crystallized twice from EtOAc. The dry acid decomposed at 193-194° (lit.⁵³ 195°), and had $\alpha^{24}D + 0.490°$ (1 dm, c 0.0244, water). Based on $[\alpha]^{25}$ D 22.1°, 53 it was 92% optically pure.

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Acknowledgments. We gratefully acknowledge financial support by the National Institutes of Health and the National Science Foundation. Helpful discussions with Professors D. S. Kemp (M. I. T.) and U. P. Strauss and S. Toby (Rutgers) were much appreciated.

Mechanisms of Elimination Reactions. XX. Stereochemistry of Photoeliminations from Some Cyclic Phenylacetates¹

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Abstract: Products and quantum yields were determined in the photolysis at 254 nm of cyclohexyl, cis- and trans-4-tert-butylcyclohexyl, cis- and trans-2-methylcyclohexyl, and cis- and trans-2-methylcyclooctyl phenylacetates. The major products are alkenes resulting from a type II photoelimination, though saturated hydrocarbons and other products derivable from free-radical processes can be found when the reaction mixtures are carefully examined. The photoelimination occurs more efficiently when the ester group is axial to the cyclohexane ring than when it is equatorial. In the 2-methylcyclohexyl system, the trans isomer yields about equal amounts of 1- and 3methylcyclohexene, but the cis isomer yields mainly but not exclusively (ca. 90%) 3-methylcyclohexene. Both cis- and trans-2-methylcyclooctyl phenylacetates, however, yield a product mixture in which 3- predominates over 1-methylcyclooctene by about 3:1. These results indicate that the preferred, but by no means exclusive, mode of elimination is syn. The bearing of the results on the mechanism of photoelimination from esters is discussed.

The pyrolysis of esters to give olefins has been known for some time, and was comprehensively reviewed in 1960.³ Its stereochemical course has been investigated by a number of groups who have shown it to be predominately or exclusively a syn elimination.⁴⁻⁷ An analogous photoeliminaton has been found to occur,⁸⁻¹⁰ but has been much less extensively investigated. The only published accounts of stereochemistry involve 1,2-dimethylbutyl esters. The phenylacetate eliminates at least 90% syn, once a sensitized isomerization of the first-formed product is allowed for,¹¹ while photoelimination from the acetate is less stereoselective.12

We undertook this research in order to gain greater insight into the mechanism and stereochemistry of ester photolysis. In this paper we will consider mainly the stereochemical aspects of the photoelimination. The effect of ring size and the nature of the excited states involved are discussed in an accompanying paper.¹³

We began with exploratory work on cyclohexyl

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benzoate, but abandoned that compound when reasonable photolysis times yielded no measurable amounts of cyclohexene. This observation is in line with a recent report that quantum yields are low in photoeliminations from benzoate esters¹⁴ and with observations on 2pentyl benzoate photolyses in our laboratories.¹⁵ Cyclohexyl phenylacetate at 254 nm, however, gave modest quantum yields (0.03-0.05) when irradiated at 0.05-0.08 M in heptane, benzene, acetonitrile, tetrahydrofuran, sec-butyl alcohol, or tert-butyl alcohol. The quantum yields decreased somewhat with photolysis time, presumably due to quenching or competitive light absorption by products. The value for photolysis of 0.03 M cyclohexyl phenylacetate in hexane at 254 nm was 0.046 ± 0.002 when extrapolated to zero reaction. This and other relevant quantum yields are summarized in Table I.

We noted that the figure for cyclohexyl phenylacetate was distinctly lower than those found for open-chain phenylacetates $(0.2-0.4)^{15}$ or cyclopentyl phenylacetate (0.127 ± 0.015) .¹³ These differences made it evident that the efficiency of the photoelimination depended markedly on conformation. In order to explore this point further, we first chose the conformationally homogeneous systems cis- and trans-4-tert-butylcyclohexyl phenylacetate, which have the ester group axial and equatorial, respectively, to the ring. The results are given in Table I. The axial (cis isomer) ester group photoeliminates with a quantum yield approximately three times that of the equatorial (trans isomer) ester. The cis and trans esters also yield significant amounts of tert-butylcyclohexane.

