6.08 (1,1,1-trichloroheptene-2) and 6.17 μ (1,1,3-trichloroheptene-1). The nmr spectrum showed a complicated pattern of absorption in the τ 3.6–4.7 region, which was shown to result from a 12-line ABX_2 system (1,1,1-trichloroheptene-2) and a doublet (1,1,3-trichloroheptene-1). The isomerization of 1,1,1-trichloroheptene-2 to its allylic isomer was easily followed by means of the nmr spectrum: 1,1,1-trichloroheptene-2: τ_A 3.73, τ_B 4.40, J_{AB} = 11.46 cps, J_{AX_2} = 1.92 cps; 1,1,3-trichloroheptene-2: τ_A 4.0, τ_B 5.4, J_{AB} = 9.7 cps.

Isomerization was accomplished by heating a sealed nmr tube containing the product in an oven maintained at 95° for 6 hr or more. The addition of thionyl chloride to the product catalyzed isomerization at room temperature.

The Addition of Bromotrichloromethane to Heptyne-1. Heptyne-1 (0.1 mole) and $BrCCl_3$ (0.4 mole) were transferred into a quartz tube, flushed with nitrogen, and sealed under vacuum. The tube was irradiated for 6 hr with ultraviolet light from a 200-w Hanovia lamp. The reaction mixture was distilled to yield one major product, bp 72–74° (0.02 mm). The infrared and nmr spectra of the distillate indicated that it was the heptyne-1–$BrCCl_3$ 1:1 normal adduct. The infrared spectrum showed bands at 6.17 (C=C) and 7.22 μ (*gem*-dimethyl); nmr: triplet at τ 3.2 (J = 0.8 cps, 1.0 H), multiplet at τ 7.2 (2.0 H), and doublet at τ 9.1 ($J \approx$ 6 cps, 6.0 H).

The addition product obtained from the addition of $BrCCl_3$ to 6-methylheptyne-1, bp 72–74° (0.02 mm), was also found to be the normal 1:1 adduct.

A Comparison of Allylic and Propargylic Radicals

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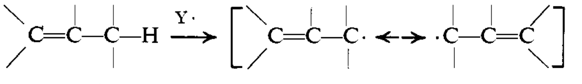
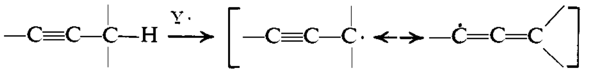
Contribution from the Department of Chemistry, University of Michigan, Ann Arbor, Michigan. *Received March 15, 1967*

Abstract: Through a study of the thermal, homolytic concerted decompositions of the β,γ-olefinic and β,γ-acetylenic peresters Ia–f, activation parameters for processes generating allylic and propargylic radicals have been determined. These activation parameters establish that the 2-buten-1-yl radical (IIa) is about 4 kcal/mole more stable than the 2-butyn-1-yl radical (IIb), but that the additional stability of the allylic radical is achieved only through the imposition of rotational restrictions not imposed upon the propargyl radical. Radical stabilization through delocalization in a propargyl radical requires no rotational restrictions as a consequence of the cylindrical symmetry of the triple bond. The γ-phenyl group of the 3-phenyl-2-propen-1-yl radical (IId) increases the stability of the radical by extending the conjugated system, whereas the γ-phenyl group of the 3-phenyl-2-propyn-1-yl radical (IIe) confers very little added stability to the propargyl radical, suggesting that the delocalization of the free electron does not extend into the benzene ring.

The formation of allylic free radicals through hydrogen abstraction is the first step in a number of synthetically useful reactions, such as allylic halogenation with N-bromosuccinimide[3] and *t*-butyl hypochlorite.[4] Analogous reactions, utilizing acetylenic substrates,[5,6] though less frequently employed, also reflect the possibility of selective hydrogen abstraction at a propargylic position. The origin of the greater ease of abstraction of an allylic or propargylic atom when compared to hydrogen abstraction from carbon atoms not adjacent to multiple bonds is obviously the formation of resonance-stabilized radicals, the contributing canonical forms for which are depicted in eq 1 and 2.


(1)


(2)

It is important to recognize, however, that there are some significant differences between allylic and propargylic radicals and consequently also between processes which generate them. For instance, the two contributing canonical forms of the allylic radical are structurally similar and therefore of very similar energies, whereas the two contributing structures of the propargyl radical, one acetylenic and one allenic, are not of equal energies. Hence, it would be anticipated that resonance stabilization of an allylic radical would be greater than for a propargylic radical. Bond energy data tend to support this contention. Although there is rather wide variation in bond disssociation values reported for allylic and propargylic bonds when measured by different methods, allylic bond dissociation energies are generally about 3–4 kcal/mole less than propargylic bond dissociation energies when measured by the same method in analogous compounds.[7–10] However, since the formation of a resonance-stabilized allylic radical requires overlap of the three p orbitals involved in the delocalized three-electron system, rotation of the bond between the allylic carbon atom and the double bond is necessarily restricted in the radical. There are no such restrictions in the propargyl radical, since the cylindrical symmetry of a triple bond permits overlap of the p orbital on the propargylic carbon atom in any rotational state. Thus an allyl radical is more stable than an analogous propargyl radical, but its added stability is purchased at the price of a loss in rotational freedom. Hence, one would be led to expect that a process leading to an allylic radical would have a lower enthalpy of

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activation and a more negative entropy of activation than one leading to a structurally analogous propargyl radical.

