61. A Regiospecific Photochemical Rearrangement of 2-Azabenzotricyclo[5.2.2.$0^{1,5}$]- to 2-Azabenzotricyclo[6.2.1.$0^{1,5}$]undecatrienone

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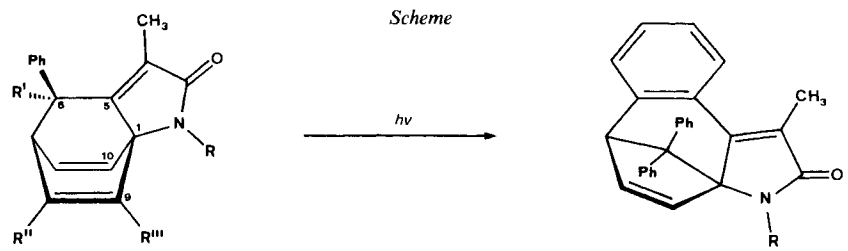
The 2-azatricyclo[5.2.2.$0^{1,5}$]undeca-4,8,10-trien-3-ones **1a** and **1b** gave on irradiation the 2-azatricyclo-[6.2.1.$0^{1,5}$]undeca-4,6,9-trien-3-ones **2a** and **2b**, respectively. The rearrangement was found to be solvent-, oxygen-, and wavelength-independant.

2-Azatricyclo[5.2.2.$0^{1,5}$]undeca-4,8,10-trien-3-ones with an electron-withdrawing group at C(4) have been recently reported to undergo a thermal rearrangement leading to the corresponding tricyclo[6.2.1.$0^{1,5}$]undeca-4,6,9-trien-3-ones [1] [2]. The basic role of such substituents at C(4) for the ionic mechanistic pathway has been convincingly demonstrated in these studies. This was, indeed, borne out by the observation that the corresponding tricyclic systems devoid of an electron-withdrawing group at C(4) failed to undergo this thermal rearrangement but led to the *retro-Diels-Alder* reaction product [3].

Compounds **1a**[1]) and **1b** with Me group at C(4) *(Scheme)* were found to be thermally stable and accordingly unreactive for a thermal rearrangement.

Surprisingly, however, the same model systems **1a** and **1b**, on irradiation, rearranged to the corresponding 2-azatricyclo[6.2.1.$0^{1,5}$]undeca-4,6,9-trien-3-ones **2a** and **2b**, respec-

Scheme



	R	R′	R″	R‴
1a	H	Ph	–(CH=CH)$_2$–	
b	$COCHPh_2$	Ph	–(CH=CH)$_2$–	
c	$COCHPh_2$	Ph	H	H
d	$COCHPh_2$	H	–(CH=CH)$_2$–	
e	$CONHC_{10}H_7$	Ph	–(CH=CH)$_2$–	

2a R = H
b R = $COCHPh_2$

[1]) Obtained on alkaline hydrolysis of **1e** [3] (see *Exper. Part*). This appears to be the only way of preparing this compound, since the *N*-unsubstituted allenic derivatives do not undergo cyclization [3].

tively, in good yields *(Scheme)*. The photochemical reaction was found to be wavelength- and solvent-independant and was unaffected, when carried out in an oxygen-saturated THF solution through which O_2 was bubbled. Attempts to sensitize the rearrangement with acetone, xanthone, acetophenone, 2-acetylnaphthalene, and anthracene-9,10-dicarbonitrile were unsuccessful. It can be concluded, on the basis of these sensitizing and quenching experiments, that the reaction probably does not proceed *via* a triplet intermediate.

It is worth noting that the benzo ring annellated along the C(8)–C(9) bond and the two Ph substituents at C(6) of **1a** and **1b** seem to play a decisive role in this reaction. Under the same reaction conditions, the tricyclic compound **1c** [3] gave a complex reaction mixture, while **1d** [4] was found to be photochemically stable.

A striking feature of this reaction is the regiospecific migration of C(9) from C(1) to C(5) and not of C(10). The isomer, which would be expected in this latter case, was not detected in the reaction mixture.

The structure of the photoproduct **2a** was assigned on the basis of the close similarity of its spectral data (see *Exper. Part*) to those of **2b** *(vide infra)*. The same product was also obtained on alkaline hydrolysis of **2b** under rigorous conditions.

The structure of **2b** was assigned on the basis of ^{1}H- and ^{13}C-NMR measurements. Apart from the normal ^{1}H- and broad-band (noise)-decoupled ^{13}C-NMR spectra, the following techniques were also used: DEPT, differential NOE, homonuclear shift correlation (HOMOCORR) for the ^{1}H,^{1}H connectivities, and heteronuclear shift correlation (HETCORR) for the ^{1}H,^{13}C connectivities, both direct and long-range coupled nuclei. The assignment of almost all signals in the ^{1}H- and ^{13}C-NMR spectra was accomplished on the basis of the above mentioned techniques without using any preliminary information from NMR chemical shifts or coupling constants. The numbering of the atoms is given in *Fig. 1*.

