

τ 1.99 (s, 1, NH), 2.08–2.60 (m, 5, indanone H and 1 NH), 3.45 (s, 1, OH), and 3.58 (s, 1, OH); tlc R_f 0.14 (ethyl acetate).

Anal. Calcd for $C_{10}H_8N_2O_4$: C, 54.55; H, 3.66; N, 12.72; mol wt, 220. Found: C, 54.41; H, 3.87; N, 12.84; mol wt, 220 (mass spectrum).

Acetylation of 6a.—A suspension of 2.0 g (9.1 mmol) of 6a in 75 ml of acetic anhydride was heated with stirring, under N_2 for 3 hr. The temperature, initially 50°, was raised to 100° over this time. The mixture was poured into 500 ml of ice-water and allowed to stand for 16 hr. The mixture was extracted with an ether-benzene mixture, and the organic layer was washed several times with water and evaporated. The residue was washed with hot water, allowed to dry, and then crystallized from benzene-petroleum ether (bp 30–60°). A yield of 1.80 g (52%) of 6b was obtained. An analytical sample, mp 186–188°, was prepared by recrystallization from benzene-petroleum ether: ir (KBr) 5.61, 5.70, 5.80, 6.22, and 6.82 μ ; uv max (MeOH) 225 m μ (ϵ 8600), 250 (9000), and 286 (1000); nmr (CD_3SOCD_3) τ 1.95–2.40 (m, 4, indanone H), 7.62 (s, overlaps CD_2HSOCD_3 peak, $COCH_3$), 7.70 (s, 3, $COCH_3$), 7.97 (s, 3, $COCH_3$), and 7.99 (s, 3, $COCH_3$); tlc R_f 0.86 (ethyl acetate).

Anal. Calcd for $C_{18}H_{16}N_2O_8$: C, 55.67; H, 4.15; N, 7.21; mol wt, 388. Found: C, 55.98; H, 4.12; N, 7.43; mol wt, 388 (mass spectrum).

Reaction of Ninhydrin with 1,3-Dimethylurea. Formation of 6c.—A solution containing 2.42 g (13.6 mmol) of ninhydrin and 2.82 g (32 mmol) of 1,3-dimethylurea in 80 ml of 0.1 N H_2SO_4 was heated at 60° for 30 min. The reaction mixture was kept at 5° for 48 hr. The precipitate that formed was filtered, washed with water, and dried to afford 3.10 g (92%) of 6c. An analytical sample, mp 259–261° dec, was prepared by recrystallization from methanol-chloroform: ir (KBr) 3.01, 3.20 (shoulder), 5.75, 5.95, 6.20, 6.74, and 6.83 μ (shoulder); uv max (MeOH) 248 m μ (ϵ 10,600) and 290 (1730); nmr (CD_3SOCD_3) τ 1.95–2.28 (m, 4, indanone H), 3.00 (s, 1, OH), 3.15 (s, 1, OH), 7.08 (s, 3, NCH_3), and 7.16 (s, 3, NCH_3); tlc R_f 0.49 (ethyl acetate).

Anal. Calcd for $C_{12}H_{12}N_2O_4$: C, 58.06; H, 4.87; N, 11.28;

mol wt, 248. Found: C, 57.77; H, 4.63; N, 11.03; mol wt, 248 (mass spectrum).

Acetylation of 6c.—A mixture of 0.5 g (2.0 mmol) of 6c, 40 ml of acetic anhydride, and a small amount of sodium acetate was heated at reflux with stirring under N_2 for 90 min. The reaction was worked up by the procedure used for 6b to afford 0.3 g (45%) of 6d. An analytical sample, mp 191–193°, was prepared by several recrystallizations from benzene-petroleum ether: ir (KBr) 3.38, 5.64, 5.80, 6.22, 6.82, and 6.95 μ ; uv max (MeOH) 250 m μ (ϵ 10,800) and 290 (1500); nmr (CD_3SOCD_3) τ 1.91–2.30 (m, 4, indanone H), 7.10 (s, 3, NCH_3), 7.17 (s, 3, NCH_3), 7.85 (s, 3, $COCH_3$), 7.88 (s, 3, $COCH_3$); tlc R_f 0.90 (ethyl acetate).

Anal. Calcd for $C_{18}H_{16}N_2O_8$: C, 57.83; H, 4.85; N, 8.43; mol wt, 332. Found: C, 57.63; H, 4.81; N, 8.44; mol wt, 332 (mass spectrum).

Reaction of Ninhydrin with Guanidine.—A solution containing 1.78 g (10 mmol) of ninhydrin and 1.80 g (15 mmol) of guanidine carbonate in 150 ml of water was stirred at 25° for 30 min and kept at 5° for 16 hr. The precipitate that formed was filtered, washed with water, and dried under vacuum. This product, 2.0 g (91%), mp 215–218° dec, was used directly for analysis: ir (KBr) 2.90–4.0 (broad), 5.82, 5.90 (shoulder), 5.98, 6.02 (shoulder), 6.08 (shoulder), 6.12 (shoulder), 6.21, 6.40, and 6.86 μ ; nmr (CF_3CO_2H) τ 2.30–2.80 (m, overlapping broad absorption, 5, indanone H + NH) and 3.50 (s, 2, NH). The mass spectrum showed numerous weak peaks beyond the expected molecular ion (m/e 219) up to about m/e 350.

