

B. With Sodium Permanganate. To 0.920 g. (0.0026 mole) of 1-phenyl-2-(2,4-dinitrobenzenemercapto)cyclohexene was added 1.0 g. of sodium hydroxide and 17.0 g. of sodium permanganate trihydrate in 125 ml. of pyridine and 10 ml. of water. The mixture was refluxed for 1 hr., the excess permanganate was reduced with a saturated solution of sodium sulfite, and the manganese dioxide was removed by filtration. The filter cake was washed with dilute sodium hydroxide and the combined filtrates were evaporated almost to dryness. The residual basic solution was extracted with ether, acidified with dilute sulfuric acid, and extracted with ether. The solvent from the second ether extract was removed through a semimicro column, and the residue was heated for several hours on the steam bath with 2 g. of tin and 10 ml. of concentrated hydrochloric acid. The mixture was poured into water and extracted with ether. The ether extract was washed with water and dried over anhydrous magnesium sulfate, and the solvent was evaporated through a semimicro column. The residue was dissolved in 10 ml. of hot water, centrifuged, and allowed to crystallize in an ice bath. After one sublimation at 100° (10 mm.), 0.078 g. (25%) of benzoic acid, m.p. 122–123 (lit.³⁵ m.p. 122.4°), was obtained.

1-Chlorocyclohexene with Sulfuric Acid. 1-Chlorocyclohexene (10.0 g., 0.086 mole) was treated with 100 ml. of 90% sulfuric acid at 50°. After 45 min., the reaction mixture was added to crushed ice and extracted with ether. The organic layer was dried over

anhydrous magnesium sulfate and the solvent was removed through a semimicro column.²⁷ The residue (6.4 g., 75%) was proved to be cyclohexanone by its infrared spectrum and by formation of a 2,4-dinitrophenylhydrazone, m.p. 161–162° (lit.³⁹ m.p. 162°), and a semicarbazone, m.p. 164–165° (lit.³⁹ m.p. 166°).

1-Phenylcyclohexanol. Cyclohexanone (9.8 g., 0.1 mole) was slowly added to 0.15 mole of phenyllithium in 250 ml. of ether. The solution was allowed to reflux for 30 min.; then it was cooled and carefully treated with water. The organic layer was washed three times with water, and the ether was evaporated on the steam bath. The residue was dissolved in ligroin and allowed to stand overnight in the refrigerator. Pure 1-phenylcyclohexanol (12.1 g., m.p. 61.5–63°) was obtained. The solvent was evaporated from the mother liquors and the residue was recrystallized from ligroin. Three additional grams of 1-phenylcyclohexanol, m.p. 61–62.5°, was obtained. The total yield was 84%.

1-Phenylcyclohexene. 1-Phenylcyclohexanol (5.5 g.) was refluxed for 5 hr. with 24 ml. of 12% sulfuric acid. The product was treated with hexane and water, and the organic layer was washed several times with water and distilled through a semimicro column.²⁷ 1-Phenylcyclohexene (4.5 g., 91%), with an infrared spectrum identical with that of an authentic sample, was obtained.

(39) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd Ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 262.

The Mechanism of a Diels–Alder Reaction. I. A Retrodiene Decarboxylation¹

M. J. Goldstein and G. L. Thayer, Jr.²

Contribution from the Baker Laboratory of Chemistry, Cornell University, Ithaca, New York. Received September 19, 1964

*The mechanistic problem of Diels–Alder addition is reconsidered and the advantages to be gained from heavy atom kinetic isotope effect studies are indicated. Decarboxylation of the maleic anhydride adduct of α -pyrone is then shown to satisfy applicable criteria for Diels–Alder retrogression: (a) production of *cis*-1,2-dihydrophthalic anhydride as the kinetically controlled product, (b) adequately first-order kinetics with $\Delta H^* = 33.2$ kcal./mole and $\Delta S^* = 2.69$ e.u., and (c) identification of the lactonic function as the source of 99.3% of the carbon dioxide liberated. The accepted structures of both reactant and product are confirmed but not that of an isomer of the product, the purported 4,5-dihydrophthalic anhydride, here identified as 1,4-dihydrophthalic anhydride. The dipole moment of the reactant (1.34 D.) is consistent with expectation for the *endo* isomer.*

(1) The study was supported by the Air Force Office of Scientific Research under Contract No. 49(038)-942 and Grant No. 142-63.

(2) Union Carbide Corporation Research Fellow, 1962–1963. Taken, in part, from the dissertation to be submitted by G. L. T. to Cornell University in partial completion of the requirements for the Ph.D. Degree, Feb. 1965.

Introduction

The range of mechanism accessible to Diels–Alder addition has been most restricted by the requirement that diene and dienophile geometry be retained.³ The problem of mechanism is thus transformed into that of the structure of a transition state whose composition has already been set by the observation of second-order kinetics. Both the dilemma and the challenge derive from an inability to deduce this structure by conventional means: the interpolation between a consecutive pair of experimentally defined, similar structures. With no intermediates nor even, as in other multicenter processes, a structurally similar reactant and product,⁴ the structure of the transition state must be deduced solely from its kinetic consequences.⁵

(3) For reviews, see (a) Ya. K. Syrkin and I. I. Moiseev, *Usp. Khim.*, **27**, 1321 (1958); (b) J. Martin and R. Hill, *Chem. Rev.*, **61**, 537 (1961); (c) R. B. Woodward and T. J. Katz, *Tetrahedron*, **5**, 70 (1959); (d) J. A. Berson and A. Remanick, *J. Am. Chem. Soc.*, **83**, 4947 (1961).

(4) W. von E. Doering and W. Roth, *Tetrahedron*, **18**, 67 (1962).

In particular, appropriate rate data must be chosen to distinguish two alternative structural hypotheses: (a) that of a one-center transition state, defined as containing *one* newly formed bond and (b) that of a two-center transition state, of more variable detailed structure, but containing *no* new intact bond. Conclusions which derive from most of the techniques thus far employed (the analysis of ΔV^* ,^{6a} of a wide range of substituents effects,^{7a} of ΔH^* and ΔS^* ,^{8a} and of π -electron localization energies^{9a}) have often only provided an opportunity for further debate.^{6b,7b,8b}

The most naive application of a linear, free-energy relationship^{9b} to the available kinetic data is not more fruitful. Were the effect of a substituent on a fully formed bond to be negligible but on an incompletely formed one a constant increment of ΔF^* , the relative rate constants of unsubstituted (k_U), monosubstituted (k_M), and symmetrically disubstituted (k_D) addends would necessarily fall into one of three distinguishable patterns. One-center transition states would require either $0.5 < (k_M/k_U) < 1$ if the substituent were deactivating or $1 < (k_D/k_M) < 2$, if activating. Two-center transition states would require $k_U k_D / (k_M)^2 = 1$.^{10a} The few data thus far available fail to reveal any consistent trend. Rates of maleic anhydride addition to furan, α -methyl-, and α, α' -dimethylfuran agree with expectation for the one-center extreme^{10b} but to anthracene, 9-methyl or ethyl, and 9,10-dimethyl or diethyl anthracenes, far more closely with that for two-center transition states.^{10c} Yet methoxylated anthracenes behave more like methylated furans. All others reported are not easily placed into any category. Perhaps this reflects the ability of such transition states to vary their structure with the number and nature of substituents in much the same way as they have already been shown to vary their polarity with those of substituents.^{10d} If so, the latter would need to be excluded as acceptable probes of structure.^{10e}

Isotopic substitution is uniquely free of this defect¹¹ and has indeed already been applied to this problem.^{12a,b} In particular it has been elegantly demon-

strated that α -deuteration at each of the two reaction sites of the maleic anhydride adduct of α -methylfuran diminishes diene retrogression identically.^{12b} The subsequent choice of a two-center transition state is the most compelling of any hitherto achieved. For this reason, it becomes important to re-emphasize that the power of the conclusion derives not from any necessary theoretical relationship between bond cleavage and α -deuterium isotope effect^{12c} but, rather empirically, from a massive correlation of such data obtained from reactions of known mechanism. It is no less important to note the existence of three anomalies which blemish this correlation.^{12d-g}

It would seem wiser to measure isotope effects at, rather than adjacent to, the sites of reaction.¹³ The necessary restriction to heavy atom (*i.e.*, nonhydrogenic) isotope effects further permits both a rigorous and (however imprecise) a quantitative deduction of transition state structure from observed phenomena, as will be shown in part II.¹⁴ The technique chosen both suggested the investigation of what is surely an atypical Diels-Alder reaction and required ancillary experimental evidence.