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Table I. Quantum Yields of Olefin in the Photolysis of Cycloalkyl Phenylacetates in Hexane at 254 nm

R in PhCH₂CO₂R	$\phi_{1- ext{ene}^a}$	$\phi_{3-{ m ene}}{}^a$	ϕ_{total^a}
Cyclohexyl			0.046 ± 0.002
cis-4-tert-			0.073 ± 0.006
Butylcyclo- hexyl ^b			
trans-4-tert-			0.025 ± 0.003
Butylcyclo- hexyl¢			
<i>cis</i> -2-Methyl- cyclohexyl ^d	0.005 ± 0.001	0.047 ± 0.005	0.052 ± 0.006
trans-2-	0.013 ± 0.002	0.014 ± 0.002	0.027 ± 0.004
Methyl- cyclohexyl ^d			
cis-2-Methyl- cyclooctyl	0.013 ± 0.001	0.033 ± 0.005	0.046 ± 0.006
trans-2-	0.013 ± 0.001	0.040 ± 0.005	0.053 ± 0.007
Methyl- cyclooctyl			

^a Quantum yields measured at various times and extrapolated to zero time. Errors are standard deviations from the mean of at least three runs, and incorporate errors in the determination of product proportions where appropriate. ^b tert-Butylcyclohexane was also formed, $\phi = 0.014 \pm 0.001$. ^c tert-Butylcyclohexane was also formed, $\phi = 0.021 \pm 0.002$. ^d Other products were found in addition to olefins. See Table II.

The distance between the ester group and a cis β hydrogen should, to a good approximation, be independent of whether the ester group is axial and the hydrogen equatorial, or vice versa. Consequently, the quantum yields suggest either a concerted process with a transition-state geometry distinctly different from that of the reactant, or a two-stage process with a biradical intermediate. The latter hypothesis permits an attractive rationalization of the quantum yields. The diradical (1) from the cis reactant has the p orbital



containing the odd electron in a position to overlap more effectively with the α carbon-oxygen bond which must break in the product-forming step than does the diradical (2) from the trans reactant. As a result, the efficiency of conversion to product relative to return to reactant (by back-donation of hydrogen from oxygen to carbon) should be higher for 1 than for 2. A more quantitative discussion of the role of the biradical intermediate is given in the accompanying paper.¹³

Another example of the conformational effect is afforded by the 2-methylcyclohexyl phenylacetates. Here the preferred conformation (3) of the cis isomer has the ester group axial, while the preferred con-



formation (4) of the trans isomer has it equatorial. Literature values of the conformational free energies of the methyl (1.5-1.9) and acetoxyl (0.4-0.7) groups¹⁶ indicate that the cis ester should prefer the conformation 3 over that with methyl axial and phenylacetoxyl equatorial by about 1.0 kcal/mol, corresponding to ca. 80-85% in the preferred conformation. The total quantum yield of olefin for the cis isomer exceeds that from the trans isomer by about 2:1, while the quantum yields of 3-methylcyclohexene differ by about 3:1.

Further comparison shows that 4, with two cis β hydrogens, yields approximately equal quantities of 1- and 3-methylcyclohexene, while 3, with no cis β hydrogen available for elimination in the direction of the methyl groups, favors 3-methylcyclohexene by ca. 10:1. Control experiments showed that 3-methylcyclohexene was not converted into 1-methylcyclohexene when irradiated at 254 nm in hexane with methyl phenylacetate. Thus, the elimination is syn stereoselective, but not stereospecific.