It is not apparent, *a priori*, how these two opposing factors will balance out. Gazith and Szwarc[11] have found that a methyl radical abstracts a hydrogen atom from a position adjacent to a triple bond about twice as readily as from a position adjacent to a double bond, whereas Walling, Heaton, and Tanner[6] have found that a *t*-butoxy radical abstracts allylic hydrogen atoms about 1.5 times as readily as propargylic hydrogen atoms. Both of these studies involve rather exothermic reactions and more likely reflect differences in ground-state energies than radical or transition-state properties. No study designed to establish the relative abilities of a double and triple bond to facilitate radical formation at adjacent positions has appeared.

In this paper a series of studies is reported in which structurally analogous allylic and propargylic radicals are generated endothermally by concerted perester decompositions (reaction 3). By a kinetic study of the

$$\underset{\mathrm{I}}{\mathrm{RCO_3C(CH_3)_3}} \xrightarrow[\Delta]{p\text{-cymene}} \underset{\mathrm{II}}{\mathrm{R}\cdot} + \mathrm{CO_2} + \mathrm{(CH_3)_3CO}\cdot \qquad (3)$$

a, R = $\mathrm{CH_3CH{=}CHCH_2}$
b, R = $\mathrm{CH_3C{\equiv}CCH_2}$
c, R = $\mathrm{CH_3C{\equiv}CCH(CH_3)}$
d, R = $\mathrm{C_6H_5CH{=}CHCH_2}$
e, R = $\mathrm{C_6H_5C{\equiv}CCH_2}$
f, R = $\mathrm{C_6H_5C{\equiv}CCH(CH_3)}$

decompositions of the peresters Ia–f, it was possible to determine and compare the enthalpies and entropies of activation of processes leading to the allylic radicals IIa and IId and the propargylic radicals IIb, c, e, and f.

Experimental Section

Materials. ***p*-Cymene** (Eastman Kodak) was shaken with one portion of concentrated sulfuric acid, one portion of water, two portions of concentrated sulfuric acid, one portion of water, three portions of 10% sodium bicarbonate solution, and one portion of water. It was then dried over calcium chloride and distilled, bp 175.5–176°.

***t*-Butyl hydroperoxide** (Wallace and Tiernan, Inc.) was dried by azeotropic distillation with benzene, then distilled at room temperature (5 mm), $n^{20}\mathrm{D}$ 1.4015.

***trans*-3-Pentenoic acid** was prepared according to the method of Linstead, Noble, and Boorman;[12] bp 102–103° (22 mm) [lit.[12] bp 95° (17 mm)]; $n^{20}\mathrm{D}$ 1.4353 (lit.[12] $n^{20}\mathrm{D}$ 1.4354); infrared (neat), $\nu_{\mathrm{O-H}}$ 3600–2400, $\nu_{\mathrm{C=O}}$ 1725, and $\nu_{\mathrm{C=C}}$ 970 cm^{-1}; nmr (neat), τ 8.33 (multiplet, area 3), 7.00 (multiplet, area 2), 4.45 (multiplet, area 2), and −1.70 (singlet, area 1).

3-Pentynoic acid was prepared according to the procedure of Jones, Whitham, and Whiting,[13] mp 103.5–106 (lit.[13] mp 103–104°); infrared (Nujol), $\nu_{\mathrm{O-H}}$ 3400–2500, $\nu_{\mathrm{C\equiv C}}$ 2260, and $\nu_{\mathrm{C=O}}$ 1705 cm^{-1}; nmr (CDCl$_3$), τ 8.17 (triplet, J = 2.5 cps, area 3), 6.70 (quartet, J = 2.5 cps, area 2), and −1.58 (singlet, area 1).

2-Methylpentyn-3-ol-1 was prepared by a reaction of the Reformatsky reagent,[14] derived from 2-bromo-3-pentyne[15] and amalgamated zinc,[16] with formaldehyde. To a 300-ml, three-necked flask containing 19.6 g (0.3 g-atom) of amalgamated zinc, 75 ml of anhydrous ether, and 75 ml of dry tetrahydrofuran was added about 2 ml of 2-bromo-3-pentyne. The initiation of the reaction was indicated by the onset of refluxing. The remainder of the 2-bromo-3-pentyne (total quantity 22 g, 0.15 mole) was added dropwise at a rate sufficient to maintain refluxing. Simultaneous addition of formaldehyde was begun as soon as the formation of the Reformatsky reagent had begun. The formaldehyde was generated by the decomposition at 180° of 18 g (0.6 mole) of paraformaldehyde, previously dried for 18 hr at reduced pressure over phosphorus pentoxide, and swept into the flask with a slow stream of nitrogen through a gas inlet tube extending to within 1 cm of the surface of the reaction mixture. Stirring was continued at room temperature for 30 min following the completion of addition of the formaldehyde. The reaction mixture was decanted into 150 ml of water and a solution of 15 g of concentrated sulfuric acid in 33 ml of water was added. The organic layer was separated and the aqueous layer extracted with two 100-ml portions of ether. The combined organic phase and ether extracts were washed with two 50-ml portions of 10% sodium carbonate and two 50-ml portions of water. After drying the ethereal solution over magnesium sulfate, solvent was removed on a steam bath, and the residue was distilled through a 6-in. Vigreux column. The yield was 9.3 g (57%); bp 62–64° (18 mm); $n^{20}\mathrm{D}$ 1.4660; infrared (neat), $\nu_{\mathrm{O-H}}$ 3350 and $\nu_{\mathrm{C\equiv C}}$ 2255 cm^{-1}; nmr (neat), τ 8.90 (doublet, J = 6 cps, area 3), 8.21 (doublet, J = 2.5 cps, area 3), 7.58 (multiplet, area 1), 6.60 (doublet, J = 6 cps, area 1), 6.54 (doublet, J = 6 cps, area 1), and 6.06 (singlet, area 1).

