

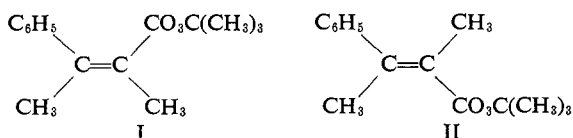
Vinyl Radicals. II.¹ The Thermal Decomposition of *t*-Butyl *cis*- and *trans*- α,β -Dimethylpercinamates²

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Abstract: *t*-Butyl *cis*- and *trans*- α,β -dimethylpercinamates (I and II) have been investigated as sources of isomeric vinyl radicals. Thermal decompositions of the peresters in cumene at 110° give the following products (I and II, respectively): CO₂ (61%, 92%), acetone (9%, 10%), *t*-butyl alcohol (80%, 81%), *cis*- and *trans*-2-phenyl-2-butene (60%, 79%), dicumyl (43%, 64%), and 3,4-dimethylcoumarin (13% from I only). Small amounts (1–2%) of the α,β -dimethylcinnamic acids are formed with retention of stereochemistry; the acids do not decarboxylate under the reaction conditions. These products clearly demonstrate the formation of vinyl radicals in good yield. Both peresters give the same ratio of *cis*-/*trans*-2-phenyl-2-butene (1.1–1.2). The peresters, intermediate acyloxy radicals, and the olefins are configurationally stable under the reaction conditions, leading to the conclusion that the vinyl radicals equilibrate more rapidly than they react with cumene.

This paper reports the preparation and thermal decomposition of *t*-butyl *cis*- and *trans*- α,β -dimethylpercinamate (I and II). α,β -Unsaturated peresters such as I and II are attractive as possible



sources of vinyl free radicals. In addition, the vinyl radicals derived from I and II are potentially isomeric and of known configuration, thereby allowing a study of the stereochemical capabilities of such radicals.

There are scattered reports of reactions that probably involve vinyl radicals. Berman and Price reported successful Hunsdiecker reactions on silver *cis*- and *trans*-cinnamate.⁴ Both isomers gave the same mixture of styryl bromides, but the configurational stability of the products under the reaction conditions was not established. Several α,β -unsaturated diacyl peroxides have been prepared and decomposed,⁵ but product studies have been incomplete or lacking. Cinnamoyl peroxide has been studied as a polymerization initiator.^{5e,f} The preparation and thermal decomposition of *t*-butyl percinamate in chlorobenzene was reported by Bartlett and Hiatt.⁶ A 70% yield of carbon dioxide suggests a respectable yield of vinyl radicals, but products incorporating these radicals were not isolated. The photolysis of 1-fluoro-2-iodoethylene apparently gives the 2-fluorovinyl radical which will add to ethylene.⁷ Nesmeyanov has indicated⁸ that

many reactions of vinyl metallics are "undoubtedly homolytic." House has recently suggested vinyl radical intermediates in metal-ammonia reductions of acetylenes.⁹ Kolbe reactions on α,β -unsaturated acids do not produce dimers; the observed products appear suspiciously ionic in origin.^{5a,b,10} Applequist and Peterson have discussed some of the theoretical reasons for studying vinyl radicals.¹¹

Vinyl radicals are presumably involved in homolytic additions to acetylenes. These reactions have been studied in some detail, but offer only limited insight into the chemistry of the intermediate vinyl radicals. The addition of radicals to acetylenes is not an attractive general route to vinyl radicals because of structural limitations on the reaction. We have previously discussed the ambiguities involved in rationalizing the stereochemical course of the over-all addition reaction.¹

Results and Discussion

Peresters I and II were prepared from the corresponding *cis*- and *trans*- α,β -dimethylcinnamic acids by reaction of the acid chlorides with *t*-butyl hydroperoxide. The preparations of the acid chlorides and peresters were conducted under mild conditions at low temperatures (0° and –20°, respectively) in order to avoid interconversion of isomers. The *cis* perester, I, was obtained as a crystalline solid, mp 39–40°; the *trans* perester was a colorless liquid. Thin layer chromatography and infrared and nmr spectra showed the perester samples to be configurationally homogeneous within the limits of sensitivity of the methods. Isomer intercontamination to the extent of >2–3% would have been detected. The configurations of the peresters follow from their preparation from acids of known stereochemistry. The structures of the α,β -dimethylcinnamic acids were convincingly assigned recently by Jackman and Lown¹² and independently established in our laboratory.¹³ In addition, the nmr spectra of *cis*- and *trans*- α,β -dimethylcinnamic acids,

(1) Part I: J. A. Kampmeier and G. Chen, *J. Am. Chem. Soc.*, **87**, 2608 (1965).

(2) Presented in part at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 16, 1965, Abstracts, p 51S.

(3) DuPont Postgraduate Teaching Assistant, 1964–1965. National Science Foundation Cooperative Fellow, 1965–1966.

(4) J. D. Berman and C. C. Price, *J. Org. Chem.*, **23**, 102 (1958).

(5) (a) F. Fichter and A. Fritsch, *Helv. Chim. Acta*, **6**, 333 (1923); (b) F. Fichter and J. Rosenzweig, *ibid.*, **18**, 238 (1935); (c) H. Erlenmeyer and W. Schoenauer, *ibid.*, **20**, 1008 (1937); (d) A. Wacek and R. Fiedler, *Monatsh.*, **80**, 179 (1949); (e) W. Cooper, *J. Chem. Soc.*, 3106 (1951); 2408 (1952); (f) N. G. Saha, N. S. Nandi and S. R. Palit, *ibid.*, 427 (1956); (g) S. Goldschmidt, H. Spath, and L. Beer, *Ann.*, **649**, 1 (1961); (h) L. F. Fieser and A. E. Oxford, *J. Am. Chem. Soc.*, **64**, 2060 (1942); (i) L. F. Fieser, *et al.*, *ibid.*, **70**, 3195 (1948).

(6) P. D. Bartlett and R. R. Hiatt, *ibid.*, **80**, 1398 (1958).

(7) H. G. Viehe, *Angew. Chem.*, 793 (1963).

(8) A. N. Nesmeyanov and A. E. Borisov, *Tetrahedron*, **1**, 158 (1957).

(9) H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, Inc., New York, N. Y., 1965, p 71.

(10) (a) J. Peterson, *Z. Elektrochem.*, **18**, 711 (1912); (b) P. Karrer and M. Stoll, *Helv. Chim. Acta*, **14**, 1189 (1931).

