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SYNTHESIS AND PROPERTIES OF 1,2-BIS(TRIMETHYLSILYL)TRICYCLO[4.1.0.0^{2,7}]HEPT-4-EN-3-ONE. A NOVEL SUBSTITUTED TROPOVALENE

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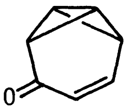
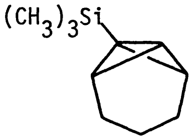
1,2-Bis(trimethylsilyl)tricyclo[4.1.0.0^{2,7}]hept-4-en-3-one (3) has been synthesized from 4-acetoxy-2-cyclopenten-1-one and bis(trimethylsilyl)acetylene. Photochemical and transition metal promoted isomerizations of 3 are described.

A valence isomer of tropone bearing bicyclo[1.1.0]butane system such as tricyclo[4.1.0.0^{2,7}]-hept-4-en-3-one (tropovalene) (1) is of interest not only because of its unique structure but also because of its reactivity. Recently 1 has been synthesized by Prinzbach et al. through the thermolysis of 7-quadricyclanone.1) Subsequently we have independently reported the alternative synthesis of 1 in good overall yield from 4-acetoxybicyclo[3.2.0]hept-6-en-2-one utilizing the oxa-di-π-methane rearrangement, and have suggested the existence of a substantial interaction between bicyclo[1.1.0]butane and enone moieties in 1.2)

Paquette et al.3) have recently demonstrated that trimethylsilyl substitution on tricyclo-[4.1.0.0^{2,7}]heptane (2) caused marked effect on their spectral characteristics and the ability of certain cationic intermediates to gain stabilization by means of hyperconjugative interaction with C-Si bond is the major determinant for the tricycloheptanes to undergo rearrangement.



1



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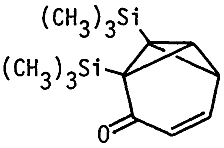
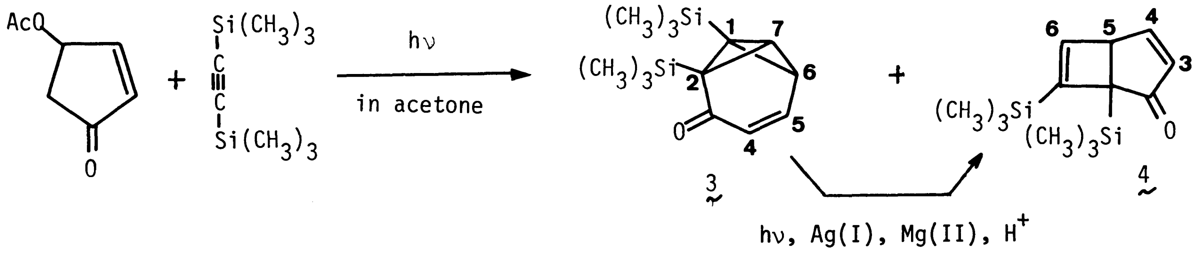


3

As a course of our study on chemical and phsical properties of valene- type isomers of cyclic conjugated systems,4) we report here a synthesis and some reactions of 1,2-bis(trimethylsilyl)-tropovalene (3).

Irradiation of a solution containing bis(trimethylsilyl)acetylene (5.07 g, 30 mmol) and 4-acetoxy-2-cyclopenten-1-one (0.125 g, 0.89 mmol) in 30 ml of acetone using a 450-W mercury lamp through a Pyrex filter for 4 h, followed by chromatographic workup on alumina (10% water) afforded 1,2-bis(trimethylsilyl)tropovalene (3), pale yellow needles of mp 49-50°C, and 1,7-bis(trimethylsilyl)bicyclo[3.2.0]hepta-3,6-dien-2-one (4), colorless liquid, IR ($CHCl_3$) 1675, 1255, 845 cm^{-1}, ^1H NMR (δ, $CDCl_3$) 0.06 (s, 9H), 0.07 (s, 9H), 3.76 (dd, 1H, H-5, $J_{4,5}$=3.0, $J_{5,6}$=1.0 Hz), 6.08 (d, 1H, H-3, $J_{3,4}$=5.5 Hz), 6.87 (d, 1H, H-6, $J_{5,6}$=1.0 Hz), 7.51 (dd, 1H, H-4, $J_{3,4}$=5.5, $J_{4,5}$=3.0 Hz), in 50 and 10% yields, respectively.