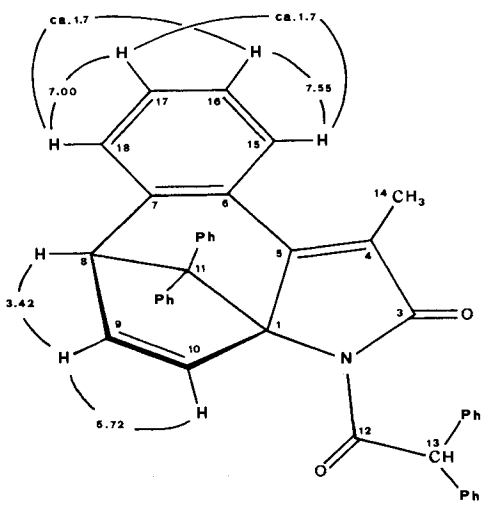


Fig. 1. *J(H,H) Values for* **2b**

The three ^{1}H-NMR signals at 4.59, 6.58, and 5.66 ppm, corresponding to H–C(8), H–C(9), and H–C(10), respectively, are assigned by their connections in the HOMOCORR spectrum and by their splitting patterns in the ^{1}H-NMR spectrum. The J(H,H) values are given in *Fig. 1*. The respective directly bonded C-atoms and the long-range couplings are listed in the *Table*.

Atoms *H*–C(8), *H*–C(10), *H*–C(9), and C(1) form an *ABCX* spin system. By irradiating H–C(8), H–C(10), and H–C(9), three sets of subspectra are obtained: *BCX*, *ACX*, and *ABX*, respectively. The *X* part is observed at 80.5 ppm. From the analysis of these spectra, the ^{1}H,^{13}C-coupling constants were evaluated (see the *Table*).

The protons H–C(15), H–C(16), H–C(17), and H–C(18) show an *ABCD* pattern of a four-spin system. It was found from the NOE-difference spectra that the signal *(doublet* of *doublets)* centered at 7.53 ppm corresponds to the proton closer to the Me group, *i.e* H–C(15). The chemical shifts and the coupling constants of the remaining protons are listed in the *Table*.

Table. *^{1}H- and ^{13}C-NMR Chemical Shifts, Direct* (++) *and Long-Range* (+) *Couplings of* **2b**. For arbitrary C-atom numbering, see *Fig. 1*.

	δ(^{13}C)	δ(^{1}H)						
		CH_3 2.14	H–C(8) 4.59	H–C(9) 6.58	H–C(10) 5.66	H–C(13) 6.75	H–C(15) 7.53	H–C(18) 6.70
C(1)	80.5		5.74	9.97	5.62			
C(3)	172.5	+						
C(4)	124.7	+						
C(5)	150.7	+					+	
C(6)	128.1	+	+				+	
C(7)	141.4		+				+	
C(11)	70.5		+					
C(12)	171.5					+		
C(arom.)–C(11)	141.7		+					+
	143.3							
C(arom.)–C(13)	139.0					+		
	139.7					+		
C(8)	55.8		126.6		+			
C(9)	133.1		+	++				
C(10)	131.1		+		++			
C(13)	56.5					119.0		
C(15)	130.0						++	
C(18)	127.7							++
C(arom.)	126.0							
	126.9							
	127.0					+		
	127.3							+
	128.2							
	128.5					+		
	129.0							
	129.5							
	129.8							
	129.9							
CH_3	11.0	++						

The two C=O C-atoms, C(3) and C(12), were assigned by the cross peaks with the Me protons (C(3), 172.5 ppm) and with *H*–C(13) (C(12), 171.5 ppm).

The two pairs of C(arom.) bonded to C(11) and C(13) gave four separate signals due to diastereotopicity. One of the Ph rings showed restricted rotation which could be seen from the ^{1}H-NMR spectrum recorded at r.t.: br. signal at *ca.* 7.0 ppm which is significantly narrowed on heating to 40°. On this ground, we ascribe the signal to *Ph*–C(11).

The lines corresponding to C(16) and C(17) as well as the Ph C-atoms remained unassigned. They give rise to 10 lines in total *(Table)*.

The structure of the photoproduct **2b** is confirmed by a single-crystal X-ray analysis[2]) performed by Dr. *B. Vincent*, University of Zurich.