(11) D. E. Applequist and A. H. Peterson, *J. Am. Chem. Soc.*, **82**, 2372 (1960).

(12) L. M. Jackman and J. W. Lown, *J. Chem. Soc.*, 3776 (1962).

(13) R. A. Silverman, M. S. Thesis, University of Rochester, 1962.

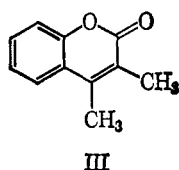
Table I. Products of Decomposition of *cis*- and *trans*- α,β -Dimethylpercinnamates (I and II)^a

Product	Yield, %	
	<i>cis</i>	<i>trans</i>
Carbon dioxide	61.3 \pm 2.5 (3)	92.0 \pm 2.6 (3)
Acetone	8.8 \pm 0.8 (9)	9.6 \pm 1.1 (16)
<i>t</i> -Butyl alcohol	79.5 \pm 1.8 (9)	81.0 \pm 2.1 (12)
<i>cis</i> - α,β -Dimethylcinnamic acid	1.2 \pm 0.3 (3)	Absent
<i>trans</i> - α,β -Dimethylcinnamic acid	Absent	1.9 \pm 0.7 (3)
3,4-Dimethylcoumarin (III)	12.8 \pm 0.9 (3)	Absent
<i>cis</i> -2-Phenyl-2-butene (IV)	32.3 \pm 1.0 (8)	41.9 \pm 1.6 (9)
<i>trans</i> -2-Phenyl-2-butene (V)	27.3 \pm 0.6 (7)	37.5 \pm 1.8 (9)
IV/V	1.18 \pm 0.03 (7)	1.14 \pm 0.05 (9)
Dicumyl	43.4 \pm 1.5 (6)	63.5 \pm 1.3 (8)

^a Under nitrogen in cumene at 110°; [perester] \cong 0.08 *M*. ^b Yields reported are the averages of results from at least three independent decompositions. Standard deviations were calculated using all of the measurements; the numbers in parentheses indicate the total number of measurements.

ethyl esters, amides, and *t*-butyl peresters show an internally consistent chemical shift pattern. With a single exception, the β -methyl of the *trans* series (*i.e.*, *cis*- to the acyl group) is shifted downfield with respect to the β -methyl of the *cis* series.^{14,15} In all cases, the α -methyls of the *trans* compounds (*i.e.*, *cis* to the phenyl) are shielded with respect to the α -methyls of the *cis* isomers.

Peresters I and II were thermally decomposed in cumene at 110° under a nitrogen atmosphere at approximately 0.08 *M* concentrations. The products of the decompositions are reported in Table I. All of the products, except carbon dioxide, were isolated and characterized by comparison with authentic materials. The yields of carbon dioxide, 3,4-dimethylcoumarin (III), and *cis*- and *trans*- α,β -dimethylcinnamic acids were determined gravimetrically. The yields of the other products were measured by vpc using internal standard methods and working curves.



The products of the decompositions of I and II in cumene clearly indicate the homolytic nature of the fragmentations. Acetone and *t*-butyl alcohol are characteristic of the formation of *t*-butoxy radicals in hydrogen-donor solvents.¹⁶ The high yield of a symmetrical coupling product derived from solvent, dicumyl, also requires a radical pathway. Although a firm conclusion will necessitate rate and scavenging studies, the formation of products retaining the acyloxy group point to an initial fragmentation involving simple dissociation of the O-O bond. The mass balance for *t*-butoxy fragments (88 and 91% for I and II, respectively) is relatively good; the accounting for acyloxy fragments (75 and 94% for I and II, respectively) is less satisfactory for the *cis* isomer.

Ionic decompositions of peresters are known, but the products are invariably different in character

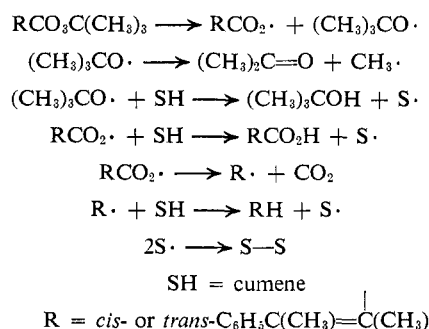
(14) L. M. Jackman, Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry, Pergamon Press Ltd., London, 1959, p 119f.

(15) The amides (in trifluoroacetic acid) are exceptional in that the β -methyl resonance occurs at the same field strength for both isomers.

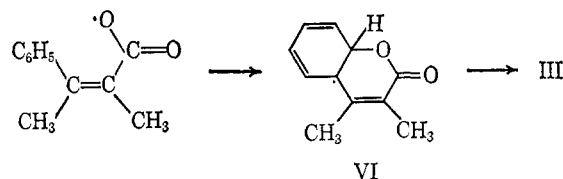
(16) J. H. Raley, F. F. Rust, and W. E. Vaughan, *J. Am. Chem. Soc.*, **70**, 1336 (1948).

from those derived from homolytic processes.¹⁷ In particular, the related acid is often a major product of ionic dissociation. Any pathway (ionic or homolytic) which involves the formation of the α,β -dimethylcinnamic acids and subsequent decarboxylation of these to form the 2-phenyl-2-butenes is ruled out by the observation that deliberately added carboxylic acid is quantitatively recovered from decomposition runs.

The scheme shown in Chart I adequately describes the formation of all of the products except 3,4-dimethylcoumarin (III). Dimethylcoumarin is formed from *cis*,

Chart I

but not from *trans* perester. The lactone logically arises *via* an intramolecular cyclization of the *cis*-acyloxy radical. Similar cyclizations are known.¹⁸



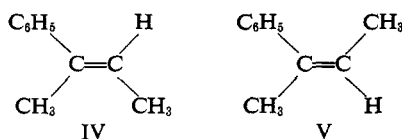
The intermediate radical VI may be diverted to products other than 3,4-dimethylcoumarin, thereby accounting for the incomplete recovery of acyloxy fragments from *cis* perester.