Spectral data of 3 are summarized in Tables 1 and 2, being compared with those of the parent tropovalene 1. As can be seen from these Tables, the characteristic features noted for 3 are (i) lower frequency shift of the carbonyl stretching band, (ii) increase in intensity of n-π* absorption band, (iii) slight downfield shift of the chemical shift of C_3, as compared with those values observed for 1. Although inspection of Dreiding models indicates that C_2-Si bond of 3 lies in a same plane with the carbonyl group, these results are explicable by the electron donating inductive effect of the trimethylsilyl group.[5)]

In contrast to the parent tropovalene 1 which is isomerized into tropone on irradiation, 3 was converted to 4 in 25% isolated yield when irradiated in acetone with a 100-W high pressure Hg lamp through a Pyrex filter. The same isomerization could be attained in quantitative yield through reaction of 3 with silver perchlorate, magnesium chloride, or *p*-toluenesulfonic acid. However, dramatic difference exists between silver perchlorate and rhodium dicarbonyl chloride dimer, $[Rh(CO)_2Cl]_2$. Thus, when 3 was treated with the rhodium catalyst in chloroform two tropone derivatives 5 and 6 in addition to 4 were obtained in 90% yield in a ratio of 9:1:1. The structure of 5 and 6 was rigorously established spectroscopically. The IR spectra of both 5 and 6 showed characteristic absorption at 1610, 1580, 1565 cm^{-1} and 1610, 1575 cm^{-1}, respectively. The ^1H NMR spectrum of 5 had absorptions at δ 7.47 (d, 1H, J=0.5 Hz) and 6.73-7.17 (m, 3H). The ^1H NMR spectrum of 6 showed symmetrical signals of an AA'BB' system at δ 6.85-7.30. NMR shift reagent allows for positive identification of the isomers.

While the reaction pathways leading to 4 and 5 are seemingly in line with those of other bicyclo[1.1.0]butane derivatives, the formation of 6 could not be explained in analogous fashion. Deuterium labeling was used to verify mechanistic assignment. When isomerization of the labeled

Table 1. Ir and Uv Spectral Data for **1** and **3**.

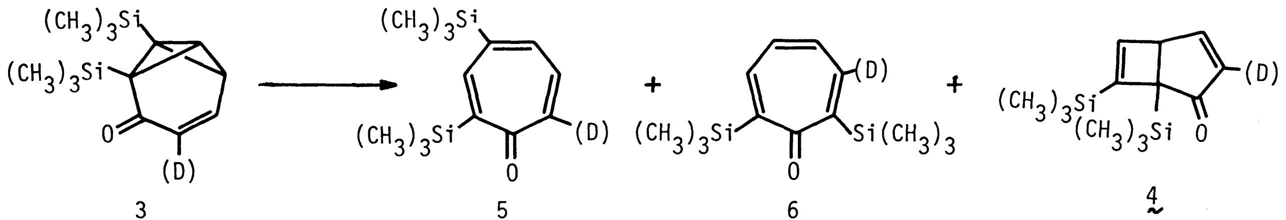
	1	**3**
IR $\nu_{C=O}$ ($CHCl_3$)	1670 cm^{-1}	1650 cm^{-1}
UV λ_{max} (EtOH)	253 nm (ε 4300), 341 (75)	283 (1750), 354 (97)
(hexane)		272 (1900), 368 (58)

Table 2. ^{13}C- and ^{1}H-Nmr Spectral Data for **1** and **3**.

