Formation and Crystal Structure of an Exocyclic Enol δ-Lactone Obtained from Dimedone and Trimethylsilylethynyl Phenyliodonium Triflate

Spyros Nikas, Nestor A. Rodios and Anastasios Varvoglis*

Laboratory of Organic Chemistry, Chemistry Department, University of Thessaloniki, Thessaloniki 54006, Greece

Aristidis Terzis and Catherine P. Raptopoulou

Institute of Materials Science, Nuclear Research Center Democritos, Aghia Paraskevi, Athens, Greece

Received February 10, 1996

Dedicated to the memory of the late Professor Nicholas Alexandrou, Aristotelian University of Thessaloniki

The reaction between dimedone anion and trimethylsilylethynyl phenyliodonium triflate leads to the formation of 4,4-dimethyl-6-(1,5-bistrimethylsilylpentane-1,4-diyne-3-ylidene)-δ-valerolactone, whose crystal structure has been determined.

J. Heterocyclic Chem., **33**, 997 (1996).

The study of alkynyl phenyliodonium salts, $RC{\equiv}CI^{+}PhX^{-}$, has revealed an interesting pattern of reactivity. These relatively new reagents are good electrophiles of tetraphilic character, reacting with a plethora of nucleophiles predominantly from the β-sp carbon [1]. The main reaction pathway observed in alkynyl iodonium salts involves the generation of alkylidene carbenes, of the general formula [R(Nu)C=C:]. These undergo normally a 1,2-shift of the nucleophile furnishing substituted alkynes, RC≡CNu. However, when the chain length of the alkynyl moiety or the nucleophile is long enough, then 1,5-carbon-hydrogen carbene insertion prevails, with formation of unsaturated five-membered rings- either cyclopentenes or heterocycles. In this way the following heterocyclic systems have been prepared: furans [2], benzofurans [3], dihydroindoles and pyrroles [4] and polycyclic tosylenamides [5]. Carbon nucleophiles in the form of 2-alkyl (or phenyl)-1,3-dicarbonyl compounds gave with several alkynyl iodonium salts either substituted alkynes or cyclic products [1,2,6].

In this note we describe the double ethynylation of the anion of dimedone **2** by trimethylsilylethynyl phenyliodonium triflate **1**. The main product obtained from their interaction, even with a 1:1 stoichiometry of reactants, was not the mono substituted dimedone but the bis-substituted isomeric enol-δ-valerolactone **3** (Scheme 1).

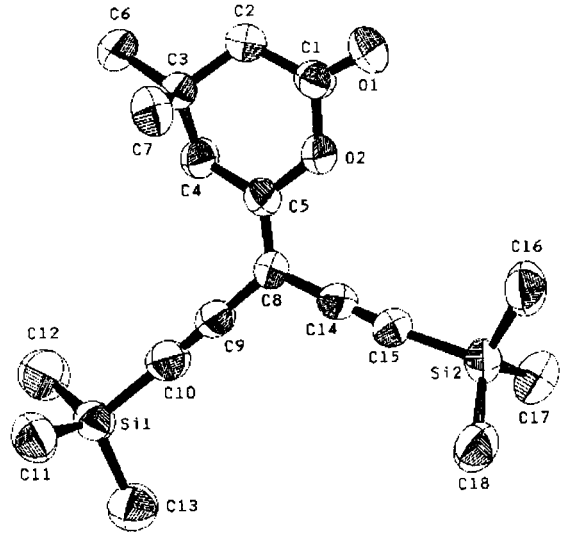
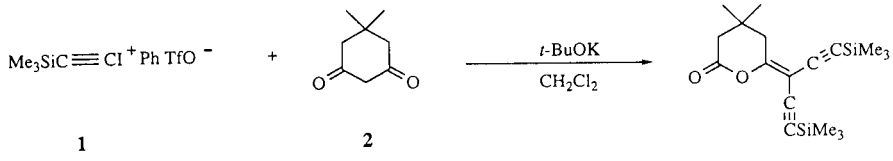


Figure 1. ORTEP Diagram of compound 3

The spectral data of **3** did not permit an unambiguous structural assignment. Therefore, this was established by a

Scheme 1



1 **2** **3**

Table 1

Positional and Equivalent Thermal Parameters ($x10^4$) of the Non H-atoms. E.s.d's in parentheses. Ueq = $1/3(U_{11}+U_{22}+U_{33})$

