Tetrahedron Vol. 44, No. 9, pp. 2427 to 2438, 1988
Printed in Great Britain.

0040-4020/88 $3.00+.00
Pergamon Press plc

DIMERS DERIVED FROM 10-TRISPIRO[2.0.2.0.2.1]DECYLIDENE: NEW HYDROCARBONS WITH INTERESTING STRUCTURAL FEATURES[1]

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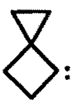
(*Received in Germany* 11 *January* 1988)

Abstract - The title carbene 3, although highly loaded with three electron donating spirocyclopropane units, does not dimerize to the olefin 4, but only undergoes ring-enlargement to the spirocyclopropane anellated bicyclo[2.2.0]hex-1(4)-ene 7. In analogy to the corresponding parent compound, 7 yields three major hydrocarbon products: the dimethylenedispirooctane 9, the dimer 11 arising from [4+2]-cycloaddition of 7 to 9 and - predominantly - dimethylenetricyclodecane 12. The expected Cope rearrangement of 12 to the interesting bis-bridgehead-diene 22 could not be detected, but the oxidation product (E)-10,10'-bi(dispiro-[2.0.2.4]decanylidene)-7,7'-dione (25) obtained upon heating 12 in nitrobenzene most probably arose from the bisallyl diradical 20 equilibrating with 12 and possibly 22 at elevated temperatures.

Introduction

Cyclopropyl groups are known to exert a multitude of influences on the chemical and spectroscopical properties of compounds.[2] Their substituent effects become especially evident on reactive intermediates. While carbenium ions with α-cyclopropyl groups are very efficiently stabilized,[3] the corresponding radicals and carbenes frequently undergo extremely facile ring opening[4] and ring enlarging reactions.[5] The high driving force in the cyclopropylcarbene to cyclobutene rearrangement becomes apparent in the fact that 4-spiro[2.3]hexylidene (1) primarily gives only the highly strained bicyclo[2.2.0]hex-1(4)-ene (2).[6] In view of the



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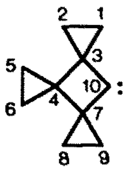

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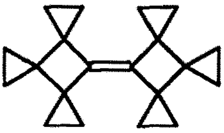

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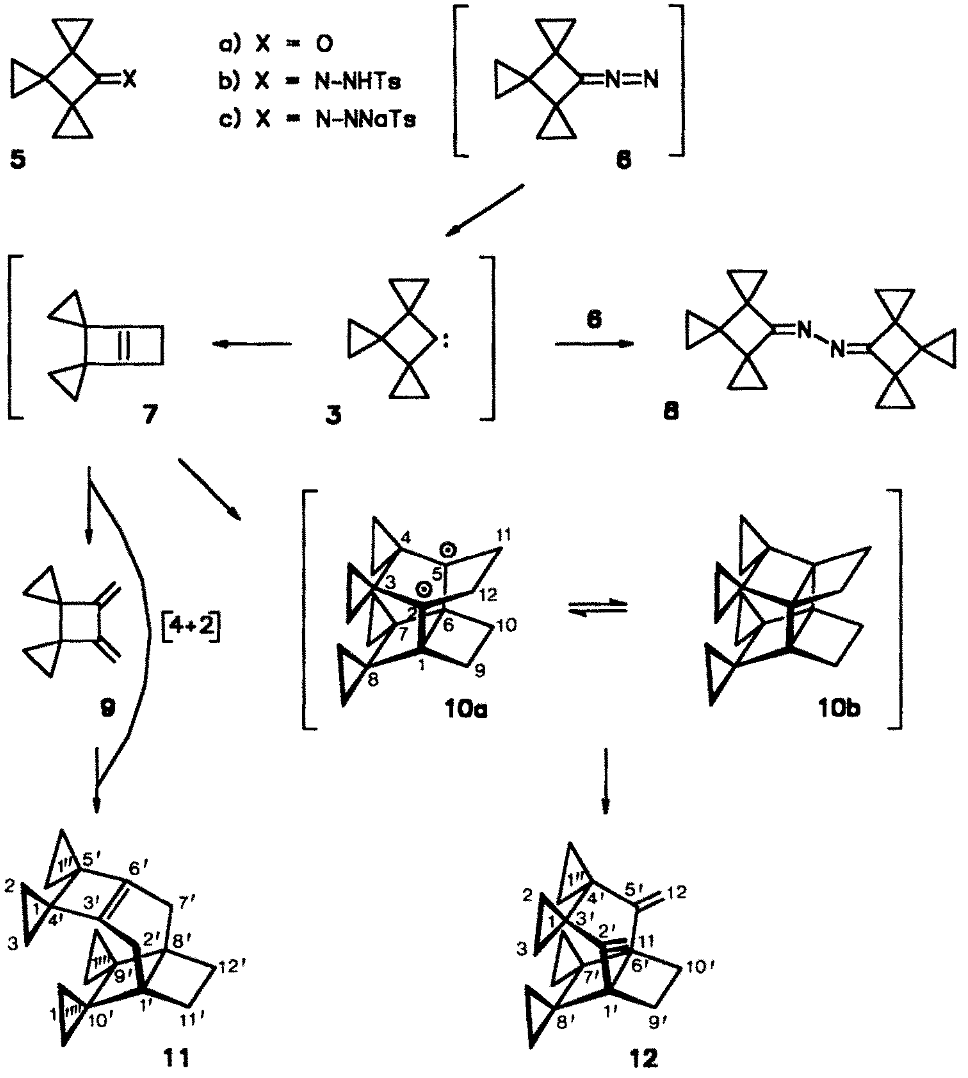
unique donor ability of cyclopropyl groups adjacent to electron deficient centres, it was not out of range that 10-trispiro[2.0.2.0.2.1]decylidene (3), like a nucleophilic carbene,[5] could dimerize to 10,10'-bi(trispiro[2.0.2.0.2.1]decylidene) (4).[7] Because of our interest in this unusual olefin,[7] we investigated the alkaline-thermal decomposition (Bamford-Stevens reaction) of the tosylhydrazone **5b**.