For practical reasons, carbon dioxide is an ideal molecule for the precise isotopic analyses needed. It is also, however, hardly a reactive dienophile and so must either be obtained (a) by selective and quantitative oxidative degradation of an appropriate addend or (b) directly by retrodiene decarboxylation. We have chosen the latter. In this part, we attempt to protect the conclusions of the next from what is surely the greatest weakness of isotope effect studies: their inability to detect structural changes anywhere but at positions of isotopic substitution. In particular, it must first be shown that decarboxylation of the maleic anhydride adduct of α -pyrone (**1**)¹⁵ satisfies the most rudimentary criteria of a Diels-Alder retrogression.

Experimental

Reported melting points are uncorrected. Microanalyses were performed by Scandinavian Microanalytical Laboratory, Copenhagen, Denmark. Infrared spectra were obtained with a Perkin-Elmer Model 21, ultraviolet spectra with a Carey Model 14, and n.m.r. spectra with a Varian Model A-60 spectrometer. Tetramethylsilane served as internal standard in all solvents except D₂O when acetone, $\tau = 7.83$ p.p.m., was employed.

α -Pyrone.¹⁶ Coumalic acid (m.p. >195° dec.) was

(5) The power of the Woodward-Katz experiment^{3c} was derived from the discovery of three nonconsecutive points from which interpolation might proceed, the structures of the two Cope rearrangement isomers and that of the monocyclic diene.

(6) (a) C. Walling and J. Peisach, *J. Am. Chem. Soc.*, **80**, 5819 (1958); C. Walling and H. J. Schugar, *ibid.*, **85**, 607 (1963); (b) S. W. Benson and J. A. Berson, *ibid.*, **84**, 152 (1962); C. Walling and D. D. Tanner, *ibid.*, **85**, 612 (1963).

(7) (a) See ref. 16 and 17 in ref. 3d; (b) M. G. Ettlinger and E. S. Lewis, Abstracts of Papers, 138th National Meeting of the American Chemical Society, New York, N. Y., Sept. 1960, p. 95P.

(8) (a) G. B. Kistiakowsky and W. W. Ransom, *J. Chem. Phys.*, **7**, 725 (1939); (b) A. Wasserman, *J. Chem. Soc.*, 612 (1942); D. Rowley and H. Steiner, *Discussions Faraday Soc.*, **10**, 198 (1951).

(9) (a) Critically reviewed by A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p. 432; (b) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963, p. 139.

(10) (a) F. D. Greene, *Bull. soc. chim. France*, 1356 (1960), has noted the failure of this last relationship in anthracene dimer dissociation; (b) H. Wynberg, W. Drenth, and W. D. Weringa, private communication; (c) J. Sauer, D. Lang, and A. Mielert, *Angew. Chem.*, **74**, 352 (1962); (d) J. Sauer and H. Wiest, *ibid.*, **74**, 353 (1962); (e) for an extreme example, see M. S. Newman, *J. Org. Chem.*, **26**, 2630 (1961).

(11) The potential energy surface of a system is independent of isotopic substitution to an overly adequate degree of approximation; G. Herzberg, "Molecular Spectra and Molecular Structure. II," D. Van Nostrand Co., Inc., New York, N. Y., 1945, p. 237; L. Pauling and E. B. Wilson, Jr., "Introduction to Quantum Mechanics," McGraw-Hill Book Co., Inc., New York, N. Y., 1935, p. 260.

(12) (a) D. E. Van Sickle and J. O. Rudin, *J. Am. Chem. Soc.*, **86**, 3091

(1964); S. Seltzer, *Tetrahedron Letters*, 457 (1962); (b) *J. Am. Chem. Soc.*, **85**, 1360 (1963); (c) M. Wolfsberg and M. J. Stern, *Pure Appl. Chem.*, **8**, 325 (1964); (d) dimethyl mercury pyrolysis: R. E. Weston, Jr., and S. Seltzer, *J. Phys. Chem.*, **66**, 2192 (1962); (e) acid-induced deoxygenation: M. M. Kreevoy and B. M. Eisen, *J. Org. Chem.*, **28**, 2104 (1963); (f) thermal- and ABN-induced polymerization of styrene- β, β' -*ds*: G. S. Hammond and K. R. Kopecky, *J. Polymer Sci.*, **60**, S56 (1962). Note that a normal C¹⁴ isotope effect had previously been observed in this reaction by E. M. Hodnett and A. W. Jensen, *ibid.*, **43**, 183 (1960). (g) A suggested explanation of the anomaly of 12d has recently been published: A. A. Zavitsas and S. Seltzer, *J. Am. Chem. Soc.*, **86**, 3836 (1964).

(13) G. A. Ropp, V. F. Raaen, and A. J. Weinberger, *ibid.*, **75**, 3697 (1953), in the only comparable investigation, failed to detect isotopic fractionation in addition of β -nitrostyrene- α -C¹⁴ to 2,3-dimethylbutadiene.

(14) M. J. Goldstein and G. L. Thayer, Jr., *ibid.*, **87**, 1933 (1965).

(15) O. Diels and K. Alder, *Ann. Chem.*, **490**, 257 (1931).

(16) The method of H. E. Zimmerman and R. M. Paufer, *J. Am. Chem. Soc.*, **82**, 1514 (1960). We have been indebted to Professor Zimmerman for providing these details prior to publication.

decarboxylated by sublimation through a 600 × 25 mm. copper turning packed Vycor tube heated at 650°. The crude material was adequately purified by distillation through a 70-cm. glass helix packed column, b.p. 93° (17 mm.).

Maleic anhydride adduct of α -pyrone (1) was prepared in 85% yield by only slight modification of the original method¹⁵ but was recrystallized from anhydrous acetonitrile. The reported melting point (185–186°¹⁷ and 187°¹⁵) is that of some transformation product, decarboxylation having already begun at 160°, and could not be used as a criterion of purity. Infrared or ultraviolet ($\lambda_{\text{max}}^{\text{acetonitrile}}$ 228 m μ (ϵ 463 \pm 7)) spectra, which remained unaffected by recrystallization, and gas or thin layer chromatography also could not be used. Purity was finally defined by satisfactory carbon-hydrogen analysis after at least three recrystallizations and was subsequently confirmed by the area ratios of n.m.r. spectra (Table II).

Anal. Calcd. for C₉H₆O₅: C, 55.68; H, 3.12. Found (batch 1): C, 55.60, 55.66; H, 3.19, 3.16. Found (batch 2): C, 55.65, 55.61; H, 3.18, 3.22.