	x	y	z	U(eq)
Si(1)	2876(2)	4788(1)	1731(3)	64(1)
Si(2)	8449(2)	2079(1)	1212(3)	62(1)
O(1)	5847(4)	376(3)	7603(8)	81(1)
O(2)	5407(3)	1497(2)	5905(7)	60(1)
C(1)	5113(5)	897(4)	7206(10)	59(1)
C(2)	3941(6)	950(5)	8068(12)	68(2)
C(3)	2973(5)	1490(4)	6882(9)	56(1)
C(4)	3667(6)	2331(4)	6630(12)	61(2)
C(5)	4687(5)	2165(4)	5374(9)	53(1)
C(6)	2112(7)	1693(6)	8344(15)	77(2)
C(7)	2323(8)	985(6)	4623(14)	78(2)
C(8)	5002(5)	2608(4)	3829(9)	52(1)
C(9)	4302(5)	3315(4)	3165(10)	58(1)
C(10)	3718(6)	3909(4)	2579(10)	67(2)
C(11)	1560(8)	4304(7)	-677(15)	89(2)
C(12)	2100(13)	5252(8)	4110(18)	98(3)
C(13)	3782(9)	5644(7)	968(18)	88(2)
C(14)	6070(5)	2420(4)	2843(9)	59(1)
C(15)	6969(6)	2283(4)	2064(10(	64(2)
C(16)	8753(9)	953(6)	1587(22)	98(3)
C(17)	9676(8)	2874(6)	3053(17)	87(2)
C(18)	8389(9)	2243(10)	-1720(16)	99(3)

Table 2

Bond Lengths [Å] and Angles [deg]

Si(1)-C(10)	1.829(7)	C(10)-Si(1)-C(13)	109.5(4)
Si(1)-C(13)	1.839(9)	C(10)-Si(1)-C(11)	107.5(4)
Si(1)-C(11)	1.845(9)	C(13)-Si(1)-C(11)	110.7(5)
Si(1)-C(12)	1.857(9)	C(10)-Si(1)-C(12)	108.4(4)
Si(2)-C(16)	1.833(9)	C(13)-Si(1)-C(12)	109.9(6)
Si(2)-C(15)	1.839(6)	C(11)-Si(1)-C(12)	110.8(6)
Si(2)-C(18)	1.844(9)	C(16)-Si(2)-C(15)	107.1(4)
Si(2)-C(17)	1.859(9)	C(16)-Si(2)-C(18)	111.2(6)
O(1)-C(1)	1.192(7)	C(15)-Si(2)-C(18)	111.3(4)
O(2)-C(1)	1.379(6)	C(16)-Si(2)-C(17)	110.7(5)
O(2)-C(5)	1.491(9)	C(15)-Si(2)-C(17)	107.8(4)
C(1)-C(2)	1.534(8)	C(18)-Si(2)-C(17)	108.7(5)
C(2)-C(3)	1.513(8)	C(1)-O(2)-C(5)	123.6(4)
C(3)-C(4)	1.523(10)	O(1)-C(1)-O(2)	116.3(5)
C(3)-C(7)	1.538(8)	O(1)-C(1)-C(2)	124.7(5)
C(3)-C(6)	1.498(8)	O(2)-C(1)-C(2)	119.0(5)
C(4)-C(5)	1.337(8)	C(1)-C(2)-C(3)	115.9(5)
C(5)-C(8)	1.437(8)	C(4)-C(3)-C(7)	111.2(6)
C(8)-C(9)	1.452(8)	C(4)-C(3)-C(2)	106.5(5)
C(8)-C(14)	1.211(8)	C(7)-C(3)-C(2)	110.6(6)
C(9)-C(10)	1.199(8)	C(4)-C(3)-C(6)	110.0(5)
C(14)-C(15)		C(7)-C(3)-C(6)	109.6(6)
		C(2)-C(3)-C(6)	108.9(5)
		C(5)-C(4)-C(3)	112.1(5)
		C(8)-C(5)-O(2)	115.9(5)
		C(8)-C(5)-C(4)	127.3(5)
		O(2)-C(5)-C(4)	116.7(5)
		C(5)-C(8)-C(9)	119.9(5)
		C(5)-C(8)-C(14)	121.9(5)
		C(9)-C(8)-C(14)	118.2(5)
		C(10)-C(9)-C(8)	179.1(6)
		C(9)-C(10)-Si(1)	177.8(5)
		C(15)-C(14)-C(8)	178.4(6)
		C(14)-C(15)-Si(2)	173.2(5)

single crystal structure determination (Figure 1). Although no unusual features were found concerning bond lengths and angles, it is worth noting a rather short carbonyl bond (1.192 Å) and rather long (1.199-1.211 Å) triple bonds. Lists of positional parameters (Table 1) and bond lengths and angles (Table 2) are presented.

Concerning the reaction pathway leading to the formation of **3**, it is not likely to proceed *via* a normal bisethynylation at C-2 of dimedone. We base this opinion on the fact that the conversion of 2,2-dimethyldimedone to the dimethyl analogue of **3** was realized photochemically [7], whereas our reaction was not influenced by light: its exclusion did not bring about any change. Further reactivity was observed with other β-dicarbonyl compounds with **1**; however under these conditions indan-1,3-dione and dibenzoylmethane gave with **1** complex mixtures of products [8].

EXPERIMENTAL

4,4-Dimethyl-6-(1,5-bis-trimethylsilylpentane-1,4-diyne-3-ylidene)valerolactone (**3**) [9].

