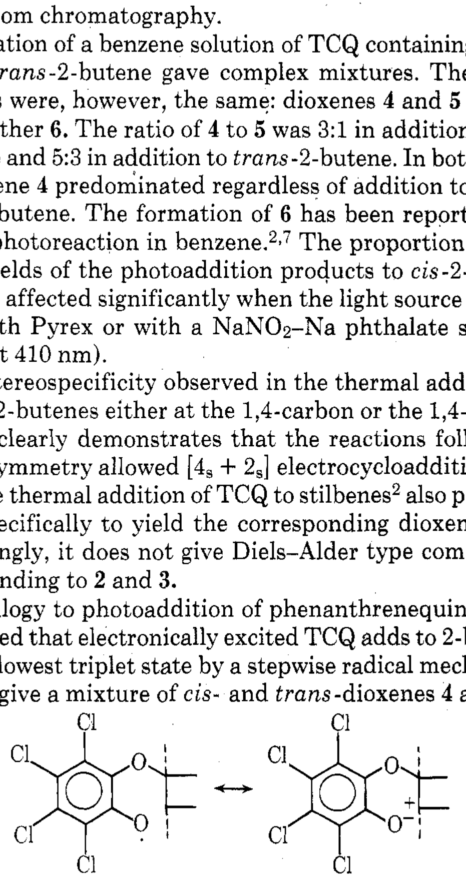
ably to slow decomposition of the major component; the spectral data indicated that α diketone **3** was contaminated by another compound.

The cis and trans configurations of dioxenes **4** and **5** were determined by the chemical shifts of the methine protons at τ 5.58 and 6.08, respectively, in analogy to the assignments made to the isomeric adducts derived from phenanthrenequinone.[4] The coupling patterns of the methyl and methine protons in the dioxenes exhibited a complex $AX_3A'X_3'$ system and were very similar to those patterns in the spectra of *cis*- and *trans*-2,3-dimethyldioxanes which had been analyzed completely.[6] This provided a further evidence indicating the cis and trans stereochemistry for dioxenes **4** and **5**. The methyl signals in both **4** and **5** exhibit two sharp lines with weaker lines in the vicinity: these patterns are similar to those observed previously in other *cis*- and *trans*-dioxene systems.[4] In both thermal additions, the absence of the alternate isomer was checked by TLC and VPC on the dioxene fractions obtained from chromatography.

Irradiation of a benzene solution of TCQ containing either *cis*- or *trans*-2-butene gave complex mixtures. The major products were, however, the same: dioxenes **4** and **5** and diphenyl ether **6**. The ratio of **4** to **5** was 3:1 in addition to *cis*-2-butene and 5:3 in addition to *trans*-2-butene. In both cases, *cis*-dioxene **4** predominated regardless of addition to *cis*- or *trans*-2-butene. The formation of **6** has been reported in a similar photoreaction in benzene.[2,7] The proportion as well as the yields of the photoaddition products to *cis*-2-butene were not affected significantly when the light source was filtered with Pyrex or with a $NaNO_2$–Na phthalate solution (cutoff at 410 nm).

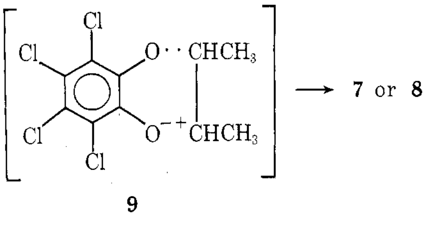
The stereospecificity observed in the thermal addition of TCQ to 2-butenes either at the 1,4-carbon or the 1,4-oxygen termini clearly demonstrates that the reactions follow the orbital symmetry allowed $[4_s + 2_s]$ electrocycloaddition process. The thermal addition of TCQ to stilbenes[2] also proceeds stereospecifically to yield the corresponding dioxenes but, interestingly, it does not give Diels–Alder type compounds corresponding to **2** and **3**.

In analogy to photoaddition of phenanthrenequinone,[4] it is expected that electronically excited TCQ adds to 2-butenes from its lowest triplet state by a stepwise radical mechanism, via **7**, to give a mixture of *cis*- and *trans*-dioxenes **4** and **5** in which the former is always in excess. The contribution of the polar resonance form **8** is obviously not significant since a "memory effect" such as that reported in the photoaddition of TCQ to stilbenes[2] is not observed. This discrepancy may be attributed to a better stabilization of the polar form **8** by the phenyl group in that case.



