filtrate was concentrated to give 45.7 g (HPLC purity 96%; yield 91%) (HPLC parameters: column, Waters μBondapak; mobile phase, MeOH–0.05 M aqueous monobasic potassium phosphate (6:4); flow rate, 1 mL/min; detection, 254 nm) of **10** as an off-white solid: mp 116–119 °C; NMR (400 MHz, CD_3OD) δ 2.0–2.2 (m, 2 H), 2.27 (s, 3 H), 2.3–2.6 (m, 4 H), 2.6–3.0 (m, 4 H) 3.3–3.6 (m, 2 H), 7.11 (d, 1 H, J = 8.17 Hz, H_{10}), 7.16 (dd, 1 H, J = 8.14, 2.07 Hz, H_9), 7.21 (d, 1 H, J = 2.07 Hz, H_7), 7.24 (dd, 1 H, J = 7.70, 4.92 Hz, H_3), 7.64 (dd, 1 H, J = 7.70, 1.55 Hz, H_4), 8.31 (dd, 1 H, J = 4.95, 1.55 Hz, H_2); mass spectrum, m/e (rel intensity) 327 $(M + 3)^+$ (28), 325 $(M + 1)^+$ (100). Anal. Calcd for $C_{20}H_{21}N_2Cl$: C, 73.94; H, 6.52; N, 8.63; Cl, 10.92. Found: C, 73.88; H, 6.48; N, 8.69; Cl, 10.80.

8-Chloro-11-(1-methyl-4-piperidinyl)-11*H*-benzo[5,6]cyclohepta[1,2-*b*]pyridine (11). A solution of **9** (6.04 g) in 120 g of polyphosphoric acid was heated at 190 °C for 8 h. The reaction mixture was poured into ice–water and adjusted to pH 9 with 50% aqueous sodium hydroxide. The aqueous solution was extracted with ethyl acetate, and the combined organic extracts were washed with brine and concentrated to a residue. Column chromatography (silica gel; toluene–CH_2Cl_2–MeOH–MeOH saturated with gaseous ammonia, 16:4:0.75:0.25) yielded 2.52 g of **10** (44%) and 0.85 g of **11**: mp 151–153 °C; NMR (200 MHz, $CDCl_3$) δ 0.8–0.9 (m, 1 H), 1.0–1.1 (m, 1 H), 1.1–1.4 (m, 2 H), 1.66 (m, 2 H) 1.8–2.0 (m, 1 H), 2.18 (s, 3 H), 2.6–2.8 (m, 2 H), 4.11 (d, 1 H, J = 8 Hz), 6.90 (dd, 2 H, J = 19, 12 Hz), 7.2–7.4 (m, 4 H), 7.67 (dd, 1 H, J = 7, 2 Hz), 8.55 (dd, 1 H, J = 5, 2 Hz); mass spectrum, m/e (rel intensity) 325 $(M + 1)^+$ (19). Anal. Calcd for $C_{20}H_{21}N_2Cl$: C, 73.94; H, 6.52; N, 8.63; Cl, 10.92. Found: C, 74.62; H, 6.53; N, 8.33; Cl, 10.51.

8-Chloro-7-(methylsulfonyl)-5-(4′-*N*-methylpiperidylidene)-4-aza-10,11-dihydro-5*H*-dibenzo[*a*,*d*]cycloheptene (12). Boron trifluoride (118 g, 1.74 mol) was added over 15 min to a solution of 40.0 g (0.117 mol) of **9** in 250 mL of methanesulfonic acid at 0–5 °C in a Teflon pressure reaction vessel. This was then sealed, and the reaction mixture was heated at 120 °C for 4 h. The reaction mixture was cooled, and the solution was poured into ice–water and adjusted to pH 10 with 50% aqueous sodium hydroxide. The product was extracted into methylene chloride, which was concentrated to a residue. The residue was triturated with hot hexanes and clarified by filtration. The filtrate was concentrated to afford 32.6 g of a crude mixture of products. Purification by chromatography (silica gel; 16:4:0.75:0.25 toluene–methylene chloride–methanol saturated with gaseous ammonia) gave 20 g of **10** and 0.3 g of **12**. NMR (200 MHz, $CDCl_3$): δ 2.2–2.6 (m, 6 H); 2.33 (s, 3 H), 2.7–3.0 (m, 4 H), 3.22 (s, 3 H), 3.4–3.6 (m, 2 H), 7.13 (dd, 1 H, J = 7, 5 Hz), 7.3–7.4 (m, 1 H), 7.49 (d, 1 H, J = 9 Hz), 8.02 (s, 1 H), 8.44 (d, 1 H, J = 5 Hz). Mass spectrum: m/e (rel intensity) 403 $(M + 1)^+$ (11).