The fate of the *cis*-acyloxy radical is complicated by cyclization. The data in the *trans* case are more clear-cut. If the *t*-butoxy radical yield (91%) is a measure of the acyloxy radical yield, then essentially all of the acyloxy radicals decarboxylate. It is apparent,

(17) (a) R. Criegee and R. Kaspar, *Ann.*, **560**, 126 (1948); (b) P. D. Bartlett and J. Kice, *J. Am. Chem. Soc.*, **75**, 5591 (1953); (c) P. D. Bartlett and T. G. Traylor, *ibid.*, **83**, 856 (1961); (d) T. Koenig and W. Brewer, *ibid.*, **86**, 2729 (1964); (e) R. E. Pincock, *ibid.*, **86**, 1820 (1964).

(18) (a) D. F. DeTar and C. Chu, *ibid.*, **82**, 4969 (1960); (b) W. H. Starnes, Jr., *ibid.*, **85**, 3708 (1963).

therefore, that *peresters I and II are useful sources of the related vinyl radicals*. The yields of the 2-phenyl-2-butenes (60 and 79% based on I and II, respectively) lead to the same conclusion. The sum of the yields of *cis*- and *trans*-2-phenyl-2-butene (IV and V) accounts



for most of the vinyl radicals produced as measured by the yields of carbon dioxide. Therefore, these vinyl radicals react predominantly to abstract hydrogen from cumene; other pathways such as addition to the ring are not particularly important.

Table I shows that both *cis* and *trans* peresters give the same ratio of *cis*- and *trans*-2-phenyl-2-butenes, *cis/trans* = 1.1–1.2. The equilibrium mixture of these two olefins is *cis/trans* \cong 4 at 100.4° in glacial acetic acid.¹⁹ Thus, the isomer ratio observed in this work is not the result of thermodynamic control. In addition, we have demonstrated that the 2-phenyl-2-butenes are not isomerized in the presence of decomposing perester. Experiments involving partial decomposition show that the peresters themselves are not equilibrated during the course of the decomposition. The configurational stability of the peresters and the intermediate acyloxy radicals is demonstrated by the fact that the α,β -dimethylcinnamic acids formed have the same configuration as the initial peresters, *i.e.*, *cis* perester gives only *cis* acid and *trans* perester gives only *trans* acid. Isomer intercontamination >2.5% would have been detected. The absence of dimethylcoumarin (III) from *trans* perester also indicates that the *trans*-acyloxy radical does not isomerize to the *cis*-acyloxy radical.

Since the precursors of the vinyl radicals and the products derived from the vinyl radicals are not isomerized under the reaction conditions, the loss of configurational integrity observed in the 2-phenyl-2-butenes must be associated with the vinyl radicals themselves.²⁰ *A priori*, this loss of stereochemistry might be explained in either of two ways.

(a) Vinyl radicals have a linear configuration at the radical center. The same vinyl radical is produced from either I or II.

(b) Isomeric, bent vinyl radicals VII and VIII are produced from peresters I and II, respectively. These radicals equilibrate more rapidly than they are trapped by reaction with cumene.

The configurations of the unsubstituted vinyl radical²¹ and the 1-methylvinyl radical²² have been determined by esr at low temperatures. Two different β -hyperfine couplings are observed in both cases, clearly indicating bent, nonlinear structures for the radicals. Case b, therefore, is the most reasonable interpretation of the data presented.^{22a} The situation is summarized in Chart II.

(19) D. J. Cram and M. R. V. Sahyun, *J. Am. Chem. Soc.*, **85**, 1257 (1963).

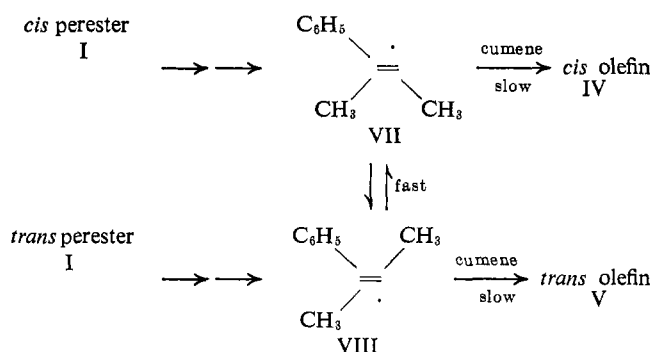
(20) Strict logic permits loss of stereochemistry in the radical-forming (decarboxylation) or radical-destroying (hydrogen abstraction) steps. These alternatives seem rather improbable.

(21) F. J. Adrian, E. L. Cochran, and V. A. Bowers, *J. Chem. Phys.*, **40**, 213 (1964).

(22) R. W. Fessenden and R. H. Schuler, *ibid.*, **39**, 2147 (1963).

(22a) NOTE ADDED IN PROOF. L. A. Singer and N. P. Kong, *Tetra-*

Chart II



Within the framework of the relative rates specified in Chart II, the *cis/trans* olefin ratio does not describe the populations of VII and VIII. Rather, the result shows that there is very little difference in the free energies of the transitions states for the reactions of VII and VIII with cumene. It is also appropriate to emphasize that these results do *not* mean that vinyl radical intermediates will isomerize under all conditions. The kinetic situation outlined in Chart II is a competitive one and with highly efficient scavengers it may be possible to trap vinyl radicals before isomerization.

The esr studies of the vinyl radical²² show that the barrier to inversion at the radical center is approximately 2 kcal/mole. The actual barrier to inversion of the 1-methylvinyl radical is unknown, but it is greater than 2.7 kcal/mole. If the unsubstituted vinyl radical is a rough model for more complicated radicals such as VII and VIII, then it may not be surprising that these radicals interconvert before they are quenched by cumene. Nevertheless, the results described in this paper constitute the first chemical evidence concerning the stereochemical capabilities of vinyl radicals.

Experimental Section

All melting points are corrected; boiling points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 421 spectrometer, ultraviolet spectra on a Cary Model 11, and nuclear magnetic resonance spectra on a Varian A-60 spectrometer. Vapor phase chromatographic analyses were performed on a Wilkins Aerograph A-90-P2 instrument using a thermal conductivity detector and helium as the carrier gas. Elemental analyses were performed by Micro-Tech Laboratories, Skokie, Ill.