In view of the strong dependence of quantum yield on conformation, it is unreasonable to suppose that the 10% of 1-methylcyclohexene from the cis ester is the result of a concerted anti elimination, which would require a highly strained cyclic transition state. Neither cis- nor trans-2-methylcyclohexyl phenylacetate is converted to the other during irradiation, so prior isomerization of reactant is excluded. If a small amount of the olefin was formed via 2-methylcyclohexyl radical (from a type I cleavage) the lack of stereospecificity could be explained. We prefer an interpretation in which the less favored conformation of the cis ester, 5, undergoes abstraction of the tertiary equatorial β



hydrogen to give a diradical. Since the radical center in the ring would presumably be either planar or able to invert readily, the diradical would be equivalent to that from 4, and could collapse to 1-methylcyclohexene and phenylacetic acid.

With the conformationally more flexible 2-methylcyclooctyl phenylacetates, stereoselectivity is almost completely absent (Table I). Here, of course, it is difficult to say a priori whether the trans or cis β hydrogen will be in a more favorable position for abstraction. A concerted syn loss of the trans 2-hydrogen and the ester group from cis-2-methylcyclooctyl phenylacetate must, however, yield 1-methylcyclooctene which is trans about the double bond. While the geometric configuration of the one known isomer of 1-methylcyclooctene has not been rigorously established, Cope and Woo¹⁷ argue persuasively that it must be cis. It follows that the 1-methylcyclooctene from the cis ester resulted in substantial part (25-30%)from a formally anti elimination. As in the 2-methylcyclohexyl system, this low stereoselectivity is most easily explained by a mechanism involving a diradical intermediate. A diradical formed by syn abstraction of

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either a cis or trans β hydrogen could collapse to the *cis*-cyclooctenes which are the only olefins observed (the 3-methylcyclooctene is also very probably cis¹⁷).

While elimination to give olefins is the major reaction observed on photolysis of these esters, other products were found when the mixtures from some of the reactions were more carefully examined. The tert-butylcyclohexane from photolysis of the 4-tert-butylcyclohexyl phenylacetates has already been noted, and probably arises from alkyl-oxygen cleavage to give tert-butylcyclohexyl radical. We also examined carefully the products from the 2-methylcyclohexyl phenylacetates. In addition to the products reported in Table I, methylenecyclohexane, bibenzyl, and traces of toluene were observed. The methylenecyclohexane was quickly shown to be a secondary product, since 1-methylcyclohexene is photoisomerized to methylenecyclohexane in the presence of methyl phenylacetate. This reaction is doubtlessly the same as the reported photoisomerization of 1-methylcyclohexene sensitized by aromatic hydrocarbons.¹⁸

In the hope of obtaining a mass balance, we determined quantitatively all the products we could isolate from the photolysis of *cis*-2-methylcyclohexyl phenylacetate. The results are given in Table II.

 Table II.
 Products from the Photolysis of cis-2-Methylcyclohexyl

 Phenylacetate in Hexane at 254 nm

Product	% yield	ϕ
3-Methylcyclohexene	12.8 ± 0.2	0.038 ± 0.001
1-Methylcyclohexene	1.4 ± 0.1	0.004 ± 0.001
Methylcyclohexane	6.7 ± 0.2	0.020 ± 0.001
Bibenzyl	2.7 ± 0.2	0.008 ± 0.001
Toluene	Trace	
Carbon monoxide	2.2 ± 0.1	0.006 ± 0.001
Carbon dioxide	9.7 ± 0.6	0.029 ± 0.002
cis-2-Methylcyclo- hexanol	~1	
Ester loss	37.8 ± 3.6	0.114 ± 0.011 .

Either our analyses were not quantitative or some products were not isolated, for the sum of the methyl-cyclohexenes, carbon monoxide, and carbon dioxide is only 70% of the ester loss. It is, of course, difficult to obtain precise mass balances in reactions involving free radicals. The high conversion (nearly 40%) necessary to obtain sufficient quantities for determination of the minor products may also lead to secondary photoreactions of the first-formed products. Some of the products of these secondary reactions might be nonvolatile and be missed in the glpc analysis.