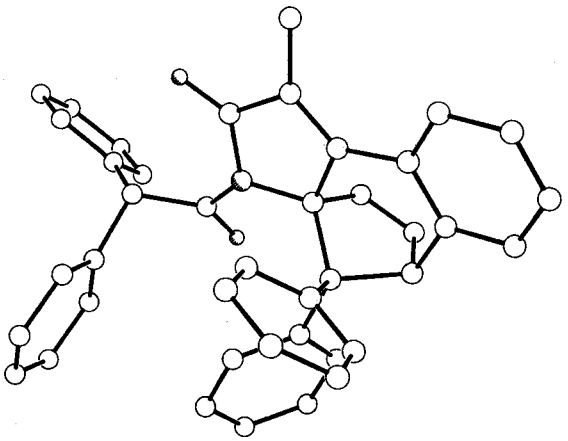


Fig. 2. *X-Ray structure of* **2b**

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Experimental Part

General. See [3]. The ^{1}H- (300 MHz) and ^{13}C-NMR (75.4 MHz) spectra of **2b** were measured on a *Varian XL-300* spectrometer.

1. *(1RS,7SR)-4-Methyl-6,6-diphenyl-2-azabenzo[8,9]tricyclo[5.2.2.0^{1,5}]undeca-4,8,10-trien-3-one* (**1a**). A soln. of **1e** [3] (400 mg, 0.74 mmol) and NaOH (100 mg, 2.5 mmol) in a mixture of THF (30 ml), EtOH (16 ml), and H_2O (10 ml) was kept at r.t. for 10 d. The solvent was removed under vacuum, and the residue was chromatographed on prep. TLC plates with petroleum ether/AcOEt/acetone 7:1:1 (4-fold development). The UV- (254 nm) active zone with R_f 0.2 was eluted with $CHCl_3$, to give, after removal of the solvent under vacuum, the crude product, which was recrystallized from 1,2-dimethoxyethane/$CHCl_3$ to afford pure **1a** (245 mg, 88%). M.p. 240.0–244.0° (dec.). IR ($CHCl_3$): 3435*m*, 2940*m*, 2880*m*, 1680*s*, 1590*w*. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.50–6.90 (*m*, 12 arom. H, NH); 6.82 (*d*, *J* = 7.5, H–C(10)); 6.54 (*dd*, *J* = 7.5, 6.0, H–C(11)); 6.45 (*dd*, *J* = 8.5, 1.5, H–C=C(8) or H–C=C(9)); 6.41 (*dd*, *J* = 8.0, 1.5, H–C=C(9) or H–C=C(8)); 4.70 (*dd*, *J* = 6.0, 1.1, H–C(7)); 1.50 (*s*, CH_3). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 177.2 (*s*, C(3)); 159.8 (*s*, C(5)); 142.9, 142.3, 140.6, 139.8 (4*s*, C(8), C(9), 2 C(arom.)); 136.5, 131.8 (2*d*, C(10), C(11)); 129.1, 128.2, 128.1, 127.6, 126.8, 126.4, 125.7, 118.9 (8*d*, arom. CH); 126.7 (*s*, C(4)); 69.6 (*s*, C(1)); 58.7 (*s*, C(6)); 55.8 (*d*, C(7)); 11.1 (*q*, CH_3). MS (70 eV): 376 (28), 375 (100, $M^{+\cdot}$), 374 (24), 360 (38), 205 (32), 165 (15), 143 (13), 127 (10, $[M - C_{10}H_7]^+$), 115 (14).

2. *(1RS,7SR)-4-Methyl-6,6-diphenyl-2-(diphenylacetyl)-2-azabenzo[8,9]tricyclo[5.2.2.0^{1,5}]undeca-4,8,10-trien-3-one* (**1b**). A soln. of 2-methyl-4,4-diphenyl-2,3-butadienoic acid (500 mg, 2 mmol) and *N*-(1-naphthyl)-3,3-diphenylketenimine (638 mg, 2 mmol) in dry THF (5 ml) was refluxed for 10 h. The solvent was removed under vacuum and the residue recrystallized from toluene/hexane 1:1 (2 ml) to afford **1b** (1.0 g, 88%) as colourless

[2]) Crystal data and atomic coordinates will be published elsewhere.