3,4-Dimethylcoumarin (III). Ethyl methylacetoacetate, bp 184–185° (lit.²³ bp 185.5°), was prepared in 78% yield by the reaction of methyl iodide with ethyl acetoacetate using directions²⁴ for the preparation of ethyl *n*-butylacetoacetate. 3,4-Dimethylcoumarin, mp 115–117.5° (lit.²⁵ mp 115°), was prepared in 14% yield by the condensation of ethyl methylacetoacetate with phenol according to the procedure described for the preparation of 4-methylcoumarin.²⁶

***cis*- and *trans*-2-Phenyl-2-Butene.**²⁷ Methylphenylcarbinol, bp 89–90° (5 mm) (lit.²⁸ bp 102° (14 mm)), was prepared in 50% yield by the reaction of ethylmagnesium bromide with propiophenone. A mixture of 35 g (0.23 mole) of methylphenylcarbinol and a solution of 25 ml of concentrated sulfuric acid in 175

hedron Letters, in press, have observed equilibration of the vinyl radicals derived from *t*-butyl *cis*- and *trans*- α -methyl- and α -phenylpercinnamates.

(23) A. Michael, *Ber.*, **38**, 2095 (1905).

(24) C. S. Marvel and F. D. Hager in "Organic Syntheses," Coll. Vol. I, H. Gilman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1941, p 248.

(25) F. Peters and H. Simonis, *Ber.*, **41**, 837 (1908).

(26) A. I. Vogel, "A Text-Book for Practical Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1962.

(27) D. J. Cram, *J. Am. Chem. Soc.*, **71**, 3883 (1949).

(28) A. Klages, *Ber.*, **35**, 3506 (1902).

ml of water was refluxed for 2 hr, cooled, and extracted with ether. The ether extract was dried over magnesium sulfate and the ether removed to yield 29 g of a colorless liquid. Vapor phase chromatographic analysis of the product (15 ft \times 0.25 in. Craig column, 20% on 30–60 Chromosorb P, oven, 120°, injector, 200°, detector, 300°, and helium flow, 200 cc/min) indicated four peaks of retention times 4.0 5.9 9.9, and 20.0 min. By co-injection of known material and infrared analysis, the material of longest retention time was identified as methylethylphenylcarbinol. The first three peaks (1.0:4.3:11.4) were assigned (see below) to *trans*-2-phenyl-2-butene, 2-phenyl-1-butene, and *cis*-2-phenyl-2-butene, in order of increasing retention time.

cis-2-Phenyl-2-butene was conveniently isolated by direct preparative vpc (conditions as described above) of the olefin mixture. Typically, 5 g of olefin mixture gave 1.8–2.2 g of *cis*-2-phenyl-2-butene, bp 192–193° (lit.²⁷ bp 194°). Reinjection showed no contamination by the other isomers and the infrared spectrum was identical with the published spectrum.²⁹ The nmr spectrum of *cis*-2-phenyl-2-butene (CCl₄) shows five aromatic protons as a multiplet centered at τ 2.81, a single vinyl proton as a quartet of quartets centered at 4.22, three methyl protons as an overlapping pair of quartets centered at 8.03, and three methyl protons as a pair of quartets centered at 8.25. If the protons at τ 4.22, 8.03, and 8.25 are labeled a, b, and c, respectively, then $J_{ab} \cong 1.4$ cps, $J_{ac} \cong 7.0$ cps, and $J_{bc} \cong 1.1$ cps.³⁰

trans-2-Phenyl-2-butene was conveniently isolated as follows.²⁷ *p*-Toluenesulfonic acid (1.0 g) was added to 10 g of the olefin mixture from the dehydration and the solution distilled slowly at atmospheric pressure to give 5 g of distillate, bp 172–178°. Preparative vpc (conditions as described above) gave 3.3 g (33% of *trans*-2-phenyl-2-butene, bp 173–174° (lit.²⁸ bp 174°). Reinjection showed no contamination by other isomers and the infrared spectrum was identical with the published spectrum.²⁹ The nmr spectrum (CCl₄) shows five aromatic protons as a multiplet centered at τ 2.82, a single vinyl proton as a quartet of quartets centered at 4.50, three methyl protons as an overlapping pair of quartets centered at 8.01, and three methyl protons as a pair of quartets centered at 8.43. If the protons at τ 4.50, 8.01, and 8.43 are labeled a, b, and c, respectively, then $J_{ab} \cong 1.5$ cps, $J_{ac} \cong 7.0$ cps, and $J_{bc} \cong 1.5$ cps.³⁰

2-Phenyl-1-butene. Methyltriphenylphosphonium iodide, mp 182–183° (lit.³¹ mp 183–183.5°), was prepared in 94% yield from triphenylphosphine and methyl iodide according to directions³² for the preparation of methyltriphenylphosphonium bromide. Reaction of methyltriphenylphosphonium iodide with propiophenone according to directions³² given for reaction with acetophenone gave 2-phenyl-1-butene, contaminated by propiophenone. Purification was effected by preparative vapor phase chromatography using a 15 ft \times 0.25 in. Carbowax 20M column at 150° to give 3.0 g (44%) of product, bp 181° (lit.²⁸ bp 182°). The infrared and nmr spectra were identical with those of material obtained from the dehydration of methylethylphenylcarbinol. Reinjection showed no contamination by the other isomers and the infrared spectrum was identical with the published spectrum.²⁹ The nmr spectrum (CCl₄) shows five aromatic protons as a multiplet centered at τ 2.75, two vinyl protons as a five-line pattern centered at 4.80 and a quartet centered at 5.00, two allylic protons as a broadened quartet centered at 7.52, and three methyl protons as a triplet centered at 8.93. If the protons (excluding aromatic) are labeled a, b, c, and d in order of increasing shielding, then $J_{ab} \cong 1.5$ cps, $J_{ac} \cong 0.75$ cps, $J_{bc} \cong 1.5$ cps, and $J_{cd} \cong 7.5$ cps.³⁰

Ethyl 2-methyl-3-phenyl-3-hydroxybutyrate prepared in 50% yield by the Reformatsky reaction of ethyl bromoacetate with acetophenone³³ had bp 93° (0.45 mm), n_D^{25} , 1.4946 (lit.³³ bp 134–135° (9 mm), n_D^{20} , 1.4975).