Alkaline Thermal Decomposition of Tosylhydrazone 5b

The reasonably well accessible trispiro[2.0.2.0.2.1]decan-10-one (**5a**)[8] was concerted to its tosylhydrazone **4b** (65% yield) and this in turn into its sodium salt **5c** by treatment with sodium hydride. The thermal decomposition of **5c** was carried out under a variety of conditions (geometry of the apparatus, heating rate, pressure), and the product composition varied accordingly. The yields of crude product ranged from 50 to 70% for batches of 1.44 - 11.4 mmol **5c** and were higher for smaller batches (0.25 - 0.41 mmol **5c**). Only in one case, when 11.4 mmol **4c** was heated to 180-230°C in a 250 ml round bottom flask under reduced pressure (0.025 torr), the azine **8** was isolated, even as the main product (59% of the total). In



Scheme 1

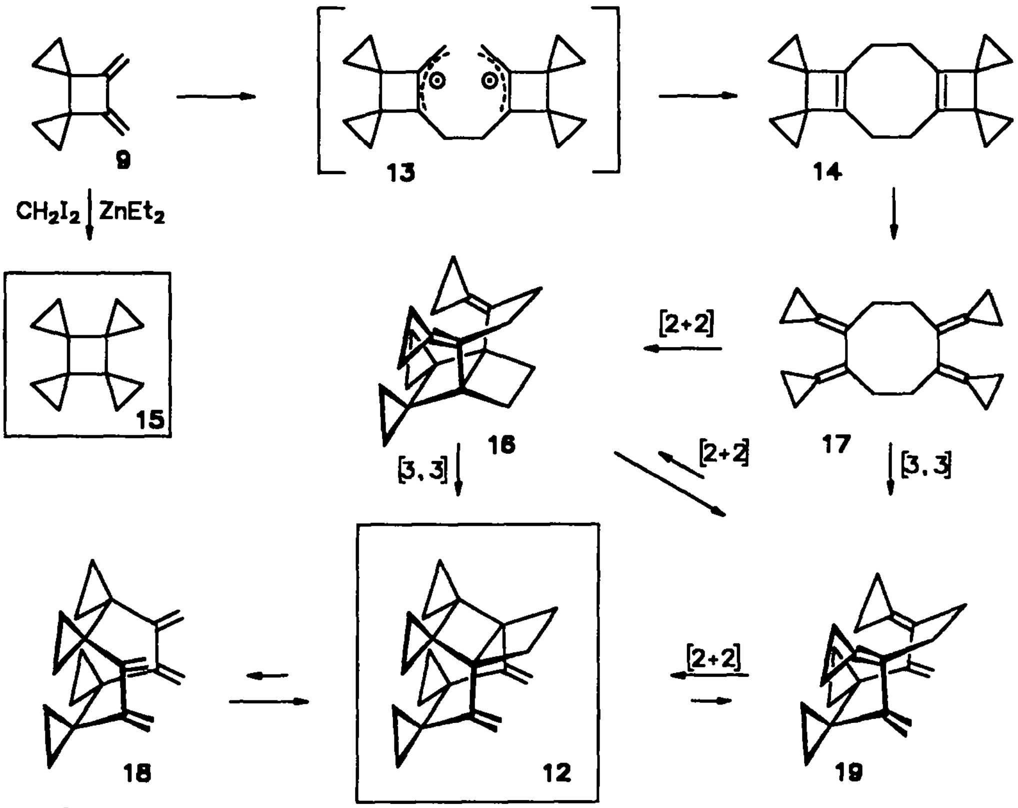
five other runs, mixtures of only three hydrocarbons were trapped at -78°C (see table 2). As analyzed by GC-MS one of them had a molecular weight of 132, formally that of the carbene 3, and the other two had m/z = 264, corresponding to dimers of 3. The ^1H NMR spectrum of the crude mixture, however, did not show any of the characteristic absorptions of the bicyclobutylidene[7] 4.

The low molecular weight product was not easily purified, since it rapidly polymerized upon vapor phase or column chromatography. A pure sample was obtained with considerable losses from the two runs on a larger scale (entries 4,5 in table 2), in which this more volatile hydrocarbon together with tetrahydrofuran was collected in a liquid nitrogen cooled trap, while the less volatile products were trapped at -78°C. The latter were readily purified by column chromatography, all three compounds were fully characterized by their MS, IR, ^1H NMR, ^{13}C NMR spectra and identified as 7,8-dimethylenedispiro[2.0.2.2]octane (9), the tetracyclic tetraspiro compound 11 and the tricyclic 12. In some experiments (entries 4,5 in table 2) 9 was the main product, in all cases 12 predominated 11 by a factor of 3.5 - 12.

Mechanism of Formation and Thermal Rearrangement of Hydrocarbon 12

Apparently, all products including the azine 8 arose from cyclobutylidene 3; when high local concentrations of the diazo compound 6 are produced, a large proportion can surprisingly be trapped by 3 to give 8 before decomposing completely. As 3 does not dimerize to 4, it obviously undergoes a rapid α-C,C insertion just like 4-spiro[2.3]hexylidene (1)[6] to give the bicyclo[2.2.0]hex-1(4)-ene derivative 7, which in turn opens one cyclobutene unit to form 9. The minor dimer 11 arises from a [4+2]-cycloaddition of 9 onto the highly strained double bond of 7. It is noteworthy that the alkaline-thermal decomposition of spiro[2.3]hexanone tosylhydrazone almost exclusively yielded the [4+2]-type dimer derived from 2 and 1,2-dimethylenecyclobutane.[6] The major dimer from 3 can be formed without intervention of 9 by a stepwise [2+2]-dimerization of 7. The initial dimer may well be the 1,4-diradical 10a, which does not have to ring-close to 10b, but opens the C^{11}-C^{12} bond right away to form the dimethylene derivative 12. This behaviour of 7 and 10 is in complete analogy to that of the parent bicyclo[2.2.0]-hex-1(4)-ene[9] and its [2+2]-dimer,[10] and the direction of ring-opening of the dispiro[2.0.2.4]deca-7,10-diyl unit in 10a totally corresponds to that of the parent cyclohexa-1,4-diyl with two α-spirocyclopropane groups.[11]