8-Chloro-6,11-dihydro-11-[1-(ethoxycarbonyl)-4-piperidylidene]-5*H*-benzo[5,6]cyclohepta[1,2-*b*]pyridine (1). Ethyl chloroformate (40.4 mL, 45.9 g, 0.423 mol) was added slowly to a hot (~80 °C) solution of **10** (45.7 g, 0.141 mol) in 320 mL of toluene. Following complete addition, the temperature was maintained at 80 °C for 1 h. The reaction mixture was cooled to ambient temperature and the toluene solution washed with water which was adjusted to pH 10 with aqueous sodium hydroxide. The organic layer was concentrated to a residue, which was dissolved in hot acetonitrile and decolorized with charcoal. The solution was concentrated to a crystalline slurry, which was cooled (5 °C). Product **1** was isolated by filtration, yielding 42.4 g: mp 134.5–136 °C (lit.[9] mp 134–136 °C); NMR (400 MHz, CD_3OD) δ 1.25 (t, 3 H, J = 8 Hz), 2.3–2.4 (m, 3 H), 2.4–2.5 (m, 1 H), 2.7–2.9 (m, 2 H), 3.1–3.2 (m, 2 H), 3.3–3.4 (m, 2 H), 3.81 (br s, 2 H), 4.13 (q, 2 H, J = 8 Hz), 7.12 (d, 1 H, J = 8.11 Hz, H_{10}), 7.17 (dd, 1 H, J = 8.11, 2.17 Hz, H_9), 7.23 (d, 1 H, J = 2.13 Hz, H_7), 2.26 (dd, 1 H, J = 7.71, 4.90, H_4), 7.65 (dd, 1 H, J = 7.73, 1.65 H_4), 8.32 (dd, 1 H, J = 4.88, 1.15 Hz, H_2); mass spectrum, m/e (rel intensity) 385 $(M + 3)^+$ (35), 383 $(M + 1)^+$ (100). Anal. Calcd for $C_{22}H_{23}N_2ClO_2$: C, 69.00; H, 6.05; N, 7.32; Cl, 9.26. Found: C, 69.37; H, 6.09; N, 7.35; Cl, 9.37.

Acknowledgment. We thank the staff of the Physical–Analytical Departments for spectra and microanalyses and Professor Ronald Breslow for helpful discussions.

Registry No. **1**, 79794-75-5; **4**, 32998-95-1; **5**, 107285-30-3; **6**, 119770-59-1; **7**, 31255-57-9; **9**, 119770-60-4; **10**, 38092-89-6; **11**, 119770-61-5; **12**, 119770-62-6; 2-cyano-3-methylpyridine, 20970-75-6; *m*-chlorobenzyl chloride, 620-20-2; (*N*-methylpiperidyl)-magnesium chloride, 63463-36-5.