crystals. M.p. 200.0–201.0°. UV (cyclohexane): 255 (10300, sh), 280 (4700, sh). IR ($CHCl_3$): 3055*m*, 3000*m*, 1720*s*, 1690*s*, 1670*m*, 1600*m*. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.68 (*d*, J = 7.7, 2 arom. H); 7.52 (*d*, J = 7.7, 2 arom. H); 7.45–6.60 (*m*, 16 arom. H, CHCO); 6.79 (*d*, J = 7.2, 1 arom. H); 6.74 (*d*, J = 7.2, 1 arom. H); 6.50–6.40 (*m*, H–C(10), H–C(11)); 6.28 (*d*, J = 7.2, 2 arom. H); 4.67 (*d*, J = 4.0, H–C(7)); 1.47 (*s*, CH_3). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 172.0, 171.3 (2*s*, 2CO); 162.5 (*s*, C(5)); 142.4, 141.9, 139.0, 138.5 (4*s*, C(8), C(9), 2 C(arom.)); 134.9, 130.7 (2*d*, C(10), C(11)); 129.6, 129.2, 128.6, 128.5, 128.4, 128.0, 127.5, 127.4, 127.1, 127.0, 126.6, 126.5, 119.7 (13 *d*, arom. CH); 125.7 (*s*, C(arom.)); 72.6 (*s*, C(1)); 59.1 (*s*, C(6)); 55.5, 55.3 (2*d*, C(7), *C*HCO); 11.4 (*q*, CH_3). MS (70 eV): 569 (11, M^+), 375 (100, $[M - Ph_2C{=}C{=}O]^+$), 205 (9), 194 (12), 167 (48, Ph_2CH^+), 165 (30).

3. *(1RS,8RS)-4-Methyl-11,11-diphenyl-2-azabenzo[6,7]tricyclo[6.2.1.0^{1,5}]undeca-4,6,9-trien-3-one* (**2a**). A soln. of **1a** (22 mg) in a mixture of THF (5 ml) and Et_2O (25 ml) was irradiated with a 15-W *Hanau* low-pressure Hg lamp under N_2 at r.t. for 90 min. The solvent was removed under vacuum and the residue chromatographed on prep. TLC plates with petroleum ether/AcOEt/acetone 10:3:3 (2-fold development). The UV-active zone with R_f 0.4 was eluted with $CHCl_3$, the solvent removed, and the residue recrystallized from CH_2Cl_2/hexane to afford pure **2a** (7.0 mg, 32%) as colourless crystals. M.p. 227.5–231.5°. IR (KBr): 3440*m*, 3250*w*, 3060*w*, 1683*s*, 1600*w*. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.67 (br. *s*, 1 arom. H); 7.40–6.80 (*m*, 12 arom. H, NH); 6.55–6.40 (*m*, 1 arom. H, H–C(9)); 5.40 (*d*, J = 6.0, H–C(10)); 4.67 (*s*, H–C(8)); 2.26 (*s*, CH_3). MS (70 eV): 376 (30), 375 (100, M^+), 360 (16, $[M - CH_3]^+$), 298 (5), 297 (8), 165 (20).

4. *(1RS,8RS)-4-Methyl-11,11-diphenyl-2-(diphenylacetyl)-2-azabenzo[6,7]tricyclo[6.2.1.0^{1,5}]undeca-4,6,9-trien-3-one* (**2b**). A soln. of **1b** (300 mg) in Et_2O (300 ml) was irradiated as described above for 6 h. The residue obtained after removal of the solvent was chromatographed on prep. TLC plates with petroleum ether/AcOEt/acetone 10:1:1 (2-fold development), and the crude product was recrystallized from Et_2O/hexane to afford pure **2b** (399 mg, 52%) as colourless prisms. M.p. 231.0–233.5°. UV (cyclohexane): 233 (sh, 29500), 297 (19500). IR ($CHCl_3$): 3080*m* (sh), 3050*m*, 3000*m*, 1710*s*, 1655*m*, 1595*m*. ^{1}H- and ^{13}C-NMR: *Table*. MS (70 eV): 569 (31, M^+), 375 (100, $[M - Ph_2C{=}C{=}O]^+$), 194 (40, $[Ph_2C{=}C{=}O]^+$), 167 (54, Ph_2CH^+), 165 (56), 152 (12), 105 (10), 74 (25), 59 (45).

5. *Preparation of* **2a** via *Hydrolysis of* **2b**. A soln. of **2b** (114 mg, 0.2 mmol) and NaOH (13 mg, 0.3 mmol) in a mixture of THF (20 ml) and H_2O (2 ml) was refluxed for 56 h. The solvent was removed under reduced pressure and the residue chromatographed on prep. TLC plates with petroleum ether/AcOEt/acetone 10:1:1 (2-fold development). The crude product eluted from the zone with R_f 0.3 with $CHCl_3$ was recrystallized from CH_2Cl_2/hexane to give pure **2a** (12 mg, 16%), identical (m.p., TLC, IR) with an authentic sample.

REFERENCES

[1] G. Himbert, K. Diehl, G. Maas, *J. Chem. Soc., Chem. Commun.* **1984,** 900.
[2] R. W. Saalfrank, K. Hilbig, F. Schutz, K. Peters, H. G. v. Schnering, *Chem. Ber.* **1988,** *121,* 1291.
[3] L. S. Trifonov, A. S. Orahovats, *Helv. Chim. Acta* **1986,** *69,* 1585; *ibid.* **1987,** *70,* 262.
[4] L. S. Trifonov, A. S. Orahovats, *Helv. Chim. Acta* **1989,** *72,* 59.