Vinyl Radicals. VIII. A Study of the Possibility of Aryl Migration in 2-Arylvinyl Radicals

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The 2,2-diphenylvinyl (I) and 1-(p-tolyl)-2,2-diphenylvinyl (II) radicals are formed by the thermal decomposition of the appropriate *tert*-butyl peresters in solvents such as cumene and *tert*-butylbenzene. The radicals are quenched by hydrogen donors to give the corresponding olefins in varying yields, according to the nature of the hydrogen donor, temperature, and perester concentration. Rearranged products, *cis*- and *trans*-stilbene and diphenylacetylene from I and 1,2-diphenyl-1-(p-tolyl)ethylene from II, are not found; depending on the particular reaction conditions, approximately 0.2–1.5% yields of rearranged products would have been detected.

1,2-Aryl migrations are firmly established in the chemistry of 2-arylalkyl cations, radicals, and carbanions (organometallics).² The corresponding aryl shift is also known for 2-arylvinyl cations.³⁻⁶ This paper reports a study of the potential for aryl migration in appropriately structured vinyl radicals.

Rearrangements of 2-aryl vinyl radicals have been considered previously. Koehl⁷ observed phenyl migration in the anodic oxidation of 3,3-diphenylacrylic acid in acetic acid. Products characteristic of radical reactions were unrearranged, while those of carbonium ion origin were both rearranged and unrearranged; the migration therefore, was attributed to the 2,2-diphenylvinyl cation rather than the radical. Köbrich⁸ observed diphenylacetylene (rearranged product) in the thermal decomposition of silver 2-halo-3,3-diphenylacrylates and 1-chloro-2,2-diphenylvinyl silver. While there is evidence for a homolytic component to these decompositions, Köbrich concludes that the rearrangement is attributable to a carbenoid species, rather than to vinyl radical intermediates. In both of these studies, the behavior and lifetimes of the 2-arylvinyl radicals are not well defined. The aim of the present work was to generate vinyl radicals I and II from the correspond-

$$(C_6H_5)_2C = \dot{C} + CH_3$$
I II

ing peresters, under conditions where the subsequent chemistry would be straightforward.

Results

tert-Butyl 3,3-diphenylperacrylate (III) and tertbutyl 2-(p-tolyl)-3,3-diphenylperacrylate (IV), the precursors of the desired radicals, are readily prepared by the reactions of the corresponding acyl chlorides with sodium tert-butyl peroxide in methylene chloride at 0°.

(1) From the Ph.D. Thesis of J. K. Haynes, Jr., University of Rochester, 1971.

(2) Reviews: Y. Pocker, C. Walling, and H. E. Zimmerman in "Molecular Rearrangements," Part I, P. de Mayo, Ed., Wiley, New York, N. Y., 1963, Chapters 1, 6, and 7.

(3) M. A. Imhoff, R. H. Summerville, P. v. R. Schleyer, A. G. Martinez, M. Hanack, T. E. Dueber, and P. J. Stang, J. Amer. Chem. Soc., 92, 3802 (1970): P. J. Stang. Proor. Phys. Gra. Chem. in press.

(1970); P. J. Stang, Progr. Phys. Org. Chem., in press.
(4) D. Y. Curtin, J. A. Kampmeier, and B. R. O'Connor, J. Amer. Chem. Soc., 87, 863 (1965).

(5) W. M. Jones and D. D. Maness, *ibid.*, **92**, 5457 (1970), and previous papers.

(6) M. S. Newman and C. D. Beard, *ibid.*, **92**, 7564 (1970), and previous papers.

(7) W. J. Koehl, Jr., J. Org. Chem., 32, 614 (1967).

(8) G. Köbrich, H. Fröhlich, and W. Drischel, J. Organometal. Chem., 6, 194 (1966); G. Köbrich and H. H. Fröhlich, Chem. Ber., 98, 3637 (1965).



Both peresters are obtained as crystalline solids and give satisfactory spectroscopic and analytical data. The peresters were thermally decomposed under a variety of conditions (solvent, temperature, concentration) to give the vinyl radicals I and II. Large-scale decompositions allowed isolation and qualitative identification of reaction products; carbon dioxide and nonvolatile products were determined quantitatively in some of these experiments. Most yields were determined by gas chromatographic (gc) analyses of reaction mixtures from small-scale decompositions in sealed, deoxygenated ampoules. The results of these product studies are presented in Table I for the diphenyl perester and in Table II for the triaryl perester.

Most of the products of the decomposition of the diphenyl perester III are anticipated by previous studies of the homolytic decomposition of α,β -unsaturated peresters.^{9,10} Thus, acetone, *tert*-butyl alcohol, and dicumyl reveal the radical nature of the perester fragmentation. 4-Phenylcoumarin and 3,3-diphenylacrylic acid reflect the intermediacy of acyloxy radicals. Decarboxylation of the acyloxy radical gives CO₂ and the desired vinyl radical I, which abstracts hydrogen to give 1,1-diphenylethylene. 1,1-Diphenylpropene-1 is presumably the result of an induced decomposition initiated by addition of methyl radical to the perester.



Similar induced pathways have been observed for other α,β -unsaturated peresters.¹¹

The dependence of the yields of diphenylpropene (induced product) and diphenylethylene (normal product) on the radical-scavenging ability of the solvent and the concentration of the initial perester are in ac-

⁽⁹⁾ J. A. Kampmeier and R. M. Fantazier, J. Amer. Chem. Soc., 88, 1959 (1966).

⁽¹⁰⁾ L. A. Singer and N. P. Kong, *ibid.*, **88**, 5213 (1966).

⁽¹¹⁾ N. Muramoto, T. Ochiai, O. Simamura, and M. Yoshida, Chem. Commun., 717 (1968).