Anal. Calcd for $C_{10}H_9N_3O_3$: C, 54.80; H, 4.14; N, 19.17. Found: C, 54.77; H, 4.12; N, 19.05.

Registry No.—1, 485-47-2; 2a, 17438-16-3; 5a, 22487-55-4; 5b, 22433-31-4; 5c, 22430-97-3; 5d, 22430-98-4; 5e, 22430-99-5; 6a, 22431-00-1; 6b, 22431-01-2; 6c, 22431-02-3; 6d, 22431-03-4; 7, 22431-04-5; 8, 22431-05-6; 9, 22431-06-7.

Attempted Epoxidation of Triphenylcyclopropene^{1a,b}

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Treatment of triphenylcyclopropene (1) with both *p*-nitro- and *m*-chloroperbenzoic acid gave the two isomeric *cis*- and *trans*- α -phenylchalcones (2a and 2b) in the approximate ratio of 82:18. No intermediates were detected when the progress of the reaction was monitored by nmr under buffered conditions. The possibility and significance of oxabicyclobutane intermediates is briefly discussed.

Oxabicyclobutanes have been postulated several times as intermediates in various thermal^{2a,b} and photochemical^{2c-h} reactions. In none of these cases, however, have oxabicyclobutanes been detected.

The report of Prinzbach and Fischer^{2b} provides the most compelling choice for an oxabicyclobutane intermediate in chemical reactions. Peracetic acid oxidation of 1,2-dimethylcyclopropenecarboxylic acid methyl ester gave a 30% isolated yield of the two isomeric *cis*- and *trans*- β -acetylcrotonic acid methyl esters in a ratio of 1:4. If the expected oxabicyclobutanes

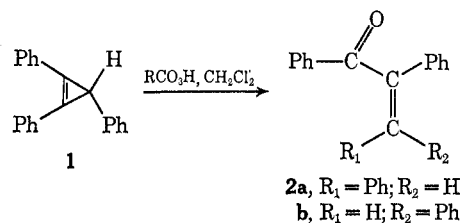
were intermediates, thermal fragmentation of the bicyclo[1.1.0] ring system³ would yield the observed products.

As part of a larger effort to synthesize oxabicyclobutanes and determine the chemistry of their ring-opening processes, we have studied the oxidation of triphenylcyclopropene with peracids.

Room-temperature treatment of a methylene chloride solution of triphenylcyclopropene (1) with 1.2 equiv of *p*-nitroperbenzoic acid in a flask wrapped with aluminum foil gave only the two isomeric *cis*- and *trans*-

(1) (a) This work was supported by National Science Foundation Grant GP-8878. (b) NOTE ADDED IN PROOF.—A communication recently appeared in which the epoxidation of several alkyl-substituted cyclopropenes was reported: J. Ciabattoni and P. J. Kocienski, *J. Amer. Chem. Soc.*, **91**, 6534 (1969). (c) To whom inquiries should be addressed.

(2) (a) S. Marmor and M. M. Thomas, *J. Org. Chem.*, **32**, 252 (1967); (b) H. Prinzbach and U. Fischer, *Helv. Chim. Acta*, **50**, 1669 (1967); (c) E. J. Corey, J. D. Bass, R. LeMahieu, and R. B. Mitra, *J. Amer. Chem. Soc.*, **86**, 5570 (1964); (d) E. J. Corey, M. Tada, R. LaMahieu, and L. Libit, *ibid.*, **87**, 2051 (1965); (e) H. E. Zimmerman, R. G. Lewis, J. J. McCullough, A. Padwa, S. W. Staley, and M. Semmelhack, *ibid.*, **88**, 1965 (1966); (f) O. L. Chapman and W. R. Adams, *ibid.*, **90**, 2333 (1968); (g) H. E. Zimmerman and W. R. Elser, *ibid.*, **91**, 887 (1969); (h) N. Furutachi, Y. Nakadaira, and K. Nakanishi, *ibid.*, **91**, 1028 (1969).



(3) Substituted bicyclobutanes fragment into butadienes in an analogous fashion; see G. Closs and P. Pfeffer, *J. Amer. Chem. Soc.*, **90**, 2452 (1968).

TABLE I
PRODUCT RATIOS FROM OXIDATION OF TRIPHENYLCYCLOPROPENE^a

Peracid	Buffer	Ratio of 2a/2b ^b	Unreacted cyclopropene, %
<i>p</i> -NO ₂	None	80:20 ± 4	16
<i>p</i> -NO ₂	None	82:18 ± 5	4
<i>m</i> -Cl	None	84:16 ± 3	5
<i>m</i> -Cl	NaHCO ₃	80:20 ± 4	10
<i>m</i> -Cl	NaHCO ₃	84:16 ± 5	10
<i>p</i> -NO ₂	NaHCO ₃	78:22 ± 5	6
<i>p</i> -NO ₂	NaHCO ₃	81:19 ± 5	8
<i>m</i> -Cl ^c	Na ₂ CO ₃	83:17 ± 9	37

^a In methylene chloride solution at room temperature using ca. 20% excess peracid. ^b All reported errors are standard deviations. ^c In ethanol-free chloroform solution.