Anal. Calcd for $\mathrm{C_6H_{10}O}$: C, 73.43; H, 10.27. Found: C, 73.38; H, 10.26.

2-Methyl-3-pentynoic acid was prepared by the Jones oxidation[13] of 2-methylpentyn-3-ol-1. To a solution of 6.86 g (0.06 mole) of 2-methylpentyn-3-ol-1 in 70 ml of acetone was added dropwise 37.1 ml of a solution of chromium trioxide in sulfuric acid (2.5 mmoles/ml). Addition required 1 hr, and stirring was continued at room temperature for an additional 2 hr. The reaction mixture was poured into 350 ml of water, and the aqueous solution was extracted with three 200-ml portions of ether. The ether extract was extracted with two 100-ml portions of 10% sodium carbonate. The basic extract was washed with 100 ml of ether, acidified with hydrochloric acid, and extracted with two 100-ml portions of ether. The combined ether extracts were dried over magnesium sulfate, and solvent was removed on a steam bath, leaving a residue which was distilled through a 6-in. Vigreux column. The yield was 3.0 g (39%); bp 67–68° (0.5 mm); $n^{20}\mathrm{D}$ 1.4543; infrared (neat), $\nu_{\mathrm{O-H}}$ 3400–2600, $\nu_{\mathrm{C\equiv C}}$ 2265, and $\nu_{\mathrm{C=O}}$ 1710 cm^{-1}; nmr (neat), τ 8.75 (doublet, J = 7 cps, area 3), 8.19 (doublet, J = 3 cps, area 3), 6.60 (multiplet, area 1), and 1.83 (singlet, area 1).

Anal. Calcd for $\mathrm{C_6H_8O_2}$: C, 64.27; H, 7.19. Found: C, 64.46; H, 7.29.

4-Phenyl-3-butynoic acid was prepared according to the method of Mansfield and Whiting[17] by the Jones oxidation of 4-phenylbutyn-3-ol-1.[18] The yield of acid was 41%; mp 71–73° (lit.[17] mp 71°); infrared (Nujol), $\nu_{\mathrm{C=O}}$ 1705, $\nu_{\mathrm{C_6H_5}}$ 755 and 685 cm^{-1}; nmr (CDCl$_3$), τ (6.45 singlet, area 2), 2.70 (multiplet, area 5), and −1.47 (singlet, area 1).

2-Methyl-4-phenylbutyn-3-ol-1 was prepared by the reaction of the Reformasky reagent derived from 3-bromo-1-phenyl-1-butyne[18] and formaldehyde using the procedure described for 2-methylpentyn-3-ol-1. The crude product corresponded to nearly a quantitative yield, but vapor phase chromatography indicated that the product was only 80% pure. It was not possible to purify the product by distillation since the alcohol decomposed on heating. This crude product was utilized successfully in the subsequent oxidation. An analytical sample was obtained by chromatographing 3.2 g of the crude product on 105 g of silica gel. Contaminants preceded the desired product, and 1.5 g (47%) of pure 2-methyl-4-phenylbutyn-3-ol-1 was eluted with 5% ether in benzene; infrared (neat), $\nu_{\mathrm{O-H}}$ 3350, $\nu_{\mathrm{C\equiv C}}$ 2235, $\nu_{\mathrm{C_6H_5}}$ 755 and 685 cm^{-1}; nmr (neat), τ 8.77 (doublet, J = 7 cps), 7.25 (singlet), 7.16 (quartet, J = 7 cps), 6.38 (doublet, J = 6.5 cps), and 2.70 (multiplet).

Anal. Calcd for $\mathrm{C_{11}H_{12}O}$: C, 82.46; H, 7.55. Found: C, 82.38; H, 7.59.

2-Methyl-4-phenyl-3-butynoic acid was prepared by the oxidation of 2-methyl-4-phenylbutyn-3-ol-1 by the same procedure[17] used to prepare 4-phenyl-3-butynoic acid. The crude acid produced in this way was contaminated with benzoic acid. The benzoic acid was sublimed out at 80° (0.4 mm). The residue was then distilled through a 6-in. Vigreux column, giving a 33% yield of purified

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acid, bp 116–120° (0.2 mm); $n^{20}\mathrm{D}$ 1.5584; infrared (neat), $\nu_{\mathrm{O-H}}$ 3500–2500, $\nu_{\mathrm{C\equiv O}}$ 1712, $\nu_{\mathrm{C_6H_6}}$ 750 and 680 cm^{-1}, no absorption attributable either to an acetylenic or allenic system; nmr (neat), τ 8.46 (doublet, J = 7 cps), 6.30 (quartet, J = 7 cps), 2.63 (multiplet), and 0.12 (singlet).

Anal. Calcd for $C_{11}H_{10}O_2$: C, 75.84; H, 5.79. Found: C, 75.75; H, 5.73.

The **acid chlorides** were prepared by the dropwise addition of 20 mmoles of oxalyl chloride to a solution of 10 mmoles of the acid at 45°. The reaction mixture was maintained at 45° for 3 hr, then at 70° for 0.5 hr. Excess oxalyl chloride and benzene were removed by distillation at reduced pressure, and the acid chloride was purified by short-path distillation.

trans-**3-Pentenoyl chloride** was obtained in 63% yield; bp 42–42.5° (30 mm); infrared (neat), $\nu_{\mathrm{C=O}}$ 1800, $\nu_{\mathrm{C=C}}$ 965, and $\nu_{\mathrm{C-Cl}}$ 700 cm^{-1}; nmr (neat), τ 8.32 (multiplet, area 3), 6.55 (multiplet, area 2), and 4.43 (multiplet, area 2).