 Table I

 Yields^a of Products from the Thermal Decomposition of *ieri*-Butyl-3,3-diphenylperacrylate (III)

	Cumana				tert-Butyl-	Banana	
	110°	110°	200°	200°	200°	200°	200°
Product	0.07 M III	0.007 M III	0.07 M III	U, 007 M III		0.07 M III	0.007 M III
Carbon dioxide	34^{b}						
3,3-Diphenylacrylic acid	176		17		4		
1,1-Diphenylethylene	13	29	33	52	17	3	5
1,1-Diphenylpropene-1	c	с	с	c	6	19	6
4-Phenylcoumarin	27	15	21	11	13		21
Acetone	9	9	27	30	63		
tert-Butyl alcohol	75	76	64	63	22		
Dicumyl	26	45	42	63			
1,1-Diphenyl-2-(x-tert- butylphenyl)ethylene ^d					25	6e	21.

^a Each entry is the average of several independent determinations. Reaction times: 5 hr at 110°; 1 hr at 200°. ^b 10-hr reaction time. ^c Present in small amounts, but not measured. ^d Mixture of isomers; ortho:meta:para, \sim 1:3:1. ^c Triphenylethylene.

 TABLE II

 THERMAL DECOMPOSITION OF tert-BUTYL

Z - (p - 101)	,YL)-3,3-DIPH	HENYLPERACR	YLATE (IV)	a
			-Yield, ^b %	
	Temp,	1,1- Diphenyl- 2-(p-tolyl)-		<i>tert-</i> Butyl
Solvent	°C°	ethylene	Acetone	alcohol
Cumened	110	82	10	78
<i>tert</i> -Butyl- benzene	110	41	45	43
<i>tert</i> -Butyl- benzene	200	43		
Benzene	200	40		

^a [IV] = $1.5 \times 10^{-2} M$. ^b Each entry is the average of several independent determinations. ^c Reaction times: 5 hr at 110°; 1 hr at 200°. ^d Dicumyl was formed in 70% yield.

cord with this induced scheme. Methyl radical attack on the O-O bond is apparently not a competing induced pathway, since methyl 3,3-diphenylacrylate is not formed $(\langle 0.3\% \rangle)$ in decompositions of the perester in solvents where diphenylpropene is an important product (e.g., benzene and tert-butylbenzene). Finally, the formation of triarylethylenes in benzene and tertbutylbenzene indicates that vinyl radicals are scavenged by addition to aromatic rings when the solvent is a poor hydrogen donor.¹² The decomposition of the triaryl perester IV is apparently more straightforward than that of perester III. The olefin derived from the triarylvinyl radical II is a major product. Acyloxy radical products are not observed and 1,1-diphenyl-2-(p-tolyl) propene-1 is, at best, a minor product (1-2%) in benzene).

While there is clear evidence in Tables I and II for competing pathways and side reactions, the main point is that both peresters give useful yields of the olefins derived from the intermediate vinyl radicals I and II. The salient point in these product studies is that products derived from rearranged vinyl radicals V and VI are not observed.



(12) P. Spagnolo and M. Tiecco, Tetrahedron Lett., 2313 (1968).

Control Experiments.-The stilbenyl radical V was generated by Singer and Kong¹⁰ by the decomposition of the isomeric tert-butyl 2,3-diphenylperacrylates in cumene and observed to give cis- and trans-stilbene (90:10) and diphenylacetylene. These products, therefore, are expected from the rearrangement of the diphenylvinyl radical I. The stability of these products to the reaction conditions was tested by decomposing the diphenyl perester III in tert-butylbenzene at 200° in the presence of the anticipated rearrangement products at concentrations of about 20% each, based on starting perester. Analysis of the reaction mixture showed that >95% of the added materials survived the perester decomposition reaction. Conservative limits of detectability of the anticipated rearrangement products were determined for representative decomposition conditions by careful gc comparison of reaction mixtures before and after addition of known amounts of authentic cis- and trans-stilbene and diphenylacetylene. In almost all experiments, there were no observable gc peaks corresponding to the rearrangement products in the undoped reaction mixtures. Detectability limits are summarized in Table III.

TABLE III Limits of Detectability of Rearrangement Products from the 2,2-Diphenylvinyl Radical, I

			Limi	t of detecta	bilitya
[III],		Temp,	Still	bene	Diphenyl-
$M imes 10^3$	Solvent	°C	cis-	trans-	acetylene
7	Cumene	110 ^b	0.75	1.2	1.3
68	Cumene	200^{b}	0.30	0.25	0.14°
7	Cumene	200	0.76	1.2	1.4
8	<i>tert</i> -Butyl- benzene	200	0.69	1.1	1.2
72	<i>tert</i> -Butyl- benzene	200		0.25^{o}	0.14

^a Expressed as per cent yield based on initial [III]. ^b Reaction times: 5 hr at 110°; 1 hr at 200°. ^c Trace peaks observed at the appropriate retention times; the areas of these peaks correspond to yields less than the conservative limits cited.

Rearrangement of the triaryl vinyl radical II would give radical VI, which should be converted to a mixture of *cis*- and *trans*-1,2-diphenyl-1-(*p*-tolyl)ethylene by reaction with hydrogen donors. The stability of the olefins to decomposing perester mixtures was tested by doping separate perester solutions with known amounts of rearranged and unrearranged olefins. The observed olefin yields were compared to those from undoped perester decompositions. In each case, \sim 75% of the added olefin remained; olefins are consumed to a small extent, but the rearranged products are not preferentially destroyed. 1,1-Diphenyl-2-(ptolyl)ethylene and the rearranged cis and trans isomers were not separated under any of our gc conditions. Control experiments with doped samples showed that rearranged olefins could be readily detected (0.2%)yield based on initial perester) by isolation of the olefin mixture by chromatography on alumina, ozonolysis of the olefin mixture, and subsequent gc analysis for 4methylbenzophenone. Actual mixtures from the decomposition of triarvl perester IV in *tert*-butylbenzene at 110° gave trace gc peaks at the retention time of 4methylbenzophenone; the area of these peaks corresponded to <0.03% yield of rearranged olefin, based on initial perester concentration. tert-Butylbenzene is the medium of choice for control tests of the stability and limits of detectability of rearranged products, since the relatively poor hydrogen donor characteristics of the solvent should accentuate any destruction of the olefins by radical reactions. Vinyl radicals should also have a longer lifetime in tert-butylbenzene than in cumene, allowing greater opportunity for a rearrangement.