α -phenylchalcones (2a and 2b). The identities of the α -phenylchalcones were established by comparison with authentic samples which were synthesized by two reported procedures.⁴ No other products were observed by ir, nmr, uv, and thin layer analysis after ca. 90% reaction. Similar experiments with commercially available 85% *m*-chloroperbenzoic acid gave identical results.

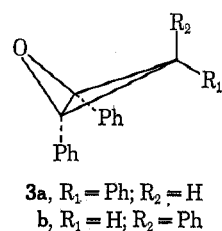
Several runs were also performed with added bases to see whether the liberated *p*-nitro- or *m*-chlorobenzoic acids were decomposing isolable intermediates. Unfortunately, control experiments established that the added bases were not effective at rapidly removing *p*-nitrobenzoic acid from chloroform (see Experimental Section).

Control experiments showed that the *cis*- and *trans*- α -phenylchalcones were individually stable to the reactions conditions and isolation procedure if the products were protected from light and if a large excess of peracid and very long reaction times were avoided. Similarly, triphenylcyclopropene was stable to *p*-nitrobenzoic acid and the isolation procedure. In the presence of light, dilute solutions of the chalcones underwent slow *cis*-*trans* isomerization. Large excesses of peracid in the epoxidation reaction led to additional unknown products. Control experiments established that these unknown materials were formed by subsequent oxidation of the chalcones and were not investigated further.

Quantitative ultraviolet analyses of the crude product mixtures obtained under various reaction conditions were performed by an unweighted least-squares regression analysis on the total optical density of the three component mixtures at ten different wavelengths. Subjection of known mixtures of the two chalcones and triphenylcyclopropene to the isolation procedure and ultraviolet analysis revealed that no analytical bias was present. The results are listed in Table I.

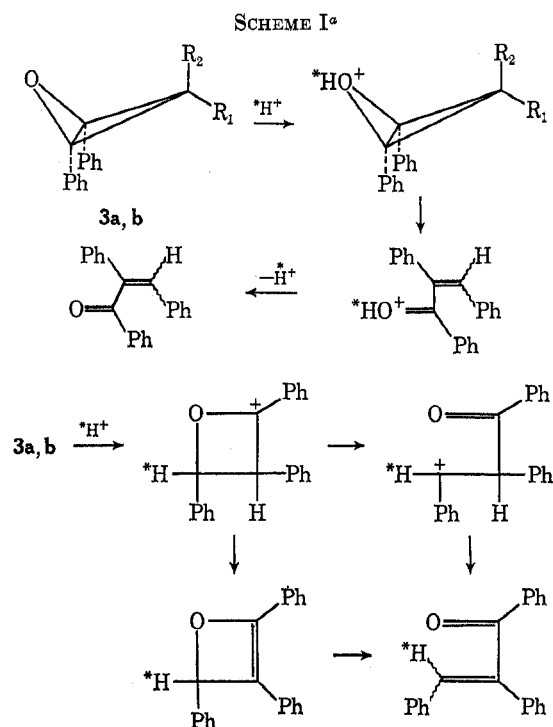
The most attractive, although completely unproven, route for formation of the two observed products is *via* oxabicyclobutane(s) 3a and/or 3b. In an effort to detect these or any other intermediates, the progress of the oxidation was followed by nmr spectroscopy in ethanol-free chloroform solution. Methylene chloride could not be conveniently used as a solvent because its proton absorption obscures the important region of the spectrum. *m*-Chloroperbenzoic acid was used both with and without the presence of sodium carbonate. In no

(4) (a) J. Parriek, *Can. J. Chem.*, **42**, 190 (1964); (b) W. Black and R. Lutz, *J. Amer. Chem. Soc.*, **75**, 5990 (1953).



instance was any evidence for 3a, 3b, or any other intermediate found; only the simultaneous disappearance of reactants and appearance of the two chalcone products 2a and 2b were observed under conditions where a minimum of 3 mol % of a product such as 3a or 3b (with an expected singlet for the tertiary benzylic proton) could be observed. The 3% minimum was established by the internal addition of a known amount of *p*-dioxane after the reaction was completed.

Since the inorganic buffers were inefficient at removing the liberated phenyl-substituted carboxylic acids, the possibility exists that the suspected oxabicyclobutane(s) 3 decompose by acid-catalyzed processes such as those shown in Scheme I. The second set of



^a R₁ = Ph or H; R₂ = H or Ph.