Benzylidene Isophorone Dimer and Its Photoproduct

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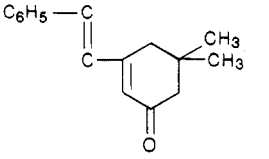
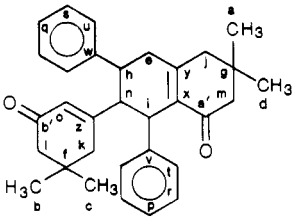
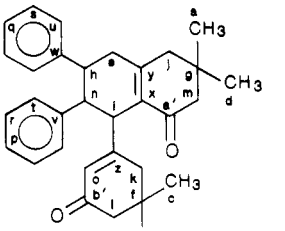
Condensation of benzaldehyde with isophorone by aqueous sodium hydroxide gives benzylidene isophorone,



mp 73.5 °C, and its dimer, mp 198–9 °C. On the basis of IR, UV, mass, and NMR spectra, Kabas[1] postulated either structure **1** or structure **2** for the dimer. We irradiated

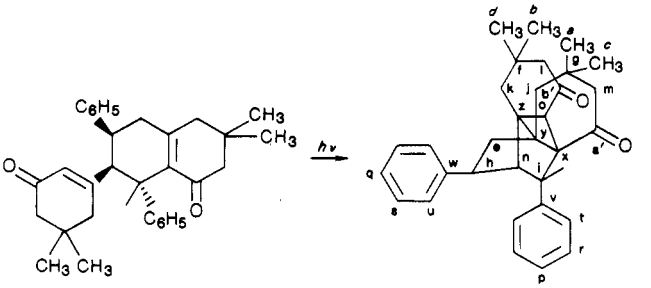


1



2

the dimer in acetone and produced a new compound mp 239–41 °C. 2D NMR and crystal structure analysis showed that the dimer had structure **1**, and the photoproduct structure **3**, derived from **1** by intramolecular 2 + 2 cycloaddition.



Although crystals of **3** tended to fall apart, appeared to be composed of several layers, and diffracted only moderately well, the data collected were sufficient to determine

(1) Kabas, G. *Tetrahedron* **1966**, *22*, 1213.

0022-3263/89/1954-2244$01.50/0

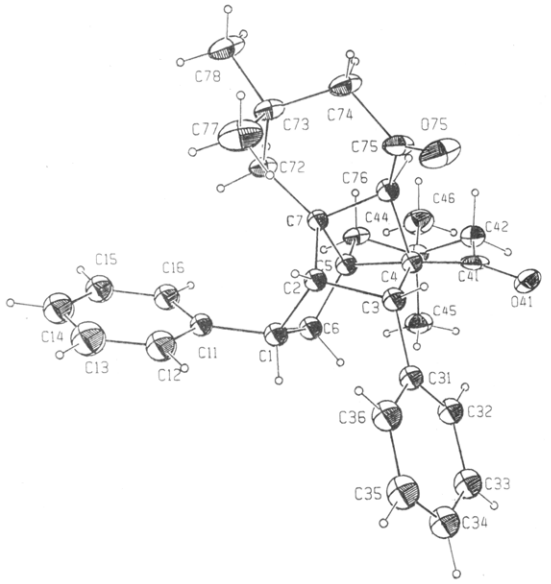


Figure 1. Molecular structure of **3**.

the structure shown in Figure 1. Figure 1 shows that the norbornane ring is twisted; bonds C1–C6 and C3–C4 are not parallel, indicating quite a bit of ring strain. The position of the phenyl ring at C3 may be the result of interaction between hydrogens at C36 and C1. The phenyl rings in the dimer probably were trans for them to give the positions in Figure 1. The carbonyl groups, almost parallel, come out of the plane of the photoadduct, as seen from the Corey–Pauling–Kolton models on the computer screen.[2]

Several aspects of the aldehyde–isophorone condensations are not clear. Of the seven studied by Kabas, only three formed dimers, those derived from benzaldehyde, 4-methoxybenzaldehyde, and furfural. Benzaldehyde gave dimer in good yield; the yields from the other two were low, about 10%, and were recovered unchanged after prolonged irradiation. We found that 4-fluorobenzaldehyde with isophorone gave 4-fluorobenzylidene isophorone mp 75–6 °C, 80%, but no dimer. Dimer forms evidently by two successive Michael additions as stated by Kabas, but the nature of the steric and electronic requirements remain to be investigated.