Dimethyl Phthalate. Commercial material was refluxed for 15 hr. over calcium hydride, rapidly distilled, and then fractionated through a 65-cm. stainless steel, helix-packed column. Only center cuts of b.p. 153° (12 mm.) and n_{D}^{24} 1.5139, 1.5140 (lit. n_{D}^{20} 1.5138^{18a} and n_{D}^{25} 1.5155,^{18b} 1.5137^{18c}) were used for kinetic experiments in this part and isotope effect determinations in the next.

trans-1,2-Dihydrophthalic acid, m.p. 206–207° dec. (lit.^{19a} 210°), was prepared in 75% yield by sodium amalgam reduction of phthalic acid,^{19a} $\tau_{\text{D}_2\text{O}}$ = 4.05 and 6.58 p.p.m. in the ratio 1.93:1.

cis-1,2-Dihydrophthalic anhydride (2) was prepared in 84% yield by brief refluxing of the *trans* diacid with acetic anhydride and then purified by sublimation: m.p. 93–102° (lit.^{19a} m.p. 99–100°); $\lambda_{\text{max}}^{\text{acetonitrile}}$ 258 m μ (ϵ 3.86 \times 10³), 293 (960), and 302 (975) (lit.¹⁷ $\lambda_{\text{max}}^{\text{ethanol}}$ 260 m μ (ϵ 3.2 \times 10³)).

*2,3-Dihydrophthalic Acid.*²⁰ 3-Acetoxy-1,2,3,6-tetrahydrophthalic anhydride was prepared in 92% yield by the addition of maleic anhydride to 1-acetoxybutadiene²¹ and distilled, m.p. 56–58° (lit.²¹ m.p. 58°). Treatment with refluxing hydrochloric acid produced 2,3-dihydrophthalic acid in 91% yield: m.p. 176–179° (lit.²⁰ m.p. 180°); $\lambda_{\text{max}}^{\text{ethanol}}$ 288 m μ (ϵ 7.68 \times 10³); $\tau_{\text{D}_2\text{O}}$ = 2.85, 3.88, 6.41, and 7.36 p.p.m. in the ratios 1:1.85:1.07:1.84.

*2,3-Dihydrophthalic anhydride (4)*²⁰ was prepared by warming the corresponding diacid with acetic anhydride. After sublimation, it showed m.p. 100–102° (lit.²⁰ m.p. 102°), $\tau_{\text{acetonitrile}}$ = 2.91, 3.63, 6.13, and 7.42 p.p.m. in the ratios 1:1.99:1.16:2.00.

1,4-Dihydrophthalic Acid. A. By Diene Synthesis.

(17) B. R. Landau, Ph.D. Thesis, Harvard University, 1950.

(18) (a) G. S. Gardner and T. E. Brewer, *Ind. Eng. Chem.*, **29**, 179 (1937); (b) W. M. Bruner and L. T. Sherwood, *ibid.*, **41**, 1654 (1949); (c) W. J. Svirbely, *et al.*, *J. Am. Chem. Soc.*, **71**, 508 (1949).

(19) (a) A. Baeyer, *Ann. Chem.*, **269**, 145 (1892); (b) W. M. Rodionow and V. C. Zvorykina, *Bull. soc. chim. France*, [5] **5**, 840 (1938); (c) V. F. Kucherov and N. Ya. Grigor'eva, *Zh. Obsch. Khim.*, **31**, 447 (1961); (d) G. Smith, C. L. Warren, and W. R. Vaughan, *J. Org. Chem.*, **28**, 3323 (1963).

(20) W. Flaig, *Ann. Chem.*, **568**, 1 (1950).

(21) H. J. Hagemeyer, Jr., and D. C. Hull, *Ind. Eng. Chem.*, **41**, 2920 (1949).

Propiolic acid (59 g., 0.84 mole) in 50 ml. of benzene was added to 250 ml. of a solution of freshly prepared vinylacrylic acid²² in the same solvent; a trace of di-*t*-butyl-*p*-cresol was added and the solution was refluxed under dry, oxygen-free nitrogen. At intervals up to 85 hr. the product was collected by cooling, yielding 12.01 g. (7.5% based on malonic acid), m.p. 224–229° dec. after two rapid recrystallizations from water: $\lambda_{\text{max}}^{95\% \text{ ethanol}}$ 285 m μ (ϵ 55.2). The n.m.r. spectrum of the disodium salt had $\tau_{\text{D}_2\text{O}}$ = 3.23, 4.15, 6.19, and 7.20 p.p.m. in the ratios 1:1.90:1.00:1.95.

B. By Isomerization of trans-1,2-Dihydrophthalic Acid.^{19a} A solution of 4.44 g. (29.6 mmoles) of *trans*-1,2-dihydrophthalic acid in 300 ml. of water was heated under nitrogen on a steam bath for 11 hr. Charcoal treatment, solvent evaporation, and four recrystallizations from water provided 3.01 g. (68%), m.p. 224–226° dec. of identical n.m.r. and infrared spectra as the synthetic material above. The ultraviolet spectrum differed: $\lambda_{\text{max}}^{95\% \text{ ethanol}}$ 284 m μ (ϵ 207).

1,4-Dihydrophthalic Anhydride (5a).^{19a} Refluxing 2.91 g. (17.3 mmoles) of synthetic 1,4-dihydrophthalic acid in 18.0 g. of acetyl chloride for 12 hr., solvent removal, and sublimation at 45° (10⁻⁵ mm.) produced 2.30 g. (81%) of anhydride: $\tau_{\text{acetonitrile}}$ = 1.92, 2.88, 3.90, 5.71, and 6.96 p.p.m. in the ratios 1.45:1.05:2.00:1:2.03. The first of these maxima is due to 26% contamination by phthalic anhydride ($\tau_{\text{acetonitrile}}$ = 1.92 p.p.m.). A value of 30% contamination was obtained from $\epsilon_{297 \text{ m}\mu}^{\text{apparent}}$ 662 and $\epsilon_{297 \text{ m}\mu}^{\text{C}_8\text{H}_4\text{O}_3}$ 2160, although the remainder of the spectrum is also essentially that of diluted phthalic anhydride. Recrystallization from carbon tetrachloride raised the m.p. to 80–82°, but only by increasing the extent of phthalic anhydride contamination as did substitution of N,N'-dicyclohexylcarbodiimide for acetyl chloride. The remarkable ease of thermal aromatization of the acid has long been known^{19a} and would appear to be a general property of 1,4-dihydrophthalic acids.²³

2-Bicyclo[2.2.2]octene-2,3,5,6-tetracarboxylic Dianhydride (3). A. By Authentic Synthesis. Refluxing a solution of 1.01 g. (6.73 mmoles) of *cis*-1,2-dihydrophthalic anhydride and 0.99 g. (10.1 mmoles) of maleic anhydride in 50 ml. of benzene, under nitrogen for 12 hr., produced 0.83 g. (50%) of product on cooling: m.p. 374–382 dec., $\lambda_{\text{max}}^{\text{KBr}}$ 5.40 μ (1852 cm.⁻¹), 5.60 μ (1785 cm.⁻¹). The tetrasodium salt had $\tau_{\text{D}_2\text{O}}$ = 3.74 (apparent triplet of J = 4.2 c.p.s.), and overlapping peaks at 7.03, 7.10, and 7.17 p.p.m. in the ratio 1:3.03.

B. By in Situ Reaction with Decarboxylation Product at 160°. Decarboxylation of 0.50 g. (2.58 mmoles) of α -pyrone adduct in 25 ml. of dimethyl phthalate, also containing 0.25 g. (2.58 mmoles) of maleic anhydride, at 160° for 170 min. was followed by solvent removal at 75° (0.015 mm.) to produce 0.52 g. (81%) of off-

(22) R. B. Woodward, F. E. Bader, H. Bickel, A. J. Frey, and R. W. Kierstead, *Tetrahedron*, **2**, 1 (1958); this material was used without purification.