**7** **8**

Alternatively, during the photolysis the exciplex of TCQ and a 2-butene, such as **9**, may be involved since *o*-benzoquinones, particularly those of halogenated ones, are known to be good electron acceptors in their electronically excited state.[8] Such an exciplex should undergo stepwise addition readily to give **4** and **5** via **7** or **8**. However, attempts to detect the presence of an exciplex in these systems have not been successful. A similar type of the exciplex between TCQ and benzene may be proposed as an alternative route to the formation of **6**.



**9**

The nonstereospecific formation of dioxenes **4** and **5** in the photoaddition of TCQ probably does not arise from isomerization of *cis*- or *trans*-2-butenes during irradiation on the same grounds as discussed previously.[4] The lowest triplet state energy of TCQ is reasonably estimated to be ~50 kcal/mol, which is much too low to sensitize the isomerization of 2-butenes, which have a lowest triplet energy[5] of ~80 kcal/mol.

## Experimental Section

**General.** Melting points were measured with a Fisher-Johns apparatus and were uncorrected. Vapor phase chromatography was done with a Varian 1400 flame ionization instrument using a column packed with 20% SE-30 on 60–80 mesh Chromosorb W. Unless specified otherwise, the NMR spectra were obtained in $CDCl_3$ solution with $Me_4Si$ internal standard in a Varian A56/60 instrument, ir spectra in Nujol mulls with a Perkin-Elmer 457 spectrophotometer, and the mass spectra with a Hitachi RMU-6E mass spectrometer at the chamber voltage of 80 eV. Elemental analysis was performed by Dr. A. Bernhardt, Mikroanalytisches Laboratorium, West Germany. TCQ was obtained from Aldrich Chemical Co., Milwaukee, Wis., and was recrystallized from petroleum ether, to give mp 121–123 °C. 2-Butenes were obtained from Mathieson of Canada, Inc.

**General Procedure of Thermal Addition of TCQ.** TCQ (8 mmol), an olefin (6–8 molar equiv), and reagent grade benzene (55 ml) were placed in a Carius tube (200 ml capacity) which was then sealed under a nitrogen atmosphere. The tube was treated at 128 °C for 5 h and cooled. The reaction product was transferred into a round-bottomed flask and solvent was removed under vacuum at ~45 °C. In some cases, the major product separated on dilution with petroleum ether and was recrystallized. The mother liquor was chromatographed to separate the minor products.

**Thermal Addition to *cis*-2-Butene.** TCQ (2 g, 8 mmol), *cis*-2-butene (3.5 g, 62 mmol), and benzene (55 ml) were sealed in a Carius tube and heated. Upon workup, **2** precipitated as a yellow solid (0.665 g). It was crystallized from benzene: mp 180–181 °C; ir 1758, 1580 cm$^{-1}$; NMR τ 8.84 (6 H, *J* = 7 Hz), 8.26 (2 H, m).

Anal. Calcd for $C_{10}H_8O_2Cl_4$: C, 39.96; H, 2.65; Cl, 46.85. Found: C, 39.86; H, 2.67; Cl, 46.94.

The mother liquor (1.54 g) was chromatographed on a silicic acid column (45 g, 10 × 3.6 cm). Dioxene **4** (0.400 g) was eluted with chloroform. An analytical sample was prepared by sublimition: mp 89–91 °C; ir 1550, 1457, 1435 (broad), 1082, 1021 cm$^{-1}$; NMR τ 8.6 (6 H, *J* = 6 Hz), 5.58 (m, 2 H); mass spectrum *m/e* 302 (M$^+$).

Anal. Calcd for $C_{10}H_8O_2Cl_4$: C, 39.96; H, 2.65; Cl, 46.85. Found: C, 39.93; H, 2.79; Cl, 46.85.

**Thermal Addition to *trans*-2-Butene.** TCQ (2 g, 8 mmol), *trans*-2-butene (3.5 g, 62 mmol), and benzene (55 ml) were sealed in a Carius tube and heated. Upon workup and chromatography using silicic acid (60 g, 20.5 × 2.4 cm), **5** (900 mg) was first eluted with chloroform. An analytical sample was prepared by sublimation: mp 141–143 °C; ir 1558, 1077, 1065 cm$^{-1}$ (shoulder); NMR τ 8.58 (6 H, *J* = 6 Hz), 6.08 (2 H, m).