In conclusion, we believe that the stereochemical results of these photoeliminations afford excellent evidence for a stepwise process involving a biradical intermediate. While we cannot exclude the possibility that the lack of stereospecificity arises from some olefin formation via cycloalkyl radicals, we believe it unlikely that radicals could be the sole source of the apparent anti elimination product. Where the saturated hydrocarbon, a probable radical product, was determined (with *cis*- and *trans*-4-*tert*-butylcyclohexyl and *cis*-2methylcyclohexyl phenylacetates), its quantum yield (0.015–0.021) was relatively insensitive to reactant

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structure. The photoelimination from the 2-methylcyclooctyl phenylacetates, on the other hand, is much less stereoselective than that from the 2-methylcyclohexyl phenylacetates. Unless the 2-methylcyclohexyl and 2-methylcyclooctyl radicals yield markedly different ratios of radical cleavage to type II photoelimination, it is hard to explain the difference in stereoselectivity. We think it more reasonable to suppose that the cycloalkyl radicals are at best a minor source of olefinic product in all cases. Experimental support for this belief comes from the observation that added 4-methyl-2-pentene substantially reduces the quantum yield of methylcyclohexane (presumably a radical product) from trans-2-methylcyclohexyl phenylacetate without affecting the quantum yields of the olefinic products.13

Experimental Section¹⁹

cis-4-tert-Butylcyclohexanol was obtained from a commercially available (Eastman Organic Chemicals) mixture by chromatog-raphy²⁰ or by fractional crystallization of the benzoates from ethanol. Its properties agreed with literature values.²⁰

trans-4-*tert*-Butylcyclohexanol was obtained from the commercial mixture by fractional crystallization of the acid phthalates,²⁰ and had properties in agreement with literature values.^{20,21}

cis-2-Methylcyclooctanol was obtained from 2-methylcyclooctanone²² by the procedure of Cope and Woo.¹⁷ Separation of the pure cis alcohol from the small amount of trans was effected by glpc on a 6 ft \times ¹/₈ in. column of 10% UCON W-98.

trans-2-Methylcyclooctanol was obtained by the hydroboration of 1-methylcyclooctene.²³ The product and its acid phthalate had properties in agreement with those in the literature,^{23,24} and glpc (see above) showed the alcohol to be the pure trans isomer.

Other alcohols were commercially available as follows: cyclohexanol (Eastman Organic Chemicals); cis-2-methylcyclohexanol (99%, Chemical Samples Co.); trans-2-methylcyclohexanol (98%, Chemical Samples Co.). They were used without further purification to make the phenylacetates.

Phenylacetate Esters. The alcohol (0.12 mol) was dissolved in 15 ml of anhydrous ether and 10 ml of dimethylaniline. To this mixture was added dropwise 0.13 mol of phenylacetyl chloride and the mixture refluxed for 1 hr. It was then cooled to room temperature, 20 ml of water added, and the ether layer separated. The water layer was extracted three times with ether, and the combined ether layers were washed several times with 10% sulfuric acid and finally with saturated sodium bicarbonate and water. The ether solution was dried over anhydrous magnesium sulfate, the ether removed, and the residue distilled. It was further purified by passing through a small alumina column (ca. 20 g of neutral Woelm alumina, grade I) and elution with hexane. The hexane was removed under vacuum and the ester checked for purity by glpc. Any esters less than 97% pure at this stage were further purified by glpc using two columns: a 6 ft \times 0.25 in. column of 30% SF-96 on Chromosorb W, and a 5 ft \times 0.25 in. column of 10% DEGS on firebrick.

Cyclohexyl phenylacetate had bp $83-84^{\circ}$ (0.005 mm). Anal. Calcd for C₁₄H₁₈O₂: C, 77.06; H, 8.26. Found: C, 76.40; H, 8.45. Purity by glpc > 99 %.

cis-2-Methylcyclohexyl phenylacetate had bp 91° (0.1 mm). Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.59; H, 8.62. Found: C, 77.45; H, 8.69. Purity by glpc >99%.

trans-2-Methylcyclohexyl phenylacetate had bp 86° (0.09 mm). Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.59; H, 8.62. Found: C, 77.59; H, 8.61. Purity by glpc >99%.

