Notes

Synthesis and Conformation of 2,4,5-Triphenyl-3-benzoylcyclopent-1-ene

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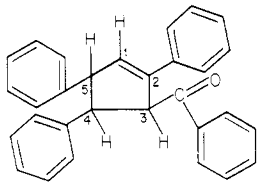
We report the synthesis and conformation of 2,4,5-triphenyl-3-benzoylcyclopent-1-ene. Chalcone (benzalacetophenone) was refluxed in dry benzene with finely divided sodium for 8 h. An ether-soluble product was isolated from a mass of insoluble material. The mass spectrum, shown in Figure 1, exhibited a molecular ion at m/e 400. Elemental analysis was consisted with the molecular formula ($C_{30}H_{24}O$). The proton NMR spectrum (Figure 2) showed chemical shifts for four unequivalent hydrogens and four monosubstituted phenyl groups. The ^{13}C NMR spectrum showed 22 peaks which contained the correct number of peaks in the off-resonance decoupled spectrum which were doublets (saturated CH, HC=C, and phenyl) and the correct number of the singlets for the ipso carbons, =C—, and carbonyl (C=O). The ^{13}C chemical shifts for C_3', C_4', and C_5' are listed in Table I. The IR spectrum showed absorption for C=C, C—O, and phenyl. This evidence suggested that we were dealing with a tetrasubstituted five-membered unsaturated ring. These data were consistent with the assigned structure (I). A reasonable radical anion mechanism shown in Scheme I supports the position of the double bond.



I

Because of the interest in cyclopentane chemistry it seemed important to study the conformation of this tetrasubstituted cyclopentene. The study of the conformation of I was made by analysis of its ^1H NMR spectrum shown in Figure 2. Karplus[2] has supported the suggestion that coupling constants in saturated molecules were largely dependent on the precise molecular geometry. Karplus[2] has carried out theoretical studies relating the coupling constant (J) to the dihedral angle (ϕ) separating the relevant carbon and hydrogen bonds. Karplus' equation (eq 1) expresses these relationships:

$$\begin{aligned} J &= 8.5 \cos^2 \phi - 0.28, \quad 0° \le \phi \le 90° \\ &= 9.5 \cos^2 \phi - 0.28, \quad 90° \le \phi \le 180° \end{aligned} \tag{1}$$

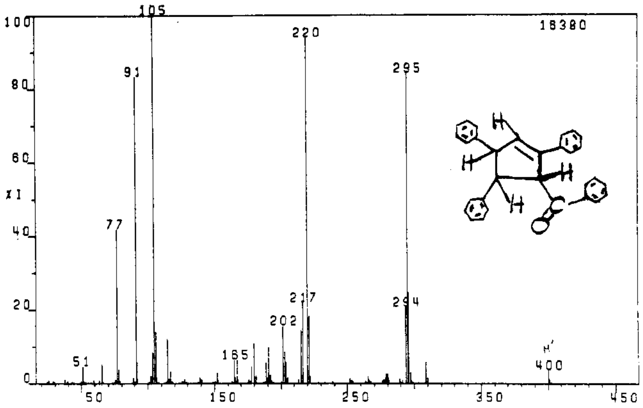
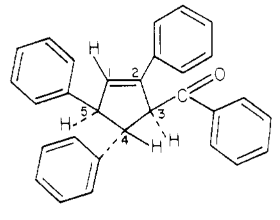


Figure 1. Mass spectrum of I.

Table I. ^{13}C Chemical Shifts[a]



Ia

entry	carbon	chemical shift	peak lines
1	C_3'	59.4	d
2	C_5'	61.4	d
3	C_4'	62.5	d

[a] Run in $CDCl_3$ at 25.16 MHz.

Table II. Diheαral Angles for I

	J(obsd), Hz	ϕ(calcd), deg	configuration
$H_{5'4'}$	5.6	144	trans
$H_{4'3'}$	5.9	147	trans
$H_{1'5}$	2.6	56	
$H_{5'3'}$	2.0	60	
$H_{1'3'}$	1.6	64	
	J(calcd), Hz	**ϕ(measured), deg**	
$H_{5'4'}$	4.1	134	trans
$H_{4'3'}$	4.4	136	trans

