phenols, but found conventional methods of ether cleavage[1,2] to be unsatisfactory. These generally involve heating in the presence of acid and caused dehydration of the carbinols with formation of the corresponding olefins. However, the desired compounds were prepared in good yield by reaction at low temperature with stoichiometric amounts of boron tribromide.[3-5]

Experimental Section

Melting points were taken on a Fisher-Johns apparatus. Infrared spectra (KBr pellet) were recorded on a Perkin-Elmer Model 237 spectrophotometer. Gas chromatography–mass spectrometry was performed using a Perkin-Elmer Model 990 gas chromatograph coupled to an Hitachi RMU-6E mass spectrometer by a modified Watson-Biemann separator. A 180 × 0.2 cm glass column was used, packed with 3% OV-225 on 100–120 mesh Supelcoport. Helium flow rate was 20 ml/min and the column was operated at 190°. Electron impact spectra were recorded at 70 eV.

Demethylation Procedure. A 5% w/v solution of the ether in dry dichloromethane was cooled to −80° and added to a similarly cooled 10% v/v solution of boron tribromide in dichloromethane. One mole of reagent was used for each mole of methoxyl to be cleaved, i.e., 3 mol of reagent per mole of compound I and 2 mol of reagent per mole of compound II. The mixture, protected from moisture by a calcium chloride drying tube, was allowed to warm to room temperature overnight. Water was added to hydrolyze the boron–ether complex and any excess reagent and the phenolic product was extracted into diethyl ether.

I. 3-Hydroxy-3-(3,4-dihydroxyphenyl)-4-(4-hydroxyphenyl)hexane. Crude material was crystallized from benzene–hexane, yield 80%, mp 120°. Anal. Calcd for $C_{18}H_{22}O_4$: C, 71.50; H, 7.33; O, 21.17. Found: C, 71.45; H, 7.20; O, 21.35.

Gas chromatography of the tristrimethylsilyl ether yielded a single peak, retention time 8.8 min.

The mass spectrum of the trimethylsilyl derivative exhibited no molecular ion. Base ion was at *m/e* 500 as a result of loss of water from the molecule. Other prominent ions were at *m/e* 485 (loss of CH_3), 472 (loss of C_2H_4), 295, 205 (hydrogen transfer followed by scission of the molecule between C-3 and C-4 of the hexane chain), 281, 219 (rearrangement followed by scission), 75, 73 (from Me_4Si).

The infrared spectrum of the parent compound exhibited the expected bands due to bonded phenolic OH at ca. 3200 and 1240 cm^{-1} and substituted aromatic CH stretch in the region 1500–1600 cm^{-1}. In addition, a sharp band appeared at 3620 cm^{-1}. This band was absent in the spectrum of 3,4-bis-(4-hydroxyphenyl)hexane (diethylstilbestrol) and may, therefore, be attributed to nonbonded carbinol OH.

II. 3-Hydroxy-3,4-bis(4-hydroxyphenyl)hexane was crystallized from benzene, yield 87%, mp 137°. Anal. Calcd for $C_{18}H_{22}O_3$: C, 75.49; H, 7.74; O, 16.76. Found: C, 75.20; H, 7.80; O, 17.00.

Gas chromatography of the bistrimethylsilyl ether yielded a single peak, retention time 6.4 min.

The mass spectrum of the trimethylsilyl derivative was similar in all respects to that of compound I with ions appearing 88 amu lower. Base ion was at *m/e* 412 and other prominent ions appeared at *m/e* 397, 384, 207, 205, 219, 193, 75, and 73.

The infrared spectrum of the parent compound was also similar to that of compound I with differences attributable to the lesser degree of substitution of compound II.

Acknowledgment. This research was supported by the Program for Applied Research on Fertility Regulation, University of Minnesota, under subcontract PARFR-65 to contact AID/csd-3608.

Registry No.—I, 57090-99-0; II, 5331-23-7; 3-hydroxy-3-(3,4-dihydroxyphenyl)-4-(4-hydroxyphenyl)hexane, 57091-00-6; 3-hydroxy-3,4-bis(4-hydroxyphenyl)hexane, 7504-83-8; boron tribromide, 10294-33-4.