Discussion

The data cited in the preceding section clearly indicate that 1,2-phenyl migration in vinyl radicals I and II does not compete to any significant extent with the reactions which consume the radicals. Control experiments certify that the rearranged products would be observed if they had been formed in yields greater than about 0.2–1.5% depending on the specific reaction conditions. It is important to note that the potential rearrangement is in competition with radical-scavenging reactions; it is conceivable that rearrangement might be observed if the radical scavenging processes were slowed dramatically.

Radicals I and II were chosen because of their different geometries. A number of studies indicate that vinyl radicals with a hydrogen in the 1 position (such as I') are bent.¹³ In contrast, several lines of evidence point to a linear structure for 1-phenyl vinyl radicals (II').^{14,15} In particular, it seemed that the linear



geometry of II' might be more suitable for rearrangement because of a more favorable spatial interaction of the radical orbital with the neighboring aromatic ring. Vinyl cations are isostructural with the linear vinyl radicals and are known to rearrange.³⁻⁴ In spite of the geometric similarities, electronic factors are apparently more conductive to the cation rearrangement.¹⁶

Experimental Section

Melting points are corrected and boiling points are uncorrected. Nuclear magnetic resonance spectra were recorded on a Varian Associates A-60 spectrometer and on a Japan Electron Optics Laboratory Company 4H-100 spectrometer by Mrs. Judy Lewis. Infrared spectra were recorded on Perkin-Elmer Model 137 and Perkin-Elmer Model 421 spectrophotometers. Ultraviolet spectra were recorded on a Cary Model 11MS spectrophotometer. Mass spectra were recorded on a Hitachi Perkin-Elmer RMU-6E mass spectrometer by Mrs. Judy Lewis and Mr. Jacob M. Hoffman, using direct sample introduction or a tandem arrangement with a Perkin-Elmer Model 900 gas chromatograph equipped with a hydrogen flame ionization detector with helium as the carrier gas. Vapor phase chromatographic studies were con-ducted on F & M Model 700 chromatographs equipped with a Vapor phase chromatographic studies were conthermal conductivity detector with WX filaments or with a hydrogen flame ionization detector. Thin layer chromatography (tlc) analyses were conducted on 25×75 mm microscope slides with E. Merck AG silica gel G as the stationary phase. Elemental analyses were conducted by the Spang Microanalytical Laboratory, Ann Arbor, Mich.

Cumene (Eastman White Label) was shaken with portions of concentrated sulfuric acid until the extracts were no longer yellow, washed three times with distilled water, dried over anhydrous magnesium sulfate, and distilled from freshly cut sodium through a 2.5×38 cm Vigreux column; a center cut was collected, bp $150-151^{\circ}$, and stored under a nitrogen atmosphere over 4 Å molecular sieves. The cumene was periodically examined for peroxide formation.¹⁷ tert-Butylbenzene (Aldrich Chemical Co.) was distilled through a 2.5×38 cm Vigreux column; a center cut was taken, bp $169-170^{\circ}$, and stored over 4 Å molecular sieves. Benzene (Mallinckrodt SpectrAR grade) was used as received.

tert-Butyl 3,3-Diphenylperacrylate (III).—To 14.54 g (0.0648 mol) of 3,3-diphenylacrylic acid^{18,19} and 0.6 ml of dimethylformamide at -78° was added dropwise with stirring 14.0 g (0.110 mol) of oxalyl chloride in 20 ml of anhydrous ether.²⁰ The solution was brought to 0° stirred for a total of 15 hr. Solvent and excess oxalyl chloride were removed at room temperature with a water aspirator and finally by evacuation at 0.06 mm for 5 hr. 3,3-Diphenylacryloyl chloride is obtained as a yellow-green, crystalline solid, 15.77 g (100%), mp 64–69° (uncorrected), ir (CCl₄) 1770 cm⁻¹.

A solution of 15.77 g (0.065 mol) of the acid chloride in 250 ml of dry methylene chloride was added to a stirred suspension of 11.65 g (0.104 mol) of sodium tert-butyl peroxide²¹ in 500 ml of dry methylene chloride at 0°. Stirring was continued for 3 hr at 0° The mixture was filtered and the methylene chloride was removed under reduced pressure to give a light tan oil which was chromatographed on alumina at 10° with petroleum ether (bp 30-60°) as eluent. Crystallization of the resulting colorless oil from petroleum ether gave 10.86 g (56.3%) of tert-butyl 3,3-diphenylperacrylate as white plates, mp $66.5-67^{\circ}$, homogeneous by tlc on silica gel with chloroform, R_f 0.76. Recrystallization from ethyl ether-petroleum ether gave perester with a peroxide content of 96.2% by iodometric titration²² and no improvement in melting point: uv $\lambda_{\text{max}}^{963}$ ^{EloH} 220 nm (shoulder) (ϵ 16,700) and 282 (15,000); ir (CHCl₃) 3045, 1750, 1605, 1365, and 1095 cm⁻¹; nmr (CDCl₃) 7 2.68 (10 H), 3.70 (s, 1 H), 8.85 (s, 9 H); mass spectrum (75 eV, inlet 60°) m/e (rel intensity) 296 (1.3, M⁺), 270 (7), 224 (17.2), 208 (24), 207 (100), 179 (30.5), 178 (37), 152 (9), and 57 (15.7).