(23) The need for a revised structure, suspected prior to this study,¹⁷ has since also been confirmed by N. Ya. Grigor'eva and V. F. Kucherov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 2196 (1962), via ozonolysis to malonic (61%), 1,1,2-ethanetricarboxylic (19%), oxalic (18%), and succinic (2%) acids; despite obvious contamination, both by 2,3-dihydrophthalic and phthalic acids, these authors successfully deduced **5a**, the structure here assigned.

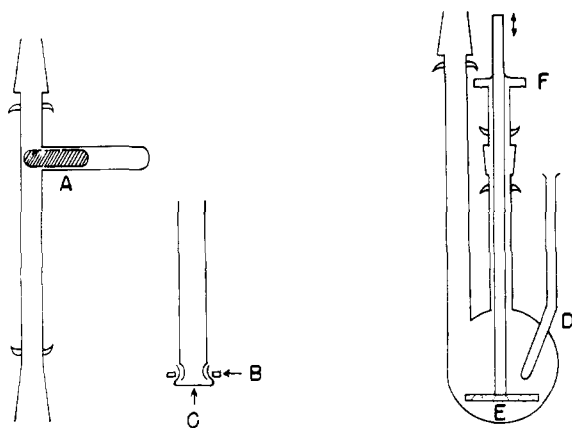


Figure 1. Drop-tube assembly and reaction flask for kinetics: A, Teflon-coated magnet; B, Teflon O-ring; C, Saran (vinyl chloride vinylidene chloride copolymer) film; D, thermocouple well; E, glass paddle with conical holes; F, pressure-tight Viton (hexafluoropropylene 1,1-difluoroethylene copolymer) gasket.

white solid. After benzene washing, it had m.p. 374–382°, m.m.p. (with material prepared above) 374–382°, and an identical infrared spectrum.

C. By Reaction with Decarboxylation Product at 50°. A solution, obtained by decarboxylation of 0.25 g. (1.29 mmoles) of α -pyrone adduct in 9 ml. of dimethyl phthalate at 160° for 180 min., was cooled to room temperature and 0.13 g. (1.33 mmoles) of maleic anhydride was added. It was then heated at 50° for 12 hr. and the solvent was removed at 105° (0.005 mm.) to produce 0.27 g. (84%) of off-white solid. After benzene washing, its infrared spectrum was identical with that of authentic material as was the n.m.r. spectrum of its tetrasodium salt. Integrated intensities of spurious peaks from $\tau = 2$ –10 p.p.m. amounted to less than 7% of the total.

Recovery of Unreacted α -Pyrone Adduct from Incomplete Decarboxylation. A solution of 1.11 g. (5.72 mmoles) of α -pyrone adduct in 55 ml. of dimethyl phthalate was maintained at 128° for 50 min. (10% reaction) and cooled to room temperature, and 10 ml. of carbon tetrachloride was added. Further cooling at 10° for 48 hr. deposited 0.80 g. (80%) of crude, recovered material whose infrared and n.m.r. spectra were nonetheless identical with those of starting material.

Isomerization Control Experiments. A. The Reactivity of 2,3-Dihydrophthalic Anhydride toward Maleic Anhydride. Heating 0.20 g. (1.33 mmoles) of 2,3-dihydrophthalic anhydride and 0.29 g. (2.04 mmoles) of maleic anhydride in 8.0 ml. of dimethyl phthalate at 160° for 185 min. produced 0.24 g. (73% assuming a 1:1 adduct) of a brown gum after solvent removal at 110° (0.005 mm.): $\lambda_{\text{max}}^{\text{acetonitrile}} = 5.43 \mu$ (1840 cm^{-1}), 5.63 (1778), and 5.80 (1724); $\tau_{\text{acetonitrile}} = 2.34, 3.43$ (broad, very weak), 6.13, and 6.5–8.3 p.p.m. (complex, very strong). A maximum contribution of the characteristic olefinic hydrogens of **3** to low-field absorption was evaluated by adding 18.1 mg. (0.070 mmole, corresponding to a 10.9% yield) of **3** to one of two identical aliquots of an acetonitrile solution of the viscous oil. Comparison of integrated intensities from $\tau = 3.49$ –3.68 p.p.m. sets an upper limit of 5.8% to the production of **3**.

B. The Reactivity of 1,4-Dihydrophthalic Anhydride toward Maleic Anhydride. A similar experiment was performed with 0.155 g. (1.03 mmoles) of 1,4-dihydrophthalic anhydride and 0.130 g. (1.33 mmoles) of maleic anhydride in 9 ml. of dimethyl phthalate, and provided 0.12 g. (47%, assuming a 1:1 adduct) of a gum of qualitatively similar n.m.r. spectrum. This time, however, integration set an upper limit of 0.6% to the yield of **3**. A control experiment showed phthalic anhydride to be quantitatively codistilled with solvent under these conditions.

Kinetics. Preliminary experiments which relied on stirring for agitation failed to provide rate constants independent of stirring speed (<2200 r.p.m.) although reproducible first-order behavior was observed at any fixed speed >200 r.p.m.. All reported rate constants were obtained using the flask, shown in Figure 1, which relied on the 60-c.p.s. vertical oscillation of a Vibromixer-driven,²⁴ perforated, circular glass paddle to provide agitation.

Typically, carbon dioxide was bubbled through approximately 70 ml. of buret-measured dimethyl phthalate in the reaction flask for at least 1.25 hr. at room temperature during agitation. The vial was charged with adduct and placed in the drop tube assembly with the magnet in the position shown. The flask was then inserted in the constant-temperature bath and connected, *via* drop-tube assembly, water-cooled condenser, and ball-jointed glass tubing to the gas-measuring manifold which included both 100- and 500-ml. water-jacketed gas burets and a sensitive, horizontal-arm, mercury manometer. Motion of the mercury thread activated a capacitance-sensitive relay to lower the appropriate mercury-leveling bulb and so to maintain atmospheric pressure.^{25a}

After temperature and phase equilibration, the supporting magnet, A, was released and volume readings were taken at each relay operation, typically 90 points per run. Three minutes were required for temperature re-equilibration after the vial had dropped; no points were recorded during this time. Atmospheric pressure and the temperatures of buret jacket, bath, and flask were measured at intervals during each run, the latter two by calibrated, triple-junction thermocouples.

Carbon Dioxide Yield. Two manometric determinations were performed by decomposing α -pyrone adduct (9.83 and 11.30 mg.) in 1.0 ml. of degassed dimethyl phthalate at 160° for 170 min. in a closed reaction vessel. The carbon dioxide was purified¹⁴ and expanded into a calibrated 7.21 \pm 0.02-ml. vol. where its pressure was compared with the calculated values (0.1330 and 0.1503 mm.) to provide the percentage yields (99.5 and 100.9%).

Dipole Moments. Both dielectric constants (ϵ_{12}) and refractive indices (n_{12}) of dioxane solutions were determined at 25.00 \pm 0.05°. The DMO1 dipole meter^{25b} was calibrated with air, Spectrograde cyclohexane (without further purification), and A.R. grade carbon tetrachloride which had been refluxed over phosphorus pentoxide, fractionally distilled (center

(24) A. G. für Chemie-Apparatebau, Mannedorf, Z. H., Switzerland.