Anal. Calcd for $C_{10}H_8O_2Cl_4$: C, 39.96; H, 2.65; Cl, 46.85. Found: C, 39.98; H, 2.81; Cl, 46.85.

A second product (287 mg) was eluted as an unknown compound using 1% methanol in chloroform, and was recrystallized from benzene–petroleum ether (2 ml, 1:4): mp 78–81 °C; ir 1603 (weak), 1470, 1420, 1360, 1295, 1270, 1175 cm$^{-1}$; NMR τ 8.35 (3 H), 6.45 (2 H), 4.55 (4 H); MS *m/e* (rel intensity) 272 (1), 270 (16), 268 (52), 266 (52), 235 (11), 233 (17), 231 (15), 218 (21), 217 (24), 216 (36), 215 (45), 213 (27), 197 (25), 195 (72), 149 (38), 103 (44), 99 (42), 51 (100).

Anal. Calcd for $C_{10}H_9O_2Cl_3$: C, 44.90; H, 3.40; Cl, 39.75. Found: C, 44.68; H, 3.45; Cl, 39.70.

Finally, **3** (481 mg) was eluted using 1% methanol in chloroform. Repeated recrystallization from petroleum ether–methylene chloride (3:1) did not give pure **3**: mp 72–75 °C; ir 3480, 1770, 1595, 1140 cm$^{-1}$; NMR τ 8.83 (m), 7.0–8.3 (m), 5.5 (m).

From the integration of the NMR spectra, the yields of **3**, **5**, and the unknown were estimated to be 38, 20, and 34%, respectively.

**General Procedure for Photoaddition of TCQ.** TCQ (8 mmol), an olefin (2–8 molar equiv), and reagent grade benzene (100 ml) were placed in a Pyrex photolysis apparatus and irradiated with a Hanovia medium-pressure mercury lamp at ice bath temperature. The solution was agitated with a magnetic stirrer and was purged with a slow stream of nitrogen. At intervals, an aliquot of the photolysate was pipetted out and was properly diluted for spectroscopic measurements in the 400–500-nm region. The photolysis was continued until the quinone absorption at 450 nm disappeared completely.

For workup of the reaction mixture, the solvent was removed under vacuum at ~45 °C. In some experiments, crystalline compound separated on dilution with petroleum ether; the mother liquor was separated by column chromatography.

**Photoaddition to *cis*-2-Butene.** TCQ (2 g, 8 mmol), *cis*-2-butene (1.25 g, 22 mmol), and benzene (100 ml) were photolyzed until the quinone absorption peak disappeared (2 h). After solvent removal, the protuct (2.1 g) was chromatographed on an alumina column (grade 1, 75 g). Dioxene **4** (512 mg) was eluted first using a mixture of benzene and chloroform (1:1) and was identified by melting point and spectral data. The last fraction eluted with methanol was mainly phenol **6** (406 mg). It was crystallized from petroleum ether: mp 138–140 °C (lit.[2] mp 134 °C); ir 793, 1488, 1590, 1600, 3340 $cm^{-1}$; NMR $\tau$ 4.4 (1 H, OH), 2.1–2.7 (5 H, aromatic protons). The middle fractions were mixtures of **4** and **5** as indicated by the NMR. On the basis of NMR analysis of the photolysis product, the ratio of **4, 5,** and **6** was 6:2:9.

In a separate experiment, TCQ (5 g, 20 mmol), *cis*-2-butene (8 g), and benzene (250 ml) were photolyzed using filter solution containing $NaNO_2$ and sodium phthalate. The photolysis was complete in 2 h. The product was worked up and examined as above. The NMR of the product was identical with the one obtained without a filter. This was further checked by silicic acid chromatography.

**Photoaddition to *trans*-2-Butene.** TCQ (2 g, 8 mmol), *trans*-2-butene (3.0 g, 50 mmol), and benzene (100 ml) were photolyzed until the 450-nm peak of TCQ disappeared (1 h). Upon solvent removal, 2.5 g of yellow gum was obtained. A portion (2.1 g) was chromatographed on an alumina column (60 g) and eluted with petroleum ether. Dioxenes **4** and **5** were eluted and were identified by mixture melting points with the samples obtained from the thermal process. Finally phenol **6** was eluted using methanol–chloroform mixtures. Total recovery from the column was 60%. The ratio of **4, 5,** and **6** was 5:3:4 as estimated from the integration of the NMR spectra of the chromatographed fractions.