It cannot be excluded that 12 is actually formed stepwise by an alternative mechanism analogous to that formulated and proved by W.S. Trahanovsky for the dimerization of several 1,2-bismethylenecycloalkenes and -heterocycloalkenes.[12] According to that (see scheme 2) the dimethylenecyclobutane 9 should be able to dimerize via the diradical intermediate 13 to yield the cyclooctadiene 14. Electrocyclic opening of the strained cyclobutene units in 14 would yield tetrakiscyclopropylidenecyclooctane 17, which consists of two 1,4- bis(cyclopropylidene)-butane units. As the parent 1,4-bis(cyclopropylidene)butane is known to undergo a facile [3,3]-sigmatropic rearrangement to 1,1'-divinylbicyclopropyl,[13] it is reasonable to assume that 17 would rapidly rearrange to the thermodynamically more stable cyclooctane derivative 19. An intramolecular [2+2]-cycloaddition between the two methylenecyclopropane units[14] in 19 would then lead to the final product 12. A [3,3]-sigmatropic rearrangement could also follow the [2+2]-cycloaddition to give 12 from 17 via 16.

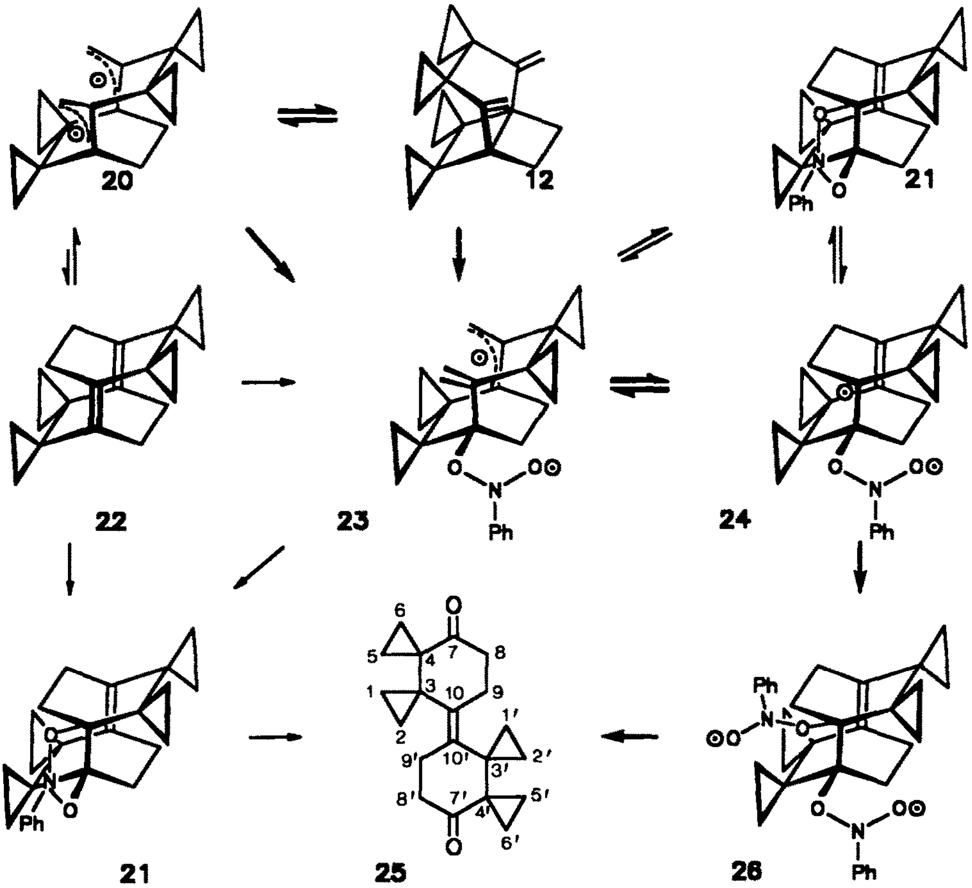


Scheme 2

Accordingly, the observation of 12 does not imply that the bicyclo[2.2.0]hex-1(4)-ene 7 is formed in high enough concentrations to undergo [2+2]-dimerization to 10. The hydrocarbon 11, however, proves that 7 must have a finite lifetime. The available evidence does not allow one to decide, along which route the major product 12 is formed. It is surprising that the tetramethylenecyclooctane 18, which could arise from 19 by a [3,3]-sigmatropic process or from 12 by an opening of the bicyclo[2.2.0]hexane unit,[15] was not found as a major end product. There was only a small fraction (<1%) of an unidentified by-product of molecular mass 264, which could actually have been 18. In order to rigorously prove that the main product in the extended scale runs was actually 9 and not 18, the crude hydrocarbon was cyclopropanated with diiodomethane/diethylzinc,[16] to give [4]rotane (15).[17] Upon heating 9 in [D$_6$]benzene to 100 - 120°C under NMR control, its signals slowly disappeared without any product peaks being detected. Upon work-up, the reaction mixture yielded only a small fraction of 12. As Wiberg et al. discovered,[9] the parent 2,5-bismethylenetricyclo[4.2.2.0^{1,6}]decane corresponding to 12 equilibrates with the unique tricyclo[4.2.2.2^{2,5}]deca-1(2),5(6)-diene. By analogy, 12 could be expected to rearrange to the corresponding tricyclic diene 22, an interesting derivative of the corresponding parent hydrocarbon, which could i.a. help to fully understand the PE spectrum of that parent.