(25) (a) Only slightly modified from an old design of E. M. Arnett; a similar apparatus has more recently been described by E. G. Janzen, *J. Chem. Educ.*, **41**, 281 (1964); (b) Wissenschaftlich-Technische Werkstätten, Weilheim, Germany.

cut, b.p. 75°), and dispensed through a 1:1 silica gel-alumina column. Fisher certified dioxane was further purified by refluxing over sodium and fractional distillation. It was stored over freshly activated Linde 4A molecular sieves until transferred, by syringe, to the dielectric constant cell. All operations involving dioxane were performed in an atmosphere of dry nitrogen. The dipole moment was calculated by Guggenheim's method²⁶

$$\mu^2 = A \frac{3M_2 (a_\epsilon - a_n)}{d_1 (\epsilon_1 + 2)^2}$$

$$A = \frac{10^{36} 9kT}{N 4\pi} = 4.897 (25.00^\circ)$$

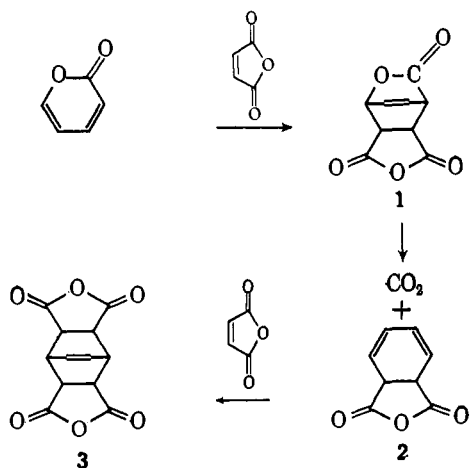
where M_2 is the solute molecular weight, d_1 and ϵ_1 are the density and dielectric constant of solvent, and a and a_n are the limiting slopes of $\epsilon_{12} - \epsilon_1$ and $n_{12}^2 - n_1^2$ vs. w_2 as $w_2 \rightarrow 0$ (see Table I).

Table I

$10^3 w_2$	ϵ_{12}	n_{12}
0	2.2073	2.0187
	2.2070	
2.266	2.2091	2.0192
	2.2089	
4.522	2.2115	2.0198
	2.2110	
9.003	2.2151	2.0207
	2.2149	

The Reactant

The only previously published information was that of the investigators who first prepared **1** and discovered its decarboxylation to *cis*-1,2-dihydrophthalic anhydride (**2**).¹⁵ The structure of the adduct was assumed by analogy. That of the product was deduced by identifying the decarboxy bisadduct **3**, prepared *in situ*, with that obtained by fusing an authentic sample of **2** with maleic anhydride. No yields were reported for any reaction save that of the initial synthesis (40%); **1** was characterized by an acceptable elemental analysis and an apparent melting point (187°). Subsequent, unpublished work¹⁷ describes some chemical transformations which were, and remain, most simply rationalized if the anhydride ring is assigned an *endo* configuration.



(26) E. A. Guggenheim, *Trans. Faraday Soc.*, **47**, 573 (1951).

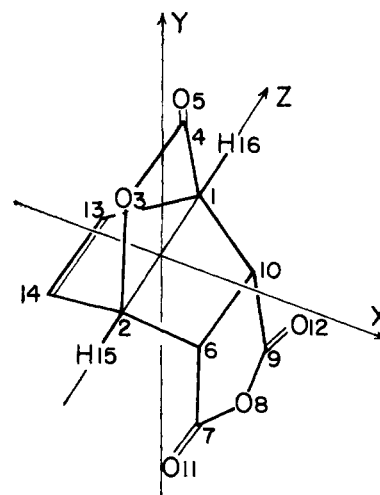


Figure 2. Numerical designation of atoms in the *endo* maleic anhydride adduct of α -pyrone.

The n.m.r. spectrum of the adduct (Table II) excludes **1b**, that product of unprecedented 1,2-addition not also excluded by infrared maxima: $\lambda_{\text{max}}^{\text{dioxane}}$ 5.35 μ (1860 cm^{-1}), 5.63 (1776), and 5.79 (1727), and confirms the gross structural assignment. The chemical shifts agree as well as might be expected with those reported for the corresponding hydrogens in the maleic anhydride adducts of furan: $\tau_{\text{acetone-triile}}$ = 3.47, 4.57, and 6.12 (*endo*) and 3.47, 4.66, and 6.75 (*exo*) p.p.m.²⁷

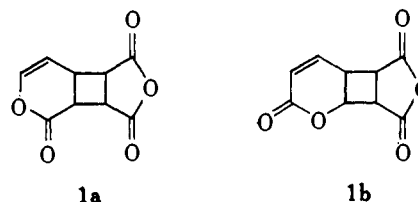


Table II

Center of absorption, τ^{DMS}	Relative integrated areas	Assignment to protons at carbons numbered ^a	Description
3.25	1.98	13, 14	Apparent triplet, separated by 4 c.p.s.; area ratios 1:1.6:1.2; half-peak height widths 1, 2, 1 c.p.s.
4.28	1	2	Apparent quadruplet; peaks equally separated by 4 c.p.s.; area ratios 1:2.5:2.3:1 half-peak height widths 1, 2, 2, 1 c.p.s.
5.95	3.00	1, 10, 6	Multiplet; highest peak at $\tau = 6.00$ p.p.m.

^a Atom numbering is assigned in Figure 2.

Only the configuration of the anhydride ring remains to be assigned and this by a comparison of the observed dipole moment with those anticipated for each of the two isomers. Atomic coordinates (numbered as in Figure 2) were used in conjunction with group

(27) F. A. L. Anet, *Tetrahedron Letters*, 1219 (1962).

moments attributed to the olefin, anhydride, and lactone functions. Dipole moments of 0.24 (mean of cyclohexene and cyclopentene),^{28a} 4.21 (succinic anhydride),^{28b} and 4.22 D. (δ -valerolactone)^{28c} were chosen. The last of these is somewhat deficient since, of the three, the lactone moment, alone, possesses a z component and so here a direction, as well as a magnitude, must be assigned to the model. This was done impartially by permitting its measured dipole moment and each of two alternate sets of "bond moments"^{28d} to determine the least predictable "bond moment," that of the C-4-O-3 bond. The procedure is illustrated in Table III and its results are compared with experiment in Table IV. The discrepancy between the observed value and those calculated for the *exo* isomer far exceeds the sum of the uncertainty in our models (*ca.* 1 D.) and those nonrandom errors (<1 D.)^{28e} often encountered in such experimental determinations.

Table III. Direction of the Lactone Dipole

	Bond moments ^a	
	Set A	Set B
C-2—O-3	0.85	1.50
Cl—C-4	0	0
C-4=O-5	3.40	3.10
C-4—O-3	$\mu_{C-4-O-3}$	$\mu_{C-4-O-3}$
Vector sum	4.22	
Whence $\mu_y^{C-4-O-3}$	0.03	-0.02
$\mu_z^{C-4-O-3}$	1.54	-0.95

^a See ref. 28d. A positive dipole moment is taken as directed toward the second atom.

An *endo* assignment is clearly to be preferred, though not unequivocally so long as the *exo* isomer remains unavailable. Our concern for homogeneity (see Experimental) was largely motivated by an unsuccessful search for this missing isomer. None was detected even in what might have appeared the most promising locations: dimethyl sulfoxide n.m.r. spectra of "crude" adduct, obtained either directly by synthesis or by recovery from incomplete reaction, and (much more dilute) dimethyl phthalate n.m.r. spectra of pure adduct observed at 126° during the course of decarboxylation.

It is clear that dipole-dipole repulsion of anhydride and lactone rings provides an attractive electrostatic justification for the predominance of *endo* adduct. But whether this is manifest in the relative rates of maleic anhydride addition or in the equilibrium constant which governs subsequent isomerization cannot be answered without the *exo* isomer in hand.