Anal. Caled for C₁₉H₂₀O₃: C, 77.00; H, 6.80. Found: C, 77.07; H, 6.75.

tert-Butyl 2-(p-Tolyl)-3,3-diphenylperacrylate (IV).—2-(p-Tolyl)-3,3-diphenylacryloyl chloride was prepared by the cautious addition of 22.3 g (0.176 mol) of oxalyl chloride in 40 ml of anhydrous ethyl ether over a period of 45 min to a rapidly stirred suspension of 15.025 g (0.0478 mol) of 2-(p-tolyl)-3,3-diphenyl-

- (18) F. Bergmann, M. Weizmann, E. Dimant, J. Patai, and J. Szmus-kowicz, J. Amer. Chem. Soc., 70, 1612 (1948).
 (19) M. S. Kharasch, S. S. Kane, and H. C. Brown, *ibid.*, 64, 333 (1942).
- (19) M. S. Kharasch, S. S. Kane, and H. C. Brown, *ibid.*, **64**, 333 (1942).
 (20) H. H. Bosshard, R. Mory, M. Schmid, and H. Zollinger, *Helv. Chim. Acta*, **42**, 1653 (1959).
- (21) J. P. Lorand and P. D. Bartlett, J. Amer. Chem. Soc., 88, 3294 (1966).
- (22) L. S. Silbert and D. Swern, Anal. Chem., 30, 385 (1958).

⁽¹³⁾ L. A. Singer in "Selective Organic Transformations," Vol. II, B. S. Thyagarajan, Ed., Wiley, New York, N. Y., 1972, p 239.
(14) R. M. Kopchik and J. A. Kampmeier, J. Amer. Chem. Soc., 90, 6733

⁽¹⁴⁾ R. M. Kopchik and J. A. Kampmeier, J. Amer. Chem. Soc., 90, 6733 (1968); L. A. Singer and J. Chen, Tetrahedron Lett., 4849 (1969).

⁽¹⁵⁾ J. E. Bennett and J. A. Howard, Chem. Phys. Lett., 9, 460 (1971).
(16) H. E. Zimmerman and A. Zweig, J. Amer. Chem. Soc., 83, 1196 (1961).

⁽¹⁷⁾ C. D. Wagner, R. H. Smith, and E. D. Peters, Anal. Chem., 19, 976 (1947).

acrylic acid²³ and 0.85 ml of dimethylformamide²⁰ in 40 ml of anhydrous ether at 0°; stirring was continued for 8 hr at 0°. Removal of the ether and excess oxalyl chloride at room temperature with a water pump followed by evacuation at 0.05 mm for 30 min yielded 17.50 g (110%) of 2-(p-tolyl)-3,3-diphenylacryloyl chloride as a pale yellow solid.

To a suspension of 10.0 g (0.0892 mol) of sodium tert-butyl peroxide²¹ in 350 ml of dry methylene chloride at 0° was added dropwise 17.50 g of chloride in 200 ml of dry methylene chloride over a period of 4 hr. The reaction was stirred for 5 hr at 0° and filtered, and the organic laver was washed with three 50-ml portions of 5% sodium bicarbonate and three 100-ml portions of water and dried over magnesium sulfate. Evaporation of the methylene chloride yielded a solid which was recrystallized from methylene chloride-petroleum ether at -78° to vield 13.73 g (74.4%) of *tert*-butyl 2-(*p*-tolyl)-3,3-diphenylperacrylate as a white solid, mp 123-124°, 89.2% peroxide by titration.²² Recrystallization from methylene chloride-petroleum ether and chromatography on alumina (Alcoa chromatographic alumina F-20) with benzene, followed by recrystallization from benzenepetroleum ether, yielded 10.57 g (57.3%) of perester: mp 123-124°; 92.3% peroxide content by titration; uv $\lambda_{\text{max}}^{95\%}$ EtoH 237 nm (ϵ 21,600) and 300 (9970); ir (CHCl₃) 1745 (s), 1440 (m), 1365 (m), 1180 (s), and 1130 cm⁻¹ (s); nmr (CDCl₃) τ 2.68–2.91 (14 H), 7.75 (s, 3 H), 8.94 (s, 9 H); mass spectrum (75 eV, inlet 140°) m/e (rel intensity) 386 (2.8, M⁺), 314 (4.7), 286 (5.3), 270 (14.3), 269 (20.4), 253 (6.2), 178 (4.4), 165 (4.3), 91 (35), 78 (88), 77 (20), and 59 (100).

Anal. Calcd for $C_{26}H_{26}O_3$: C, 80.80; H, 6.78. Found: C, 80.93; H, 6.93.

1,1-Diphenyl-2-(p-tolyl)propene-1.—To 0.30 g (0.0432 g-atom) of lithium metal, flattened into thin disks, in 30 ml of anhydrous ethyl ether under a nitrogen atmosphere was added with stirring at 25° 2.44 g (0.0172 mol) of methyl iodide in an additional 30 ml of ether over a period of 30 min. The mixture was refluxed for 15 min, during which time all of the lithium dissolved. To this was added 2.01 g (7.02 mmol) of α, α -diphenyl-4-methylacetophenone²⁴ in 50 ml of ether, and the mixture was refluxed for 11 hr. Water (5 ml) was added dropwise and the mixture was stirred for 1 hr. The reaction mixture was washed with two 30-ml portions of water and dried over anhydrous sodium sulfate, and the ether was removed to yield a viscous oil whose infrared spectrum (film) showed absorptions at 3640 and 3540 cm^{-1} . The oil was dissolved in 50 ml of acetyl chloride and refluxed for 5.5 hr. Removal of the excess acetyl chloride gave a red oil, which was dissolved in 50 ml of ether and extracted with three 10-ml portions of 5% sodium bicarbonate and then chromatographed on silica gel with petroleum ether as eluent. The total olefin fraction was refluxed in 200 ml of benzene with 0.5 ml of methanesulfonic acid for 3 hr. Work-up and crystallization from petroleum ether gave 1.073 g (53.8%) of 1,1-diphenyl-2-(ptolyl)-propene-1 as white needles: mp 83-84°; ir (CCl₄) 3150, 3090, 2980, 2910, 1595, 1510, 1490, 1440, 1375, 1020, and 910 cm⁻¹; nmr (CDCl₃) τ 2.70 (5 H), 2.98 (9 H), 7.75 (s, 3 H), and 7.90 (s, 3 H).