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Stereochemistry of the Type II Elimination from 4-*tert*-Butylcyclohexyl Phenylacetate

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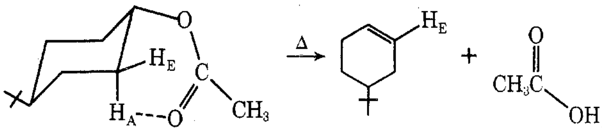
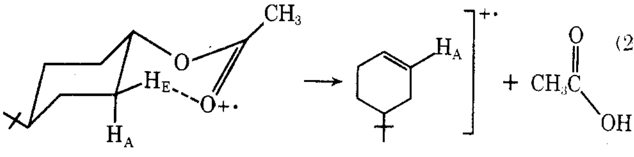
Recently, it has been observed that the stereochemistries of the electron impact induced and pyrolytic elimination of acetic acid from *trans*-4-*tert*-butylcyclohexyl acetate (I) differ.[1] The near-exclusive cis elimination observed in the pyrolysis (eq 1) is related to the greater ease of forcing cis cyclohexyl substituents toward coplanarity than trans substituents.[2] Since the pyrolysis is a concerted elimination, introduction of a double bond into the cyclohexyl ring system must involve a movement toward coplanarity of the eliminated substituents.[2,3] Conversely, it was suggested that the predominantly trans elimination observed in the electron impact induced process (eq 2) was evidence for the nonconcerted nature of this process.[4] In order to test this hypothesis, it appeared desirable to examine the stereochemistry of a bona fide stepwise unimolecular elimination occurring in an accessible phase. Because of the considerable recent interest in the type II photoelimination from phenylacetates, this reaction was an obvious choice for further investigation.



I

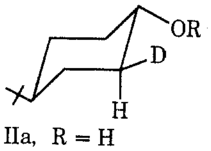
(1)



I

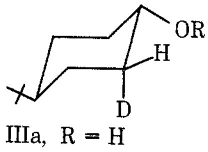
(2)

The photolytic elimination of phenylacetic acid has been suggested to be a syn intramolecular, nonconcerted process proceeding predominantly or exclusively through a singlet state.[5] Thus, the phenylacetates of the stereospecifically labeled alcohols IIa–Va were prepared and irradiated. Mass spectrometry was utilized to establish the isotopic composition of the 4-*tert*-butylcyclohexene product and thus the



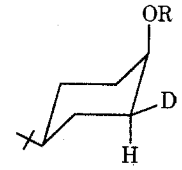
IIa, R = H

b, $R = C_6H_5CH_2\overset{O}{\overset{\|}{C}}$



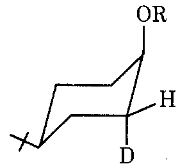
IIIa, R = H

b, $R = C_6H_5CH_2\overset{O}{\overset{\|}{C}}$



IVa, R = H

b, $R = C_6H_5CH_2\overset{O}{\overset{\|}{C}}$



Va, R = H

b, $R = C_6H_5CH_2\overset{O}{\overset{\|}{C}}$

Table I
Isotopic Composition of Phenylacetic Acid Eliminated in the Photolysis of Stereospecifically Labeled 4-*tert*-Butylcyclohexyl Phenylacetates in Hexane at 254 nm

Compd	H loss/D loss [a]
trans-4-*tert*-Butylcyclohexyl phenylacetate-*trans*-2-*d* (IIb)	3.9 ± 0.3
trans-4-*tert*-Butylcyclohexyl phenylacetate-*cis*-2-*d* (IIIb)	8.4 ± 0.5
cis-4-*tert*-Butylcyclohexyl phenylacetate-*cis*-2-*d* (IVb)	1.6 ± 0.2
cis-4-*tert*-Butylcyclohexyl phenylacetate-*trans*-2-*d* (Vb)	>50

[a] Errors are standard deviations from the mean of at least four runs.

stereochemistry of the elimination. The results appear in Table I.

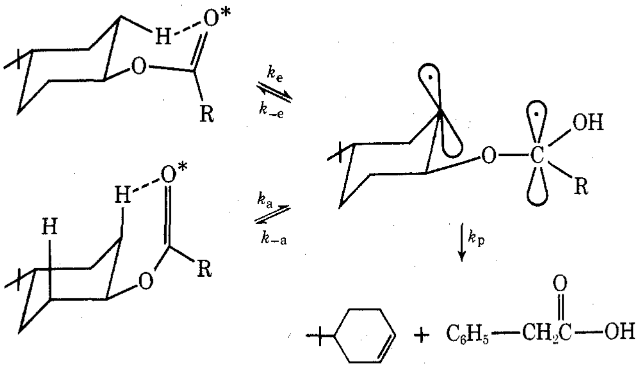
The trans labeled phenylacetate IIb eliminates deuterium ca. twice as frequently as the cis labeled phenylacetate IIIb, consistent with predominant trans elimination.[6] This unusual behavior is not attributable to the intervention of an intermolecular radical-type process. Added 4-methyl-2-pentene has been shown to suppress radical-type products in these systems;[5a,b] photolysis of the labeled phenylacetates IIb and IIIb in the presence of 0.5 *M* 4-methyl-2-pentene gives 4-*tert*-butylcyclohexene of the same isotopic composition as photolysis in the absence of 4-methyl-2-pentene. Further, the complete absence of trans elimination from the axial phenylacetate Vb is most consistent with an intramolecular reaction.