	^{13}C-NMR[a)]		^{1}H-NMR[a)]			
	1	**3**	**1**		**3**	
Position	δ (J_{C-H})[b)]	δ (J_{C-H})[b)]	δ (mult.)	J (Hz)	δ (mult.)	J (Hz)
1	29.9 (215)	41.4	3.35 (t)	$J_{1,2}$=2.5		
2	49.7 (162)	51.3	2.72 (dtd)	$J_{2,7}$=2.5		
3	195.6	200.0		$J_{1,6}$=2.5		
4	121.8 (167)	120.0 (168)	5.46 (dt)	$J_{6,7}$=2.5	5.25 (dd)	$J_{6,7}$=2
5	149.5 (160)	149.0 (159)	7.00 (dd)	$J_{2,6}$=4.0	6.92 (dd)	$J_{5,6}$=5
6	33.3 (162)	37.8 (159)	2.55 (m)	$J_{5,6}$=4.0	2.14 (ddd)	$J_{4,6}$=1
7	29.9 (215)	42.7 (210)	3.35 (t)	$J_{4,5}$=10.0	3.56 (d)	$J_{4,5}$=10
$SiMe_3$		-1.29 (120)			0.07 (s)	
		0.00 (120)			0.15 (s)	

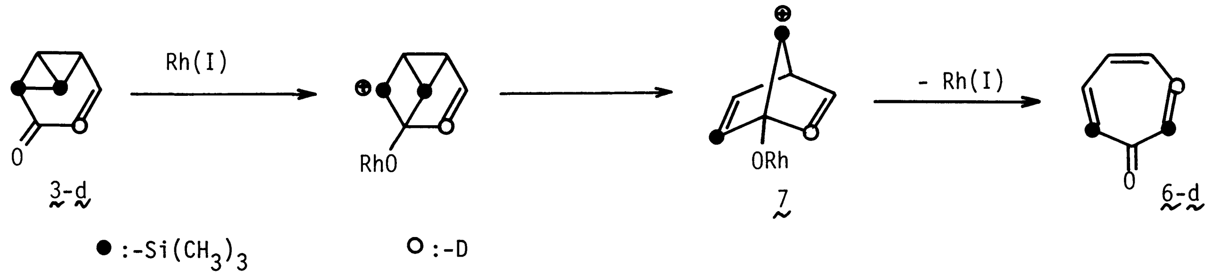
a) Chemical shifts are recorded in δ downfield from TMS.

b) Coupling constants with directly bonded hydrogens are given in parentheses in Hz.



3 **5** **6** **4**

tropovalene **3**-*d*[6)] was carried out with the rhodium catalyst, the tropone **6**-*d* obtained was found to be 3-deuterated 2,7-bis(trimethylsilyl)tropone as revealed by its ^{1}H NMR spectrum in which the peaks at lower half of an AA'BB' system were diminished in intensity. Although the precise mechanism for the formation of **6** is not clear, the deuterium labeled experiment suggested that the 2,5-norbornadien-7-yl cation 7 seemed to be one plausible intermediate. Thus, the formation of 6 from 3 can be rationalized by coordination of the metal at the carbonyl oxygen and ring opening with bicyclobutane participation to give 7 which undergoes successive cationic rearrangement$^{7)}$ with loss of a metal to produce 6-d as shown in the following scheme.$^{10)}$



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5) W. K. Musher and G. L. Larson, *J. Organomet. Chem.*, 6, 627 (1966); idem., *J. Org. Chem.*, 31, 4237 (1966).

6) The labeled tropovalene 3-d was prepared from 4-acetoxy-2-cyclopenten-1-one-5-d_2 as with the unlabeled material.

7) Rearrangement of tricyclo[4.1.0.0^{2,7}]hept-3-en-5-yl cation to the 2,5-norbornadien-7-yl cation$^{8)}$ and its conversion to the tropylium ion$^{9)}$ are well docummented.

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10) The activation energy for the pyrolysis of 1 in pyridine-d_5 was found to be 29.8 kcal/mol suggesting the presence of a biradical intermediate.$^{11)}$ In order to clarify the effect of trimethylsilyl substitution, pyrolysis of 3 was carried out. The reaction took place immediately, however, none of the products could be identified.

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