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(2+2)-CYCLOADDITION OF TRIAZOLINEDIONES TO STRAINED BICYCLOALKENES

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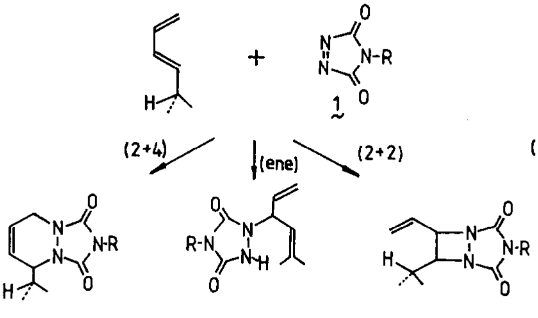
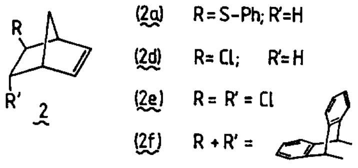
SUMMARY: Substituted norbornenes and dibenzobarrelene react under forced conditions with N-methyl-1,2,4-triazolin-3,5-diones to afford urazoles via (2+2)-cycloaddition.

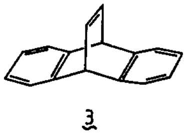
The similarity of triazoline-3,5-diones (TAD) and singlet oxygen in their dienophilic reactivity, i. e. (2+4)-cycloaddition[2], ene-reaction[3] and (2+2)-cycloaddition[4] (eq.1), has recently been accentuated by the interesting discovery[5] that TAD exhibits the same regioselective deuterium isotope effect as singlet oxygen in the reaction with tetramethylethylene. Moreover, the fact that bisadamantylidene, a simple olefin without electron-donating substituents [4a,c], undergoes (2+2)-cycloaddition[5], prompts us to communicate our experiences



(eq.1)

of such reactions with the strained bicycloalkenes of the norbornene (2) and dibenzo-barrelene (3). Admittedly, our motivation for examining the reaction

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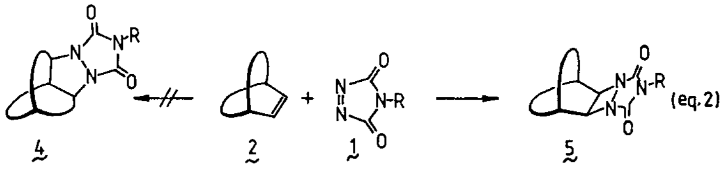
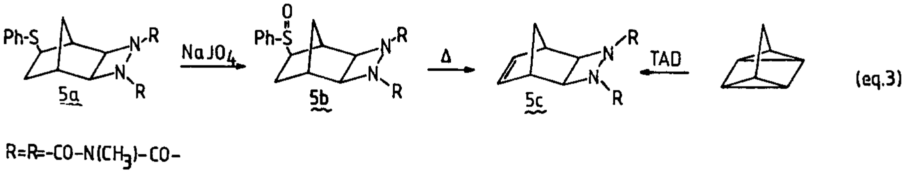
of TAD with these substrates was to extend the generality of our recently discovered[6] dipolar cycloaddition process (eq.2) to afford the rearrangend



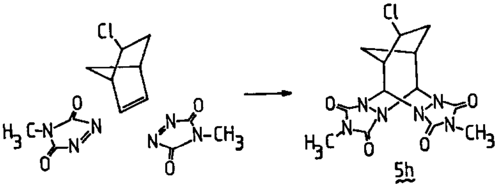
urazoles (4), but instead the urazoles (5) were formed via (2+2)-cycloaddition. Besides the very recent bisadamantylidene example, such (2+2)-cycloadditions of TAD with simple bicycloalkenes appear not to have been reported as yet to the best of our knowledge.

Under the usual conditions (refluxing methylene chloride) the bicycloalkenes appeared to be unreactive towards TAD. However, at elavated temperatures (ca. 80°C in $Cl_2CHCHCl_2$ for 12-15 h) these substrates[7] proved reactive, affording the corresponding (2+2)-cycloadducts (5). The yields, physical constants and spectral data are summarized in Table I. In addition, rigorous structure proof was secured for urazole (5a) through chemical transformations (eq.3).



Thus, sodium periodate oxidation of (5a) to the sulfoxide (5b) and thermolysis (refluxing toluene and pyridine as base) gave urazole (5c) in 83% overall yield. Authentic (5c) was prepared in quantitative yield from quadricyclane (eq.3) and authentic (5a) can be obtained from (5c) by radical addition of thiophenol.

It is mechanistically obscure to us why the unsubstituted norbornene affords, albeit in low yield (ca. 10%) the rearranged urazole (**4**) with TAD, while the substituted derivatives (**2**) lead to the (2+2)-cycloadducts (**5**). Still more puzzling is the formation of urazole (**5h**), in which two moles of TAD have been added to the 5-chloronorbornene with cleavage of the double bond (eq.4). An X-ray analysis was essential for the unequivocal elucidation of this unusual product, for which we have no analogy nor precedence in TAD chemistry.


5h

(eq.4)

Work is in progress to rationalize the mechanism of this unique cleavage process. Furthermore we intend to convert the urazoles (**5**) into their corresponding azoalkanes and examine their thermal and photochemical denitrogenations.