Dehydration of ethyl 2-methyl-3-phenylhydroxybutyrate with potassium bisulfate³⁴ gave a 68% yield of product, bp 105–108° (3 mm). The nmr spectrum of this material showed it to be a mixture of ethyl *cis*- and *trans*- α,β -dimethylcinnamate and an unsaturated ester containing a terminal methylene group. The relative areas of the vinylic and allylic regions of the spectrum showed the terminal methylene ester to be the major product ($\cong 90\%$). The ultraviolet spectrum showed λ_{max}^{EtOH} 2380 Å (ϵ

9700), indicating that the terminal methylene ester is ethyl 2-methyl-3-phenyl-3-butenolate.¹³

2-Methyl-3-phenyl-3-butenic Acid.¹³ To 59.5 g (0.29 mole) of the ester mixture described above (mainly ethyl 2-methyl-3-phenyl-3-butenolate) was added a solution of 30.0 g (0.54 mole) of potassium hydroxide in 400 ml of methanol and 30 ml of water. The solution was heated at reflux for 2 hr, the methanol was removed, 100 ml of water was added, and the solution was extracted with ether. The aqueous solution was acidified and more water was added to dissolve the inorganic salts. Extraction of the solution with ether, drying of the ethereal solution over magnesium sulfate, and removal of the ether gave 47.0 g (93%) of a yellow oil. This oil (0.27 mole) was dissolved in 65 ml of ethyl acetate and added to a less than equimolar amount of cyclohexylamine, 17.0 g (0.17 mole) in 40 ml of ethyl acetate. The white solid that formed immediately was collected, washed with ethyl acetate, and recrystallized twice from acetone to give 32.0 g of the cyclohexylammonium salt, mp 156–157° dec. The salt was dissolved in 5% potassium hydroxide and the solution was extracted with ether to remove the cyclohexylamine. The aqueous solution was acidified with cold, dilute sulfuric acid and extracted with ether. The extract was dried over magnesium sulfate and the ether was removed. The residue, 20.7 g of a cloudy, colorless oil, was distilled to give 17 g of 2-methyl-3-phenyl-3-butenic acid, bp 116–117° (1 mm). After cooling at 0° for 20 hr, the oil had solidified to give a white solid which, after three recrystallizations from ligroin, had mp 33.5–34.5°, λ_{max}^{EtOH} 2375 Å (ϵ 9400).³⁵ The infrared spectrum (CCl₄) shows carboxylic acid absorption at 1701 and terminal methylene at 900 cm⁻¹. The nmr spectrum shows a single carboxylic acid proton, five aromatic protons as a multiplet centered at τ 2.74, two olefinic protons as singlets at 4.64 and 4.81 (fine structure), a single tertiary proton as a quartet centered at 6.38 ($J \cong 7$ cps), and three methyl protons as a doublet centered at 8.65 ($J \cong 7$ cps).³⁰ Anal. Calcd for C₁₁H₁₂O₂: C, 75.0; H, 6.8. Found: C, 75.0; H, 6.9.

Ethyl *cis,trans*- α,β -Dimethylcinnamate. To a solution of 101 g (2.25 g-atoms) of sodium in 1500 ml of absolute ethanol purified according to Vogel²⁶ was added 140 g (0.69 mole) of the ester mixture described in the preceding section (predominantly ethyl 2-methyl-3-phenyl-3-butenolate). The solution was refluxed slowly in an atmosphere of dry nitrogen for 8 hr, then approximately 500 ml of the ethanol was distilled from the solution. The reaction mixture was cooled to room temperature and poured into 3500 ml of cold, distilled water, and the resulting mixture was extracted with four 500-ml portions of ether and the combined ether extracts were dried over magnesium sulfate. Removal of the ether left 111 g of a red-brown oil, which was distilled to give 93.1 g (66.5%) of a colorless liquid, bp 79–80° (0.4 mm). The nmr spectrum showed the material to be a mixture of 39% ethyl *cis*- and 61% *trans*- α,β -dimethylcinnamate, with no detectable amount of ethyl 2-methyl-3-phenyl-2-butenolate. The composition of the mixture was determined by integration of the triplets at τ 8.68 and 9.27, due to the CH₃ portion of the ethyl group of the *trans* and *cis* isomers, respectively. In addition to aromatic absorption and the methyl resonance indicated above, the *cis* ester shows a quartet absorption centered at τ 6.25 due to the methylene of the ethyl groups and the allylic methyls as multiplets centered at 7.92 and 8.00. The *trans* ester shows methylene absorption at τ 5.81 as a quartet and allylic methyls as quartets at 7.73 and 8.30.

***cis*- and *trans*- α,β -Dimethylcinnamic Acids.** To a solution of 45 g (0.8 mole) of potassium hydroxide in 300 ml of methanol and 60 ml of water was added 112.0 g (0.55 mole) of ethyl *cis*- and *trans*- α,β -dimethylcinnamate. The mixture was heated at reflux for 4 hr and approximately 250 ml of methanol was removed by distillation. The solution was cooled to room temperature, acidified with hydrochloric acid, and extracted with ether, and the ethereal solution was washed with water and dried over magnesium sulfate. Removal of the ether left 90 g (94%) of a pale yellow oil which slowly solidified on standing, mp 70–95°. The nmr spectrum showed the product to be a mixture of 38% *cis*- and 62% *trans*- α,β -dimethylcinnamic acid. Laborious fractional crystallization from ligroin (bp 100–115°) gave the pure isomers. The *cis* acid (needles) is less soluble than the *trans* acid (prisms). The different crystalline forms make it relatively easy to follow the course of the separation. *cis*- α,β -Dimethylcinnamic acid, 20 g, 22%, was obtained as needles, mp 111–112° (lit.¹² mp 112–113°), amide mp 174–175°, cyclo-

(29) D. J. Cram, *J. Am. Chem. Soc.*, **74**, 2137 (1952).

(30) Coupling constants were measured directly from line separations.

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hexylammonium salt¹³ mp 182–184°, $\lambda_{\text{max}}^{\text{EtOH}}$ 2415 Å (ϵ 7450). The nmr spectrum shows one carboxylic acid proton, five aromatic protons as a multiplet centered at τ 2.72, three methyl protons at 7.84 (fine structure), and three methyl protons at 7.94 (fine structure). *trans*- α,β -Dimethylcinnamic acid, 45 g, 50%, was obtained as prisms, mp 108–109° (lit.¹² mp 109–110°), amide mp 190–191°, cyclohexylammonium salt¹³ mp 152–153°, $\lambda_{\text{max}}^{\text{EtOH}}$ 2370 Å (ϵ 9400). The nmr spectrum shows one carboxylic acid proton, five aromatic protons as a multiplet centered at τ 2.73, three methyl protons at 7.61 (fine structure), and three methyl protons at 8.23 (fine structure). The infrared spectra (CCl₄) of the *cis* and *trans* acids are virtually identical, both showing carboxylic acid absorption at 1681 cm⁻¹.