Experimental Section

The dimer of benzylidene isophorone was prepared by a modification of the method of Ensor and Wilson.[3] To a stirred mixture of 65 mL, 0.434 mol, of isophorone, 44 mL (0.434 mol) of benzaldehyde, and 200 mL of 95% ethanol at 10–15 °C was added 20 mL of 50% aqueous sodium hydroxide dropwise. The mixture was stirred at 25 °C for 48 h and then filtered. The solid on the filter was washed with 10% aqueous methanol, followed by two ether washes. The dimer, 41 g, 43% yield, remained on the filter. Crystallized from toluene, it melted at 198 °C. Workup of the filtrates gave 41.7 g, 43% yield, of benzylidene isophorone, bp 155–60 °C, mp 76 °C.

A solution of 4.52 g, 10 mmol, of dimer and 0.1 g of benzophenone in 200 mL of acetone was irradiated in a Pyrex Erlenmeyer flask over two 15-W black light fluorescent bulbs for 5 days. The solution was evaporated to 15 mL, 10 mL of ether was added, and the mixture was chilled at 0 °C for 1 h. Filtration gave 1.81 g, 40% yield, of white photoproduct, melting at 239–241 °C from toluene. Anal. Calcd for $C_{32}H_{36}O_2$: C, 85.0; H, 8.0. Found: C, 84.8; H, 8.1.

(2) A crystallographic summary, tables of final atomic coordinates, anisotropic thermal parameters, bond lengths and angles, and hydrogen final atomic coordinates are available as supplementary material.
(3) Ensor, G. R.; Wilson, N. *J. Chem. Soc.* **1956**, 4068.

Table I. 2D NMR Data for Structure 1, Dimer

carbon	$^{13}C\delta_{TMS}$	type	^{13}C–^{13}C connectivity	^{13}C–^{1}H[a] connectivity	^{1}H–^{1}H connectivity
				(ppm)	
a	27.5	CH_3	g	1.04	
b	27.7	CH_3	f	0.67	
c	28.3	CH_3	f	0.79	
d	29.3	CH_3	g	1.08	
e	32.5	CH_2	h, *y*[b]	2.50	
f	32.8	C_q	b, c, k, l		
g	33.0	C_q	a, d, j, m		
h	35.9	CH	e, n, *w*	3.2	2.5, 2.6, 2.4
i	43.4	CH	n, *v*, *x*	4.1	
j	45.3	CH_2	g, *y*	2.5	2.5, 2.6, 3.2
k	46.1	CH_2	f, *z*	1.55	
l	50.5	CH_2	f, *b′*	2.0	
m	51.5	CH_2	g, *a′*	2.28	
n	54.8	CH	h, i, *z*	2.6	12.6, 3.2
o	125.5	=CH		5.6	5.6, 1.8, 1.3
p	126.2	=CH			
q	126.5	=CH			
r	127.7	=CH			
s	127.4	=CH			
t	128.1	=CH			
u	128.2	=CH			
v	144.4	$=C_q$			
w	141.1	$=C_q$			
x	131.0	$=C_q$			
y	155.1	$=C_q$			
z	163.4	$=C_q$			
a′	197.1	C=O			
b′	199.4	C=O			

[a] Proton chemical shifts confirmed by HETCOR experiment. [b] Italicized = calculated from correlation folded into SCCM spectra.

NMR spectra were acquired at 300 MHz on a Nicolet NT-300 spectrometer. Spectra were obtained with 90° pulse (12 μs). The spectral width and number of data points were adjusted to give a digital resolution of 0.2 Hz. Spin–lattice relaxation times were obtained by using an inversion–recovery sequence and standard Nicolet software on a Nicolet 1280 computer.

