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REGIOSPECIFIC ADDITION OF TCNE TO 2-exo-METHYL-endo-TRICYCLO [3.2.1.$0^{2,4}$] OCT-6-ENE

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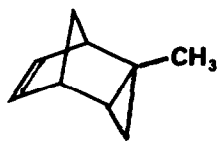
We report a novel reaction involving regiospecific corner attack by TCNE at C(4) of 2-exo-methyl-endo-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene 1. Hydrocarbon 1,



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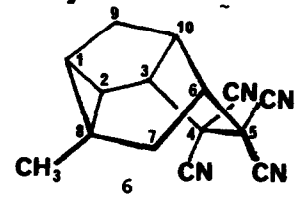

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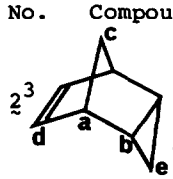
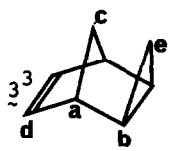
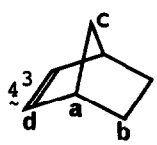
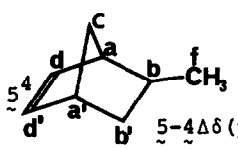
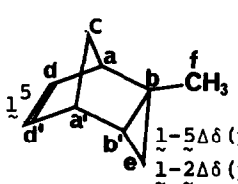
prepared by reaction of cyclopentadiene with 1-methylcyclopropene, was reported by Magid et al[1] and the stereochemistry assigned from the known preference[2] for endo-adduct formation. For the present study it was necessary to establish the stereochemistry of the adduct beyond doubt. The ^{13}C FT N.m.r. spectra of endo- and exo-tricyclo[3.2.1.$0^{2,4}$]oct-6-enes 2 and 3 exhibit an extraordinarily large γ-shift[3]; for the exo-isomer 3,C(8) is shielded (-11.1 ppm) and the vinyl carbons deshielded(5.9 ppm) and for the endo-isomer 2, C(8) is deshielded (15.2 ppm) and the vinyl carbons shielded (-4.8 ppm) with respect to the corresponding carbons of norbornene 4. An effect similar to endo-isomer 2 is observed for adduct 1; C(8) is deshielded (16.4 ppm) and the vinyl carbons shielded ((-5.4 ppm), (-4.4 ppm)) relative to the appropriate carbons of 5-exo-methylnorbornene (Table I). These observations unambiguously establish the stereochemistry of adduct 1 as endo.

Reaction of hydrocarbon 1 with TCNE in methylene chloride at room temperature for one week gave in high yield (> 80%) a compound (m.p. 170-2°) shown from elemental analysis and the mass spectrum to be a 1 : 1 adduct.

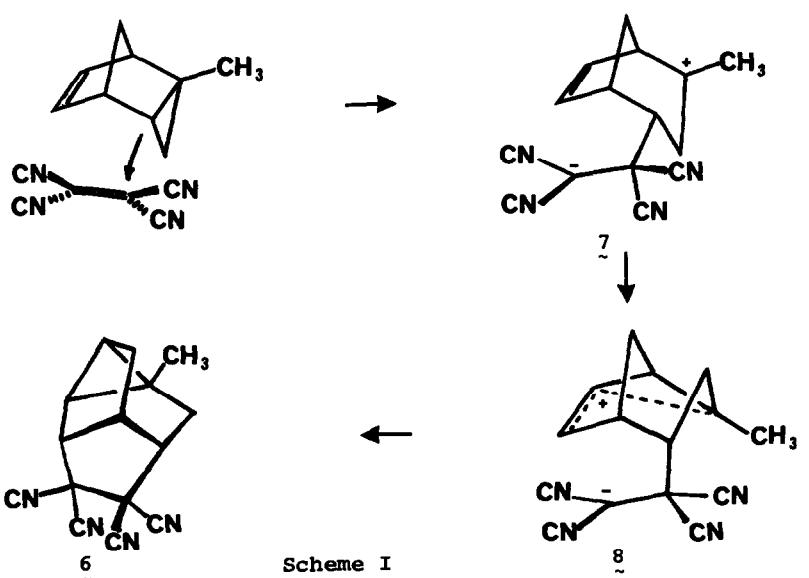
Table 1. ^{13}C N.m.r. Data in $CDCl_3$

No.	Compound	a	a'	b	b'	c	d	d'	e	f
2		42.3		12.3		63.7	130.4		17.1	
	2-4Δδ (ppm)	0.5		-12.3		15.2	-4.8			
3		41.4		21.9		37.4	141.1		19.2	
	3-4Δδ (ppm)	-0.4		-2.7		-11.1	5.9			
4		41.8		24.6		48.5	135.2			
5		48.7	42.7	(33.0)	35.0	45.0	(136.2)	(137.2)		21.7
	5-4Δδ (ppm)	6.9	0.9	8.4	10.4	-3.5	(1.0)	(2.0)		
1		48.2	44.1	19.7	19.5	61.4	(130.8)	(132.8)	24.2	20.8
	1-5Δδ (ppm)	-0.5	1.4	(-13.3)	-15.5	16.4	(-5.4)	(-4.4)		-0.9
	1-2Δδ (ppm)	5.9	1.8	7.4	7.2	-2.3	(0.4)	(2.4)	7.1	