The *cis* and *trans* acids are cleanly separated by thin layer chromatography. Glass plates (50 × 200 mm, Pyrex) were coated with silica gel G³⁶ to a thickness of 0.2 mm, and were dried in air overnight. The plates were then sprayed with a solution consisting of one part saturated boric acid and one part 0.5 M silver nitrate and dried for 30 min at 110°. Typically, 3 μ l of a 1% solution of acid in benzene gave well-defined spots. Ascending chromatograms were run using 5:4:1 petroleum ether–benzene–ether with the solvent front traveling 10 cm above the spot. The acids were located by spraying the plates with dichlorofluorescein (0.1% in 1:1 ethanol–water), giving yellow spots on a pink background, R_f *cis*, 0.16; *trans*, 0.27. A series of known mixtures of the *cis* and *trans* acids were prepared and chromatographed. The results showed that 2.5% of either isomer in the presence of the other could be detected by this method.

Photoisomerization of *trans*- α,β -Dimethylcinnamic Acid. In a typical run, 2.5 g of *trans*- α,β -dimethylcinnamic acid was dissolved in 50 ml of cyclohexane and placed in a 100-mm cylindrical quartz spectrophotometer cell fitted with a water jacket for cooling. The cell was irradiated with a medium pressure mercury lamp (Hanovia Type SH). After 67 hr, the irradiation was stopped and the solvent was evaporated. The residue contained only *trans* and *cis* acids in the ratio *trans/cis* = 1.8 as indicated by the nmr spectrum. The inside of the quartz cell was coated with a thin layer of a yellow material, but the solution itself was colorless and the nmr spectrum showed no extraneous peaks. Since the synthetic procedure gives a predominance of *trans* acid, this photoisomerization was a useful method of converting *trans* acid to a *cis/trans* mixture from which *cis* acid could be isolated.

Cyclization Rates of *cis* and *trans* Acids in Concentrated Sulfuric Acid. To 5 ml of concentrated sulfuric acid at –10° was added 0.2071 g (1.17 mmoles) of *cis*- α,β -dimethylcinnamic acid, and the mixture was stirred rapidly for 130 sec, and then poured onto 20 g of ice. The mixture was extracted with ether, the ether extract was washed with saturated sodium bicarbonate, dried over magnesium sulfate, and the ether was removed to yield, after one recrystallization from heptane, 0.203 g (103%) of 2,3-dimethylindenone, mp and mmp 79–80° (lit.³⁸ mp 80°). The sodium bicarbonate extract, after acidification, extracting with ether, and drying over magnesium sulfate, yielded 0.002 g (0.9%) of *cis*- α,β -dimethylcinnamic acid, mp 110–111°.

In an identical experiment, 0.2027 g (1.16 mmoles) of *trans*- α,β -dimethylcinnamic acid yielded 0.0015 g (0.9%) of 2,3-dimethylindenone and 0.200 g (99%) of *trans*- α,β -dimethylcinnamic acid, mp 108–109°.

***cis*- and *trans*- α,β -Dimethylcinnamoyl Chloride.** Conventional methods for converting carboxylic acids to acid chlorides were unsuccessful in the present case. Treating either *cis*- or *trans*- α,β -dimethylcinnamic acid with refluxing thionyl chloride or with thionyl chloride in refluxing benzene produced 2,3-dimethylindenone almost quantitatively. In a typical experiment, 0.8361 g (4.74 mmoles) of *trans*- α,β -dimethylcinnamic acid in 10 ml of dry benzene was refluxed for 4 hr with 2.1 g (18 mmoles) of purified thionyl chloride. The solvent and unreacted thionyl chloride were removed under reduced pressure to yield 0.715 g (97%) of a bright yellow oil which slowly solidified on standing. The infrared spectrum of the crude oil was identical with that of authentic 2,3-dimethylindenone. Recrystallization from heptane gave mp and mmp 78–80° (lit.³⁸ mp 80°). Additional experiments showed that if the *trans* acid–thionyl chloride mixture was warmed above room temperature, the bright yellow color of 2,3-dimethylindenone developed, while with the *cis* acid the color developed above 10°.

The acid chlorides can be prepared with thionyl chloride at low temperatures using a dimethylformamide catalyst³⁹ as described in the preparation of *cis*- and *trans*- α,β -dimethylcinnamide. A more satisfactory procedure⁴⁰ is described below.

A solution of 6.0 g (0.0473 mole) of oxalyl chloride in 10 ml of anhydrous ether at –5° was added with stirring over 30 min to a solution of 5.674 g (0.0325 mole) of *cis*- α,β -dimethylcinnamic acid and 0.3 ml of dimethylformamide. The solution was allowed to warm to 0° and stirring was continued for 12 hr. The ether and unreacted oxalyl chloride were removed under reduced pressure while keeping the temperature below 5°. This required approximately 6 hr at water pump pressure followed by an additional 6 hr at 0.05 mm. The acid chloride (6.345 g, 101%) was obtained as a colorless liquid. Further purification was not attempted. The *trans* acid chloride was prepared in an identical manner. The infrared spectrum (CHCl₃) of the *cis* acid chloride shows the carbonyl at 1770 cm⁻¹. The *trans* acid chloride shows a doublet at 1758 and 1791 cm⁻¹ (liquid film). Both spectra were free of hydroxyl absorption.

***cis*- and *trans*- α,β -Dimethylcinnamide.** *cis*- α,β -Dimethylcinnamic acid (0.278 g, 1.60 mmoles) was added to a solution of 1.0 ml of purified thionyl chloride and 0.1 ml of dimethylformamide at 0°, and the mixture was stirred for 5 min and poured into 10 ml of ice-cold concentrated ammonium hydroxide. The resulting white precipitate was filtered from the solution, dried, and recrystallized from ethanol–water to give 0.154 g (55%) of *cis*- α,β -dimethylcinnamide, mp 174–175°, $\lambda_{\text{max}}^{\text{EtOH}}$ 239 m μ (ϵ 6800). The infrared spectrum (CHCl₃) shows absorption at 3537 (m), 3411 (m), 1671 (s), and 1590 (m) cm⁻¹. The nmr spectrum (CF₃CO₂H) shows two quartets centered at τ 7.80 (3 H) and 7.68 (3 H) and aromatic absorption.