The Product

The assignment of *cis*-1,2-dihydrophthalate anhydride (**2**) to the structure of the product could also benefit from less ambiguous evidence than had been

(28) (a) W. D. Kumler, S. Winstein, R. Boikess, and P. Radlick, Abstracts of Papers, 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 1962, p. 80Q; a more recent publication by this group, *J. Am. Chem. Soc.*, **86**, 3226 (1964), revises this value, insignificantly, to 0.21 D.; (b) M. A. G. Rau and N. Anantanarayanan, *Proc. Indian Acad. Sci.*, **5A**, 185 (1937); (c) R. Huisgen and H. Wieland, *Angew. Chem.*, **69**, 341 (1957); (d) J. W. Smith, "Electric Dipole Moments," Butterworth and Co. (Publishers) Ltd., London, 1955, p. 92; (e) R. J. W. LeFevre, "Dipole Moments" Methuen and Co. Ltd., London, 1947, Chapter III.

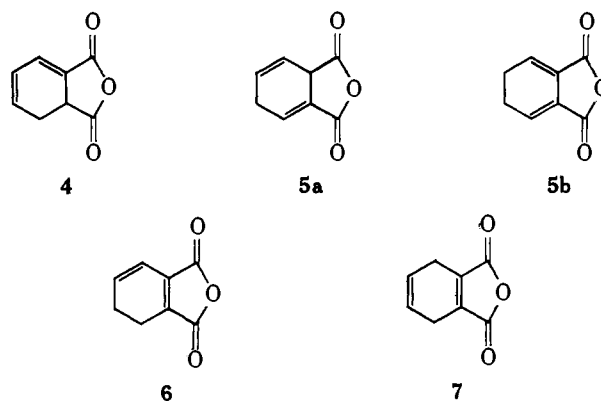
Table IV. Predicted and Observed Dipole Moments

	Group Moments				
	Anhydride		Olefin	Lactone ^a	
	<i>endo</i>	<i>exo</i>		A	B
x	0	3.65	-0.21	0	0
y	-4.21	2.11	-0.12	2.89	4.05
z	0	0	0	3.07	1.19
Molecular moments predicted for	<i>endo</i>		<i>exo</i>		
	A	B	A	B	
x	-0.21	-0.21	3.44	3.44	
y	-1.20	-0.28	4.88	6.04	
z	3.07	1.19	3.07	1.19	
Vector sum	3.30	1.24	6.71	7.05	
Observed	1.34 ± 0.07				

^a Derived from each of the two sets of bond moments in Table III.

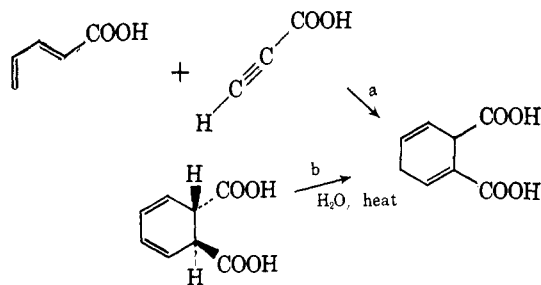
available¹⁵ and this too is now provided. In particular, decarboxylation of **1** in the presence of maleic anhydride permitted isolation of the decarboxy bisanhydride **3** in 81% yield. N.m.r. and infrared spectra are consistent with this structure as is repetition of the independent synthesis,¹⁵ though more efficiently and under less drastic conditions. It is noteworthy that maleic anhydride scavenging appears to be a matter of convenience, not necessity. When decarboxylation of **1** (in dimethyl phthalate solution at 160°) had been completed, a comparable yield of **3** (84%) could still be obtained by subsequent maleic anhydride addition at 50°. The product **2** is therefore quite stable under decarboxylation conditions.

It remains to be shown that **2** is also the initially formed product and not an artifact of subsequent isomerization. Although all the structurally isomeric dihydrophthalic anhydrides are initially suspect, only the two proximate tautomers, 2,3-dihydrophthalic anhydride (**4**) and 1,4-dihydrophthalic anhydride (**5a**), deserve serious consideration. Of these, **4** was the more simply obtained and this by a procedure due to Flaig.²⁰



The only previous report of **5a** describes melting points of anhydride (73–74°) and acid (175°), a preparative method unlikely to have produced this isomer, and no proof of structure.²⁹ A rational⁷ synthesis seemed appropriate and was achieved simply, if in poor yield, by the addition of propiolic to vinylacrylic acid (a, below). The resulting diacid displayed an n.m.r. absorption pattern characteristic of two dis-

(29) G. Abati, *Gazz. chim. ital.*, **38**, 153 (1908).



similar vinylic and two dissimilar allylic groups of protons in the expected ratios 1:2:1:2. A similar pattern is also expected of **4** but ultraviolet spectra clearly distinguish the conjugated ($\epsilon_{\text{max}}^{90\% \text{ ethanol}} 7670$) from the unconjugated ($\epsilon_{\text{max}}^{90\% \text{ ethanol}} 285 \text{ m}\mu$ **55**) acid. The melting points of **5a** and of its acid (81–82° and 224–229°) are strongly reminiscent of those (83–84°, ^{19a} 84–85°, ^{19b}; 213°, ^{19c} 215°, ^{19a} 222–223°, ^{19b} 224–225°, ¹⁷ and 215° ^{19d}) reported for a far more thoroughly investigated isomer, one to which the 4,5-dihydrophthalic structure **5b** had long been assigned. Indeed, repetition of Baeyer's original preparation (b, above) of the purported "**5b**" produced the very same compound whose structure is now unambiguously that of **5a**. The ultraviolet spectrum of the acid obtained by isomerization, however, reveals isomeric contamination; $\epsilon_{\text{max}}^{90\% \text{ ethanol}} 289 \text{ m}\mu$ decreases only gradually from ca. 800 to 207 even after four recrystallizations and this, no doubt, suffices to explain the persistence of this error.²³

With both **4** and **5a** available, each was subjected to maleic anhydride treatment under precisely the same conditions as was the α -pyrone adduct **1**. In neither case could the decarboxy bisadduct **3** be isolated. Quantitative n.m.r. analysis of the viscous oils obtained sets an extreme upper limit of 5.8 and 0.6% to the yields of **3** that could have been obtained from **4** and from **5a**.³⁰ Were any of the other tautomers **5b**, **6**, or **7** produced by decarboxylation they would need isomerize *via* **4** and **5a**. Since the latter have been excluded, so too have the former, and *cis*-1,2-dihydrophthalic acid (**2**), produced in greater than 80% yield, may confidently be assumed to be the initially formed product.

Kinetics

Isotope effect studies do not need highly precise rate data but do require that carbon dioxide be quantitatively recovered and rigorously purified. This suggested the use of a high-boiling solvent, soon restricted to dimethyl phthalate because of solubility problems, and so left little choice but to employ a gasometric technique for rate measurement. The dangers inherent in such methods are well known³¹ and were anticipated by demonstrating that apparent first-order rate constants were insensitive to extent of agitation or to the incorporation of varying amounts of powdered glass (runs 14, 15, 16; Table V). Points (50–100) were

(30) The absence of an appreciable yield of any adduct from **4** is presumably due to side reactions under these conditions (see Experimental) and contrasts with the ease of maleic anhydride addition to the corresponding dimethyl ester at lower temperatures: J. Kazan and F. D. Greene, *J. Org. Chem.*, **28**, 2964 (1963); the previously reported unreactivity of the dimethyl ester of **5a**^{19d} is now fully consistent with the revised structure.