When 12 was heated in [D$_6$]benzene, no new product was observed at temperatures up to 210°C, but only slow polymerization. After one day in chloroform at 70°C, 12 remained unchanged. In nitrobenzene at 160 - 180°C, however, 12 completely disappeared within one day. The reaction proceeded by first order kinetics with an estimated $k=(7.7 \pm 0.8)\cdot 10^{-5}\ s^{-1}$ as monitored by NMR spectroscopy. The only product was the unsaturated diketone **25**. Its IR spectrum showed a carbonyl band at 1690 cm^{-1}, but no C=C stretch absorption. This may be taken to indicate that the product was the centrosymmetric (E)-isomer (E)-**25** rather than (Z)-**25**. This is in accord with molecular models which render a (Z)-configuration virtually impossible. The (E)-configuration was verified by a NOE experiment proving the spatial proximity of the 9(9')- and 5,6(5',6')-protons.

This facile and clean oxidative opening of **12** in nitrobenzene is surprising, since normal olefins are totally inert under thermal conditions,[18a] but are attacked by nitrobenzene upon UV irradiation and cleaved to carbonyl compounds similarly as by ozone.[18b] 2-Aza-1,3-dioxolanes (1,3,2-dioxazolidines) have been postulated as intermediates in such photochemical reactions. Although **25** could arise from the azadioxolane **21** formed by 1,3-dipolar cycloaddition of nitrobenzene to the strained bridgehead diene **22** in a thermal equilibrium with the dimethylenetricyclodecane **12**, it is more likely that the bisallylic diradical **20** is formed as an intermediate en route to **22** and trapped by nitrobenzene to yield **23** (see scheme 3). Either **24** or **21**, which might equilibrate with **24** or **23**, could react with a second molecule of nitrobenzene. The intermediate **26** thus formed corresponds to the adduct formed in the oxidation of benzyl radicals by nitrobenzene,[18c] and it is reasonable that **26** would thermally decompose to yield **25** along with nitrosobenzene.[18c] It is unlikely that **25** is formed directly by thermal cleavage of **21**. Although **20** might be expected to be trapped also by other reagents at elevated temperature, no reaction was observed when **12** was heated in benzene/methanol or isopropanol to 170°C for one day in sealed ampoules.



Scheme 3

Crystal Structure of Dimethylenetricyclodecane[19] 12

Under flash vacuum pyrolysis conditions, 12 showed only 50% conversion even at 500°C/$6 \cdot 10^{-3}$ torr, but the only products were four unidentified low molecular weight fragments of 12. In order to better understand the thermal behaviour of 12, its structure was analyzed by X-ray crystrallography.

The triclinic crystals (space group $P\bar{1}$) were mounted on a Syntex $P2_1$ diffractometer and 1883 out of 2754 symmetry independent reflections were significant with M_O-K_α out to $\theta_{max}=25°$. The structure was solved with direct methods (SHELXS-84)[20] and refined (SHELX-76)[21] to R=9.4% (R_w=5.8%).

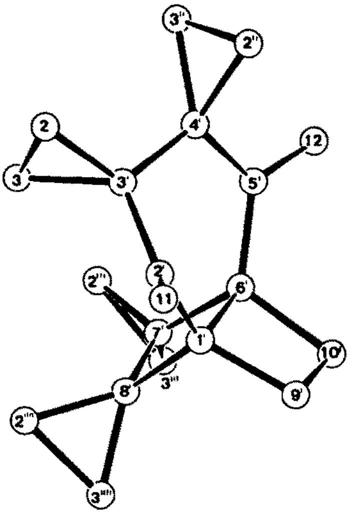


Fig. 1. Crystal structure of 12.[19] (Triclinic, space group $P\bar{1}$, a = 760.2(4), b = 898.8(4), c = 1264.6(5) pm, α = 76.78(2), β = 75.72(2), γ = 70.26(2)°, V = 778.07 x 10^6 pm^3, ρ = 1.13 g/cm^{-3}).

Surprisingly, the four spirocyclopropane groups are *syn*-oriented on the tricyclic skeleton (see fig. 1). The six-membered ring C^1-C^6, however, adopts a rather flat boat conformation holding the two exomethylene groups at a distance of 300 (C^2,C^5) and 544 pm (C^{11}, C^{12}), respectively. In a [3,3]-sigmatropic rearrangement of 12 to 22 the latter two carbon atoms would become C^{11} and C^{12}, and this would require a considerable conformational change of the six-membered ring C^1-C^6 on the way to the transition state for this Cope rearrangement. It cannot easily be foreseen how much energy this would require, and molecular mechanics force fields do not well enough account for strain effects in three-membered ring systems. One factor, which definitely contributes to and probably increases the overall strain energy of the bridgehead diene 22 (with respect to 12) arises from the necessity of eclipsing the spiroanellated bicyclopropyl unit on C^3, C^4. This unit has a high tendency to be staggered,[22,23] and it so is on the six-membered ring in 12 with a dihedral angle of 53.7°.

The other bicyclopropyl unit on C^7, C^8 of **12** is forced into an eclipsed synperiplanar conformation (dihedral angle ~8°, see Fig. 1), as it is linked to the rigid bicyclo[2.2.0]hexane subunit. Surprisingly, the C^7-C^8 bond in the four-membered ring is shorter (150.5 vs. 152 pm) than the corresponding C^3-C^4 bond in the six-membered ring. All the other structural parameters (see table 1) show no peculiarities or abnormalities.

Table 1. Relevant structural parameters of crystalline 2,5-dimethylenetricyclodecane **12**.