The key to NMR determination of dimer structure is the unequivocal assignment of the substituent on carbon "i" of the structures. In order to do this, the ^{1}H–^{1}H correlation (COSY)[4] experiment, the ^{1}H–^{13}C heteronuclear correlation (HETCOR)[5] experiment, and the ^{13}C–^{13}C correlation (INADEQUATE)[6] experiment were recorded. We were able to make unequivocal chemical shift assignments for the carbons based upon the 2D data and establish that the spectra are consistent with the proposed structure of isomer **1**. The chemical shift assignments, carbon–carbon connectivities, carbon–proton connectivities, and proton–proton connectivities are listed in Table I. The assignment of structure to that of isomer **1** is based primarily on detailed analysis of the INADEQUATE spectrum. The correlations among the aliphatic carbons and the aromatic and olefinic carbons are based on cross peaks that have been aliased or folded back into the spectrum at least two times. The corresponding connectivities have been calculated mathematically based upon the position of the folded peak. This calculation procedure is subject to some error, but we feel confident that the assignments are correct.

The rationale for our assignments of the dimer are as follows.

1. The APT[7] spectra clearly shows that there are three aliphatic methine carbons located at 35.9, 43.4, and 54.8 ppm; four methyl carbons located at 27.5, 27.7, 28.3, and 29.2 ppm; five methylene carbons located at 32.5, 45.3, 46.1, 50.5, and 51.5 ppm; and two quaternary carbons at 32.8 and 33.0 ppm. Further, the APT spectrum shows that there are seven =CH carbons at 125.5, 126.2, 126.5, 127.1, 127.4, 128.1, and 128.2 ppm; five quaternary =C

(4) Bax, A.; Freeman, R.; Morris, G. A. *J. Magn. Reson.* **1981**, *42*, 169.
(5) (a) Bax, A.; Morris, G. A. *J. Magn. Reson.* **1981**, *42*, 501. (b) Bax, A. *Ibid.* **1983**, *53*, 512.
(6) Mareci, T. H.; Freeman, R. *J. Magn. Reson.* **1982**, *48*, 158.
(7) Patt, S. L.; Shoolery, J. N. *J. Magn. Reson.* **1982**, *46*, 535–539.

Table II. Photoproduct NMR Data

carbon	X-ray carbon no.	type	$^{13}C\delta_{TMS}$, ppm	$^{1}H\delta_{TMS}$,[a] ppm	^{13}C–^{13}C[b] connectivity	^{1}H–^{1}H[c] connectivity
a	C45	CH_3	28.9	1.21	g	
b	C77	CH_3	31.1	0.86	f	
c	C46	CH_3	32.6	1.22	g	
d	C78	CH_3	33.8	0.92	f	
e	C6	CH_2	36.5	2.0, 2.23	h, y	h,
f	C73	C_q	38.8		b, d, k, l	
g	C43	C_q	37.3		a, c, m, j	
h	C1	CH	45.1	2.77, 2.80	e, n, w	e, n
i	C3	CH	42.9	4.40, 4.42	v, n, x	n
j	C44	CH_2	39.9	1.77, 1.82, 2.28, 2.33	g, y	
k	C72	CH_2	37.3	0.96, 1.0, 1.44, 1.46	f, z	
l	C74	CH_2	54.8	2.16, 2.09	f, b′	
m	C42	CH_2	53.2	2.47, 2.42	g, a′	
n	C2	CH	56.7	3.25, 3.22	h, i, z	i, h
o	C76	CH	57.0	2.89	b′, x, z	
p	C34	=CH	125.7	7.0	r	r
q	C14	=CH	125.6	7.0	s	s
r	C33,35	=CH	127.0	7.0	p, t	p, t
s	C13,15	=CH	127.7	7.4	u, q	u, q
t	C32,36	=CH	128.6	7.4	v, r	r
u	C12,16	$=C_q$	128.0		w, s	s
v	C31	C_q	139.3		i, t	
w	C11	C_q	143.5		h, u	
x	C4	C_q	62.5		a′, i, y, o	
y	C5	C_q	62.7		x, z, j, e	
z	C7	C_q	61.6		o, y, n, k	
a′	C41	C=O	206.9			
b′	C75	C=O	207.8			

[a] Chemical Shift confirmed by HETCOR experiment. [b] Connectivities confirmed by INADEQUATE experiment. [c] Connectivities confirmed by COSY experiment.

carbons at 131.0, 141.1, 144.4, 155.1, and 163.4 ppm; and two carbonyl carbons at 197.1 and 199.3 ppm.