Anal. Calcd for $C_{22}H_{20}$: C, 92.91; H, 7.09. Found: C, 93.03; H, 7.08.

 α, α -Diphenyl-4-tert-butylacetophenone.—Diphenylacetic acid (8.50 g, 0.040 mol) was refluxed with thionyl chloride for 30 min. Excess thionyl chloride was removed under reduced pressure and the resulting acid chloride was dissolved in 20 ml of tert-butylbenzene and added dropwise to a stirred suspension of 12.0 g (0.090 mol) of aluminum chloride powder in 10 ml of tert-butylbenzene. After 3.5 hr at 95°, the reaction mixture was poured into 100 ml of ice-cold, dilute hydrochloric acid and stirred for 14 hr at 25°. The mixture was extracted with ether, and the ether solution was washed with two 50-ml portions of 5% sodium bicarbonate and two 50-ml portions of water. The ether solution was boiled with 15 g of activated charcoal for 15 min, filtered, and evaporated to yield an oil which was treated with cold petroleum ether to yield 1.93 g of α, α -diphenyl-4-*tert*-butylaceto-phenone as a white solid, mp 119-121°. Chromatography on silica gel gave an additional 4.89 g of material in the fraction eluted with 4:1 petroleum ether-benzene for a total yield of 6.82 g (51.9%) of the ketone. The of these two fractions on silica gel with 1:1 petroleum ether-benzene showed single spots of identical Rf values; ir (CCl4) 3120, 3080, 3015, 1685, 1600, 1495, 1450, and

1110 cm⁻¹; nmr (CDCl₃) showed an A_2B_2 quartet centered at τ 2.00 and 2.56 (4 H), 2.69 (s, 10 H), 3.93 (s, 1 H), and 8.71 (s, 9 H).

Anal. Caled for C₂₄H₂₄O: C, 87.76; H, 7.37. Found: C, 87.88; H, 7.31.

1,1-Diphenyl-2-(p-tert-butylphenyl)ethylene.-To 0.144 g (3.79 mmol) of lithium aluminum hydride in 25 ml of dry tetrahydrofuran under nitrogen was added dropwise a solution of 1.004 g (3.06 mmol) of α, α -diphenyl-4-tert-butylacetophenone in a total of 15 ml of tetrahydrofuran over a period of 15 min. The reaction mixture was refluxed for 19.5 hr, cooled, and hydrolyzed by the careful addition of 5 ml of water. Extraction with three 50-ml portions of methylene chloride followed by evaporation to dryness yielded a pale yellow oil presumed to be 1-hydroxy-1-(ptert-butylphenyl)-2,2-diphenylethane. Without further characterization, this oil was dehydrated by refluxing in benzene with a trace of sulfuric acid for 15 hr. Work-up gave an oil which solidified. Gc analysis of the oil on Apiezon \overline{L} (6 ft \times 0.25 in., 10% on Chromosorb W, temperature programmed from 150 to 275° at 5°/min, He = 100 ml/min) and also on silicon rubber SE-30 (methyl) (6 ft \times 0.25 in., 10% on Chromosorb W, 250°, He = 100 ml/min) showed two peaks with retention times of 41.0 and 44.6 and 7.6 and 8.4 min, respectively. The first peak was tentatively assigned to the *m*-tert-butyl isomer (4.5%) while the major component is the desired *p*-tert-butyl isomer (95.5%). Column chromatography on silica gel with petroleum ether as eluent yielded 0.744 g (77.9% crude) of 1,1-diphenyl-2-(p-tertbutylphenyl)ethylene as an amorphous white solid, mp 63.5-71.5°. Recrystallization of the isomer mixture from petroleum ether yielded pure (by gc analysis) 1,1-diphenyl-2-(p-tert-butyl-phenyl)ethylene: mp 74-76°; ir (CHCl₃) 3020, 1595, 1500, 1490, 1440, 1360, 1270, 1105, 1070, 1025, 890, and 830 cm⁻¹; nmr (CDCl₃) τ 2.75-3.08 (15 H) and 8.76 (s, 9 H).

Anal. Caled for $C_{24}H_{24}$: C, 92.26; H, 7.74. Found: C, 92.32; H, 7.67.

Small-Scale Perester Decompositions.—The following procedures are typical. Solutions of perester III were introduced into glass tubes, and the samples were degassed at 0.02 mm with three freeze-pump-thaw cycles and sealed. Each tube was placed in a stainless steel bomb with 1.0 ml of cumene to minimize tube breakage and to aid in heat transfer, and heated. The tubes were cooled and opened, and known amounts of the internal standard were added. The tubes were analyzed for 1,1-diphenylethylene, dicumyl, and 4-phenylcoumarin on an Apiezon L column [6 ft \times 0.25 in., 10% on Chromosorb W (acid washed), temperature programmed from 150 to 275° at 5°/min, detector 278°, injector 258°, He 100 ml/min], using biphenyl and triphenylmethane as internal standards. Triplicate injections were made for each tube analyzed.

Acetone and *tert*-butyl alcohol yields were determined in a similar fashion on a Carbowax 20M column [10 ft \times 0.25 in., 25% on Chromosorb P (acid washed), 60/80 mesh, column 80°, detector 275°, injector 245°, He 100 ml/min] using ethanol as internal standard.