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1. NIH Career Awardee (1975-80); direct correspondence to the Würzburg address.
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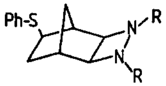
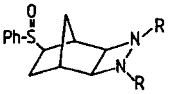
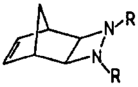
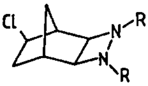
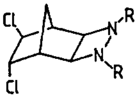
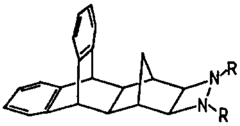
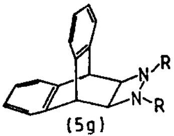
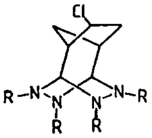
6. Adam, W.; De Lucchi, O.; Erden, I. *J. Am. Chem. Soc.* **1980**, *102*, 4806.
7. Bicycloalkenes (**2a**) and (**2d**) were prepared from norbornadiene via addition of PhSH and HCl, respectively and contained the respective tricyclic isomers as impurities.
8. Kindly determined for us by Dr. K. Peters, Max-Planck-Institute, Stuttgart.

TABLE I: Yields, Physical Constants and Spectral Data for Urazoles (5).

		mp (°C)	^{1}H NMR (CDCl$_3$,TMS)					
Urazole[a,b]	% Yield[c]	Solvent (Shape)	Type[d]	#H's	δ (ppm)	Pattern	J (Hz)	IR(KBr) ν (cm^{-1})
 (5a)		170-174	H_6	2	1.53	m		2980, 1780, 1700,
	30	CH$_2$Cl$_2$/Ether	H_7	1	2.10	A part AB	J_{gem}=11	1440, 1390, 1330,
		(plates)	H_7	1	2.40	B part AB		1190, 1033, 1000,
			$H_{1,4,5}$	3	2.63-2.93	m		980, 790, 755, 690.
			N-CH$_3$	3	3.05	s		
			$H_{2,3}$	2	4.27	m		
			S-Ph	5	7.33	m		
 (5b)		198-203	$H_{5,6,7}$	5	1.92-2.67	m		2980, 1780, 1715,
	91	(dec.)	bridgehead	1	2.82	m		1440, 1390, 1200,
		CH$_2$Cl$_2$/Ether	bridgehead	1	3.03	m		1190, 1180, 1040,
		(powder)	N-CH$_3$	3	3.05	s		780, 690.
			$H_{2,3}$	2	4.60	br.s		
			SO-Ph	5	7.57	br.s		
 (5c)		148	H_7	1	1.98	A part AB	J_{gem}=10	2980, 1765, 1690,
	91	EtOH	H_7	1	2.43	B part AB		1440, 1395, 1325,
		(needles)	N-CH$_3$	3	3.10	s		1310, 1190, 1020,
			H_1,H_4	2	3.30	br.s		1000, 990, 955, 790,
			H_2,H_3	2	4.28	br.s		700.
			H_5,H_6	2	6.13	narrow m		
 (5d)		175	H_6	2	1.53-2.07	m		2990, 2950, 1775,
	10	EtOH	H_7	1	2.15	A part AB	J_{gem}=11,7	1710, 1440, 1390,
		(powder)	H_7	1	2.50	B part AB		1210, 1190, 1030,
			H_1	1	2.78	narrow m		980, 785, 770, 735,
			H_4	1	2.88	br.s		660.
			N-CH$_3$	3	3.07	s		
			H_5	1	3.60	m		
			$H_{2,3}$	2	4.27	br.s		
 (5e)		165-166	H_7	1	2.27	A part AB	J_{gem}=12	2980, 1775, 1710,
	20	EtOH	H_7	1	2.68	B part AB		1440, 1390, 1210,
		(needles)	bridgehead	1	2.92	br.s		1190, 1020, 990,
			bridgehead	1	3.00	m		920, 800, 775, 735,
			N-CH$_3$	3	3.10	s		680.
			CHCl	1	3.48	app.t	J=2.7	
			CHCl	1	4.27	app.q	J=3	
			CHN	1	4.43	d	J=5.4	
			CHN	1	4.93	d	J=5.7	
 (5f)		165-168	H_7	1	0.00	A part AB	J_{gem}=ca. 13	3040, 2960, 2920,
	28	EtOH	bridgehead	2	1.60	br.s		1780, 1720, 1460,
		(prisms)	H_7	1	1.70	B part AB		1440, 1390, 1290,
			bridgehead	2	2.50	br.s		1260, 1185, 1030,
			N-CH$_3$	3	3.02	s		1010, 970, 920, 780,
			bridgehead	2	4.15	br.s		755, 720, 630, 610.
			bridgehead	2	4.30	br.s		
			Anthracene	8	7.20	m		3070, 3970, 1775,
 (5g)		281-283	N-CH$_3$	3	2.75	s		1710, 1460, 1440,
	25	EtOH	H_2,H_3	2	4.68	m		1390, 1340, 1300,
		(prisms)	H_1,H_4	2	4.87	m		1275, 1190, 1160,
			C_6H_4	8	7.10-7.57	m		1035, 1000, 965, 950,
								835, 750, 625.
 (5h)		190-194	$H_{6,7}$	4	1.92-3.05	m		3000, 2960, 1800,
	35	(with dec.)	N-CH$_3$	3	3.05	s		1735, 1460, 1400,
		EtOH	N-CH$_3$	3	3.07	s		1390, 1280, 1180,
		(powder)	bridgehead	2	3.33	m		1005, 920, 800, 760,
		CHCl$_3$	H_5	1	4.63	m		700, 650.
		(prisms)	CHN	1	6.43	d	J=10.5	
			CHN	1	6.55	d	J=9	

a) R+R = -CO-N(CH$_3$)-CO- ; b) correct elemental composition according to combustion analysis; c) yield corrected for recovered bicycloalkene for urazoles (5a,d,e,f,h); d) the numbering refers to the bicycloalkene; e) obtained together with the rearranged product (4) (see Ref.6).

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