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**Registry No.**—**1,** 2435-53-2; **2,** 58866-14-1; **3,** 58894-39-6; **4,** 58866-15-2; **5,** 58866-16-3; **6,** 21464-64-2; *cis*-2-butene, 590-18-1; *trans*-2-butene, 624-64-6.

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# Asymmetric Adsorption of DL-Alanine Hydrochloride by Quartz

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In 1938 Karagunis and Coumoulos,[1] after reporting the resolution of an asymmetric chromium complex using a chromatography column consisting of powdered quartz, first suggested that asymmetric adsorption of racemic adsorbates on the surfaces of optically active minerals might have been the genesis of the first optically active molecules in nature. This suggestion appeared to receive abundant (if marginal) documentation[2] until 1968, when Amariglio et al.[3] were unable to repeat several critical quartz-mediated asymmetric adsorption experiments reported in the earlier literature, and thereupon concluded that all previous successful reports were uniformly erroneous. Because of these contradictions, we recently undertook[4,5] a reexamination of this question using experimental techniques not depending upon the polarimetric measurement of optical activity as a criterion for asymmetric adsorption, and using adsorbates more realistic from the viewpoint of prebiotic chemical evolution, namely, amino acids. We found[4,5] that radioactive D- and L-alanine hydrochloride enantiomers in $10^{-5}$ M dimethylformamide solutions were adsorbed by *d*- and *l*-quartz to the extent of 20–30% (as shown by radioactivity loss), and that *d*-quartz preferentially adsorbed D-alanine hydrochloride and *l*-quartz L-alanine hydrochloride. The extent of asymmetric (differential) adsorption was rather small, however, being only 0.96–1.75% (at the 99.9% confidence level). We have now extended these studies to DL-alanine hydrochloride, with the observation of significantly higher and more reproducible extents of asymmetric adsorption.

Several dilute solutions (ca. $10^{-5}$ M) of DL-alanine hydrochloride in anhydrous dimethylformamide were prepared, one set having the L enantiomer only labeled with $^3H$ and the other having the D enantiomer only labeled with $^{14}C$. The radioactivity count for an aliquot of each stock solution was established by liquid scintillation counting, whereupon equal volumes of each solution were exposed to identical weights of carefully dried *d*- and *l*-quartz (average particle size, 96 $\mu$m) under anhydrous conditions. After equilibration, similar sized aliquots of the supernatant in each experiment were removed and recounted for radioactivity. The radioactivity counting data, percent total adsorption, and percent differential adsorption for the three experiments conducted are calculated and summarized in Table I.

It should be emphasized that each pair of *d*- and *l*-quartz experiments in Table I is mirror symmetric with respect to the quartz. That is, identical quantities of *d*- and *l*-quartz samples of identical particle size range were employed with identical quantities of each amino acid solution. Thus it follows in expt I, for example, that the amount of *unlabeled* D-alanine hydrochloride adsorbed from the racemate by the *l*-quartz must have been 17.58%, i.e., the same as the quantity of *labeled* L enantiomer adsorbed by the *d*-quartz. Thus the *total* racemate which was adsorbed by the *l*-quartz (or the *d*-quartz) in this experiment was 43.93%, the sum of no. 5 and no. 6. As seen in no. 7 of Table I, the total adsorption in the three experiments varied from 38 to 48%.

No. 8 in Table I shows the differential adsorption ($A$) of the D and L components of the racemic alanine hydrochloride solutions by *d*- and *l*-quartz, defined in terms of the difference in the amount of each enantiomer left in the supernatant divided by the amount of that enantiomer originally present. On this basis, the differential adsorption ($A$) in the three sets of experiments ranges from ca. 5.7 to 8.8% (a compared to only 1–1.8% in our earlier study[4,5]). It is even more striking if we look at the differential adsorption ($B$) in terms of the percent of each enantiomer adsorbed divided by the total percent of racemate adsorbed. From this viewpoint (no. 9) the differential adsorption ($B$) ranges from ca. 11.8 to 20.3%. From either viewpoint we see clearly that *l-quartz preferentially adsorbs* L*-alanine hydrochloride from a racemic mixture, whereas d-quartz favors the* D *enantiomer*—results which unambiguously confirm the conclusions of our earlier exper-