Studies of the conformation of substituted cyclopentanes and cyclopentenes using ^1H NMR spectra have been reported in the literature.[2-6] In five-membered rings which cannot deviate appreciably from plainarity, it was found that Karplus' rule applied (J_{cis} was always appreciably larger than J_{trans}) and that a double bond in the ring did not appear to appreciably influence the magnitude of the vicinal coupling constants in the saturated fragments in

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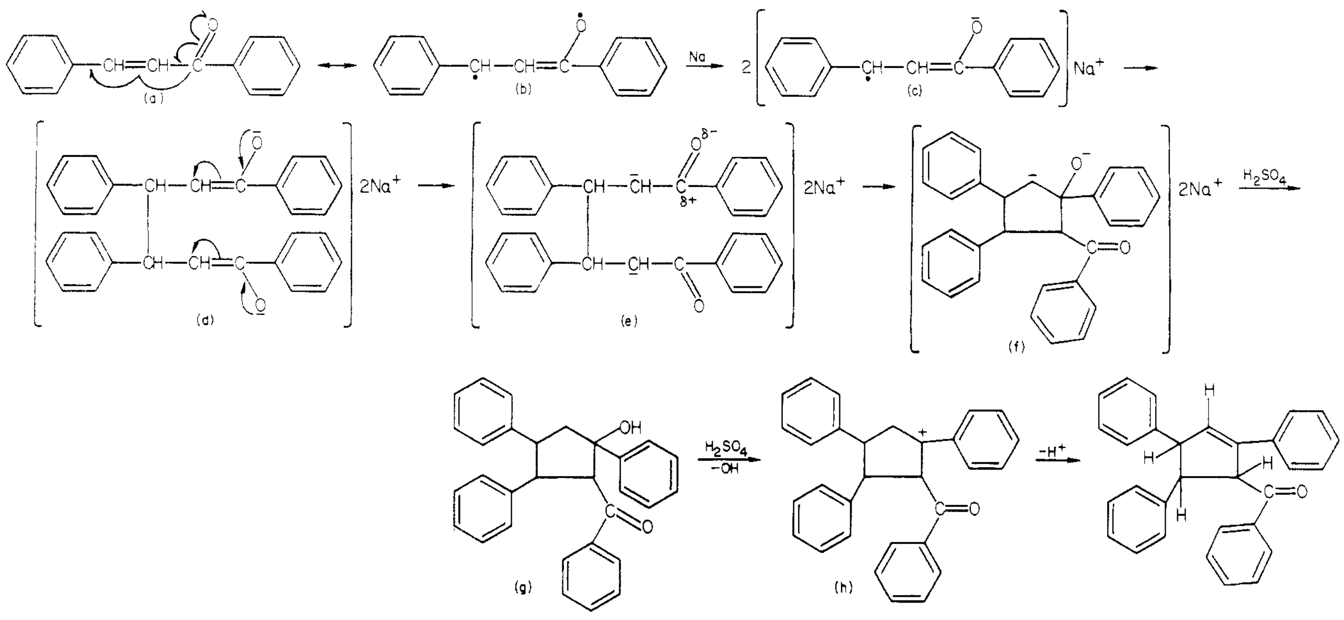
Scheme I



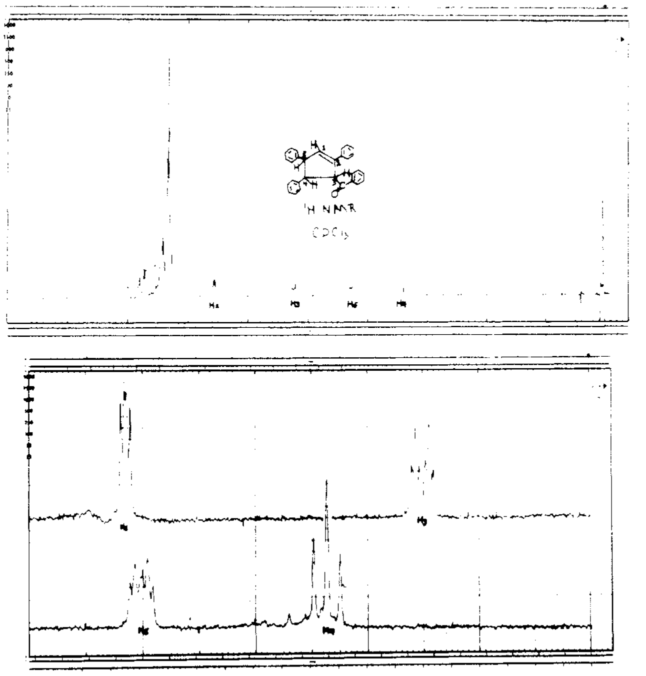


Figure 2. Proton NMR spectrum and signal assignments for I.