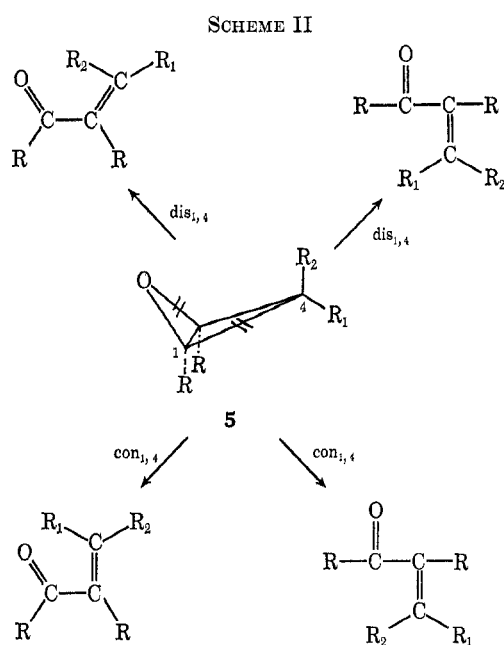
equations in this scheme predicts a shuffling of the atoms in the products. This possibility was tested through the use of *m*-chloroperbenzoic acid-*O*-*d*₁, which should introduce deuterium at the β carbon of the α,β -unsaturated ketone products. Mass spectral analysis of both products showed only undeuterated material, which invalidates the second acid-catalyzed fragmentation. The first mechanism in Scheme I, which involves protonation on oxygen, cannot be eliminated.

If oxabicyclobutanes 3a and/or 3b are the immediate precursors of the two chalcones, it is reasonable but not necessary to expect that a stereoselective fragmentation would occur that is controlled by the orbital symmetry characteristics of oxabicyclobutane.⁵ The qualitative

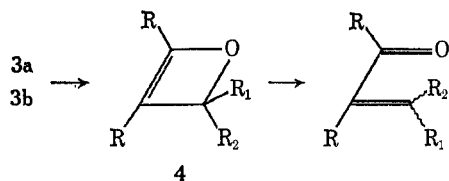
(5) R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968).

prediction of fragmentation preferences for oxabicyclobutanes, however, is complicated by the lack of symmetry elements which are preserved throughout the reaction. Furthermore, since there is no stereochemistry associated with the oxygen atom, only two theoretical concerted fragmentation modes are possible for oxabicyclobutanes. This situation is contrasted with that for bicyclobutanes, where the extra two hydrogen atoms or other substituents on the additional bridged carbon atom lead to four distinguishable fragmentation pathways.³

As is the case with bicyclobutanes,⁶ oxabicyclobutanes in theory may fragment to form initially either cisoid or transoid α,β -unsaturated carbonyl products. In order to form the same *cis* or *trans* isomer, opposite rotational modes must prevail in forming cisoid or transoid product (Scheme II).



Another possibility is that oxabicyclobutanes may prefer to rearrange first to oxetenes⁷ of general structure 4. If so, the product chalcones could be formed by a



cyclobutene-butadiene-type fragmentation. In such a case, only the developing nonbonded interactions of R_1 with R and R_2 with the oxygen atom would direct the ring-opening process to the cisoid α,β -unsaturated carbonyl product; as mentioned before, the presence of the oxygen atom destroys the disrotatory and conrotatory distinctions for fragmentation.

We have performed extended Hückel calculations on the four fragmentation modes of oxabicyclobutane to

(6) K. B. Wiberg, *Tetrahedron*, **24**, 1083 (1968); K. B. Wiberg and G. Szeimies, *Tetrahedron Lett.*, 1235 (1968).

(7) (a) This reaction pathway is most likely "allowed" because of the results from the CNDO^{7b} calculations performed by Wiberg⁶ on the analogous reaction of bicyclobutane to cyclobutene. The results of Closs,³ however, effectively rule out this process for the dimethylbicyclobutanes. (b) Complete neglect of differential overlap molecular orbital.

acrolein (Scheme II). These calculations, subject to their theoretical and practical limitations, fortunately enable distinct predictions to be made. The transoid- $dis_{1,4}$ mode is clearly favored over the transoid- $con_{1,4}$ mode, on the basis of total energy as well as symmetry arguments; in the transoid- $con_{1,4}$ mode the highest occupied orbital of oxabicyclobutane correlates with the lowest unoccupied π orbital of acrolein. A similar result was found for the two cisoid modes. The cisoid- $dis_{1,4}$ mode was clearly favored over the cisoid- $con_{1,4}$ mode for the same two reasons. The use of these predictions must await firm knowledge of whether oxabicyclobutane 3 is indeed an intermediate and, if so, knowledge of the ratio of 3a/3b.

In both our work on triphenylcyclopropene and Prinzbach's work on 1,2-dimethylcyclopropenecarboxylic acid methyl ester, a kinetically controlled epoxidation of the double bonds should give a predominance of oxabicyclobutane 5, where R_2 is hydrogen and R_1 is phenyl or carbomethoxy. In both cases, a disrotatory opening of the cyclopropane ring (Scheme II) to form a transoid α,β -unsaturated ketone or a conrotatory opening to form a cisoid ketone (energetically unfavorable) would produce the observed major reaction product. It appears fortuitous that both Prinzbach and we observed a 4:1 ratio of the two possible *cis* and *trans* products.