Another explanation for the observed net trans elimination postulates that the stereochemistry of the label is reversed prior to elimination. This possibility is excluded by two observations. The isotopic composition of the alkene produced by the photolysis of either labeled equatorial phenylacetate did not vary significantly as the extent of the reaction was varied from 10% to 80%. Further, photolysis of phenylacetate recovered after photolysis was 80% complete gave alkene of the usual isotopic composition. Thus, the elimination reaction must occur faster than loss of stereochemistry. The photolysis of *trans*-4-*tert*-butylcyclohexyl phenylacetate then provides a rare example of an intramolecular elimination with preferred trans stereochemistry.[7]

These data do not suffice to permit rigorous determination of the exact extent of cis and trans elimination from unlabeled *trans*-4-*tert*-butylcyclohexyl phenylacetate. However, if the gross simplifying assumptions are made that the primary isotope effects for cis and trans elimination are identical, and that secondary isotope effects can be neglected, the data for the labeled compounds IIb and IIIb require $\Phi_{\text{trans-H}}/\Phi_{\text{cis-H}} = 1.8 \pm 0.2$, and $\Phi_{\text{hydrogen}}/\Phi_{\text{deuterium}} = 1.8 \pm 0.2$. The latter figure is in reasonable agreement with the more rigorously determined isotope effect observed in the elimination proceeding from *cis*-4-*tert*-butylcyclohexyl phenylacetate-*cis*-2-*d* (IVb) ($\Phi_{\text{hydrogen}}/\Phi_{\text{deuterium}} = 1.6 \pm 0.2$).

Consideration of the formulation of Scheme I provides a possible explanation for the observed stereochemistry. If abstraction of an axial or an equatorial hydrogen atom generates a common biradical intermediate from which product formation and reverse hydrogen transfer occur, the ratio of equatorial hydrogen elimination to axial hydrogen elimination corresponds to k_e/k_a.[8] The half-vacant n orbital of the n,π* carbonyl group can assume a coplanar relationship[9] with either C–H bond without distortion of the cyclohexyl ring system. The *trans*-decalin-like transition state for abstraction of the equatorial hydrogen appears strain free. Conversely, a 1,3-diaxial interaction exists between the axial hydrogen at C-6 and the phenylacetyl moiety in the *cis*-decalin-like transition state for axial hydrogen abstraction. Thus, the transition state for cis axial hydrogen abstraction is destabilized relative to the transition state for trans equatorial hydrogen atom abstraction.

Scheme I



These experiments demonstrate a clear dichotomy between the stereochemistries of representative concerted and nonconcerted unimolecular eliminations proceeding through six-membered transition states. If this result proves general, the stereochemistry of elimination from the *trans*-4-*tert*-butylcyclohexyl system may provide a simple test for the concertedness or nonconcertedness of such reactions, a subject of current interest in mass spectrometry[4] and photochemistry.[10]

Experimental Section

The stereospecifically labeled alcohols IIa–Va were prepared as previously described.[1] Conversion to the corresponding phenylacetates IIb–Vb was accomplished by analogy to the procedures of Yarchak, Dalton, and Saunders.[5a]

Photolyses were also conducted according to the general procedures of Yarchak, Dalton, and Saunders.[5a] The phenylacetates were irradiated as thoroughly degassed 0.01 *M* solutions in hexane using an eight-lamp Rayonet preparatory reactor equipped with Rayonet RPR 2537-Å lamps.

The alkene product was isolated by preparative gas chromatography on a Hewlett-Packard F & M Model 5750 containing a 20-ft UCW-98 column operated at 90°. Control experiments demonstrated that the unreacted phenylacetate was not undergoing detectable elimination of phenylacetic acid under the conditions of the gas chromatographic analysis.