Distance [pm]		Equivalent distance		Angle [°]	
C1' -C2'	150.4(6)	C5' -C6'	148.4(8)	C6' -C1'-C9'	90.7(3)
C1' -C6'	157.9(7)			C6' -C1'-C8'	87.1(3)
C1' -C8'	156.6(5)	C6' -C7'	154.0(6)	C2' -C1'-C9'	123.7(4)
C1' -C9'	152.4(6)	C6' -C10'	156.3(7)	C2' -C1'-C8'	117.1(3)
C2' -C3'	149.2(8)	C4' -C5'	152.7(6)	C2' -C1'-C6'	115.1(4)
C2' -C11	131.7(7)	C5' -C12	133.2(8)	C1' -C2'-C11	121.0(5)
C2 -C3'	151.8(6)	C2'' -C4'	151.6(7)	C1' -C2'-C3'	112.9(4)
C3 -C3'	153.4(6)	C3'' -C4'	149.8(9)	C1' -C9'-C10'	90.4(4)
C2 -C3	150.0(6)	C2'' -C3''	146.5(8)	C3' -C2'-C11	126-0(5)
C3' -C4'	151.5(7)			C2' -C3'-C4'	115.2(4)
C7' -C8'	150.5(7)			C2' -C3'-C3	118.6(4)
				C2' -C3'-C2	119.6(5)
C7' -C2'''	148.0(8)	C8' -C2''''	149.7(6)	C3 -C3'-C4'	115.5(5)
C7' -C3'''	149.1(6)	C8' -C3''''	148.0(8)	C2 -C3'-C4'	117.4(4)
C2'''-C3'''	150.5(8)	C2''''-C3''''	150.1(7)	C2 -C1 -C3	58.9(3)
C9' -C10'	153.2(7)			C1 -C2 -C3	61.1(3)
				C1' -C8'-C7'	91.8(3)
				C1' -C8'-C2''''	125.4(4)
				C2''''-C8'-C3''''	60.5(3)

Torsional angle [°]	
C2' -C3'-C4'-C 5'	46.2(6)
C2 -C3'-C4'-C 2''	52.6(6)
C3 -C3'-C4'-C 3''	52.0(6)
C2''-C7'-C8'-C 2''''	7.5(9)
C3''-C7'-C8'-C 3''''	7.5(9)
C6' -C7'-C8'-C 1'	5.8(4)
C9' -C1'-C6'-C10'	5.9(4)

EXPERIMENTAL PART

General remarks: ^1H NMR: Bruker WH 270, WM 400; δ = 0 for tetramethylsilane, 7.15 for [D_5]benzene, 7.26 for chloroform; s = singlet, bs = broad singlet, d = doublet, t = triplet, m = multiplet, mc = centrosymmetric multiplet. - ^{13}C NMR: Bruker WM 400 (100.62 MHz); δ = 0 for tetramethylsilane, 77.0 for $CDCl_3$, 128.0 for C_6D_6; assignments were made on the basis of DEPT (distortionless enhancement by polarization transfer) spectra.- IR: Perkin-Elmer 125, 297, 399. - MS: Varian MAT CH 7 coupled with Varian Aerograph 1740 and Varian MAT 112 with Varian Aerograph 1400 (25 m fused silica capillary column Oribond SE 54, carrier gas: helium). High resolution MS: Varian MAT 311 A. - GC (analytical): Siemens Sichromat 3. - GC (preparative): Varian Aerograph 920, 3/8" PTFE columns with Chromosorb W-AW-DMCS 60-80 mesh.

Trispiro[2.0.2.0.2.1]decan-10-one-p-toluenesulfonylhydrazone (**5b**): A mixture of 2.0 g (14 mmol) **5a**, 3.77 g (20 mmol) p-toluenesulfonylhydrazid and 40 ml dry ethanol was heated under reflux for 7 d. After cooling to room temperature the reaction mixture was concentrated on a rotary evaporator to a volume of 20 ml, the precipitate was collected on a Büchner funnel and washed with 20 ml dry ethanol, yield 2.54 g (60%) **5b**. A second crop of 308 mg (7.2%) **5b** was obtained from the solutions to give a total of 2.85 g (67%) **5b** as white crystals, m.p. 169 °C (dec.). - ^1H NMR (270 MHz, $CDCl_3$): 0.25 (AA'BB', 4H, 5,6-H_2), 0.68 and 1.07 (AA'BB', 4H, 1,2,8,9-H_{endo}), 0.74 and 1.59 (AA'BB', 4H, 1,2,8,9-H_{exo}), 2.44 (s, 3H, $C\underline{H}_3$), 6.42 (bs, 1H, N-$\underline{H}$), 7.31 and 7.78 (AA'BB', 4H, Aryl-C-$\underline{H}$). - IR (KBr): 3430 (N-H), 3100, 3000, 1680 (C=N), 1600 (C=C), 1335 and 1170 (S=O), 1090, 1050, 1010, 980 cm^{-1}. - MS (70 eV): m/z = 316 (5%, M^+), 161 (43%, M-$C_7H_7SO_2^+$), 155 (4%, $C_7H_7SO_2^+$), 146 (9%, $C_{10}H_{12}N^+$), 132 (14%, $C_{10}H_{12}^+$), 123 (15%, $C_7H_7S^+$), 117 (45%, $C_9H_9^+$), 115 (20%, $C_9H_7^+$), 105 (30%, $C_8H_9^+$), 91 (100%, $C_7H_7^+$), 77 (40%, $C_6H_5^+$), 65 (38%, $C_5H_5^+$). Calcd. for $C_{17}H_{20}N_2O_2S$ (316.4) : C, 64.53; H, 6.37; N, 8.85; S,10.13. Found: C, 64.21 (64.22); H, 6.46 (6.46); N, 8.62 (8.65); S, 10.04%.

Alkaline thermal decompositions of the tosylhydrazone **5b**: *a) General procedure (for details see table 2)*: To a solution of **5b** in dry tetrahydrofuran (THF) was added in portions a 30 per cent excess of sodium hydride (freed from paraffin by washing with hexane). During this operation the reaction mixture warmed up, started to foam heavily and turned slightly yellow. It was then stirred for 10 to 15 min at room temperature and 4-5 h under reflux. After evaporation of the solvent on a rotary evaporator the finely ground light brown trispiro[2.0.2.0.2.1]-decan-10-one-p-toluenesulfonylhydrazone sodium salt (**5c**) was dried for at least 1 d at 25°C/0.1 torr. Even then it was not completely free of THF. Upon heating the dry salt under reduced pressure (10^{-1}-10^{-2} torr), decomposition started at about 180 °C and was completed at 200 °C. Most pyrolysis runs (see table 2) were conducted in a "Kugelrohr" connected to a cold trap kept at -78°C and in series with a second trap at -196°C to condense the highly volatile fractions. The colourless crude condensates were first checked by ^1H NMR spectroscopy and subsequently flash-chromatographed over silica gel with n-pentane.