One final set of experiments was performed, even though the results cannot yet be applied to an overall understanding of the oxidation of cyclopropenes. Piperidine-catalyzed equilibration of the α -phenylchalcones was effected in both ethanol and methylene chloride solution until the composition of the mixture no longer changed. Even though the solutions turned yellow, nmr analyses revealed no detectable decomposition of the chalcones, nor did the previously employed least-squares regression analysis reveal any noticeable presence of decomposition products, which should have led to large residuals and standard deviations. The equilibration results are shown in Table II. As is indicated, the thermodynamically favored α -phenylchalcone is the same chalcone that was formed in major amounts in the irreversible, kinetically controlled oxidation of triphenylcyclopropene.

TABLE II
EQUILIBRATION^a STUDIES ON CHALCONES 2a AND 2b

Solvent	Temp, °C	Starting chalcone	Equilibrium ratio of 2a/2b ^b
EtOH	80	2a	68:32 \pm 3
EtOH	80	2b	69:31 \pm 3
CH ₂ Cl ₂ ^c	120-130	2a	64:36 \pm 3
CH ₂ Cl ₂ ^c	120-130	2b	66:34 \pm 2

^a All equilibrations employed a 10-mol excess of piperidine.

^b All reported errors are standard deviations. ^c Undegassed solutions employing undistilled piperidine gave a 2a to 2b ratio of 66:34 \pm 3 from 2a and a 64:36 \pm 2 ratio from 2b.

Experimental Section

General.—Nmr spectra were obtained with a Varian Model A-60 spectrometer using tetramethylsilane as internal standard. A Cary Model 11 MS spectrophotometer was used to obtain uv spectra. Ir spectra were recorded with a Perkin-Elmer Model 137 spectrometer. Melting points were obtained on a calibrated Fisher-Johns melting point apparatus. Mass spectra were obtained at both 20 and 75 eV on a Perkin-Elmer Hitachi RMU6E spectrometer. A direct inlet probe was used.

1,2,3-Triphenylcyclopropene (1).—The cyclopropene was prepared from triphenylcyclopropenyl bromide⁸ according to the procedure of Breslow and Dowd⁹ and recrystallized to constant uv in 95% EtOH: mp 114.0–115.5°; uv max (95% EtOH) 330 m μ (ϵ 24,200), 313 (29,000), and 228 (30,600); uv max (CHCl₃) 334 m μ (ϵ 23,700) and 317 (29,000); ir (CCl₄) 1820 cm⁻¹ (cyclopropene double bond); nmr (CDCl₃) δ 7.77–7.20 (m, 15 H, aromatic) and 3.26 (s, 1 H, allylic H) [lit.⁸ mp 112–113°; uv max (95% EtOH) 334 m μ (ϵ 22,800), 318 (28,800), and 218 (27,800); ir 1818 cm⁻¹; nmr δ 7.1 (m, 15 H) and 3.2 (s, 1 H)].

***p*-Nitroperbenzoic Acid.**—The peracid was prepared by either Na₂O₂¹⁰ or sodium peroxide¹¹ oxidation of *p*-nitrobenzoic acid or *p*-nitrobenzoyl chloride, respectively. The peracid analyzed to 99+ % purity by iodometric analysis with standardized Na₂S₂O₃ in CHCl₃–HOAc solution: mp 138–139° dec (sealed tube) [lit.⁹ mp 138° dec (sealed tube); lit.¹⁰ mp 136–137° dec (sealed tube)]; ir¹² (Nujol) 3200 (OH), 1750 (C=O), and 870 cm⁻¹ (O–O).

***m*-Chloroperbenzoic Acid.**—The peracid was 85% assay and was used as obtained from Research Organic/Inorganic Chemical Co.

***cis*- and *trans*- α -Phenylchalcones (2a and 2b).**—The chalcones were synthesized according to the procedures of Parrick and of Black and Lutz.⁴ Mixtures of isomers were separated by a Woelm neutral alumina chromatography (activity II) using benzene–hexane as the eluent. The individual isomers were recrystallized from 95% EtOH to constant uv. Data for *cis*- α -phenylchalcone (2a) follow: mp 89–90° (lit.⁴ mp 89–90°); uv max (95% EtOH) 260 m μ (ϵ 26,200) and 281 (24,400) [lit.^{4b} uv max (95% EtOH) 260 m μ (ϵ 24,600) and 280 (22,900)]; uv max (CHCl₃) 260 m μ (ϵ 21,800) and 284 (20,800); ir (CCl₄) 1666 (C=O) and 1224 cm⁻¹ (lit.^{4a} ir 1666 cm⁻¹); nmr (CDCl₃) δ 8.09–7.92 (m, 2 H, benzoyl *ortho* protons) and 7.55–6.98 (m, 14 H, remaining protons). Data for *trans*- α -phenylchalcone (2b) follow: mp 103–104° (lit.⁴ mp 98–99°, 103–103.5°); uv max (95% EtOH) 255 m μ (ϵ 16,500) and 300 (14,500) [lit.^{4b} uv max (95% EtOH) 255 m μ (ϵ 15,100) and 300–302.5 (13,700)]; uv max (CHCl₃) 253 m μ (ϵ 14,300) and 303 (12,700); ir (CCl₄) 1650 (C=O), and 1250 cm⁻¹ (lit.^{4a} ir 1649 cm⁻¹); nmr (CDCl₃) δ 7.97–7.82 (m, 2 H, benzoyl *ortho* protons) and 7.49–7.15 (m, 14 H, remaining protons).