The deuterium content of the purified 4-*tert*-butylcyclohexene was determined by analysis of the molecular ion region of the alkene at 70 eV ionizing voltage on an AEI MS-902 mass spectrometer. The calculated ratios of protium loss to deuterium loss varied by less than 10% as the ionizing voltage was varied from 70 eV to threshold.

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Registry No.—IIb, 57172-70-0; IIIb, 57172-71-1; IVb, 57172-72-2; Vb, 57172-73-3; phenylacetic acid, 103-82-2.

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(6) The high ratios of hydrogen loss to deuterium loss observed for IIb and IIIb are due to the operation of an isotope effect; photolysis of *trans*-4-*tert*-butylcyclohexyl phenylacetate-*2,2,6,6-d_4* proceeded with >98% elimination of phenylacetic acid-d_1.

(7) A referee has suggested that this conclusion is contradicted by the data reported by Saunders et al. (ref 5a) for photoelimination from *cis*- and *trans*-2-methylcyclohexyl phenylacetate. Actually, however, Saunders' data permit no conclusions concerning the preferred stereochemistry of elimination from *trans*-4-*tert*-butylcyclohexyl phenylacetate. For example, *cis*-2-methylcyclohexyl phenylacetate photoeliminates to give ca. 10% 1-methylcyclohexene (trans elimination) and ca. 90% 3-methylcyclohexene (cis and trans elimination). However, since this compound exists largely (80–85%) in the conformer in which the phenylacetate group is axial,[5a] and since the quantum yield for elimination from certain axial phenylacetates is ca. three times greater than that from the corresponding equatorial phenylacetates,[5a] this result has little relevance to the stereochemistry of elimination from an equatorial phenylacetate. *trans*-2-Methylcyclohexyl phenylacetate exists very predominantly in the conformer with an equatorial phenylacetate; photoelimination gives roughly equal amounts of 1-methylcyclohexene (trans elimination) and 3-methylcyclohexene (cis and trans elimination). However, since the relative reactivities of secondary and tertiary hydrogens in this reaction are unknown, conclusions concerning the preferred stereochemistry of elimination from *trans*-4-*tert*-butylcyclohexyl phenylacetate are hazardous. Nevertheless, the relatively large amount of 1-methylcyclohexene observed is indicative of appreciable trans elimination from this system, and fully consistent with the results in this paper.

(8) Alternatively, if alkene formation and/or reverse hydrogen transfer occur from isomeric biradicals, the overall stereochemistry will depend on the relative rates of axial and equatorial hydrogen abstraction, and on the relative rates of reverse hydrogen transfer and alkene formation from each biradical.

(9) K. Dawes, J. C. Dalton, and N. J. Turro, *Mol. Photochem.*, **3,** 71 (1971); N. J. Turro and D. S. Weiss, *J. Am. Chem. Soc.*, **90,** 2185 (1968).

(10) See, for example, L. M. Stephenson, P. R. Cavigli, and J. L. Partlett, *J. Am. Chem. Soc.*, **93,** 1984 (1971); P. J. Wagner and R. G. Zepp, *ibid.*, **94,** 287 (1972); F. D. Lewis, *ibid.*, **92,** 5602 (1970).

Methoxycarbonylation of Substituted Benzenes. Effect of the Electronic Configuration of Carbon Radicals in Homolytic Substitutions