3-Pentynoyl chloride was obtained in 78% yield; bp 63–64° (32 mm); infrared (neat), $\nu_{\mathrm{C\equiv C}}$ 2250, $\nu_{\mathrm{C=O}}$ 1800, $\nu_{\mathrm{C-Cl}}$ 740 and 695 cm^{-1}; nmr (neat), τ 8.17 (triplet, J = 2.5) and 6.20 (quartet, J = 2.5 cps).

2-Methyl-3-pentynoyl chloride was obtained in 75% yield; bp 59–60.5° (17 mm); infrared (neat), $\nu_{\mathrm{C\equiv C}}$ 2260, $\nu_{\mathrm{C=O}}$ 1790, and $\nu_{\mathrm{C-Cl}}$ 720 cm^{-1}; nmr (neat), τ 8.54 (doublet, J = 7 cps, area 3), 8.18 (doublet, J = 3 cps, area 3), and 6.23 (multiplet, area 1).

4-Phenyl-3-butynoyl chloride was obtained in 70% yield; bp 82–84° (0.4 mm); infrared (neat), $\nu_{\mathrm{C\equiv C}}$ 2240, $\nu_{\mathrm{C=O}}$ 1790, $\nu_{\mathrm{C_6H_5}}$ 775 and 685, $\nu_{\mathrm{C-Cl}}$ 750 cm^{-1}; nmr (neat), τ 6.19 (singlet) and 2.68 (multiplet).

2-Methyl-4-phenyl-3-butynoyl chloride was obtained in 82% yield; bp 74–77° (0.2 mm); infrared (neat), $\nu_{\mathrm{C\equiv C}}$ 2245, $\nu_{\mathrm{C=O}}$ 1790, $\nu_{\mathrm{C_6H_5}}$ 755 and 690, and $\nu_{\mathrm{C-Cl}}$ 715 cm^{-1}; nmr (neat), τ 8.45 (doublet, J = 7 cps), 6.12 (quartet, J = 7 cps), and 2.72 (multiplet).

The **peresters** were prepared by the reaction of the acid chloride with *t*-butyl hydroperoxide in the presence of pyridine. In a typical preparation a solution of 10.5 mmoles of pyridine in 25 ml of petroleum ether (bp 30–60°) was added over a 30-min period to a solution of 10 mmoles of the acid chloride and 21 mmoles of *t*-butyl hydroperoxide in 50 ml of petroleum ether (bp 30–60°) maintained at 0°. The reaction mixture was stirred for an additional 3 hr at room temperature, then poured into 75 ml of water. The organic phase was separated and washed with 50 ml of cold 10% sulfuric acid, 50 ml of cold 10% sodium carbonate, and 50 ml of cold water. The petroleum ether solution was dried over magnesium sulfate. Removal of the solvent at reduced pressure gave the crude perester, which was then chromatographed on Florisil (10 g of Florisil/g of perester), eluting the perester with petroleum ether (bp 30–60°). The aliphatic peresters Ia–c were all purified further by distillation at reduced pressure through a short-path apparatus. *t*-Butyl 3-phenyl-2-propyne-1-percarboxylate (Ie), a solid, was recrystallized. *t*-Butyl 4-phenyl-3-butyne-2-percarboxylate (If) which could be neither distilled nor recrystallized was purified by chromatography on two different adsorbents, first on silica gel (30 g of silica gel/g of perester), eluting with 5% ether in petroleum ether, then on Florisil as described above.

t-**Butyl** *trans*-**2-butene-1-percarboxylate (Ia)** was obtained in 44% yield; bp 56.5° (0.8 mm); infrared (neat), $\nu_{\mathrm{C=O}}$ 1775, $\nu_{\mathrm{C-CH_3}}$ 1380 and 1360, $\nu_{\mathrm{C=C}}$ 960 cm^{-1}; nmr (CCl_4), τ 8.73 (singlet), 8.28 (multiplet), 7.03 (multiplet), and 4.45 (multiplet).

Anal. Calcd for $C_9H_{16}O_3$: C, 62.77; H, 9.36. Found: C, 62.75; H, 9.17.

t-**Butyl 2-butyne-1-percarboxylate (Ib)** was obtained in 39% yield; bp 67–68° (1 mm); infrared (neat), $\nu_{\mathrm{C\equiv C}}$ 2250, $\nu_{\mathrm{C=O}}$ 1780, $\nu_{\mathrm{C-CH_3}}$ 1395 and 1365 cm^{-1}; nmr (CCl_4), τ 8.70 (singlet), 8.20 (triplet, J = 2.5 cps), and 6.88 (quartet, J = 2.5 cps).

Anal. Calcd for $C_9H_{14}O_3$: C, 63.45; H, 8.29. Found: C, 63.18; H, 8.20.

t-**Butyl 3-pentyne-2-percarboxylate (Ic)** was obtained in 40% yield; bp 56–57° (0.7 mm); infrared (neat), $\nu_{\mathrm{C=O}}$ 1780, $\nu_{\mathrm{C-CH_3}}$ 1390 and 1360 cm^{-1}; nmr (CCl_4), τ 8.68 (singlet), 8.19 (doublet, J = 2.5 cps), 8.61 (doublet, J = 7 cps), and 6.80 (multiplet).

Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 65.18; H, 8.66.

t-**Butyl 3-phenyl-2-propyne-1-percarboxylate (Ie)** was obtained in 23% yield; mp 45–46.5° (recrystallized from petroleum ether); infrared (Nujol), $\nu_{\mathrm{C=O}}$ 1780, $\nu_{\mathrm{C_6H_5}}$ 760 and 695 cm^{-1}; nmr (CCl_4), τ 8.70 (singlet), 6.65 (singlet), 2.70 (multiplet); ultraviolet (hexane), $\lambda_{\max}$ 239 mμ (ϵ 20,600) and 250 mμ (ϵ 19,500).

Anal. Calcd for $C_{14}H_{14}O_3$; C, 72.39; H, 6.90. Found: C, 72.52; H, 7.02.

t-**Butyl 4-phenyl-3-butyne-2-percarboxylate (If)** was obtained in 45% yield; infrared (neat), $\nu_{\mathrm{C\equiv C}}$ 2205, $\nu_{\mathrm{C=O}}$ 1780, $\nu_{\mathrm{C-CH_3}}$ 1395 and 1370, and $\nu_{\mathrm{C_6H_5}}$ 755 and 690; nmr (CCl_4), τ 8.67 (singlet), 8.48 (doublet J = 7 cps), 6.44 (quartet, J = 7 cps), and 2.67 (multiplet); ultraviolet (hexane), $\lambda_{\max}$ 239 mμ (ϵ 20,000) and 250 mμ (ϵ 18,500).

Anal. Calcd for $C_{15}H_{16}O_3$: C, 73.15; H, 7.37. Found: C, 72.98; H, 7.44.

Methyl 3-pentynoate and methyl 2-methyl-4-phenyl-3-butynoate were prepared from the corresponding acids and boron trifluoride–methanol.[19] These two esters were heated in *p*-cymene for 6 hr at 96 and 80°, respectively. At the end of this time, gas–liquid partition chromatography indicated only the initial ester to be present, and the infrared spectra of the initial and final solutions were identical. No isomerizations had occurred.

Determination of Carbon Dioxide Yield. The amount of carbon dioxide evolved during a decomposition was determined gravimetrically by noting the increase in weight of a tube filled with Ascarite. The procedure is described elsewhere.[20]

Procedure for Kinetic Runs. A weighed sample of the perester in a 5.00-ml volumetric flask was dissolved in *p*-cymene, and aliquots of this solution were transferred to glass ampoules. The ampoules were carefully degassed by freezing the sample in Dry Ice–acetone, allowing it to thaw while under vacuum, and then filling the ampoule with nitrogen. Degassing was effected by two such freeze–thaw–flush operations on each ampoule. Ampoules were sealed under nitrogen. Effective removal of oxygen was very important, since it was found that in the presence of air, the production of substances which absorbed in the carbonyl region of the infrared resulted, apparently oxidation products derived from intermediate radicals, which rendered perester concentration measurements very inaccurate. Chlorobenzene, toluene, and cumene were rejected as decomposition solvents because of the formation of similar oxidation products which absorbed in the carbonyl region of the infrared. The ampoules were immersed simultaneously in an oil bath maintained at constant temperature. Ampoules were removed at fixed intervals and stored at 0° until analyzed. Points were taken until 75–90% of the original perester had decomposed. One ampoule was allowed to remain in the oil bath until decomposition was complete. This sample was taken to represent infinite time, whereas a sample of the original solution was taken to represent zero time.

Determination of Relative Concentration of Peresters. The method of Bartlett and Hiatt[21] was utilized. Analyses were carried out in matched 0.125-mm sodium chloride cells on a Perkin-Elmer Model No. 21 infrared spectrophotometer. Each sample was allowed to warm to room temperature, and the intensity of the carbonyl peak at 1780 cm^{-1} was measured twice. An average value was used for calculating the rate of decomposition.

Treatment of Data. The rate constants for perester decomposition were calculated from a least-squares slope of plots of log P/P_0 *vs.* t, where P is perester concentration at any given time, t, and P_0 is initial perester concentration. The ratio P/P_0 was calculated from the expression $P/P_0 = (\log T_\infty - \log T_t)/(\log T_\infty - \log T_0)$ where T_∞, T_0, and T_t represent percentage transmission at infinite time, zero time, and time t, respectively. Correlation coefficients and 99% confidence limits were calculated by standard statistical methods.[22] The enthalpies of activation were calculated from least-squares slopes of plots of ln (k/T) *vs.* $(1/T)$ using mean values of k for three or four runs at each of three different temperatures. The entropy of activation was calculated from the expression $k = (k'T/h)e^{-\Delta H^*/RT}e^{\Delta S^*/R}$, where k is the first-order rate constant at temperature T, k' is the Boltzmann constant, h is the Planck constant, R is the gas constant, and ΔH^* is the enthalpy of activation.