(31) K. J. Pedersen, *J. Am. Chem. Soc.*, **49**, 2681 (1927); M. G. Peard and C. F. Cullis, *Trans. Faraday Soc.*, **47**, 616 (1951), and references cited.

Table V. Summary of Kinetic Data

Temp., °C.	Run no.	Concn., <i>M</i>	<i>f</i> _{max} ^a	10 ³ <i>k</i> , sec. ⁻¹	
128.10 ± 0.12 ^b	12	0.1262	0.348	2.73	
	13	0.1440	0.223	2.83	
	14 ^c	0.1379	0.161	2.90	
	15 ^d	0.1143	0.174	2.48	
	16 ^e	0.1392	0.180	2.67	
	17	0.1456	0.198	2.83	
	18 ^f	0.1619	0.299	2.55	
	19 ^f	0.2132	0.193	2.79	
					mean, 2.73 ± 0.29 ^b
	140.00 ± 0.01	29	0.07239	0.405	9.18
30		0.08944	0.381	9.24	
31		0.07957	0.410	9.22	
32		0.07147	0.415	9.18	
				mean, 9.19 ± 0.05	
149.98 ± 0.04	25	0.06515	0.690	24.0	
	26	0.06255	0.724	25.1	
	27	0.06165	0.723	23.6	
	28	0.06306	0.674	23.6	
					mean, 24.1 ± 0.7
160.34 ± 0.08	20	0.05457	0.984	64.4	
	21	0.04942	0.934	67.0	
	22 ^g	0.05641	0.923	67.5	
	23 ^h	0.05878	0.814	65.8	
	33	0.3132	0.883	62.6	
					mean, 65.5 ± 2.0
				$\Delta H^* = 33.2 \pm 0.2 \text{ kcal/mole}$	
				$\Delta S^* = 2.69 \pm 0.05 \text{ e.u.}$	

^a Maximum extent of reaction followed. ^b These are pooled results of runs taken over a sufficiently extended period to suffer from long term bath temperature instability. Temperature variation in any run never exceeded ±0.01°. Activation parameters were calculated using individually measured temperatures for each rate constant. ^c Vibromixer set at its maximum amplitude. ^d 0.4 g. of Pyrex powder added. ^e 4.0 g. of Pyrex powder added. ^f Solvent passed through alumina column prior to kinetic run. ^g Solution contained 0.058 *M* maleic anhydride. ^h Adduct added *via* an all-glass sample vial.

obtained for each run and conveniently fitted to eq. 1 by a least-squares regression program.³² Activation parameters were similarly obtained *via* eq. 2.

$$\ln(V_{\infty} - V) = \ln(V_{\infty} - V_0) - kt \quad (1)$$

$$\ln(k/T) = -\Delta H^*/RT + \ln(k/h) + \Delta S^*/R \quad (2)$$

In general, these experiments provide little opportunity for other mechanisms. A typical kinetic run (Figure 3) reveals only random scatter from the calculated regression line. The activation parameters (Table V), and in particular ΔS^* (2.69 e.u., log *A* = 13.94), recall those of more conventional Diels–Alder retrogressions^{33,34} but still more emphatically exclude chain mechanisms. Runs 18, 19, and 33 exclude catalysis by impurities, whether in adduct or in solvent. Run 22 ensures that *in situ* formation of the decarboxy bisanhydride **3** is kinetically irrelevant.

(32) MLRA, written by Mrs. P. L. Primer of the Cornell Computing Center for the C.D.C. 1604.

(33) A total variation of log *A* from 12.6–15.1 is available in the literature; cf. M. Uchiyama, T. Tomioka, and A. Amano, *J. Phys. Chem.*, **68**, 1878 (1964), and W. C. Herndon, W. B. Cooper, Jr., and M. J. Chambers, *ibid.*, **68**, 2016 (1964), for recently determined values and references to previous work.

(34) We note, without comment, that both activation parameters are experimentally indistinguishable from those reported^{34a} for the Cope rearrangement referred to earlier.^{3c}

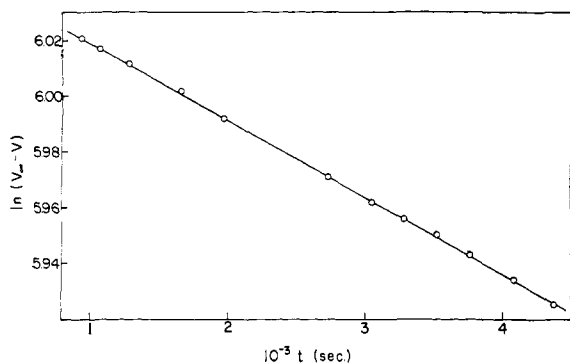
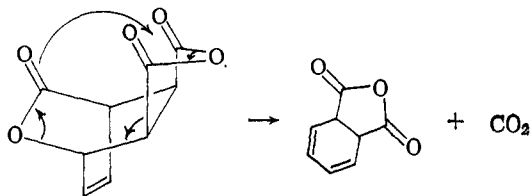


Figure 3. Calculated slope and experimental points of run 19. Only every fifth point has been included.

Mechanistic Considerations

The prime criterion for Diels–Alder retrogression, retention of geometry, clearly cannot be applied. The decarboxylation can only be forced into this class by exclusion of reasonable alternatives. To the pertinent data thus far presented, we now add that carbon dioxide is quantitatively ($100.2 \pm 1\%$) obtained, that undecomposed adduct is recovered in 80% of the anticipated yield after 10% decomposition, and that the magnitude of the carbon isotope effect ($k_{12}/k_{13} = 1.030$)¹⁴ requires that C–C cleavage be somehow contained in the rate-controlling step.³⁵

These exclude all but two alternatives. The first derives from the proximity of lactone and anhydride functions in the *exo* isomer, a permissible intermediate if not reactant, and is summarized by the expression



Preparation of **1** from maleic-1,4- C^{14} anhydride and subsequent radiocarbon analysis, which detected only $0.72 \pm 0.08\%$ of initial specific activity in evolved carbon dioxide excluded this and similar alternatives (Table VI).

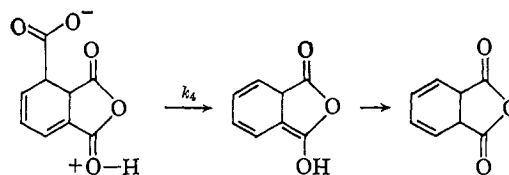
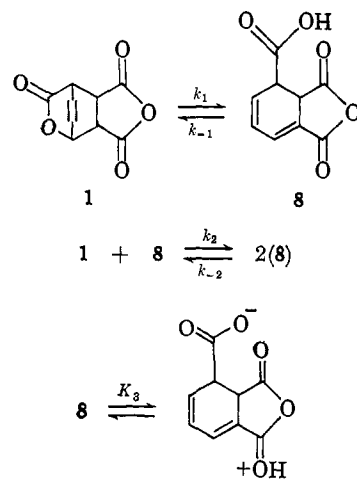
Table VI

Specific activity	Adduct	CO ₂ of decarboxylation
$m\mu\text{c./mg. C}$	0.853 ± 0.007	0.67 ± 0.08
$m\mu\text{c./mmole}$	92.12 ± 0.76	0.056 ± 0.007

The second was first suggested by detection of slight, but unmistakable, curvature in the kinetic plots of runs 20–23 (e.g., Figure 4) but *not in run 24 or any other*. This behavior is consistent with, though not demanded, by³⁶ the scheme

(35) If only by analogy. Compare malonic acid, 1.037; mesitoic acid, 1.032; and trichloroacetate ion, 1.034.