Anal. Calcd for C₁₁H₁₃NO: C, 75.40; H, 7.48; N, 7.99. Found: C, 75.31; H, 7.26; N, 8.27.

trans- α,β -Dimethylcinnamide (0.261 g, 1.50 mmoles) and 0.1 ml of dimethylformamide were added to 1.0 ml of purified thionyl chloride at 0° and stirred in a dry atmosphere for 20 min, then poured into 10 ml of ice-cold, concentrated ammonium hydroxide. The resulting white precipitate was filtered from the solution, dried, and recrystallized from ethanol–water to give 0.1455 g (55%) of *trans*- α,β -dimethylcinnamide, mp 190–191°, $\lambda_{\text{max}}^{\text{EtOH}}$ 233 m μ (ϵ 8700). The infrared spectrum (CHCl₃) shows absorption at 3529 (m), 3405 (m), 1673 (s), and 1588 (s) cm⁻¹. The nmr (CF₃CO₂H) shows two quartets at τ 8.05 (3 H) and 7.68 (3 H) and aromatic absorption.

Anal. Calcd for C₁₁H₁₃NO: C, 75.40; H, 7.48; N, 7.99. Found: C, 75.18; H, 7.44.

***t*-Butyl *cis*- α,β -Dimethylpercinnamate.** To a solution of 0.328 g (0.0325 mole) of *cis*- α,β -dimethylcinnamoyl chloride in 10 ml of anhydrous ether at –20° was added 3.56 g (0.0395 mole) of *t*-butyl hydroperoxide. The hydroperoxide (Wallace and Tiernan) was purified by the method of Bartlett and Hiatt⁶ and had bp 35–36° (20 mm), 98.4% purity by iodometric titration.⁴¹ The solution was stirred while 6.0 g (0.075 mole) of pyridine was added dropwise over 30 min. The temperature was maintained between –25 and –20° and the stirring was continued for 3.5 hr. The mixture was poured into 50 g of ice, the layers were separated, and the ether layer was washed with ice-cold 10% sulfuric acid, 10% sodium carbonate, water, and dried over magnesium sulfate. Removal of the ether by vacuum distillation at 0° left 7.318 g of a pale yellow liquid. The crude product was chromatographed on alumina (Woelm, activity grade 1) using a jacketed column maintained at 10°. The perester was eluted in petroleum ether (bp 30–60°), and its infrared spectrum showed it to be free of *t*-butyl hydroperoxide. The perester was dissolved in petroleum ether and cooled in Dry Ice to effect crystallization. After two recrystallizations at –78°, 3.499 g (43%) of material was obtained as white prisms, mp 39–40°, 98.2% peroxide by iodometric titration, $\lambda_{\text{max}}^{\text{EtOH}}$ 232 m μ (ϵ 7200). The infrared spectrum (CHCl₃) has bands at 2990 (m), 1749 (s), 1498 (m), 1447 (m), 1371 (s), 1302 (m), 1186 (m), 1109 (m), and 1089 (m) cm⁻¹. The nmr spectrum (CCl₄) has a singlet at τ 9.09 (9 H), quartets centered at 8.01 (3 H) and 7.94 (3 H), and a multiplet at 2.82 (5 H).

Anal. Calcd for C₁₅H₂₀O₃: C, 73.14; H, 8.18. Found: C, 72.50; H, 8.30.

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***t*-Butyl *trans*- α,β -Dimethylpercinamate.** The *trans* perester was synthesized in a manner analogous to the *cis* perester. *trans*- α,β -Dimethylcinnamoyl chloride (3.894 g, 0.020 mole) yielded, after chromatography of the crude product on alumina at 9°, 3.172 g (64.5%) of perester as a colorless liquid which did not crystallize. Iodometric titration indicated 99.2% peroxide and the infrared spectrum showed the absence of *t*-butyl hydroperoxide. *trans* perester has $\lambda_{\text{max}}^{\text{EtOH}}$ 238 m μ (ϵ 9500). The infrared spectrum (liquid film) has strong bands at 2985, 2930, 1760, 1221, 1192, 1080, 1048, and 1022 cm⁻¹. The nmr spectrum (neat) shows a singlet at τ 8.66 (9 H), quartets centered at 8.26 (3 H) and 7.81 (3 H), and a multiplet at 2.8 (5 H).

Anal. Calcd for C₁₅H₂₀O₃: C, 73.14; H, 8.18. Found: C, 72.80; H, 8.24.

Small-Scale Decompositions. The procedure described below was used for all decompositions on a small scale (5 ml of solvent) in which product analyses were done by vpc. *t*-Butyl *cis*- α,β -dimethylpercinamate (0.0973 g, 0.395 mmole) was dissolved in 5.0 ml of purified cumene⁴² in a 10-ml Pyrex tube ([perester] = 0.079 M). The tube was cooled in Dry Ice-acetone, evacuated to 0.05 mm for 15 min, dry nitrogen was introduced, and the tube was allowed to warm to room temperature. The cycle was repeated three times and the tube was cooled, evacuated, and sealed. The tube was placed in an oil bath maintained at 110.0° \pm 0.1° for 13 hr. The tube was removed, cooled in Dry Ice, and opened. Immediately the internal standards were added as follows: 0.30 ml of 1.019 M ethanol in cumene, 0.0268 g (0.2027 mmole) of 2-phenyl-1-butene, and 1.0 ml of 0.0452 M fluorene in cumene. A 30- μ l sample was injected into the chromatograph for analysis of acetone and *t*-butyl alcohol, using a Carbowax 20M column (15 ft \times 0.25 in., 20% on 30-60 Chromosorb P) with a column temperature of 70°, an injector temperature of 120°, a detector temperature of 300°, and a helium flow of 100 ml/min. The retention times were acetone, 4.0 min, *t*-butyl alcohol, 6.3 min, and ethanol, 8.1 min. Three injections gave the results: acetone, 10.0, 9.3, and 9.3%; *t*-butyl alcohol, 82.8, 78.9, and 80.6%.

The column temperature was raised to 120° and the injector to 170° and a 50- μ l sample was injected for analysis of the 2-phenyl-2-butenes. The retention times were *trans*-2-phenyl-2-butene, 13 min; 2-phenyl-1-butene, 20 min; and *cis*-2-phenyl-2-butene, 30 min. Three injections gave the results *trans*-2-phenyl-2-butene 27.7, 27.7, and 27.7%, and *cis*-2-phenyl-2-butene, 33.9, 33.9, and 32.3%.