Results

Synthesis of the Peresters. The peresters were prepared in a straightforward manner from the corresponding acid chloride, *t*-butyl hydroperoxide, and pyridine. Peresters prepared and purified as described in the

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Experimental Section exhibited no extraneous bands in the infrared which might have suggested contamination by *t*-butyl hydroperoxide or any carbonyl-containing compounds. The two α-substituted β,γ-acetylenic acids were new compounds, synthesized by the route depicted in eq 4. This is the first potentially general

$$RC{\equiv}CCH(R')Br \xrightarrow[2.\ CH_2O]{1.\ Zn\text{–}Hg} RC{\equiv}CCH(R')CH_2OH \xrightarrow[H_2SO_4,\ acetone]{CrO_3} RC{\equiv}CCH(R')CO_2H \quad (4)$$

route to α,γ-disubstituted β,γ-acetylenic acids which has been reported. The acids, acid chlorides, and peresters were all established to be the desired β,γ-acetylenic compounds and not α,β-acetylenic or allenic compounds by infrared, ultraviolet, and nmr data, all of which are reported in the Experimental Section.

The Reaction. Perester decomposition is a well-studied reaction,[3,21] and the decompositions reported in this paper have all of the characteristics of a concerted free-radical process. The enthalpies of activation (Table VII) are considerably less than those of simple nonconcerted decompositions. The first-order rate plots are nicely linear with correlation coefficients of 0.99 or better. Significant complications resulting from induced decompositions are ruled out by the absence of any systematic or significant change in rate constants (Tables II–VI) with an increase in initial perester concentrations. Isomerizations of the triple bond of the perester prior to decomposition are rendered unlikely by the observation that the simple methyl esters of 3-pentynoic acid and 2-methyl-4-phenyl-3-butynoic acid can be recovered unchanged after being subjected to the conditions of perester decomposition. Likewise the high yields of carbon dioxide (Table I) and the absence of any carbonyl absorption in the infrared spectra of the completely decomposed peresters rule out any double or triple bond induced decomposition, which should lead to lactonic products, or any isomerizations prior to decomposition, which should lead to α,β-unsaturated peresters which would decompose more slowly than the β,γ isomers. Hence, we conclude that the measured rates of decomposition of the peresters studied do constitute rates of production of the allylic and propargylic radicals IIa–f.

Table I. Carbon Dioxide Yields during Decomposition in *p*-Cymene

Perester	Temp, °C	Init concn, *M*	% CO_2
Ia	79.9	0.0952, 0.1008	100, 94
Ib	94.7	0.1002, 0.1031	96, 101
Ic	80.5	0.0932, 0.1261	86, 90
Ie	93.3	0.1316, 0.1278	98, 94
If	79.9	0.0961, 0.0978	94, 93

Rate Constant. The kinetic data for the decompositions of the peresters IIa–c, e, and f are tabulated in Tables II–VI. The 99% confidence limits for all of the kinetic runs vary from 1.8 to 13.5% of the value of the first-order rate constant, having an average value of 7.2%.

Activation Parameters. Enthalpies and entropies of activation for the concerted decompositions of peresters

Table II. Rates of Decomposition of *t*-Butyl *trans*-2-Butene-1-percarboxylate (Ia) in Cumene

Init concn, *M*	Temp, °C ±0.05°	$k \times 10^3$, min^{-1}
0.1352	67.94	4.33 ± 0.10[a]
0.0738	67.94	4.33 ± 0.35
0.0305	67.94	4.14 ± 0.45
0.0158	67.94	4.10 ± 0.19
0.1352	74.46	8.82 ± 0.79
0.0738	74.46	8.80 ± 0.35
0.0305	74.46	9.37 ± 0.52
0.0158	74.46	9.72 ± 0.72
0.1352	82.15	19.2 ± 1.10
0.0738	82.15	19.8 ± 1.30
0.0305	82.15	20.3 ± 0.60
0.0158	82.15	19.1 ± 1.00

[a] Confidence limits, 99%.

Table III. Rates of Decomposition of *t*-Butyl 2-Butyne-1-percarboxylate (Ib) in *p*-Cymene

Init concn, *M*	Temp, °C ±0.05°	$k \times 10^3$, min^{-1}
0.1444	80.90	3.16 ± 0.26[a]
0.0563	80.90	3.27 ± 0.36
0.0270	80.90	3.09 ± 0.27
0.1516	87.09	6.61 ± 0.39
0.0561	87.09	6.70 ± 0.12
0.0273	87.09	6.40 ± 0.26
0.1444	95.63	17.6 ± 1.10
0.0563	95.63	17.7 ± 1.40
0.0270	95.63	18.0 ± 1.80

[a] Confidence limits, 99%.

Table IV. Rates of Decomposition of *t*-Butyl 3-Pentyne-1-percarboxylate (Ic) in *p*-Cymene

Init concn, *M*	Temp, °C ±0.050	$k \times 10^2$, min^{-1}
0.1435	68.31	1.08 ± 0.07[a]
0.0606	68.31	1.08 ± 0.08
0.0530	68.31	1.14 ± 0.06
0.1568	74.57	2.22 ± 0.11
0.0499	74.57	2.34 ± 0.11
0.0302	74.57	2.18 ± 0.06
0.1592	80.45	4.69 ± 0.20
0.0560	80.45	4.70 ± 0.19
0.0304	80.45	4.68 ± 0.26

[a] Confidence limits, 99%.

Table V. Rates of Decomposition of *t*-Butyl 3-Phenyl-2-propyne-1-percarboxylate (Ie) in *p*-Cymene

Init concn, *M*	Temp, °C ±0.05°	$k \times 10^3$, min^{-1}
0.1520	79.14	4.84 ± 0.36[a]
0.0832	79.14	5.48 ± 0.69
0.0382	79.14	4.77 ± 0.37
0.0223	79.14	4.42 ± 0.50
0.1421	85.46	10.7 ± 0.80
0.0832	85.46	10.2 ± 1.00
0.0382	85.46	10.2 ± 0.90
0.0223	85.46	9.6 ± 0.80
0.1421	92.18	22.0 ± 1.20
0.0383	92.18	22.1 ± 0.60
0.0223	92.18	22.3 ± 1.90

[a] Confidence limits, 99%.