1,1-Diphenyl-2-(p-tolyl)ethylene from decomposition of perester IV and dicumyl were determined on Apiezon L as described above using triphenylethylene and triphenylmethane, respectively, as internal standards. Replicate determinations gave about $\pm 5\%$ agreement.

Large-Scale Perester Decompositions.—A 100-ml flask fitted with a nitrogen bubbler was connected to two Dry Ice-acetone traps in series which led to a three-way stopcock connected to two pairs of Ascarite/Mg(ClO₄)₂ absorption tubes arranged in parallel so that tubes could be periodically removed and weighed while the gases were vented through the other side of the system. In a typical run, a solution of 1.003 g (3.384 mmol) of *tert*-butyl 3,3-diphenylperacrylate in 60 ml of purified cumene ([perester] = 0.0564 M) was cooled to -78° , evacuated to 0.35 mm for 10 min, warmed to 25°, and purged with purified nitrogen. This cycle was repeated three times. The flask was connected to the decomposition train, purged with a 75 ml/min flow of purified nitrogen, and placed in an oil bath at 110 \pm 0.2° for 10 hr. The Ascarite/Mg(ClO₄)₂ tubes absorbed a total of 0.0528 g (35.5%) of carbon dioxide.

The materials in the first trap were analyzed by gc on a 10 ft \times 0.25 in. Carbowax 20M column (column 80°, He 100 ml/min). Acetone, *tert*-butyl alcohol, and cumene were characterized by coinjection with authentic samples.

The reaction mixture was extracted with five 50-ml portions of 10% sodium carbonate; the carbonate solution was back-

⁽²³⁾ N. P. Buu-Hoi and J. Lecocq, J. Chem. Soc., 641 (1947).

⁽²⁴⁾ P. I. Pollak and D. Y. Curtin, J. Amer. Chem. Soc., 72, 961 (1950).

extracted with ether, acidified, and extracted with ether, and the ether was worked up to give 0.1113 g (14.7%) of 3,3-diphenyl-acrylic acid, mp 157–159°, ir (CHCl₃) superimposable with that of known acid.18,19

The remaining cumene solution was evaporated at approximately 0.25 mm at room temperature to a mixture of a viscous oil and needlelike crystals. The nonacidic materials from three such large-scale runs were combined and chromatographed on neutral Woelm alumina, grade I. Dicumyl, mp 116–118°, 1,1-diphenyl-ethylene,²⁶ and 4-phenylcoumarin,¹⁸ mp 105–107°, were isolated and characterized by comparison of ir and nmr spectra with those of authentic materials.

Large-scale decompositions of IV gave 1,1-diphenyl-2-(p-tolyl)ethylene,²⁶ isolated by molecular distillation and column chromatography, mp 69.5-71.5°, mmp 69-72°, ir and nmr superimposable with those of authentic samples. 1,1-Diphenyl-2-(ptolyl)propene-1 was characterized by coinjection with an authentic sample as a trace product of the decomposition of IV. Procedures similar to those described for perester III did not give identifiable samples of 2-(p-tolyl)-3,3-diphenylacrylic acid or 3-(p-tolyl)-4-phenylcoumarin from the decomposition of perester IV.

In another series of experiments, large-scale decompositions of III in benzene and tert-butylbenzene were carried out on deoxygenated solutions in sealed Carius tubes. The nonpolar olefin fraction of each decomposition was isolated by chromatography on alumina; the olefin fractions from the runs in tert-butylbenzene were further fractionated by molecular distillation at 0.11 mm by varying the bath temperature from 34 to 190°. The fraction distilling at 115-190° (0.11 mm) from the experiments in tertbutylbenzene and the total olefin fraction from the benzene run were examined by vpc on a 6 ft \times 0.125 in. 10% UC-W98 silicone rubber column. The gas chromatographic eluents were vented via a gas separator into an RMU-6E mass spectrometer, and their mass spectra (ionization voltage 75 eV) were scanned and compared with the spectra obtained in a similar manner for authentic 1,1-diphenyl-2-(p-tert-butylphenyl)ethylene and triphenylethylene.

Triphenylethylene (column 255°, retention time 2.5 min) showed a M^+ ion at m/e (rel intensity) 256 (12.6) and other prominent peaks at 178 (20.4), 168 (64.5), 167 (58.7), 165 (30.3), 92 (54), 91 (100), 78 (83.6), and 77 (38.8). Identical fragmentation pattern and gc behavior were obtained for authentic material.

The 1,1-diphenyl-2-(o-, m-, and p-tert-butylphenyl)ethylenes [column 270°, o- (3.0), m- (3.25), and p- (3.45 min)] partially overlapped under the conditions of vpc analysis. In all cases, however, consecutive scans of the eluting isomer mixture as a function of time gave a M^+ ion at m/e 312 and other prominent peaks at m/e 209, 207, 179, 178, 168, 167, 165, 152, 134, 133, 119, 105, 92, 91, and 78. These peaks were common to all three isomers but varied in intensity. The peak eluting at 3.45 min and known para isomer (3.5 min) showed nearly identical fragmentation patterns. Besides the above fragments, major peaks were observed at m/e 297, 282.7 (metastable), 256, 224, and 219 of similar relative intensities for both known and suspected para isomer. Further, both of these compounds had identical retention times (44.5 min) on a 10% Apiezon L column (temperature programmed $150-275^{\circ}$ at $5^{\circ}/\text{min}$). The major isomer (3.25) min) was assigned as the meta isomer by analogy.¹²

Control Experiments. cis- and trans-Stilbene and Diphenylacetylene.-A stock solution of the two stilbenes and diphenylacetylene in tert-butylbenzene was prepared. Run 1 represents the decomposition of two solutions of tert-butyl 3,3-diphenylperacrylate (III) in the stock solution. Run 2 is the stock solution and provides a reference point for the analyses. Detector response factors were determined for cis- and trans-stilbene and diphenylacetylene using the data from the control tubes of run 2. Because cis-stilbene has the same retention time as 1,1-diphenylethylene under the analysis conditions, the yields of cis-stilbene in run 1 were obtained by subtracting an average yield for 1,1-diphenyl-2ethylene of 17.2%, determined in separate experiments (Table I), from the total yield of cis-stilbene and 1,1-diphenylethylene. The data are presented in Table IV and show that cis- and transstilbene and diphenylacetylene are consumed to only a small extent in the presence of decomposing perester.