2. The HETCOR spectrum clearly shows that the methyl protons that resonate at 0.67, 0.79, 1.04, and 1.08 ppm in the proton spectrum are attached to the carbons that resonate at 27.7, 28.3, 27.5, and 29.2 ppm in the carbon spectrum. The methylene protons are all indicating some degree of nonequivalence in so far as they all are represented as quartets with various coupling constants. These multiplets are attached to their corresponding carbon in the following order: the quartets centered at about 1.6, 2.0, 2.3, and 2.4 ppm in the proton spectrum are attached to the carbons that resonate at 46.1, 50.5, 51.5, and 45.3 ppm, respectively, in the carbon spectrum and have been assigned as carbons k, l, m, and j based on our analysis of model isophorone type compounds; the multiplet centered at about 2.6 ppm in the proton spectrum is attached to the carbon that resonates at 32.5 ppm in the carbon spectrum and therefore is assigned to carbon e since it is the only remaining methylene carbon in the spectrum.

There are only three methine protons in the proposed structure and they resonate at 2.7, 3.2, and 4.1 ppm respectively. These methine resonances are attached to the carbons which resonate at 54.8, 35.9, and 43.4 ppm in the carbon spectrum. The olefinic proton that resonates at 5.6 ppm is attached to the carbon that resonates at 125.5 ppm. This evidence enables us to assign the resonance at 125.5 ppm to the carbon labeled "o" in the structures given above. The remaining aromatic protons that resonate around 7.2 ppm also clearly show correlating resonances to the carbons near 127 ppm, which is the typical resonance position of aromatic carbons attached to hydrogen.

3. The COSY spectrum shows the coupling patterns of the protons on adjacent carbons. The coupling patterns for the three methine protons on carbons h, i, and n are critical for the understanding of the analysis. The proton on carbon h will be coupled to the two nonequivalent methylene protons on carbon e and to the proton on carbon n, which will result in a more complex coupling pattern. The methine proton on carbon n will be coupled to the methine protons on carbons h and i, while the methine proton on carbon i will only be coupled to the proton an carbon n and not to the one on carbon h.

The only methine proton resonance that shows evidence of the more complex coupling pattern mentioned above is the one at about 3.2 ppm. The COSY spectrum also clearly shows that this resonance is coupled to the complex multiplet centered around 2.5 ppm, which we have assigned to carbon e from the HETCOR data.

4. The detailed analysis of the INADEQUATE spectrum is the key to the entire assignment. This experiment allows us to observe the carbon to carbon couplings between adjacent carbon atoms. Therefore, it gives a roadmap of the molecule to connect the carbons to each other and reconstruct the molecule carbon by carbon. All of the connections between the various carbons in the molecule are listed in the attached table. The key to the assignment is to determine if carbons n and i are attached to an aromatic ring or to the olefinic carbon of the free isophorone ring. Carbons i and n clearly show the following couplings: carbon i is attached to carbon n and two other carbons, which have been aliased back into the spectrum and calculated to be at 131.0 and 144.4 ppm; carbon n is attached to carbons i and h and one aliased resonance, which calculates to be at 163.4 ppm. The typical resonance position for the quaternary carbon of a monosubstituted aromatic ring is about 145 ppm. Therefore, we can assign carbon i to be attached to the aromatic ring carbon v at 144.4 ppm and to the internal olefinic ring carbon x at 131.0 ppm. Carbon n is clearly attached to the resonance at 163.4 ppm, which is the typical resonance position of the substituted olefinic ring carbon of a cyclohexenone ring system and is assigned to carbon z. This evidence clearly establishes that the spectrum is consistent with the proposed structure for isomer **1** and not with isomer **2**.