Table VI. Rates of Decomposition of *t*-Butyl 4-Phenyl-3-butyne-2-percarboxylate (If) in *p*-Cymene

Init concn, *M*	Temp, °C ±0.05°	$k \times 10^2$, min^{-1}
0.1599	64.90	1.16 ± 0.08[a]
0.0788	64.90	1.19 ± 0.09
0.0381	64.90	1.11 ± 0.08
0.0223	64.90	1.10 ± 0.13
0.1599	71.26	2.42 ± 0.21
0.0788	71.26	2.67 ± 0.36
0.0381	71.26	2.37 ± 0.17
0.0223	71.26	2.46 ± 0.23
0.1599	79.14	6.40 ± 0.80
0.0788	79.14	6.31 ± 0.59
0.0381	79.14	5.20 ± 0.40
0.0223	79.14	5.76 ± 0.51

[a] Confidence limits, 99%.

Ia–f, along with half-lives and rate constants at 60°, are presented in Table VII. A statistical analysis of the error in ΔH^* is unrealistic when applied to an Arrhenius plot utilizing only three points, but it is estimated that the error in ΔH^* is of the order of 1.0 kcal/mole.

Table VII. Activation Parameters, Rate Constants, and Half-Lives at 60° for the Peresters $RCO_3C(CH_3)_3$

R	k, min^{-1}	$t_{1/2}$, min	ΔH^*, kcal/mole	ΔS^*, eu
$CH_3CH{=}CHCH_2$ (Ia)	1.75×10^{-3}	396	25.8	−2.5
$CH_3C{\equiv}CCH_2$ (Ib)	2.24×10^{-4}	3094	29.8	5.9
$CH_3C{\equiv}CCH(CH_3)$ (Ic)	3.93×10^{-3}	176	28.0	6.2
$C_6H_5CH{=}CHCH_2$ (Id)	6.93×10^{-3}	100[21]	23.5[21]	−5.9[21]
$C_6H_5C{\equiv}CCH_2$ (Ie)	4.63×10^{-4}	1497	28.9	4.6
$C_6H_5C{\equiv}CCH(CH_3)$ (If)	6.54×10^{-3}	106	26.7	3.2

Discussion

The most instructive approach to the interpretation of the data is to consider the peresters in selected pairs. The comparison of the activation parameters of decomposition of pesters Ia and Ib, which generate the 2-buten-1-yl (IIa) and 2-butyn-1-yl (IIb) radicals, respectively, is the comparison fundamental to this entire study. Thus it is observed that the process leading to the allylic radical IIa has an enthalpy of activation 4 kcal/mole less than that of a process leading to the structurally analogous propargyl radical IIb, and an entropy of activation 8.4 eu more negative. These findings are entirely in accord with the considerations presented in the introductory section. The allyl radical derives greater stabilization through delocalization than the propargyl radical, but only at the expense of greater rotational constraint. Indeed, the activation parameters for the decomposition of Ib are very similar to those of peresters which generate stable radicals having no rational constraints (Cl_3CCO_3-*t*-Bu, $\Delta H^* = 30.1$ kcal/mole, $\Delta S^* = 8.9$ eu),[21] leading to the conclusion anticipated in the introductory section that the resonance stabilization of a propargyl radical imposes no rotational restrictions on the bond between the newly generated radical carbon atom and the triple bond.

The comparison of Ib and Ic, which generate the 2-butyn-1-yl (IIb) and 3-pentyn-2-yl (IIc) radicals, respectively, or Ie and If, which generate the 3-phenyl-2-propyn-1-yl (IIe) and the 4-phenyl-3-butyn-2-yl (IIf) radicals, respectively, only shows that in going from a process generating a primary propargyl radical to one generating a secondary propargyl radical, the only change is in the enthalpy of activation, resulting from the greater stability conferred upon the radical by the additional methyl group. The entropies of activation of Ib and Ic and of Ie and If are very similar and reflect transition states of similar rotational characteristics.

When one comes to consider the peresters Id–f, in which a γ-phenyl group extends the conjugated system, several features emerge which were not anticipated in the introductory section. In comparing Ia and Id, the effect of a phenyl group extending the π system into which the free electron of the resulting radical is delocalized is clearly reflected in the lower enthalpy of activation for Id ($\Delta\Delta H^* = 2.3$ kcal/mole). Correspondingly the entropy of activation for Id is more negative ($\Delta\Delta S^* = 3.4$ eu), since one more bond, the one between the phenyl group and the double bond, must be restricted to permit overlap of the relevant π orbitals. No such dramatic effect on the activation parameters is observed when a methyl group is replaced by a phenyl group in a propargyl system. Indeed, the activation parameters for Ib and Ie differ very little ($\Delta\Delta H^* = 0.9$ kcal/mole, $\Delta\Delta S^* = 1.3$ eu). Hence, it must be concluded that the phenyl group of a γ-phenylpropargyl radical contributes very little to the stabilization of the radical, in spite of the fact that it would seem superficially to be a completely conjugated system analogous to the corresponding γ-phenylallyl system in which the phenyl group contributes significantly to the stabilization of the radical. It would seem that the delocalized system of a γ-phenylpropargyl radical does not encompass the benzene ring. It is interesting to note that the epr spectrum of the 3-phenyl-2-propyn-1-yl radical (IIe) exhibited only three lines, also indicating that the free electron is not delocalized into the benzene ring.[23] The cylindrical symmetry of the triple bond and the resulting rotational properties of propargyl radicals can explain the failure of a γ-phenyl group to increase the stability of a propargyl radical. Since no rotational constraints on the bond between the triple bond and the benzene ring are necessary to permit overlap between the two π systems, and similarly, no rotational constraints on the bond between the triple bond and the newly generated radical carbon atom are imposed to permit overlap of the orbital containing the free electron and the π system of the triple bond, these two bonds are essentially rotating independently. Consequently, the probability that the π orbitals of the phenyl group and the p orbital of the sp^2 radical carbon atom are coplanar is very small, with the result that the free electron is