General Procedure for Peracid Oxidation of Triphenylcyclopropene (1).—A solution of 3.60 mmol of peracid in 45 ml of CH₂Cl₂ (*m*-chloroperbenzoic acid was dissolved in 10 ml of CH₂Cl₂) was added rapidly with stirring in a nitrogen atmosphere to 3.00 mmol of 1 in 5 ml of CH₂Cl₂ at room temperature. All reaction flasks were wrapped with aluminum foil to exclude light. Stirring was continued for *ca.* 6 hr and the unreacted peracid was destroyed with 10% aqueous Na₂SO₃ to give a negative starch-iodide test. The resulting mixture was washed with three 25-ml portions of 5% aqueous NaHCO₃ and one 25-ml portion of water. The organic layer was dried over anhydrous Na₂SO₃ and the solvent was evaporated without heating on a rotary evaporator to give a pale yellow oil which solidified. Thin layer chromatography on Merck silica gel G with 5% ether in hexane showed only two spots, corresponding first to the *R_f* value of a mixture of 2a and 2b and second to an *R_f* value identical with that of unreacted olefin 1. Uv, ir, and nmr spectroscopy showed only the presence of the two chalcones and unreacted 1.

Control experiments performed in the same manner showed that in the absence of large excesses of peracid or long reaction times, the product chalcones were stable to the reaction conditions and work-up. Similarly, triphenylcyclopropene (1) was stable to a CH₂Cl₂ solution of *p*-nitrobenzoic acid and the work-up conditions.

When the oxidations were performed with a >20% excess of peracid, at least one additional component was detected in small amounts, nmr (CDCl₃) δ 4.1 (s). This or some other additional component absorbed strongly in the 250–270-m μ region of the uv spectrum. This minor product(s) was not further investigated.

Several reactions were performed with added solid NaHCO₃ or Na₂CO₃. No additional products were observed. Only when the reaction was buffered as a two-phase mixture with

aqueous NaHCO₃ was an additional product found which exhibited in the crude reaction mixture a weak, 1770-cm⁻¹ absorption in the ir. No further investigations were performed with aqueous buffers.

Several experiments were performed in which the course of the oxidation of 1 was followed in an nmr tube. *m*-Chloroperbenzoic acid and ethanol-free CHCl₃ were employed. The spectrum was repeatedly scanned in the region δ 1.0–7.0. Only the disappearance of 1 at δ 3.26 and the appearance of chalcone products were observed. Addition of *p*-dioxane to the nmr tube after the reaction was complete indicated that a minimum of a 3 mol % yield of an intermediate with a one-proton singlet could have been detected in the region scanned. Similar oxidations with *m*-chloroperbenzoic acid in ethanol-free CHCl₃ with an added 15-mol ratio of solid Na₂CO₃ also failed to produce any detectable intermediates.

Analytical Method for Product Composition.—Quantitative uv analyses of the various crude multicomponent reaction mixtures were performed by a linear unweighted least-squares regression analysis¹⁴ on the total optical density of the product at ten different wavelengths (eq 1). The determined extinction

$$OD_{\text{total}}^{\lambda_i} = \epsilon_{2a}^{\lambda_i} c_{2a} l + \epsilon_{2b}^{\lambda_i} c_{2b} l + \epsilon_1^{\lambda_i} c_1 l \quad (1)$$

coefficients of 2a, 2b, and 1 which were used in this analysis are given in Table III. Solutions for analyses were prepared by dissolving a small sample of the product in *ca.* 50 ml of CHCl₃ (Mallinckrodt AR grade) and the concentration was adjusted to give approximately unit optical density at 260 m μ . The spectra of all solutions were run immediately because control experiments established that *ca.* 10⁻⁵ M solutions of the chalcones underwent significant *cis*–*trans* isomerization when not protected from light. No isomerization occurred in the dark. A control experiment in which a 73:17:10 mole ratio of 2a, 2b, and 1 was subjected to the work-up and uv analysis gave an analyzed ratio of 73:18:9. The analytical results of several peracid oxidations of 1 are summarized in Table I.