cis-4-tert-Butylcyclohexyl phenylacetate had bp 113-117° (0.1

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⁽²⁴⁾ E. S. Waight in "Rodd's Chemistry of Carbon Compounds," Vol. IIB, S. Coffey, Ed., Elsevier, New York, N. Y., 1968, p 404.

mm). Anal. Calcd for C₁₈H₂₆O₂: C, 78.83; H, 9.49. Found: C, 79.00; H, 9.71. Purity by glpc 97 %.

trans-4-tert-Butylcyclohexyl phenylacetate had bp 115–118° (0.1 mm). Anal. Calcd for $C_{18}H_{26}O_2$: C, 78.83; H, 9.49. Found: C, 78.70; H, 9.59. Purity by glpc >99%.

cis-2-Methylcyclooctyl phenylacetate had bp $110-112^{\circ}$ (0.08 mm). Anal. Calcd for $C_{17}H_{24}O_{2}$: C, 78.46; H, 9.23. Found: C, 78.40; H, 9.42. Purity by glpc >99%.

trans-2-Methylcyclooctyl phenylacetate had bp 125-126° (0.45 mm). Anal. Calcd for $C_{17}H_{24}O_2$: C, 78.46; H, 9.23. Found: C, 79.30; H, 9.45. Purity by glpc >99%.

Olefins. Those olefins which were commercially available were: cyclohexene (Chemical Samples Co.), 1-methylcyclohexene (Aldrich Chemical Co.), 3-methylcyclohexene (Aldrich Chemical Co.), methylenecyclohexane (Chemical Samples Co.), and 1-methylcyclooctene (Aldrich Chemical Co.). The others were prepared as described below.

3-Methylcyclooctene was prepared from 3-bromocyclooctene and methylmagnesium bromide by the procedure of Cope and Woo.¹⁷ It had bp 68° (30 mm) (lit.¹⁷ bp 78° (56 mm)), and the nmr spectrum expected for 3-methylcyclooctene.

4-*tert***-Butylcyclohexene** was prepared by heating overnight near the reflux temperature 11 g (0.035 mol) of 4-*tert*-butylcyclohexyl *p*-toluenesulfonate in 50 ml of 2,4-lutidine. The mixture was poured into ice-water and extracted with pentane. The pentane extract was washed in 10% sulfuric acid and water, and dried over anhydrous magnesium sulfate. After removal of the pentane, the residue was fractionated to give material of bp 66-67° (23 mm) (lit.²⁵ bp 54-55° (10 mm)).

Other Photoproducts. The sources of comparison samples of other photoproducts were as follows: toluene (Mallinckrodt Spectral Grade), bibenzyl (Aldrich Chemical Co.), methylcyclohexane, and *tert*-butylcyclohexane (Chemical Samples Co.).

Analysis by Glpc. All measurements were made using a Hewlett-Packard F&M Model 700 or a Perkin-Elmer Model 900 gas chromatograph with flame ionization detectors. All photoproducts were identified by coinjection on at least two different columns. All quantitative measurements were made against standards to calibrate detector response. The columns used (all 1/8 in. diameter) for the various products, along with the conditions, were as follows: a 20-ft column of 15% silver nitrate in ethylene glycol on firebrick (Varian) for cyclohexene (50°, 54 psi); a 15-ft column of 30% Carbowax 20M (Applied Science) on Anakrom ABS (Analabs) for 4-tert-butylcyclohexene (145°, 45 psi), 1- and 3methylcyclohexenes (80°, 30 psi), 1- and 3-methylcyclooctenes (120°, 40 psi), methylcyclohexane (80°, 30 psi), methylenecyclohexane (80°, 30 psi), and tert-butylcyclohexane (130°, 40 psi); a 6-ft column of 10% DEGS (Applied Science) on firebrick (Varian) for cis- and trans-2-methylcyclohexyl phenylacetates (150°, 30 psi), toluene (110°, 30 psi), and bibenzyl (150°, 30 psi).