Table 2. Experimental conditions for pyrolysis of 5c

Run	Prep. of 5c 5b/NaH in mg (mmol)	THF in ml	Pyrolysis temp. in C pressure in Torr	Crude in mg (%)	Yields rel. in crude in % (isolated in mg)				Isol.
					9	12	11	8	
1	105 (0.33)/	5	160-250a)	37.5	8	81	11	-	GC
	15 (0.63)		0.03	(86)	-	(9)	(2)	-	
2	79 (0.25)/	(3)	190-220	26	7	65	6	-	-
	-b)		0.005	(79)	-	-	-	-	
3	128 (0.41)/	10	200-250	37.5	10	37	7.5	-	GC
	51 (2.1)		0.1	(69)	-	(12)	(4)	-	
4	454 (1.44)/	8	200-250	97	65	27	8	-	SCc)
	50 (2.1)		0.1-0.4	(51)	(7)	(27)	(11)	-	
5	2540 (8.0)/	40	170-230	752	60d)	37	3	-	SCe)
	300 (12.5)		0.05	(71)	(57)	(143)	(18)	-	
6	3590 (11.4)/	80	180-230f)	1280	23	14	4	59	Dist.
	354 (15)		0.025	(54)	(156)	(111)	(38)	(870)	SC

a) Pyrolysis carried out in a 100 ml round-bottomed flask, products collected in two traps in series (-78 and -196 C). - b) **5b** reacted with sodium methoxide from 24 g (1.0 mmol) sodium and 3 ml dry methanol. - c) Chromatographed over 150 g silica gel (3.5 x 45 cm, 1.3 bar n-pentane). - d) Including 90 mg of a mixture of 52% **9** and 48% THF which were trapped at -196 C. - e) Chromatographed over 160 g silica gel (column 3 x 61 cm, n-pentane). - f) Pyrolysis in a flask with a short-path glass connection to a cold flask cooled to -196 C; 249 mg of a mixture of 51% **9** and 49% THF was collected in this trap. The united crude pyrolysates were distilled in a "Kugelrohr" to yield 410 mg (27%) of a mixture containing **9** and **12**, the residue weighed 870 mg (27%) and was almost pure azine **8**; the distillate was chromatographed over 42 g of silica gel (column 2 x 32 cm, 1.2 bar, n-pentane).

Fraction I (R_F = 0.76): Small amount of an unidentified white solid. - MS (70 eV): m/z = 264 (2%, M^+), 237 (3%, M-C_2H_3), 223 (5%, M-C_3H_5), 209 (12%, M-C_4H_7), 195 (7%), 181 (10%), 179 (11%), 167 (20%), 165 (15%), 155 (25%), 143 (21%), 141 (25%), 128 (43%), 117 (48%, $C_9H_9^+$), 115 (43%, $C_9H_7^+$), 105 (49%, $C_8H_9^+$), 91 (100%, $C_7H_7^+$), 79 (62%), 77 (68%), 67 (37%), 65 (35%), 55 (36%), 53 (35%).

II (R_F = 0.69): *endo*-tetraspiro[cyclopropane-1,3'-[2',5']bismethylenetricyclo-[4.2.2.$0^{1,6}$]decane-4,1''-cyclopropane-7,1'''-cyclopropane-8,1''''-cyclopropane] **12**, white solid, m.p. 69°C. - ^1H NMR (270 MHz, $CDCl_3$): 0.16-0.34 (m, 4H), 0.34-0.52 (m, 8H), 0.52-0.62 (m, 2H), 0.68-0.78 (m, 2H), 2.30 and 2.55 (AA'BB', 4H, 9',10'-H_2), 4.08 (s, 2H, 2',5'-H_{exo}), 4.51 (s, 2H, 2',5'-H_{endo}). - IR (KBr): 3100, 3080, 3000, 1645 and 1625 (C=C), 1030, 900 cm^{-1}. - ^{13}C NMR (100.62 MHz, $CDCl_3$): 7.10 and 9.61 (C-2''',3''',2'''',3''''), 10.99 and 11.71 (C-2,3,2'',3''), 26.67 (C-7',8'), 31.45 (C-9',10'), 32.62 (C-3',4'), 48.46 (C-1',6'), 102.99 (2',5'-$\underline{C}H_2$), 154.95 (C-2',5'). - MS (70 eV): m/z = 264 (1%, M^+), 249 (5%, M-CH_3), 236 (100%, M-C_2H_4), 221 (52%, M-C_3H_7), 207 (54%, M-C_4H_9), 193 (48%, M-C_5H_{11}), 179 (50%, M-C_6H_{13}), 165 (55%, M-C_7H_{15}), 153 (25%), 141 (15%), 128 (20%, $C_{10}H_8^+$), 115 (21%, $C_9H_7^+$), 91 (15%, $C_7H_7^+$), 89 (17%), 77 (14%), 65 (6%). - Calcd. for $C_{20}H_{24}$: 264.1878. Found: 264.19036 (MS).

III (R_F = 0.56): 7,8-dimethylenedispiro[2.0.2.2.]octane (**9**), colourless oil. - ^1H NMR (270 MHz, C_6D_6): 0.40 and 0.68 (AA'BB', 8H), 4.36 (s, 2H), 4.97 (s, 2H). - ^{13}C NMR (100.62 MHz, C_6D_6): 11.87 (C-1,2,5,6), 31.94 (C-3,4), 95.73 (7,8-$\underline{C}H_2$), 154.79 (C-7,8). - MS (70 eV): m/z = 132 (68%, M^+), 131 (35%, M-H), 117 (100%, M-CH_3), 115 (86%, $C_9H_7^+$), 104 (32%, $C_8H_8^+$), 91 (61%, $C_7H_7^+$), 77 (44%, $C_6H_5^+$), 65 (33%, $C_5H_5^+$), 51 (48%), 39 (78%). - Calcd. for $C_{10}H_{12}$: 132.0939. Found: 132.0909 (± 0.003) (MS).