(36) $k_{obsd} = (k_4 k_3 k_2 / k_{-2}) (1 + k_{-1} k_2 / k_1)$ is derived by application of the steady-state approximation to both **8** and its zwitterion and by the requirement that k_4 be less than either k_{-1} or k_2 (**1**).



This too is dismissed, if in several ways, of which we note three. (a) In the absence of strong acids, lactone-olefinic acid equilibria are only slowly attained even with temperatures significantly above 160° and undiluted reactants.³⁷ This mechanism requires bi-

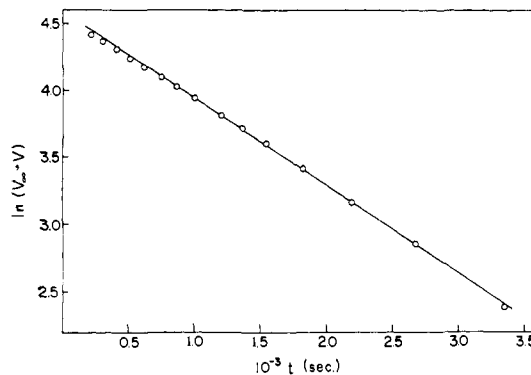


Figure 4. Calculated slope and experimental points of run 20. Only every fifth point has been included.

molecular equilibration to be rapid in dilute solution at still lower temperatures. (b) Such equilibria, as well as those related to K_3 , are commonly accompanied by prototropic isomerism which, in this system, would destroy the integrity of the C^{14} -labeled lactonic carboxyl. (c) 2,3-Dihydrophthalic acid was shown to be destroyed under the same conditions which resulted in a quantitative yield of carbon dioxide from **1**. The hypothesis that **8**, a carboxyl-substituted 2,3-

(37) W. S. Johnson and R. H. Hunt, *J. Am. Chem. Soc.*, **72**, 935 (1950), and references cited; J. v. Braun and W. Munch, *Ann. Chem.*, **465**, 52 (1928); H. Kröper in "Methoden der Organischen Chemie, (Houben-Weyl) Sauerstoff-Verbindungen I2," Vol. 6/2, E. Muller, Ed., Georg Thieme Verlag, Stuttgart, 1963, p. 571; M. F. Ansell and M. H. Palmer, *Quart. Rev.* London, **18**, 211 (1964); the thermal stability of gibberellic acid is most relevant; P. W. Brian, J. F. Grove, and J. MacMillan in "Fortschritte der Chemie Organischer Naturstoffe," Vol. XVIII, Springer-Verlag, Vienna, 1960, p. 350; its hydrolytic instability resembles that of **1**.²³

dihydrophthalic anhydride, be immune to similar side reactions contradicts all experience.

It is simpler to believe the origin of the anomaly to be no more profound than its magnitude and to attribute it to the incursion of a marginal side reaction. The predominant reaction path avoids all such inter-

mediates. It is to be regarded as a retrodiene decarboxylation.

Acknowledgment. We are grateful to Dr. A. P. Wolf and Dr. D. R. Christman for C¹⁴ analyses, to Dr. A. W. Laubengayer for use of the dipole meter, and to Dr. R. B. Woodward for informing us of ref. 17.

The Mechanism of a Diels–Alder Reaction. II. The Structure of the Transition State¹

M. J. Goldstein and G. L. Thayer, Jr.²

Contribution from the Baker Laboratory of Chemistry, Cornell University, Ithaca, New York. Received September 19, 1964

Carbon and oxygen kinetic isotope effects ($k_{12}/k_{13} = 1.030$ and $k_{16}/k_{18} = 1.014$) have been determined for decarboxylation of the maleic anhydride adduct of α -pyrone. Subjected to both approximate and exact theoretical analysis, they require a one-center transition state: the C–C bond connecting the labile lactone to the remainder of the molecule is effectively broken in the transition state whereas the C–O connecting bond remains virtually intact. Exact analysis provides a more quantitative description and relates structural to experimental uncertainties. The reliability of these conclusions is shown to depend critically on the use of heavy atom kinetic isotope effects measured at multiple, adjacent sites. Some more general aspects of the one-center and two-stage descriptions of Diels–Alder addition are discussed.

Introduction

In Part I,³ decarboxylation of the maleic anhydride adduct of α -pyrone was experimentally classified as a Diels–Alder retrogression and the accepted structures of reactants and products were confirmed. In this part, kinetic isotope effects are evaluated and used to explore the structure of the transition state.

Experimental

α -Pyrone maleic anhydride adduct and dimethyl phthalate were prepared and purified as described.³

Apparatus and Procedure. The decarboxylations were carried out in a long-necked, round-bottom flask connected to a high-vacuum stopcock by the sample drop tube.³ With 1.2108 g. of adduct in the

drop tube-supported vial and 55.74 ml. of dimethyl phthalate in the flask, the latter was degassed to 10^{-5} mm. by 12 repetitions of the sequence: freeze (carbon dioxide–trichloroethylene), evacuate, and melt. The flask and contents were permitted to reach temperature equilibrium with a constant-temperature ($130.21 \pm 0.05^\circ$) bath (1 hr.), the vial was dropped into the solvent, and the flask was agitated while the sample dissolved (<1.5 min.). After 55 min. (10% decomposition) the flask was removed from the bath, rapidly cooled, and returned to the vacuum line. The carbon dioxide was purified by sublimation through a 70×1 cm. column kept at 100° and packed with 14–20 mesh silica gel into a cooled (nitrogen) trap. Samples from complete reaction were identically obtained and purified except that reaction time exceeded 10 half-lives at 160° (170 min.). Silica gel was regenerated by heating for at least 5 hr. at 200° *in vacuo*. Variations of traditional bulb-to-bulb distillation technique failed to remove traces of dimethyl phthalate (b.p. 153° at 12 mm.!) easily detected by mass spectrometry at m/e 59 (COOCH_3^+). A similar problem has been reported.⁴

Isotopic Analysis. A Consolidated Engineering Corporation 21–401 mass spectrometer was employed in both its analytical and isotope ratio modes. In the latter, one of its dual collectors records ions of m/e while the second records the sum of those at $m/e - 1$ and $m/e - 2$. Ratio measurements on any one sample were reproducible to ± 0.02 – 0.05% for carbon, ± 0.03 – 0.08% for oxygen, and were always preceded, and often immediately followed, by (a) a background scan, (b) a scan of m/e 4–100 for impurities which were never observed, and (c) isotope ratio determination of commercially obtained carbon dioxide.⁵ Optimum resolution was ensured by maximizing the isotope ratio with respect to accelerating voltage and provided results identical with those obtained by the more tedious variation with respect to magnetic field. Each observed ratio of Table I is the average of four observations on each of two samples obtained from the same reaction vessel.

(1) The study was supported by the Air Force Office of Scientific Research under Contract No. 49(038)-942 and Grant No. 142-63. Preliminary experimental results and approximate analysis were the subject of a previous communication: M. J. Goldstein and G. L. Thayer, Jr., *J. Am. Chem. Soc.*, **85**, 2673 (1963). The results of exact calculations were presented at the "International Symposium on Organic Reaction Mechanisms" held in Cork, Ireland, July 25, 1964.

(2) Union Carbide Corporation Research Fellow, 1962–1963. Taken, in part, from the dissertation to be submitted by G. L. T. to Cornell University in partial completion of the requirements for the Ph.D. Degree, Feb. 1965.

(3) M. J. Goldstein and G. L. Thayer, Jr., *J. Am. Chem. Soc.*, **87**, 1925 (1965).

(4) A. A. Bothner-By and J. Bigeleisen, *J. Chem. Phys.*, **19**, 755 (1951).

(5) Coleman grade, 99.99% minimum.