Synthesis of 8,9,10,11,12,13,13a,14-Octahydro-7,11; 9,13-dimethanoazonino[1,2-b]isoquinolin-5(7H)-ones and Some Related Derivatives by Photocyclization Reactions of 5-Methylene-4-aroyl- and -acryloyl-4-azatricyclo[4.3.1.1^{3,8}]undecanes (4-Azahomoadamantanes)[1]

Shoji Eguchi,* Koji Asai, Hisato Takeuchi, and Tadashi Sasaki
Institute of Applied Organic Chemistry, Faculty of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464, Japan

5-Methylene-4-aroyl- and -acryloyl-4-azatricyclo[4.3.1.1^{3,8}]undecanes (2a—h) have been prepared by acylation of 5-methyl-4-azatricyclo[4.3.1.1^{3,8}]undec-4-ene (1). Irradiation of 4-aroyl derivatives (2a—d) afforded 2- or 4-substituted 8,9,10,11,12,13,13a,14-octahydro-7,11; 9,13-dimethanoazonino-[1,2-b]isoquinolin-5(7H)-ones (3a—d) in good yields *via* enamide photocyclization. DDQ oxidation of (3a—d) gave the corresponding hexahydroisoquinolin-5(7H)-ones (4a—d). Among the acryloyl derivatives, only the methacryloyl derivative (2g) afforded the enamide photocyclization product (5) in a lower yield, the other acryloyl derivatives (2e,f,h) when irradiated yielding the corresponding vinylogous amide derivatives (6a—c) *via* a 1,3-acyl shift.

The six-electron photocyclization of enamides provides a useful route to a nitrogen-containing six-membered ring and has been widely applied to the synthesis of alkaloids and related products.[2,3] We now report the results of the synthetic application of such enamide photocyclizations to some novel 8,9,10,-11,12,13-hexa- and 8,9,10,11,12,13,13a,14-octahydro-7,11; 9,13-dimethanoazonino[1,2-b]isoquinolin-5(7H)-ones.

Results and Discussion

5-Methyl-4-azatricyclo[4.3.1.1^{3,8}]undec-4-ene (1) was the compound of choice as starting material since it is both readily prepared from 2-methyladamantan-2-ol and known to be converted exclusively into 5-methylene derivatives on acylation.[4] Thus, acylation of (1) with benzoyl chloride in the presence of triethylamine in ether afforded the corresponding 4-benzoyl-5-methylene compound (2a) (enamide-II type)[2b] (82%), the structure of which was supported by appearance of characteristic i.r. absorption at 1 620 cm^{-1}, ^{1}H n.m.r. signals at δ 4.52 and 4.07 (C=CH$_2$), and by elemental analysis (Table 1). Similar acylation of (1) with p-methyl-, p-methoxy-, and o-methylbenzoyl chlorides gave the corresponding 5-methylene-4-aroyl-compounds (2b—d) in good yields (see Table 1), whilst acryloyl-, crotonyl-, methacryloyl-, and cinnamoyl chlorides afforded the corresponding 5-methylene-4-acryloyl derivatives (2e—h) (enamide-I type) in good yields (Scheme). The structure of all these products was confirmed by spectral and analytical data (Table 1).

Irradiation of (2a) in ether with a low-pressure Hg-lamp through a quartz filter under argon for 0.5 h afforded a cyclization product (3a) (66%), the structure of which was evidenced by appearance of characteristic ^{1}H n.m.r. signals at δ 3.78 (dd, J 13.5 and 3.0 Hz), 3.10 (dd, J 15.0 and 13.5 Hz), and 2.50 (dd, J 3.0 and 15.0 Hz) (13a-H and 14-H × 2) and also by the appearance of signals for only four aromatic protons (Tables 2 and 3). Similar irradiation of *para*-substituted (2b) and (2c) gave cyclization products (3b) and (3c) in 75 and 83% yields respectively. The irradiation of the o-methyl substituted derivative (2d) yielded regioselectively the 4-methyl-octahydro compound (3d) accompanied with the corresponding hexahydro compound (4d) (Table 2); there was no trace of the isomeric compound (3d') which might arise from regioisomeric