the ring. Coupling constants and dihedral angles shown in Table II were determined; dihedral angles were calculated by using Karplus' method. The dihedral angles for vicinal coupling constants in I were compared with results obtained from ^1H NMR studies of rigid and semirigid substituted cyclopentanes and cyclopentenes reported in the literature, relating coupling constants and dihedral angles to the configuration of vicinal hydrogens.[3,6] The assignment of the conformation of structure I rested on the configuration of the central ring hydrogens H_5', H_4', and H_3', since H_1' and phenyl at C_2 should be fixed in the plane of the ring. It has been shown that the range of cis coupling constants in rigid and semirigid five-membered rings was 7.7–8.5 Hz and that the range for trans coupling constants under similar conditions was 2.1–6.5 Hz.[3,5,6] The coupling constants observed for I were 5.6 Hz for H_5',H_4' and 5.9 Hz for H_4', H_3', with dihedral angles of 144° and 147°, respectively. These values were found to be in good agreement with coupling constants and dihedral angles for five-membered-ring hydrogens assigned the trans configuration reported in the literature.[3,5,6] Dihedral angles were calculated with Dreiding models. These results are shown in Table II. Signal assignments for I are given in Table III.

Table III. Signal Assignments for I

	peak	δ	proton	resolved lines
$J_{1'3'} = 1.64$; $J_{1'5'} = 2.59$	4	6.486	1	4
$J_{3'4'} = 5.93$; $J_{3'1'} = 1.64$; $J_{3'5'}$	3	5.485	3	6
$J_{5'4'} = 5.65$; $J_{5'1'} = 2.59$; $J_{5'3'} = 2$	2	4.222	5	6
$J_{4'5'} = 5.65$; $J_{4'3'} = 5.93$	1	3.400	4	3

On the basis of the evidence obtained for structure I and the comparison of this evidence with evidence for the assignment of trans configurations for vicinal hydrogens in substituted rigid and semirigid five-membered rings reported in the literature,[3,5,6] we assigned the trans configuration to hydrogens H_5', and H_4' and H_4' and H_3' in I to give the conformation Ia where only potential buckling of the ring would be expected to occur at C_4. As the compound contains chiral centers, the pure compound would be expected to be a recemic modification.

Experimental Section

General Procedures. ^1H NMR spectra were recorded with an XL-100 spectrometer at Jackson State University, Jackson, MI, and reported in parts per million ($CDCl_3$) downfield from tetramethylsilane. Mass spectra were recorded with a Varian MAT CH_5-DF double-focusing mass spectrometer coupled to a VG data system at Burroughs Welcome. IR spectra were recorded with a Beckman IR-10 infrared spectrometer. ^{13}C analyses were performed in the spectroscopy laboratory at the University of North Carolina, Chapel Hill. Carbon and hydrogen analyses were performed by Micro Tech Laboratories, Skokie, IL. Melting points were taken on a Thomas-Hoover melting point apparatus. Chemicals were from Aldrich Chemical Company.

2,4,5-Triphenyl-3-benzoylcyclopent-1-ene (Ia). To 12.5 g (0.54 mol) of finely divided sodium in (250 mL) of refluxing dry benzene was added with stirring 52.15 g (0.25 mol) of chalone dissolved in 100 mL of dry benzene at a very slow rate, 2 h. The reaction was run in a three-neck flask with a sealed stirrer and a condenser protected with a $CaCl_2$ tube. The excess sodium was destroyed with 37% H_2SO_4. The benzene layer was separated from the aqueous layer, extracted with four 50-mL portions of 20% Na_2CO_3 solution, washed with two 50-mL portions of H_2O, and dried over anhydrous Na_2SO_4. The filtered benzene solution was evaporated under reduced pressure. The resulting yellow slurry was heated to boiling in 150 mL of acetone, filtered, and allowed to cool, and placed in the refrigerator. Crystals formed. After standing 3 or 4 days, the crystals were collected, 8.1 g (16%). A pure sample from 2-ethoxyethanol melted at 181–182 °C; exact mass calcd for $C_{30}H_{24}O$ *m/e* 400.1821, found *m/e* 400.1826. Anal. Calcd for $C_{30}H_{24}O$: C, 89.96; H, 6.04. Found: C, 89.70; H, 5.85.