TABLE III
EXTINCTION COEFFICIENTS^a OF α -PHENYLCHALCONES 2a AND 2b AND TRIPHENYLCYCLOPROPENE (1)

λ , m μ	10 ⁻³ ϵ (2a)	10 ⁻³ ϵ (2b)	10 ⁻³ ϵ (1)
250	17.9	14.0	3.1
260	21.8	13.6	2.8
270	19.7	10.4	5.1
280	20.4	10.1	8.8
290	20.4	11.4	14.0
300	16.9	12.6	19.9
310	11.7	12.3	23.3
320	6.8	9.6	27.2
330	3.3	6.1	21.1
340	1.8	3.6	12.3

^a Measured in CHCl₃ solution. The extinction coefficients were invariant within the measured concentration ranges of 2 \times 10⁻⁵ to 12 \times 10⁻⁵ M.

Neutralization Rates of *p*-Nitrobenzoic and *p*-Nitroperbenzoic Acid with Inorganic Bases. A. Sodium Bicarbonate.—Solid, anhydrous NaHCO₃ was added to a saturated CHCl₃ solution of *p*-nitrobenzoic acid and the mixture was stirred at room temperature. The acid concentration was monitored by uv analysis. After 1 hr, 1 equiv of NaHCO₃ had only reduced the concentration of *p*-nitrobenzoic acid by 18%.

B. Sodium Carbonate.—A similar experiment as above employing a 25-mol excess of anhydrous Na₂CO₃ reduced the acid concentration by 50% after 15 min. When a saturated CHCl₃ solution of *p*-nitroperbenzoic acid was treated with a 100-mol excess of Na₂CO₃, the peracid concentration was reduced by 28% after 1 hr.

C. Disodium Hydrogen Phosphate.—A 50-mol excess of solid, anhydrous Na₂HPO₄ reduced the acid concentration by 13% after 1 hr.

(13) Ethanol-free chloroform was prepared by passing Mallinckrodt AR grade CHCl₃ through a column of Merck alumina (100 g of alumina per 200 ml of CHCl₃).

(14) J. Mandel, "The Statistical Analysis of Experimental Data," Interscience Publishers, Inc., New York, N. Y., 1964, p 136.

(8) R. Breslow and H. W. Chang, *J. Amer. Chem. Soc.*, **83**, 2367 (1961).

(9) R. Breslow and P. Dowd, *ibid.*, **85**, 2729 (1963).

(10) L. S. Silbert, E. Siegel, and D. Swern, *J. Org. Chem.*, **27**, 1336 (1962).

(11) M. Vilkas, *Bull. Soc. Chim. Fr.*, **26**, 1401 (1959).

(12) Absorptions characteristic of aliphatic peracids are found at 3200, 1745, and 880 cm⁻¹; see L. T. Man, *ibid.*, **33**, 652 (1966).

Oxidation with *m*-Chloroperbenzoic Acid-*O*-*d*₁.—*m*-Chloroperbenzoic acid of 99+ % purity was prepared by extraction of an ethereal solution of the commercially available material with a neutral phosphate buffer prepared from 35.5 g of disodium hydrogen phosphate and 34.0 g of potassium dihydrogen phosphate dissolved in 1 l. of water. A solution of 3.4 g (0.020 mol) of 99+ % *m*-chloroperbenzoic acid in 50 ml of dry, ethanol-free chloroform was stirred with 4.0 g (0.20 mol) of deuterium oxide at room temperature. After 1 hr the organic layer was separated and dried over anhydrous sodium sulfate. The dried chloroform solution was treated with a second 4.0-g (0.20 mol) portion of deuterium oxide for 1 hr. Work-up as before and removal of the solvent on a rotary evaporator without heating gave 2.7 g (80%) of deuterated peracid: ir (Nujol) 2375 (OD), 1715 (C=O), and 861 cm⁻¹ (O-O); nmr (CDCl₃) δ 8.26–7.33 (m, 4 H, aromatic protons).

A 5.0-mmol sample of triphenylcyclopropene was oxidized with an equimolar amount of *m*-chloroperbenzoic acid-*d*₁ as previously described. Uv analysis of the product showed 94% reaction with a ratio of 2a/2b of 80:20 ± 6. The crude product was chromatographed on 75 g of Woelm neutral alumina (activity II), *d* 2.2 cm. Application with 25% benzene in hexane and elution with benzene-hexane (increasingly greater amounts of benzene) gave 0.10 g (7%) of 1, 0.66 g (49%) of 2a (99:1 ± 4 ratio of 2a/2b), and 0.13 g (10%) of 2b (88:12 ± 3 ratio of 2a/2b). Infrared analysis of the materials established their identity. The impure *trans* isomer (2b) was rechromatographed to yield 63 mg (5%) of a mixture of 2a and 2b, and 43 mg (3%) of 2b (91:9 ± 2 ratio of 2b/2a). No further attempt was made to purify this sample.

Mass spectral analysis at 20- and 75-eV ionizing voltage of these samples showed the absence of deuterium incorporation. The peak intensities in the molecular ion region were virtually identical with those of standard undeuterated samples. The mass spectrum of a control sample of 2b which had been passed through Woelm neutral alumina (activity II, deactivated with deuterium oxide) was also identical with that of a standard sample of 2b. The alumina had previously been treated with deuterium oxide and dried at 200–205° (1.0 mm) for 15 hr before deactivation.