TABLE IV

DECOMPOSITION OF III IN THE PRESENCE OF cis- AND trans-Stilbene and Diphenylacetylene at 200° in tert-Butylbenzene

			Yiel	d. %———		· · · ·
	cis-St	ilbene	-trans-S	tilbene-	Diph acet;	enyl- ylene
Run	Found	Added	Found	Added	Found	Added
1^a	21.8^{b}	23.5	20.4	21.8	19.4	19.8
	22.1^{b}	23.5	20.5	21.8	18.9	19.8
2^{c}	23.4	23.5	21.9	21.8	19.6	19.8
	23.9	23.5	21.8	21.8	20.1	19.8

 a [III] = 7.83 \times 10⁻³ M, cis-stilbene (2.76 \times 10⁻⁶ mol), trans-stilbene (2.56 \times 10⁻⁶ mol), and diphenylacetylene (2.32 \times 10⁻⁶ mol) added per tube. ^b Corrected yield (see text). ° cis-Stilbene (2.76 \times 10⁻⁶ mol, 1.84 \times 10⁻³ M), trans-stilbene (2.56 \times 10⁻⁶ mol, 1.71 \times 10⁻⁸ M), diphenylacetylene (2.32 \times 10⁻⁶ mol, 1.55 \times 10⁻³ M).

Limits of Detection of Products from the Decomposition of tert-Butyl 3,3-Diphenylperacrylate.-Several tert-butyl 3,3-diphenylperacrylate decomposition mixtures were selected as representative of all of the reaction conditions investigated. Detection limits were established for cis- and trans-stilbene, diphenylacetylene, and methyl 3,3-diphenylacrylate by comparing the hydrogen flame detector gc chromatograms of known amounts of these decomposition mixtures with identical samples doped separately with known amounts of these compounds. The analysis for *cis*-stilbene was conducted on a Carbowax 20M column [20 ft \times 0.125 in., 25% on Chromosorb P (acid washed), 60/80 mesh, column 220°, injector 240°] to give retention times of 46.6, 49.9, and 52.5 min for 1,1-diphenylethylene, cis-stilbene, and 1,1diphenylpropene-1, respectively. The analysis for diphenylacetylene and trans-stilbene in the 7 \times 10⁻³ M perester range was conducted on an Apiezon L column (6 ft \times 0.125 in., 3% on Chromosorb G, column 160°, injector 285°) to give retention times of 11.1 and 17 min, respectively. In the 7 imes 10⁻² M perester range, limits were established for diphenylacetylene on a 3% Apiezon L column (column 167°, injector 276°), while transstilbene was determined under similar conditions on a SE-30 (methyl) column (6 ft \times 0.125 in., 10% on Chromosorb W, column 170°). The data are reported in Table III. Limits (<0.3%) for the formation of methyl 3,3-diphenylacrylate²⁷ in tert-butylbenzene and in benzene were determined on the 3% Apiezon L column (column 195°, injector 286°). In all cases, the limit of detectability is taken as the concentration necessary to give a well-defined unambiguous gc peak; the limits are conservative.

Decomposition of tert-Butyl 2-(p-Tolyl)-3,3-diphenylperacrylate in the Presence of Added 1,1-Diphenyl-2-(p-tolyl)ethylene and cis- and trans-1,2-Diphenyl-1-(p-tolyl)ethylene.-tert-Butyl 1-(ptolyl)-3,3-diphenylperacrylate was decomposed in tert-butylbenzene at 110° for 5 hr in the presence of added 1,1-diphenyl-2-(p-tolyl)ethylene (run 1) and, in a separate experiment, cis- and trans-1,2-diphenyl-1-(p-tolyl)ethylene (run 2). In run 3, perester IV was decomposed in the absence of added olefin to establish the expected yield of 1,1-diphenyl-2-(p-tolyl)ethylene. 1,1-Diphenyl-2-(p-tolyl)ethylene and the cis-trans isomer mixture of 1,2-diphenyl-1-(p-tolyl)ethylene were not separated under the analysis conditions. The yields of added olefin remaining after reaction were obtained by subtracting the yield of 1,1-diphenyl-2-(p-tolyl)ethylene in run 3 from the measured total olefin yields in runs 1 and 2. The results are presented in Table V; it is apparent that both olefins are consumed to comparable extents under these reaction conditions.

Limit of Detection for 1,2-Diphenyl-1-(p-tolyl)ethylene.—The validity of the ozonization procedure employed in the analysis for 1,1-diphenyl-2-(p-tolyl)ethylene and rearranged 1,2-diphenyl-1-(p-tolyl)ethylene was tested. Synthetic mixtures of unrear-ranged and rearranged triaryl olefin were prepared corresponding to 5.01, 2.64, and 1.08% rearrangement on a mole basis. These samples were ozonized in the presence of a slight mole excess of TCNE in ethyl acetate. Analysis on the dual column F & M 700 flame gas chromatograph on matched FFAP columns [10 ft \times 0.125 in., 15% on Chromosorb P (acid washed) 60/80 mesh, column 222°, injector 240°] gave four peaks which were assigned

⁽²⁵⁾ C. F. H. Allen and S. Converse, "Organic Syntheses," Collect. Vol. H. Gilman, Ed., Wiley, New York, N. Y., 1941, p 226.
 (26) A. C. Cope, P. A. Trumbull, and E. R. Trumbull, J. Amer. Chem.