Photolysis Procedures. An eight-lamp Rayonet Preparatory Reactor containing a merry-go-round apparatus was used in all photolyses. For irradiation at 254 nm, unfiltered light from Rayonet RUL 2537 Å lamps was used. Irradiations were run using quartz tubes joined by graded seals to high-vacuum stopcocks and a standard joint for connection to a vacuum line. Apiezon N highvacuum grease (J. G. Biddle Co.) was used on all joints and stopcocks. Samples were degassed at $<10^{-5}$ mm by at least five freeze-pump-thaw cycles. All quartz tubes used for photolyses were calibrated for transmittance of light, and found to transmit the same amount of light within experimental error. Commercially available spectral grade solvents were used without further purification, but were tested by glpc before use to ensure that they contained nothing which would interfere with the analyses. Direct photolyses of the phenylacetates were conducted on 0.025–0.035 M solutions (absorbance of 3.5–4.8). Conversion was usually to <5%, and always <10% except in the mass balance studies.

Uranyl oxalate actinometry was used for all quantum yield studies.²⁶ The actinometer solution was 0.01 M uranyl sulfate (Fisher) and 0.05 M oxalic acid (Eastman Organic Chemicals.). It was titrated with potassium permanganate before and after each irradiation. The quantum yield for the uranium-sensitized decomposition of oxalate was taken as 0.60 at 254 nm.

A correction had to be applied in the quantum yield calculations because the lamps used emit an appreciable amount of light in the vicinity of 310 nm which is absorbed by the actinometer but not by the phenylacetate solutions. The correction factor was determined as follows. The light intensity into the quartz tubes was 1.05×10^{18} photons/(ml min). With a Pyrex filter to remove light below 290 nm, the intensity was 0.25×10^{18} photons/(ml min). The Pyrex filter transmits about 91% of the 310-nm light transmitted by the quartz tubes alone. Thus

$corrn = (0.25 \times 10^{18}/0.91 \times 1.05 \times 10^{18}) \times 100 = 26.2\%$

Photoisomerization of Methylcyclohexenes. Irradiation at 254 nm of 4.0×10^{-6} mol of 3-methylcyclohexene and 1.27×10^{-4} mol of methyl phenylacetate in 5 ml of hexane for a time comparable to that used in the ester photolysis runs led to no isomerization or loss of 3-methylcyclohexene. Similar treatment of 4.0 $\times 10^{-6}$ mol of 1-methylcyclohexene and 1.21×10^{-4} mol of methyl phenylacetate in 5 ml of hexane resulted in approximately 40% conversion to methylenecyclohexane, as shown by glpc analysis.

Mass Balance Studies in the Photolysis of cis-2-Methylcyclohexyl Phenylacetate. Solutions of 1.31×10^{-4} mol of cis-2-methylcyclohexyl phenylacetate in 5 ml of dodecane (Eastman Organic Chemicals, Spectrograde) were degassed and irradiated in quartz tubes for 3 hr. The quartz tube was connected to a vacuum line, frozen in liquid nitrogen for 15 min, and the stopcock opened, and uncondensed gas was pumped into a Toepler pump reservoir. The tube was closed, thawed, and frozen, and the process was repeated four times. The resulting gas (assumed to be carbon monoxide because the amount was insufficient for a mass spectrum) was measured in a gas buret. It was then pumped out of the system, the sample tube was frozen in Dry Ice-acetone, and the above process was repeated to measure carbon dioxide, the identity of which was shown by its mass spectrum.

In a separate experiment, 1.34 g (0.058 mol) of *cis*-2-methylcyclohexyl phenylacetate in 50 ml of pentane was irradiated for 6 hr at 254 nm. The solution was carefully concentrated by distillation and then 2-methylcyclohexanol isolated by preparative glpc on a 5 ft \times 0.25 in. column of 10% DEGS on firebrick. The material collected was coinjected with authentic *cis*-2-methylcyclohexanol and had a mass spectrum identical with that of the authentic material. Toluene and bibenzyl were identified among the products by coinjection on three separate columns: DEGS, Carbowax 20M, and SF-96.

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