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Endo Selectivity of Allenic Esters in Diels–Alder Additions to Cyclopentadiene. The Effect of Added Aluminum Trichloride and an Approach to Dehydrosantalene Analogues[1]

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In contrast to the massive research effort that has gone into the study of Diels–Alder reactions with acrylic and acetylenic esters, surprisingly little use has been made of allenic esters as dienophiles.[2] Occassionally, the literature has also been confusing with respect to configurational assignments.[2c] In the course of some model experiments for the synthesis of santalenes, we have investigated Diels–Alder additions of cyclopentadiene to a number of allenic esters. Our results are summarized in Table I.

The endo and exo configurations of the cycloadducts were assigned by ^1H NMR and GC retention times. For instance, the endo 2-H proton (R = H) in exo adduct **1x** appeared as a multiplet centered at 2.83 ppm, i.e., 0.63 ppm upfield from the exo 2-H proton in endo adduct **1n** (anisotropic shielding by the 5,6 double bond in **1x**). Consistently, the *endo*-methoxy signal in endo adducts **3bn** appeared upfield from the signal of the exo epimer **3bx**. On GC (glass capillary column) the endo epimers **2bn**, **3bn**, and **4n** had longer retention times than the corresponding exo epimers. An elegant chemical proof of configurations **3an** and **3ax** has been described by Barnett and McKenna.[2f]

Clearly, the α-alkylated allenic esters **3b** and **4** as well as allenic acid **3a**[2f,g] violate the Alder endo rule, formation of the exo adduct being preferred. This behavior is reminiscent of the special position held by dienophiles of the methacrylic ester type, which also favor exo addition (exo with respect to the ester grouping).[3] The decreased endo selectivity of methacrylic ester has recently been ascribed to decreased reactivity of the dienophile.[3a]

Addition of $AlCl_3$ to esters **2b** and **3b** increased the reaction rate, the reaction temperature being lowered from that of boiling benzene to room temperature. Simultaneously, the proportion of endo adduct increased: for **2b** from an endo/exo ratio of 64:36 to 86:14. For the less reactive dienophile **3b**, the validity of the endo rule was restored: from an endo/exo ratio of 40:60 in the uncatalyzed reaction to 76:24 in the presence of $AlCl_3$. Since the reactivity and endo selectivity of allenic esters with long α side chains R (cf. **4** and **5**) are comparatively poor, the sequential introduction of the alkyl group R, as described by Bertrand,[2k] may be used if R is to be exo.

In summary, endo selectivity of allenic dienophiles appears to depend on reactivity. While Lewis acids have been used successfully in many Diels–Alder reactions[3,4] as well as ene reactions,[5] their utility for activating allenic esters seems to have been overlooked.[2] As with more conventional dienophiles, Lewis acid catalysis lowers the reaction temperature and increases the yield and endo selectivity.

Experimental Section

Preparation of Allenic Esters. 2,3-Butadienoic acid (**1**) was prepared according to Jones et al.[2a] Its ethyl ester (**2b**) was obtained conveniently via the modified Wittig reaction as described by Hansen.[6] 2-Alkyl-2,3-butadienoic esters **3b** and **4** were prepared by the method of Taylor, Robey, and McKillop.[7] The procedure may be exemplified by the synthesis of **5** which was previously unknown.

Methyl 2-Ethenylidene-6-methylhept-5-enoate (5). (i) 4-Methyl-3-pentenyl Iodide (6).[8] Cyclopropyldimethylmethanol (50 g, 0.5 mol) was dissolved in absolute ether (500 mL), and zinc iodide (160g, 0.5 mol) was added in portions with stirring. After 1 h at room temperature, the mixture was refluxed for 0.5 h and suction filtered. The filtrate was washed with water, dried (Na_2SO_4), and freed from ether to leave an oil which was distilled, giving 4-methyl-3-pentenyl iodide (100 g, ca. 95%). In our hands, the fragmentation with ZnI_2 proceeded more smoothly and gave fewer byproducts (GC) than the reaction with MgI_2.[8]

(ii) Alkylation of Acetoacetic Ester. Ethyl acetoacetate (5.25 g, 40 mmol) in 1,2-dimethoxyethane (25 mL) was treated with several portions of sodium hydride (50%; 1.90 g, 40 mmol). After

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