chloride, 7669-54-7; *p*-nitrobenzenesulfenyl chloride, 937-32-6; 6-aminopenicillanic acid, 551-16-6; 6-(dibenzenesulfenimido)penicillanic acid, 58816-32-3; 6-(benzenesulfenamido)penicillanic acid, 58816-33-4; diazomethane, 334-88-3; methyl 6-(dibenzenesulfenimido)penicillanoate, 58816-34-5; methyl 6-(benzenesulfenamido)-penicillanoate, 58816-35-6; penicillin G, 61-33-6.

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An Anomeric Effect in Photochemical Hydrogen Abstraction Reactions of Tetrahydropyranyl Ethers[1]

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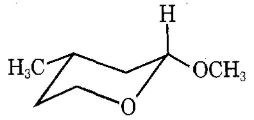
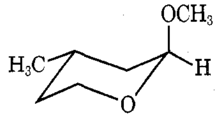
In our previous paper[3] on excited-state ketone initiated hydrogen abstraction reactions of 2-methoxytetrahydropyran, there was some indication that conformational effects might be important. *cis*- and *trans*-2-methoxy-4-methyltetrahydropyran (1) exist primarily in single conformations,[4] and therefore provide an ideal system for studying these effects. The cis isomer exists almost completely in the conformation having the methoxy group equatorial since, in the alternative conformation, a severe 1,3-diaxial interaction between the methyl and methoxy groups is unfavorable. On the other hand, the trans isomer exists almost completely in the conformation with the methyl group in the more favorable equatorial position and the methoxy group axial, which is favored owing to the anomeric effect. A mixture of *cis*- and *trans*-1 was prepared according to literature procedures[5] and a portion was separated by gas chromatography. Assignment of the isomers, based on NMR of the "anomeric" hydrogen, was in agreement with the literature.[5]

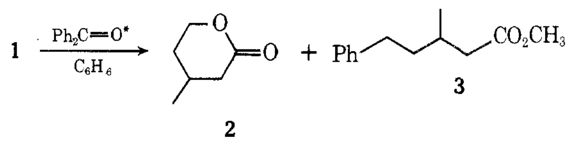


cis-1

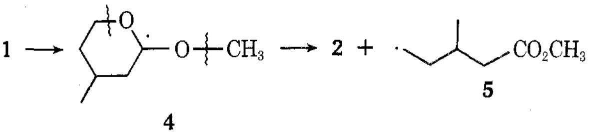


trans-1

Irradiation of mixtures of benzophenone and either the individual isomers of 1 or an isomeric mixture in benzene gave 3-methyl-δ-valerolactone (2) and methyl 3-methyl-5-phenylvalerate (3). The ratio of these products varied somewhat with conditions, but in a typical run, the yields, based on unrecovered starting material, were 29 and 5% for 2 and 3, respectively. Interestingly, no methyl 3-methylvalerate was detected for irradiations in benzene, even though the analogous product was found previously in the 2-methoxytetrahydropyran system.[3]



The products are analogous to those observed previously[3] in the 2-methoxytetrahydropyran system, and can be rationalized by initial hydrogen abstraction by excited benzophenone to give free radical **4**, which can then undergo carbon–oxygen bond cleavage in either of two modes to give lactone **2** or open-chain radical **5** which reacts with benzene solvent to give **3**.

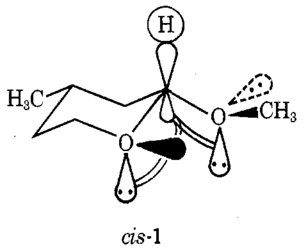


The most interesting aspect of the observed chemistry is that the cis isomer of 1 was consumed much more rapidly than the trans isomer. This was obvious when either the individual isomers or isomeric mixtures were irradiated. Relative quantum yields are not a good measure of relative rates of excited state processes. In the present system, the lifetime of benzophenone triplet might be different in the presence of the two individual isomers. Therefore, irradiations of mixtures of the isomers in the presence of benzophenone were carried out and the ratio of rate constants for the disappearance of the individual isomers was calculated by the following formula:[6]

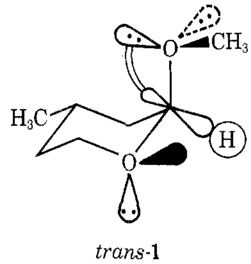
$$k_{\text{cis}}/k_{\text{trans}} = \ln([\text{cis}]/[\text{cis}]_0)/\ln([\text{trans}]/[\text{trans}]_0)$$

The ratio was found to be 8.0 ± 1.4 for several samples irradiated for consumptions of total starting material ranging from 40 to 54%. It was necessary to go to these high conversions to get a large enough change in the trans isomer concentration to determine an accurate ratio. The apparently large variations in the ratio were due to the fact that the function is very sensitive to small changes in the value for the amount of *trans*-1 remaining. The preferential abstraction of an axial hydrogen in this system is even more impressive when comparison is made with 4-*tert*-butylcyclohexanol, which does not contain a ring oxygen. In the latter system, *equatorial* hydrogen abstraction was preferred.[7]

The greater reactivity of *cis*-1, which undergoes abstraction of an axial hydrogen atom, can be rationalized nicely in terms of overlap of nonbonding orbitals on both oxygens with the C–H bond being broken. Thus, the cis isomer has a nonbonding orbital on each of the two oxygens which is antiperiplanar to the bond being broken. The trans isomer, on the other hand, has only one such nonbonding orbital antiperiplanar to the bond being broken and, therefore, the transition state leading to the common free radial 4 is stabilized to a lesser degree by orbital overlap. A similar rationale has been



cis-1



trans-1

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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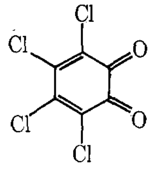
Tetrachloro-*o*-quinone (**1**, TCQ) is known to add to various conjugated and reactive olefins by thermal or photolytic initiation[1,2] to give 1,4-dioxenes and bicyclic α diketones. It has been reported[2] that thermal addition of TCQ to *cis*- and *trans*-stilbenes is stereospecific giving *cis*- 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 τ 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-



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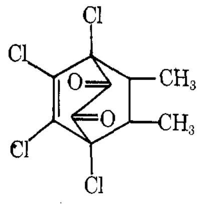
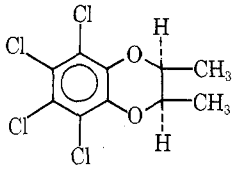


2 or **3**



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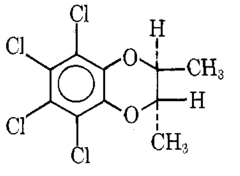

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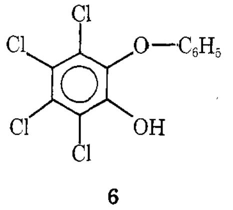

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