NMR Analysis of the Photoproduct of Benzylidene Isophorone Dimer. The definitive assignment and structure confirmation evidence are found in the analysis of the INADEQUATE spectrum. The INADEQUATE data contains the carbon–carbon connectivity data used to reconstruct the molecule via the NMR information. The assignment of the C4 ring carbons and the CH carbons unequivocally confirms the structure as that suggested by the X-ray data. The proposed structure is shown in Figure 1. The NMR chemical shift assignments are listed in Table II.

The rationale for our assignment of the photoadduct are as follows.

1. The assignments of the CH carbons h, n, and i of the C7 ring are confirmed by these facts: (a) Only carbon h is connected to a CH_2 carbon and an aromatic quaternary carbon, and the CH peak at 45.1 ppm clearly shows that connection as well as the connection to the CH at 56.7 ppm. (b) This CH peak at 56.7 ppm

has to be carbon n because it is the only CH carbon that clearly shows a connection to two other CH carbons that are also connected to aromatic ring carbons. (c) Carbon i is then confirmed by the above connections and the connection to the quaternary carbon x at 62.5 ppm.

2. The assignments of the C4 ring carbons x, y, z, and o are confirmed by these facts: (a) The peak at 57.0 ppm is assigned to the CH carbon o because it shows no coupling in the proton spectrum and only couplings to quaternary carbons x and z at 62.5 and 61.6 ppm in the carbon 13 spectrum. (b) The peak 62.7 ppm is assigned to the quaternary carbon y because it is the only quaternary carbon that shows connections to two CH_2's (j and e) and another quaternary carbon z. (c) The peak at 61.6 ppm is assigned to the quaternary carbon z because it shows connections to the two CH carbons n and o at 56.7 and 57.0 ppm. (d) The peak at 62.5 ppm is assigned to the quaternary carbon x because it is the only quaternary carbon to show coupling to a CH carbon that is also coupled to an aromatic ring carbon i at 42.9 ppm.

We also see an interesting proton coupling situation in the COSY spectrum for the CH carbons on the C7 ring. The formation of the C4 ring in this molecule locks the CH carbons h, n, and i into a configuration that results in the protons on carbons n and i being in the eclipsed position and therefore shows a strong coupling, while the dihedral angle between the protons on carbons h and n is locked at 90° and shows zero coupling.

Acknowledgment. We are indebted greatly to Kurt L. Loening of Chemical Abstracts who has suggested these names for the photoproduct **3**: (6α,7α,8β)-7-(5,5-dimethyl-3-oxo-1-cyclohexen-1-yl)-3,4,5,6,7,8-hexahydro-3,3-dimethyl-6,8-diphenyl-1(2*H*)-naphthalenone and (1α,2β,3a*S**,7aα,7bβ,11a*R**,12*R**)-hexahydro-5,5,10,10-tetramethyl-2,12-diphenyl-9*H*-1,7a-methano-1*H*-cyclopenta[*e*]biphenylene-7,8(4*H*,7b*H*)-dione; and to one of the reviewers for his suggestions concerning the NMR analysis.

Registry No. 1, 119680-89-6; 3, 119680-90-9; isophorone, 78-59-1; benzaldehyde, 100-52-7.

Supplementary Material Available: Crystallographic summary, tables of final atomic coordinates, anisotropic thermal parameters, bond lengths and angles, and hydrogen final atomic coordinates (16 pages). Ordering information is given on any current masthead page.