IV (R_F = 0.47): tetraspiro[cyclopropane-1,4-tetracyclo[6.2.2.$0^{1,8}$.$0^{3,6}$]dodec-3,6-ene-5,1''-cyclopropane-9,1'''-cyclopropane-10,1''''-cyclopropane] (**11**): white solid, m.p. 121 °C. - ^1H NMR (270 MHz, C_6D_6): 0.11 (AA'BB', 4 H), 0.38 (AA'BB', 8H), 0.72 (AA'BB', 4H), 1.47 and 1.70 (AA'BB', 4H, 11',12'-H_2), 1.99 and 2.39 (AA'BB', 4H, 2',7'-H_2). IR (KBr): 3120, 2990, 1015 cm^{-1}. - ^{13}C NMR (100.62 MHz, C_6D_6): 4.78 and 4.83 (C-2''',3''',2'''',3''''), 6.95 and 8.21 (C-2,3,2'',3''), 25.93 (C-11',12'), 32.03 (C-2',7'), 33.85 (C-9',10'), 35.51 (C-4',5'), 42.22 (C-1',8'), 140.29 (C-3',6'). - MS (70 eV): m/z = 264 (28%, M^+), 249 (40%, M-CH_3), 335 (64%, M-C_2H_5), 221 (76%, M-C_3H_7), 207 (90%, M-C_4H_9), 205 (67%, M-C_4H_{11}), 193 (95%, M-C_5H_{11}), 191 (76%, M-C_5H_{13}), 181 (55%, M-C_6H_{11}), 179 (84%, M-C_6H_{13}), 165 (100%, $C_{13}H_9^+$), 155 (65%), 153 (63%), 141 (69%), 128 (73%), 117 (62%, $C_9H_9^+$), 115 (64%, $C_9H_7^+$), 91 (65%, $C_7H_7^+$), 77 (40%, $C_6H_5^+$). - Calcd. for $C_{20}H_{24}$: 264.1878. Found: 264.18807 (MS).

a) *Additional remarks*: The mass spectra were obtained with a GC/MS-system (2 m SE 30; 60°C, then 20°C/min; rel. retention times: **9** 1.0; **12** 2.94; product in fraction I 2.99, **11** 3.14). The relative proportions of products were determined by gaschromatography (GC). In some runs the crude pyrolysate was chromatographed over silica gel and the products then separated by preparative scale GC (GC 920, 1.2 m 10% SE 30, 150°C, rel. retention times: **12** 1.0, product in fraction I 1.13, **11** 1.24). Most of the dimethylenedispirooctane **9** decomposed upon either column chromatography (CC) or GC, the spectral data for **9** were obtained for samples from the two larger scale experiments (entries 5,6 in table 2), collected in the cold traps at -196°C together with THF.

The trispiro[2.0.2.0.2.1]decan-10-onazine (**8**) obtained in one run (entry 6 in table 2) was identical in all respects with an authentic sample obtained from **5a** and hydrazine.

Trispiro[2.0.2.0.2.1]decan-10-onazine (**8**): A solution of 148 mg (1mmol) **5a** and 150 mg (3 mmol) 99 per cent hydrazine hydrate in 5 ml dry diethyleneglycol was heated to 120°C under argon for 15 h. According to TLC (pentane/ether 1:1) the reaction was complete (R_F(5a) = 0.74), and the product (R_F = 0.81) was chromatographed on 10 g silica gel (column 1.2x21 cm, ether/pentane 1:1), yield 140 mg (96%) **8**, white crystals, m.p. 207-210°C (from ethanol). - ^1H NMR (270 MHz, $CDCl_3$): 0.25 (AA'BB', 8H, 5,6,5',6'-H_2), 0.64 (AA'BB', 8H, 1,2,8,9,1', 2',8',9'-H_{endo}), 1.10 and 1.58 (AA'BB', 8H, 1,2,8,9,1',2', 8',9'-H_{exo}). - IR (KBr): 2980, 2910, 1690 (C=N), 1040, 970 cm^{-1}. - ^{13}C NMR (20.15 MHz, $CDCl_3$): 5.42 (C-5,6,5',6'), 11.31 (C-1,8,1',8'), 12.08 (C-2,9,2',9'), 27.51 (C-3,3'), 32.55 (C-4,4'), 34.51 (C-7,7'), 176.31 (C-10,10'). - MS (70 eV): m/z = 292 (100%, M^+), 146 (24%, $C_{10}H_{12}N^+$), 130 (60%, $C_{10}H_{10}^+$), 105 (40%, $C_8H_9^+$), 91 (75%, $C_7H_7^+$). - Calcd. for $C_{20}H_{24}H_2$ (292.4): C,82.15; H 8.27; N 9.58. Found: C,82.37 (82.51); H,8.16 (8.18); N,9.44 (9.39)%.

Cyclopropanation of **9**: To a solution of 52.3 mg (0.40 mmol) **9** and 80 µl (0.80 mmol) diethylzinc in 2 ml dry diethyl ether with a little silver wool was added dropwise at room temperature within 1.5 h 96 µl (1.19 mmol) diiodomethane, and the mixture was stirred for 3d at room temperature. It was then diluted with 5 ml diethyl ether, poured onto 8 ml 1 N HCl; the organic phase was separated and the aqueous layer extracted with 3 portions of 5 ml of diethyl ether each. The organic phases were washed twice with 5 ml each of saturated $NaHCO_3$, three times with 5 ml each of NaCl solution and three times with 2 ml of water. After drying it over Na_2SO_4 and evaporating the solvent over a 30 cm packed column the crude product was chromatographed on 52 g silica (column 2x40 cm, 1.3 bar, n-pentane).
Fraction I (R_F=0.69): 5.8 mg (11%) **12**.
II (R_F=0.61): 5.2 mg (12%) tetraspiro[2.0.2.0.2.0.2.0]dodecane (**15**), white solid. - ^1H NMR (270 MHz, C_6D_6): 0.20 (s, 16H). - MS (70 eV): m/z = 160 (23%, M^+), 145 (15%, M-CH_3), 131 (38%, M-C_2H_5), 117 (100%, M-C_3H_7), 115 (39%, $C_9H_7^+$), 105 (24%, $C_8H_9^+$), 91 (64%, $C_7H_7^+$), 77 (20%), 65 (10%). The spectroscopic data are identical to those reported previously.[17]
III (R_F=0.59): 11.2 mg unidentified product, colourless oil. - ^1H NMR (270 MHz, C_6D_6): 0.09-2.29 (multitude of multiplets), 4.21 (s), 4.36 (s), 4.56 (s).
IV (R_F=0.47): 2.9 mg (5%) **11**.