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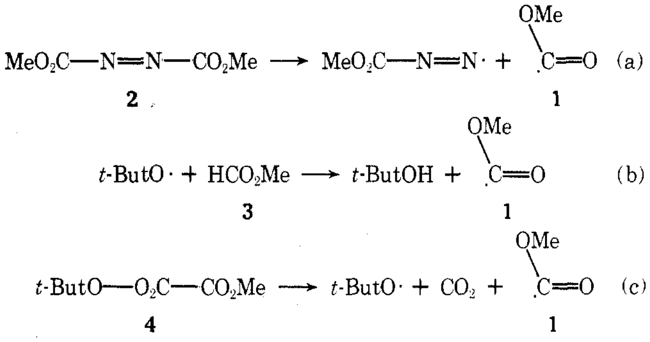
From studies of relative rates and isomer distributions in homolytic substitutions it emerged that one of the factors affecting the polar nature of carbon-centered radicals is the hybridization of the orbital carrying the unpaired electron; because the s orbital has higher electronegativity than the p orbital, it can be expected that the greater the s character of an orbital, the greater will be its electronegativity and hence the lower will be the nucleophilicity of the corresponding radical. Thus for carbon radicals the nucleophilicity should decrease along the series p > sp^3 > sp^2 > sp; substituents linked to the radical carbon atom will modify the polar character and it can be expected that this effect should be more pronounced with π than with σ radicals. Simple alkyl and bridgehead polycyclic alkyl radicals present various degrees of nucleophilicity depending upon their structure, while acetylenic radicals are slightly electrophilic.[1] Radicals produced on carbon having an sp^2 configuration, like phenyl,[2] vinyl,[3] and cyclopropyl,[4] present substantially similar neutral properties; only in the case in which they react with strongly deactivated substrates, like the protonated pyridines, some degree of nucleophilicity can be evidenced, which, however, is much less pronounced than that of simple alkyl radicals.[5] The effect of substituents on σ radicals having an sp^2 configuration has been studied in the case of the phenyl radical; the presence of electron-withdrawing or electron-donating groups makes the resulting aryl radical respectively more electrophilic or more nucleophilic than the phenyl radical.[2]

We report in this paper the results of a study on the methoxycarbonyl radical, $\cdot CO_2Me$, carried out with the aim of investigating the effect of the oxygen functions on the electronic nature of this radical, where the unpaired electron still occupies an sp^2 orbital.[6] Alkoxycarbonyl radicals have been formulated as reaction intermediates[7–11] and have been spectroscopically detected and studied;[12,13] indications that these radicals can effect homolytic substitutions on aromatic[8] and heteroaromatic[14] compounds have also been obtained. In the present investigation methoxycarbonyl radicals, **1**, have been produced in three different ways: (a) the thermal decomposition, at 130°C, of dimethyl azodicarboxylate (**2**); (b) the hydrogen abstraction from methyl formate (**3**) by *tert*-butoxy radicals, photolytically generated at room temperature;[12] and (c) the thermal decomposition,[7] at 65°C, of the methyl *tert*-butylperoxyoxalate (**4**).



$$\underset{\mathbf{2}}{MeO_2C{-}N{=}N{-}CO_2Me} \longrightarrow MeO_2C{-}N{=}N\cdot + \underset{\mathbf{1}}{\cdot C(OMe){=}O} \quad (a)$$

$$t\text{-}ButO\cdot + \underset{\mathbf{3}}{HCO_2Me} \longrightarrow t\text{-}ButOH + \underset{\mathbf{1}}{\cdot C(OMe){=}O} \quad (b)$$

$$\underset{\mathbf{4}}{t\text{-}ButO{-}O_2C{-}CO_2Me} \longrightarrow t\text{-}ButO\cdot + CO_2 + \underset{\mathbf{1}}{\cdot C(OMe){=}O} \quad (c)$$

Experiments carried out in benzene showed that the substitution product, the methyl benzoate, was formed in every case. Small quantities of toluene were also detected indicating that the radical **1** suffers fragmentation to CO_2 and methyl radicals; in the cases b and c the methyl radicals can obviously be produced also from the *tert*-butoxy radicals.

$$\begin{aligned}\cdot CO_2Me + C_6H_6 &\longrightarrow C_6H_5CO_2Me\\ \cdot CO_2Me &\longrightarrow CO_2 + Me\cdot\\ t\text{-}ButO\cdot &\longrightarrow Me_2CO + Me\cdot\\ \cdot Me + C_6H_6 &\longrightarrow C_6H_5Me\end{aligned}$$

Diphenyl was also formed as a by-product in the reactions b and c, but not from the decomposition of **2**; the formation of this compound has already been reported from the decomposition of the ethyl *tert*-butylperoxyoxalate[7] and of the di-*tert*-butyl peroxide[15] in benzene and has been attributed to the production of phenyl radicals from the reaction of *t*-ButO· with benzene.[16] Finally, from the reactions b and c in benzene traces of dibenzyl were also detected as a result of the dimerization of the benzyl radicals produced from toluene; the dibenzyl obviously constituted the major reaction product when toluene was used as solvent for the studies on the relative reactivities described below. In the thermolysis of dimethyl azodicarboxylate (**2**), other unidentified products were also present and this reaction was therefore not employed for further studies.

In order to evaluate the polar character of methoxycarbonyl radicals, reactions were carried out in several differently substituted benzenes and in an equimolecular mixture of substituted benzenes and benzene; these experiments allowed the reactivity of the various nuclear posi-