A slurry of dimedone **1** (0.462 g, 3.3 mmoles) in dichloromethane (10 ml) was stirred for 30 minutes under argon with potassium *t*-butoxide (0.370 g, 3.3 mmoles). Then a solution of trimethylsilylethynyl phenyliodonium triflate **2** (0.675 g, 1.5 mmoles) in dichloromethane (7 ml) was added through a septum with a syringe. After 24 hours of stirring, the reaction mixture was filtered and the solid residue was transfered to a beaker and washed with dichloromethane (3 x 15 ml). The combined washings and filtrate were concetrated and the residue was chromatographed on column (silica gel, hexane-ethyl acetate 10:1). After iodobenzene, the second fraction afforded 0.039 g (16%) of **3** as white crystals, mp 144-145° (from hexane); ir (nujol): ν 2140, 1779, 1582 cm^{-1}; ^{1}H-nmr (300 MHz, deuteriochloroform): δ 0.22 (s, 18H), 1.09 (s, 6H), 2.47 (s, 2H), 2.64 (s, 2H); ^{13}C nmr (75 MHz) (deuteriochloroform): δ -0.13, 27.8, 29.8, 39.0, 44.0, 89.4, 96.3, 98.7, 98.9, 100.4, 163.7, 165.7; ms: m/z 332 (M^+, 34), 317 (11), 206 (4), 83 (100).

Anal. Calcd. for $C_{18}H_{28}O_2Si_2$: C, 65.00; H, 8.49. Found: C, 64.88; H, 8.31.

X-ray Structure Analysis of **3**.

This compound had a molecular formula $C_{18}H_{28}O_2Si_2$, M = 332.58. The intensity data were collected at room temperature on a Crystal Logic Dual Goniometer diffractometer; λ (Mo-Kα) = 0.7107 Å, graphite monochromator. 25 Reflections in the range 11°≤ 2θ ≤ 23° were chosen to refine the unit cell parameters; triclinic system, space group p1, a = 11.02(2) Å, b = 15.48(3)Å, c = 6.19(1) Å, α = 98.07(4)°, β = 101.04(5)°, γ = 93.42(4)°, V = 1021(3) $Å^3$, z = 2, μ = 0.178 mm^{-1}, d_{calc} = 1.081 g cm^{-3}, F(000) = 360, 3154 reflections up to 2θ = 46° were collected (-11 ≤ h ≤ 12, -16 ≤ k ≤ 17, -6 ≤ I ≤ 0) of which 2846 unique reflections (R_{int} = 0.0242) were kept in refinement calculations. The structure was solved with SHELXS86 [10] and

refined by full-matrix least-squares techniques with F^2 with SHELXL93 [11]. Non-hydrogen atoms were refined with anisotropic temperature factor, hydrogen atoms were located in difference Fourier map and refined with isotropic temperature factor. The final values for R, R_w and GOF [1787 reflections with $I > 2\sigma(I)$] are 0.0716, 0.1928 and 1.034 respectively and for all data are 0.1186, 0.2470 and 1.034 respectively. The maximum and minimum residual peaks in the final difference map were 0.311 and -0.345 e/Å^3. The largest shift/esd in the final cycle was 0.006. Lists of the atomic coordinates, thermal parameters, bond distances and angles have been deposited at the Cambridge Crystallographic centre, U.K.

Acknowledgment.

A. T. is grateful to Ms. Athina Athanasiou for financial support.

REFERENCES AND NOTES

[1] P. J. Stang and V. V. Zhdankin, Ang. Chem., *Int. Ed. Engl.*, **31**, 274 (1992).

[2] M. Ochiai, M. Kunishima, Y. Nagao, K. Fuji, M. Shiro and E. Fujita, *J. Am. Chem. Soc.*, **108**, 8281 (1995).

[3] T. Kitamura, L. Zheng, H. Taniguschi, M. Sakurai and R. Tanaka, *Tetrahedron Letters*, **34**, 4055, (1993).

[4] K. S. Feldman, M. M. Bruendl and K. Schildknegt, *J. Org. Chem.*, **60**, 7722 (1995).

[5] K. Schildknegt, A. C. Bohndtedt, K. S. Feldman and A. Sambandam, *J. Am. Chem. Soc.*, **117**, 7544 (1995).

[6] M. Ochiai, T. Ito, Y. Takaoka, Y. Masaki, M. Kunishima, S. Tani and Y. Nagao, *J. Chem. Soc., Chem. Commun.*, 118 (1990).

[7] H. Nozaki, Z. Yamaguti, T.Okada, R. Noyori and M. Kawanisi, *Tetrahedron*, **23**, 3993 (1967).

[8] S. Nikas, Unpublished results.

[9] Ir spectra were obtained with a Perkin-Elmer 297 spectrometer. The ^1H and ^{13}C nmr spectra were recorded on a Brucker AM 300 spectrometer at 300 MHz and 75 MHz respectively, and the mass spectra were obtained with a VG 250 spectrometer.

[10] G. M. Sheldrick, SHELXS-86: Structure Solving Program. University of Göttingen, Germany, 1986.

[11] G. M. Sheldrick, SHELXL-93: Crystal Structure Refinement. University of Göttingen, Germany, 1993.