Soc., 80, 2844 (1958).

⁽²⁷⁾ D. D. E. Newman and L. N. Owen, J. Chem. Soc., 4722 (1952).

TABLE	v
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Decomposition of IV in the Presence of Added
1,1-DIPHENYL-2-(p-TOLYL)ETHYLENE AND cis- AND
trans-1,2-DIPHENYL-1-(p-TOLYL)ETHYLENE IN
AND tert-BUTYLBENZENE AT 110°

		Added olefin, %			
Run	Found olefin, % ^a	1,1-Diphenyl- 2-(p-tolyl)- ethylene	1,2-Diphenyl- 1-(p-tolyl)- ethylene		
1^b	15.2 15.4	19.3 19.3			
2^{c}	15.2 14.4		19.1 19.1		
3 ^d	40.1 38.7		2012		

^a Corrected yield (see text). ^b [IV] = $1.51 \times 10^{-2} M$, 1,1-diphenyl-2-(*p*-tolyl)ethylene added (2.92 × 10^{-6} mol/tube). ^c [IV] = $1.51 \times 10^{-2} M$, 1,2-diphenyl-1-(*p*-tolyl)ethylene added (2.88 × 10^{-6} mol/tube). ^d [IV] = $1.50 \times 10^{-2} M$, no added olefin.

to benzaldehyde (2.5), 4-methylbenzaldehyde (3.5), benzophenone (23), and '4-methylbenzophenone (33 min) on the basis of retention times and relative peak heights. Assuming a detector response ratio of unity for the two ketones, relative yields of 4.91, 2.67, and 1.12% were calculated for 4-methylbenzophenone derived from rearranged olefin in the three samples. Analysis of these same samples on an Apiezon L column (6 ft \times 0.25 in., 10% on Chromosorb W, column 150–275° at 5°/min, He 100 ml/min) showed that no olefin remained.

Two 100-ml samples, $0.0139 \ M$ IV in tert-butylbenzene, were placed in Carius combustion tubes, degassed at 0.02 mm by three freeze-pump-thaw cycles, sealed, and heated in an oil bath at 110° for 5 hr. A control sample was prepared which was 5.79 \times $10^{-8} M$ in 1,1-diphenyl-2-(p-tolyl)ethylene and $2.93 \times 10^{-5} M$ in 1,2-diphenyl-1-(p-tolyl)ethylene in tert-butylbenzene. This synthetic mixture contained 0.50% rearranged olefin and was carried through the work-up and analytical procedures in parallel with the perester decomposition mixtures. The three samples were each concentrated at 0.25 mm and 60° for 2 hr to yield a viscous oily residue which was chromatographed on a $1.3 \times 16.0 \text{ mm}$ column of silical gel with benzene as eluent. Thin layer, nmr, and gc indicated that the samples from the perester decompositions were still badly contaminated with several extraneous uni-dentified materials. The decomposition mixtures and the control sample were rechromatographed on silica gel; the olefin fraction was shown by tlc to be in the fractions eluted with 9:1 hexanebenzene.

Each of the three olefin samples was examined on an F & M 700 flame gas chromatograph on a silicone rubber UC-W98 column (column 235°, injector 250°, detector 360°, N₂ 1.0 on flow meter). The olefinic fractions from the perester decompositions contained at least four contaminants of shorter retention time than that of the 1,1-diphenyl-2-(p-tolyl)ethylene; the major contaminant had the same retention time as authentic 1,1-diphenyl-2-(p-tolyl)propene-1. On the basis of relative peak area measurements, the decomposition samples contained 94% of the potential triaryl olefin mixture; the control sample was shown to contain only the synthetic mixture of unrearranged and rearranged triaryl olefins.

Each of the three olefin mixtures was dissolved in ethyl acetate containing a slight molar excess of tetracyanoethylene²⁸ and treated with an ozone-oxygen mixture. After 30 min, excess ozone was purged from the mixtures with oxygen. The reaction mixtures were analyzed on a matched pair of 15% FFAP column (column 226°, injector 230°) on an F & M 700 flame instrument. All four control ozonolysis samples were analyzed as standards along with the ozonolysis mixtures from the two perester decompositions. From the sums of the area measurements for the benzophenone and 4-methylbenzophenone peaks in each of the 5.01, 2.64, 1.08, and 0.50% control samples, a working curve was constructed converting measured 4-methylbenzophenone area percentages to 1,2-diphenyl-1-(p-tolyl)ethylene mole percentages. A very small peak in both perester decomposition mixtures had the same retention time under the analysis conditions as the peak assigned to 4-methylbenzophenone in the control sample; this peak was determined to be equivalent to 0.075 mol $\frac{1}{2}$ of rearranged 1,2-diphenyl-1-(p-tolyl)ethylene in the perester decomposition mixtures. On the basis of the purity established for the olefin mixtures of 94%, this peak corresponds to 0.08 mol % of rearranged olefin or 0.03% yield of rearranged olefin, based on initial perester. Since neither 4-methylbenzophenone nor rearranged olefin were rigorously shown to be present, 0.03% represents a maximum yield for rearranged olefin.

Registry No.—I, 36595-08-1; II, 36595-09-2; III, 35286-77-2; IV, 35286-78-3; 3,3-diphenylacrylaryl chloride, 4456-79-5; 1,1-diphenyl-2-(p-tolyl)-propene-1, 36601-67-9; α, α -diphenyl-4-*tert*-butylacetophenone, 36601-68-0; 1,1-diphenyl-2-(p-*tert*-butylphenyl)ethylene, 36601-69-1.

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(28) R. Criegee and P. Günther, Chem. Ber., 96, 1564 (1963).