Molecular Orbital Calculations.—A probable geometry of oxabicyclobutane was deduced from the known geometries of cyclopropane, oxirane, and bicyclobutane.^{15,16} The reaction coordinate was chosen to lie along a pathway defined by a linear variation of the bond angles and bond lengths of oxabicyclobutane to those of acrolein.¹⁶ The exponents of the atoms were chosen as 1.625, 2.275, and 1.000 for carbon, oxygen, and hydrogen, respectively. The respective Coulomb integrals in eV were as follows: C_{2s}, 21.43; O_{2s}, 35.30; C_{2p}, 11.42; O_{2p}, 17.76. Resonance integrals were calculated by the Wolfsberg-Helmholz equation using *K* = 1.75. Eigen vectors and eigen values were calculated for eight intermediate geometries by the usual extended Hückel program.¹⁷ The matrix diagonalization was performed in double precision.¹⁸

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(16) L. E. Sutton, Ed., "Tables of Interatomic Distances and Configurations in Molecules and Ions," The Chemical Society, London, 1958, Supplement, 1965. All angles were chosen as 120° and the C_{1,2} distance as 1.43 Å. All C-H bond lengths were 1.08 Å.

(17) Quantum Chemistry Program Exchange, Department of Chemistry, Indiana University, Bloomington, Indiana 47001.

(18) Acknowledgment is made to the Computer Center at the University of Rochester for machine time on their IBM 360/65 computer.

Catalytic Equilibration of α -Phenylchalcones (2a and 2b).

A. Piperidine in Ethanol.—A 284-mg (1.0 mmol) portion of 2a was added with stirring to a solution of 850 mg (10.0 mmol) of piperidine (Eastment Practical) in 25 ml of absolute EtOH. The resulting solution, excluded from light, was heated to 80° internal temperature (reflux) in an oil bath. A 1-ml aliquot was removed at selected times and added to a mixture of 400 ml of water and 10 ml of CHCl₃. After thorough mixing, the CHCl₃ solution was separated and diluted with additional CHCl₃ to give a unit optical density at 260 m μ . The diluted solutions were analyzed for the per cent of *cis*- and *trans*-chalcones 2a and 2b by uv analysis as described previously. After 24 hr the ratio of 2a to 2b was constant (Table III). At the end of the equilibration a portion of the remaining ethanolic solution was added to a mixture of water and CHCl₃ as described above and the CHCl₃ layer was analyzed by ir and nmr spectroscopy. No absorptions other than those of the *cis*- and *trans*- α -phenylchalcones were observed.

The *trans*- α -phenylchalcone was allowed to equilibrate under the same reaction conditions as above (Table III). Only the two chalcone absorptions were observed in the ir and nmr spectra of the crude reaction product.

When the 24-hr aliquots from both equilibrations were added to water and CHCl₃ and the CHCl₃ solution was successively washed with 5% aqueous HCl, 5% aqueous NaHCO₃, and water, the uv analyses gave slightly different equilibrium mixtures. *cis*- α -Phenylchalcone (2a) led to a 71:29 ± 3 ratio and the *trans*-chalcone 2b gave a 73:27 ± 3 ratio of 2a/2b, respectively.

B. Piperidine in Methylene Chloride.—A solution of 142 mg (0.500 mmol) of 2a and 425 mg (5.00 mmol) of piperidine in 4 ml of CH₂Cl₂ was heated in a stainless steel sealed tube at 120–130°. At selected times the tube was cooled in ice and a 0.5-ml sample of the orange solution was added to a mixture of 400 ml of water and 15 ml of CHCl₃ and shaken well. The colorless CHCl₃ layer was filtered through anhydrous Na₂SO₄ and the solvent was removed on a rotary evaporator. The colorless, oily residue was analyzed by uv, ir, and nmr spectroscopy. Only the two chalcones were observed. After 24 hr the composition of the equilibration mixture was constant at 66:34 ± 3 for 2a and 2b, respectively.

Similar treatment of 2b gave a 64:36 ± 2 equilibrium mixture of 2a and 2b.

When the two equilibrations were performed with freshly distilled piperidine and when nitrogen gas was bubbled through the reactants for 0.5 hr prior to reaction, 2a led to a 64:36 ± 3 ratio and 2b gave a 66:34 ± 2 ratio of 2a and 2b, respectively. See Table II for a summary of the results.

C. Other Conditions.—Several equilibrations were attempted with aqueous perchloric acid catalysis as well as with anhydrous *p*-toluenesulfonic acid catalysis in benzene. In the case of aqueous perchloric acid,¹⁹ no isomerization was observed after 48 hr at room temperature using ca. 35% aqueous HClO₄ and 5 × 10⁻⁶ M 2a. With *p*-toluenesulfonic acid in benzene, decomposition of 2a occurred. Thermal, iodine-catalyzed equilibration²⁰ also led to decomposition of 2a and was not investigated further.

Registry No.—1, 16510-49-9; 2a, 7512-67-6; 2b, 7474-65-9.

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