The ^{13}C chemical shifts[5] (17.9(s), 22.3(q), 26.0(d), 26.6(t), 27.9(t), 30.0(d), 42.6(d), 46.0(s), 48.8(d), 52.0(s), 55.2(d), 110.3(s), 111.0(s), 111.9(s), 112.1(s)) are inconsistent with those expected for a $[_{\pi}2 + _{\pi}2]$ cycloadduct. The product was identified as 4,4,5,5-tetracyano-8-methyltetracyclo-$[4.2.2.0^{2,8}.0^{3,10}]$decane 6 as follows. In the P.m.r. spectrum[6] (Table II) C(3)H was coupled to C(2)H and C(10)H and exhibited long range coupling with C(6)H and a C(9)H. The C(2)H was coupled with C(1)H which appeared as a multiplet and sharpened to the upfield doublet of an AB quartet when $C(9)H_2$ was irradiated. The C(10)H multiplet sharpened on irradiation of $C(9)H_2$. The $C(7)H_2$ appeared as an AB quartet with the downfield proton further coupled to C(6) - the downfield proton of the C(6)H, C(10)H multiplet.

Table II N.m.r. data[6] for adduct 6

Functional group	Position of signal(s) δ (p.p.m.)		Apparent coupling constants (Hz)	
C(3)H	3.36		$J_{3,10}$	6.5
			$J_{3,2}$	3.6
			$J_{3,6}$	<0.5
C(10)H, C(6)H	2.95	($W_{\frac{1}{2}}^{h}$ 20Hz)		
C(7)exo-H	2.29		$J_{7exo,7endo}$	15.8
			$J_{7exo,6}$	8.2
C(7)endo-H	2.09		$J_{7endo,7exo}$	15.8
			$J_{7endo,6}$	~1.0
			$J_{7endo,10}$	<1.0
$C(9)H_2$	2.06	($W_{\frac{1}{2}}^{h}$ 5Hz)		
C(2)H	1.69		$J_{2,1}$	6.5
			$J_{2,3}$	3.6
C(1)H	1.52		$J_{1,2}$	6.5
$C(8)CH_3$	1.07			



Scheme I

Reaction of TCNE with hydrocarbon 1 is regiospecific involving cleavage of the strained C(2),C(4) bond by corner attack at C(4)[7]. The reaction proceeds probably via the ionic species 7 which has a sufficient lifetime for conformational inversion to the boat conformation 8 to occur allowing overlap of the tertiary carbonium ion with the π-bond (Scheme I). The C(2)-methyl substituent has a marked influence[8] on the course of the reaction since the intermediate tertiary ion 7 is sufficiently stable to permit the conformational change necessary to facilitate C(7),C(2) bond formation.

References

1. R.M. Magid, T.C. Clarke and C.D. Duncan, J.Org.Chem., 36, 1320(1971)
2. R.B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry" Academic Press: New York 1970 p.145 and references therein.
3. K. Tori, M. Ueyama, T. Tsuji, H. Matsumura and H. Tanida, Tetrahedron Lett. 327 (1974).
4. J.B. Grutzner, M. Jautelat, J.B. Dence, R.A. Smith and J.D. Roberts, J.Amer.Chem.Soc., 92, 7107 (1970).
5. ^{13}C FT N.m.r. spectra recorded on a Varian CFT20 spectrometer in the $CDCl_3$-locked mode at 20 MHz. Sample concentrations were about 1M in $CDCl_3$ containing TMS as an internal reference.
6. Recorded on a Bruker HF X90 spectrometer in $CDCl_3$.
7. No product resulting from electrophilic attack at the alkene was observed.
8. This effect can be seen from a comparison with the reaction of endo-tricyclo $\left[3.2.1.0^{2,4}\right]$oct-6-ene(i) with TCNE to give 5,5,6,6-tetracyanotricyclo$\left[5.2.1.0^{4,8}\right]$dec-2-ene(ii).

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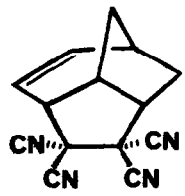

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This work is being written up for publication by Professor M.A. Battiste at the University of Florida.