For analysis of dicumyl, a 5 ft \times 0.25 in. Apiezon L column (20% on 30-60 Chromosorb P) at 225° with an injector temperature of 250° and a helium flow of 150 ml/min was used. The retention times were dicumyl, 7.6 min and fluorene, 4.6 min. Three 50- μ l injections gave dicumyl yields of 43.6, 43.8, and 43.8%.

Large-Scale Decompositions. In a typical run, 1.0299 g (4.154 mmole) of *cis* perester was dissolved in 50 ml of cumene ([perester] = 0.083 M) in a 100-ml flask arranged for bubbling nitrogen through the solution and conducting the exit gases through two Dry Ice traps and two Ascarite-magnesium perchlorate absorption tubes.⁴³ The solution was degassed and placed in the oil bath at 110.0 \pm 0.1°, and a stream of prepurified nitrogen was passed through the solution throughout the course of the decomposition at a rate of 100 ml/min. The Ascarite-magnesium perchlorate tubes absorbed 0.116 g of carbon dioxide (61%). The material that had collected in the Dry Ice traps was shown to be acetone, *t*-butyl alcohol, and cumene by vpc retention times, co-injection of authentic samples, and comparing their infrared spectra with those of authentic materials.

The cumene solution was extracted with aqueous sodium carbonate (10%). Acidification, extraction of the acid with ether, and drying over magnesium sulfate yielded, on removal of the ether, 5.8 mg (0.8%) of *cis*- α,β -dimethylcinnamic acid, shown to be isomerically pure by thin layer chromatography.

The cumene was then removed from the solution by distillation under reduced pressure. The residue partially crystallized on standing. The crystals were filtered and recrystallized from ethanol to give dicumyl, mp and mmp 118.5-119.5°. The infrared spectrum of the isolated material was identical with that of authentic material.

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The noncrystalline residue was chromatographed on Woelm alumina (activity 1). Additional dicumyl was obtained using petroleum ether as eluent. 3,4-Dimethylcoumarin was obtained in the fraction eluted by 5:1 benzene-ether; 0.871 g (13%), mp and mmp 115-117.5°, nmr and infrared spectra identical with those of authentic material. In the large-scale decomposition of *trans* perester, similar work-up yielded no material whose infrared or nmr spectra were similar to those of 3,4-dimethylcoumarin.

In a separate run, the *cis*- and *trans*-2-phenyl-2-butenes were identified by their vpc retention times, by co-injection of authentic material, and by collecting the peaks and comparing the infrared and nmr spectra with those of authentic samples.

Decomposition of *t*-Butyl *trans*- α,β -Dimethylpercinamates in the Presence of *cis*- and *trans*-2-Phenyl-2-butene. Two samples of *t*-butyl *trans*- α,β -dimethylcinnamate were decomposed in cumene at 110° for 11 hr in the presence of deliberately added *cis*- and *trans*-2-phenyl-2-butene. The resulting mixtures were analyzed in the usual fashion. The yields of olefin were corrected by subtracting the moles of olefin initially added from the measured yield of that olefin. The results are shown in Table II and are to be compared with the data in Table I. Some of the added olefin is apparently destroyed in the course of the decomposition since the corrected yield is less than that reported in Table I. There is no increase in the yield of the olefin not added, indicating that the olefins are not isomerized under the decomposition conditions.

Table II

Sample	Acetone	<i>t</i> -Butyl alcohol	2-Phenyl-2-butenes <i>cis</i>	<i>trans</i>	Dicumyl
I ^a	9.5	81.7	41.6	28.6 ^c	62
	9.5	79.2	46.0	27.4 ^c	61
	8.8	79.2	39.2		
II ^b	8.8	82.3	33.4 ^c	35.6	
			31.8 ^c	36.7	

^a [perester] = 0.084 M; *trans*-2-phenyl-2-butene (0.204 mmole) added. ^b [perester] = 0.084 M; *cis*-2-phenyl-2-butene (0.190 mmole) added. ^c Corrected yield (see text).

Decomposition of *trans*- α,β -Dimethylpercinamate in the Presence of *cis*- and *trans*- α,β -Dimethylcinnamic Acid. To a solution of 0.6393 g (2.60 mmole) of *t*-butyl *trans*- α,β -dimethylpercinamate in 50.0 ml of cumene ([perester] = 0.052 M) was added 0.3808 g (2.16 mmole) of pure *trans*- α,β -dimethylcinnamic acid. The resulting solution was degassed and decomposed at 110° for 20.5 hr. Carbon dioxide (0.1058 g, 92.3%) was absorbed on Ascarite-magnesium perchlorate. The cumene solution was extracted with 10% aqueous sodium carbonate to give, after acidification, 0.3698 g (97.3% recovery) of *trans*- α,β -dimethylcinnamic acid, mp and mmp 105-107°. Thin layer chromatography showed that <2.5% of the *cis* isomer was present.

In an analogous experiment *t*-butyl *trans*- α,β -dimethylpercinamate was decomposed in the presence of *cis*- α,β -dimethylcinnamic acid to give a 93% yield of carbon dioxide and 92% recovery of *cis*- α,β -dimethylcinnamic acid, mp and mmp 111-112.5°. Thin layer chromatography indicated the presence of 1-2% of the *trans* acid contaminating the *cis* acid.

Perester Stability. A solution of 0.05 g of *t*-butyl *trans*- α,β -dimethylpercinamate in 2 ml of cumene was placed in an oil bath at 110° for 25 min. The half-life of *trans* perester at 110° is approximately 25 min. A sample of the reaction mixture was spotted on a 50 \times 200 mm glass plate coated to a thickness of 0.2 mm with alumina. Pure *cis* and pure *trans* peresters were spotted on the same plate and the ascending chromatogram developed with 2:1 petroleum ether-benzene. The partially decomposed sample showed a single spot corresponding to the known *trans* perester. The spots were indicated by spraying with a solution of aqueous potassium iodide and acetic acid and warming slightly, giving brown spots with *R_f* values of *cis*-, 0.15 and *trans*-, 0.29. From a series of mixtures of *cis* and *trans* peresters, it is estimated that 2% of either isomer in the presence of the other can be detected.

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