Radical Reaction of Ketene Alkyl Trimethylsilyl Acetals with Divinyl Sulfone Promoted by Titanium(IV) Chloride

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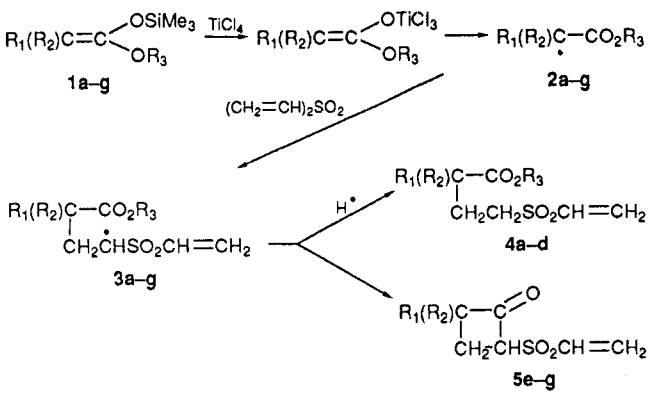
In the course of our studies on the synthetic utility of ketene alkyl trimethylsilyl acetals (**1**), we conducted the reaction of **1** with divinyl sulfone in the presence of titanium(IV) chloride. During the past decade several groups have demonstrated the synthetic utility of these ketene acetals.[1-4] Very recently we have accomplished the synthesis of α-nitroso esters, oximes of α-oxo esters, and malonic ester derivatives using **1**.[5,6] The usefulness of **1** would be more enhanced if they could be converted to new type of ester derivatives that are difficult to prepare by known methods. Thus, we have investigated the interaction between divinyl sulfone and the radical species derived from **1** and titanium(IV) chloride, because it was anticipated that the reaction would lead to the formation of either a simple addition product or a cyclobutanone derivative by subsequent cyclization.

Scheme I



a: R_1 = Me; R_2 = H; R_3 = Et
b: R_1 = Et; R_2 = H; R_3 = Et
c: R_1 = Pr; R_2 = H; R_3 = Me
d: R_1 = *i*-Pr; R_2 = H; R_3 = Et
e: R_1 = R_2 = Me; R_3 = Et
f: R_1 = Et; R_2 = Me; R_3 = Et
g: R_1 = R_2 = R_3 = Et

The reactions using several ketene alkyl trimethylsilyl acetals (**1a–g**) proceeded smoothly as anticipated, providing excellent yields of alkyl γ-(vinylsulfonyl)butyrate derivatives (**4a–d**) or 2-(vinylsulfonyl)cyclobutanone derivatives (**5e–g**) (Scheme I). The divergence in the formation of products, which is somewhat surprising, indicates that the reaction process is highly controlled by the number of alkyl substituents situated on the α-carbon of the starting acetals (**1a–g**). The products obtained have been characterized on the basis of spectral properties (IR, ^{1}H NMR, ^{13}C NMR, MS, and UV spectra), elemental analyses, chemical transformations, and further by comparison with reported data if available.

In a preliminary experiment, it was ascertained that divinyl sulfone shows no interaction with titanium(IV) chloride. The formation of radical species **2** from **1** and titanium(IV) chloride, followed by dimerization into alkyl succinate derivatives, is well documented.[7] In the present experiments, however, the reactions of divinyl sulfone with radical species **2** dominate over their dimerization and afford another intermediate, radical species **3**. It should be noted that, when both substituents (R_1 and R_2) of **3** are alkyl groups, **3** prefers cyclization to give the corresponding 2-(vinylsulfonyl)cyclobutanone derivatives (**5e–g**), and that when one of the above substituents is hydrogen, **3** abstracts a hydrogen radical to afford the corresponding alkyl γ-(vinylsulfonyl)butyrate derivatives (**4a–d**). Although the reason for this reactivity difference is not clear, it is thought that the steric requirements of two alkyl substituents of **3** cause the radical site and carbonyl group of **3** to approach each other and assist cyclization. The radical nature of reaction was further supported by experiments in which a small amount of hydroquinone or *p-tert*-butylpyrocatechol was added to the reaction mixture. In these cases, the yields of **4** and **5** were depressed to less

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