(23) V. I. Smirnova, T. S. Zhuravleva, D. N. Shigorin, E. P. Gracheva, and M. F. Shostakovskii, *Zh. Fiz. Khim.*, **38**, 469 (1964).

delocalized only into the π system of the triple bond and not further into the benzene ring. The slight decrease in enthalpy of activation which does result from replacing the γ-methyl group of Ib with the phenyl group of Ie (0.9 kcal/mole) may reflect the increased stabilization of the radicals produced by that fraction of Ie which happens to be in a rotational state at the instant of decomposition in which the p orbitals of the phenyl group and the p orbital of the terminal radical sp^2 carbon atom are coplanar or nearly so.

The inability of a triple bond to transmit the resonance-stabilizing effect of a phenyl group on a carbonium ion has been indicated earlier in studies by Kochi and Hammond[24] in which they solvolyzed *m*- and *p*-2-phenylethenyl and 2-phenylethynylbenzyl tosylates. They found that the σ_p and σ_p^+ values for the 2-phenylethenyl group were -0.070 and -1.00, respectively, whereas for the 2-phenylethynyl group, σ_p and σ_p^+ had values of 0.165 and -0.03. Thus, the phenyl group conjugated with the benzyl cation through an intervening double bond at the *para* position serves as an excellent electron reservoir ($\sigma_p^+ - \sigma_p = -0.93$) whereas when the conjugating link is a triple bond, the phenyl group only contributes modestly to the added stabilization of the benzyl cation ($\sigma_p^+ - \sigma_p = -0.19$). Here, as in the case of the radical discussed in this paper, free and independent rotation about both bonds between the triple bond and the two phenyl groups precludes through conjugation of the γ-phenyl group with the benzylic cationic center.

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Directly Observable Carbonium Ion–Carbonium Ion Rearrangements. I. Kinetics and Equilibria in the Interconversion of Trialkylcyclopentenyl Cations

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Abstract: The kinetics of several observable carbonium ion–carbonium ion reversible rearrangements in an alkyl-substituted cyclopentenyl system have been measured. By conducting these reactions in variable acid concentrations and in deuterated acids, it has proven possible to suggest a plausible mechanism for the rearrangements. The equilibrium constants for these reversible reactions have been obtained in a variety of acid concentrations and a preliminary discussion of the possible structural features responsible for the varying *K* values is presented. An unrelated rearrangement involving the *t*-butyl-substituted ions is also described and a detailed measurement and comparison of the nmr and ultraviolet spectra of these ions are presented.

Physical chemical studies of carbonium ion rearrangements have almost exclusively[1] involved a kinetic or product study of the general sequence

starting material (neutral molecule of known structure)	⟶	[ionic transition states of deduced structure]	⟶	product (neutral molecule of known structure)

This paper reports the study of a rearrangement where the starting material and products are both carbonium ions and while these correspond to no known transition-state intermediates, both in structure and solvating solvent, it may be possible in the future to make certain direct correlations with these.

Previous work[1a–d,f,g,2,3] has shown that cyclopentenyl cations are readily prepared in highly acidic solution and that they appear to be more stable than other allylic cations. A study of deuterium substitution in some nonrearranging cyclopentenyl cations has also been made.[1a]

This study originated from an attempt to test the relative ability of alkyl groups in stabilizing carbonium ion centers, and it was considered that the cyclization of dienylic ions of structure A (a known reaction type[1b,c,f,h]) would lead to two cyclopentenyl ions whose relative amounts would be determined by their thermodynamic stabilities.

This hypothesis proved to be wrong. However, it was observed that the proportion of the two ions in the mixture *slowly changed* but eventually reached a constant value. Furthermore the reaction was clean, *i.e.*, no further significant products or polymer formed during this change, except where R was *t*-butyl.

This study reports the experimental evidence showing that the two ions reach a true equilibrium, reports the

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[1] Exceptions include some recent ion rearrangement studies given in the following references: (a) N. C. Deno, N. Friedman, J. D. Hodge, and J. J. Houser, *J. Am. Chem. Soc.*, 85, 2995 (1963); (b) T. S. Sorensen, *Can. J. Chem.*, 42, 2768 (1964); (c) N. C. Deno, C. U. Pittman, Jr., and J. O. Turner, *J. Am. Chem. Soc.*, 87, 2153 (1965); (d) N. C. Deno and J. J. Houser, *ibid.*, 86, 1741 (1964); (e) N. C. Deno and C. U. Pittman, Jr., *ibid.*, 86, 1744 (1964); (f) T. S. Sorensen, *Can. J. Chem.*, 43, 2744 (1965); (g) T. S. Sorensen, *J. Am. Chem. Soc.*, 87, 5075 (1965); (h) G. A. Olah, C. U. Pittman, Jr., and T. S. Sorensen, *ibid.*, 88, 2331 (1966).

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