Thermolysis of **12**: a) A solution of 6 mg (23 µmol) **12** in 300 µl C_6D_6 in a sealed ampoule was first heated to 30°C for 5 h, then to 40°C for 13.5 h and eventually to 70°C for 2 d. In each case the ^1H NMR spectrum depicted only the presence of unrearranged **12**.

b) A solution of 12.3 mg (47 µmol) **12** in 450 µl C_6D_6 in a sealed ampoule was heated to 160°C for 66 h, then to 200-210°C for 174 h. Except for a deterioration of the signal to noise ratio no changes were visible in the ^1H NMR spectrum.

c) Upon heating a sample of **12** in $CDCl_3$ in a sealed ampoule to 70°C for 22 h no reaction could be detected.

d) Upon flash-vacuum pyrolysis of **12** through a quartz tube (1x 30 cm) a 50 per cent reaction was observed at 500°C/$6\cdot10^{-3}$ torr; the gaschromatographic retention times (Sichromat 3, 25 m OV 1701 Oribond fused silica capillary, 210°C) of the products were much shorter (0.48, 0.54, 0.64 and 0.81) relative to that of **12** (1.00) except for one component (1.08) present in 2.6% proportion. At 650°C/0.05 Torr the turnover was 98% with the four fragmentation products accounting for 62% besides several others.

e) A solution of 14 mg (53 µmol) **12** in 25 µl dry methanol and 0.4 ml dry benzene was heated to 170°C in a sealed ampoule for 18.5 h. The thin layer chromatogram (TLC) developed with n-pentane showed only the presence of **12** (R_F = 0.69).

f) An analogous experiment with 14 mg (53 µmol) **12** in 0.5 ml isopropanol showed the same negative result.

(E)-10,10'-Bi(dispiro[2.0.2.4]decanylidene)-7,7'-dione (**25**): a) A solution of 45 mg (0.17 mmol) **12** in 3.0 ml dry nitrobenzene was kept under argon at 175°C for 21 h. According to TLC (n-pentane, R_F(12)=0.69 the reaction was complete. The solvent was condensed (50°C/0.012 Torr) into a cold trap and the residue sublimed at 100-150°C/0.01 Torr, yield 33 mg (73%) **25**, yellow solid, m.p. 198°C (recryst. from diethyl ether). - ^1H NMR (270 MHz, C_6D_6): 0.05(m, 4H), 0.27 (m, 8H), 1.10 (mc, 4H, 5,6,5',6'-H_{exo}), 2.39 and 2.53 (AA'BB', 8H, 8,8'-H_2 and 9,9'-H_2). The (E)-configuration of **25** was assigned on the basis of NOE difference spectroscopy: only saturation of the signal at 2.53 showed a significant NOE for the signal at 0.27 ppm. - IR (KBr): 3070, 2995, 1690 (C=O), 1020 cm^{-1}. - ^{13}C NMR (100.62 MHz,

$CDCl_3$): 11.35 (C-1,2,1',2'), 14.48 (C-5,6,5',6'), 23.46 (C-3,3'), 27.25 (C-9,9'), 36.25 (C-4,4'), 40.76 (C-8,8'), 134.18 (C-10,10'), 211.26 (C-7,7'). The assignment of the ^{13}C NMR signals was verified by $^1H,^{13}C$ COSY spectroscopy. - MS (70 eV): m/z = 296 (3%, M^+), 281 (8%, $M-CH_3$), 268 (19%, $M-C_2H_4$), 267 (21%, M- C_2H_5), 239 (33%, $M-C_4H_9$), 211 (27%, $M-C_6H_{13}$), 187 (100%, $C_{13}H_{15}O^+$), 172 (48%, $C_{12}H_{12}O^+$), 159 (26%, $C_{11}H_{11}O^+$), 148 (47%, $C_{10}H_{12}O^+$), 115 (34%, $C_9H_7^+$), 91 (46%, $C_7H_7^+$), 77 (36%, $C_6H_5^+$), 65 (21%, $C_5H_5^+$).- Calcd. for $C_{20}H_{24}O_2$: 296.1776. Found: 296.16595 (MS).

b) A solution of 2 mg (7.6 µmol) **12** in 300 µl [D_5]nitrobenzene was heated in a sealed NMR tube to 160°C and the reaction followed by ^1H NMR (400 MHz) spectroscopy integrating the signals of the adduct **12** at δ = 4.08 (s, 2H), 4.50 (s, 2H) and of the product **25** at δ = 2.76 and 2.91 (AA'BB', 8H). After 170 min the turnover was approximately 50% and after 25 h almost complete (94%). A rough estimate of the rate constant was obtained from the integrations after 20, 40, 90 and 170 min with $k = (7.67 \pm 0.83)\cdot 10^{-5}\ s^{-1}$.

c) An analogous experiment was carried out with 10.6 mg (40 µmol) **12** in 0.40 ml [D_5]nitrobenzene under argon in a sealed ampoule at 170°C; it was complete after 15 h with **25** as the sole product.

Acknowledgement - This work was supported by the Deutsche Forschungsgemeinschaft (Project Me 405/15-1/2), the Fonds der Chemischen Industrie as well as Hoechst AG, BASF AG and BAYER AG. We are grateful to Dr. V. Sinnwell for extensive help with non-routine NMR experiments. H.W. is indebted to the Fonds der Chemischen Industrie for a Doktoranden-Stipendium.

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