photocyclization of (2d), followed by a suprafacial [1,5] migration of the o-methyl group (Scheme). These results are compatible with the reported substituent effects in the photocyclization of N-benzoylenamines by Ninomiya and co-workers.[5] The latter workers obtained 5-benzyl-7-methyl-1,2,3,4,4a,10b-hexahydrophenanthridin-6(5H)-one selectively on irradiation of o-methyl-N-benzylcyclohex-1-enylbenzamide, whilst regiospecific photocyclization followed by a [1,5] shift of the substituent occurred for o-methoxy- or o-methylenedioxy substituted N-benzyl-N-benzoylenamines.[5] These results suggest that the steric effect on geometrical conformation is greater than the electronic effect for an o-methyl substituent in the photocyclization of N-benzoylenamines.

The cyclization products (3a—d) were readily converted into the corresponding hexahydro derivatives (4a—d) in high yields by 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) oxidation in benzene under reflux (Scheme). The structural assignments for these oxidation products were supported by spectral and analytical data (Table 3). Thus, appearance of singlet signals at δ 6.00—6.12 for one proton (14-H) instead of the ABX pattern mutiplet of (3a—d) was compatible with the structures shown.

The photochemical behaviour of the acryloyl derivatives (2e—h) was quite different from that of aroyl derivatives. Thus, irradiation of the acryloyl derivative (2e) under conditions similar to those described above afforded a complex mixture, from which the sole product, after preparative t.l.c., was the vinylogous amide derivative (6a) (40%); this was a 1,3-acyl rearrangement product.[2a,3c] Compound (6a) had an i.r. absorption at 1 590 cm^{-1} and a ^{1}H n.m.r. signal at δ 11.75 (NH, D$_2$O exchangeable) which permitted the structural assignment shown. Similarly, irradiation of (2f) and (2h) afforded the corresponding vinylogous amides (6b) and (6c) in 44 and 61% yields, respectively (Tables 2 and 3). The irradiation of the methacryloyl derivative (2g) also yielded a complex mixture, from which, however, the corresponding cyclization product (5) was isolated (25%) after preparative t.l.c.; the structural assignment was supported by spectral and analytical data (Table 3).

In the photocyclization of N-acryloylenamines and N-acryloylanilides, the α-substituent of the acyl moiety is known to improve the cyclization as a result of a steric effect which favours the requisite s-*trans* conformation of the α,β-unsaturated

Table 1. Physical and analytical data for 5-methylene-4-aroyl- and -acryloyl-4-azatricyclo[4.3.1.1$^{3.8}$]undecanes (2a—h)

Compound [M.p., °C]^a	% Yield	$v_{max}.cm^{-1}$ ^{b}	δ_H		% Found (requires)		
					C	H	N
(2a) [122—125]	(82)	3 060, 2 920, 2 840, 1 620, 1 580, 1 450, 1 395, 1 335, 870, 690	7.6—7.1 (m, 5 H), 5.10 (br s, 1 H), 4.52 (s, 1 H), 4.07 (s, 1 H), 2.90 (br s, 1 H), 2.3—1.5 (m, 12 H)^d	$C_{18}H_{21}NO$	80.85 (80.86)	7.8 (7.92)	5.35 (5.24)
(2b) [93—94]	(74)	3 100, 3 030, 2 920, 2 850, 1 630, 1 575, 1 510, 1 440, 1 395, 1 330, 835, 790, 770	7.50—6.85 (m, 4 H), 5.10 (br s, 1 H), 4.46 (s, 1 H), 4.00 (s, 1 H), 2.88 (br s, 1 H), 2.34 (s, 3 H), 2.3—1.4 (m, 12 H)	$C_{19}H_{23}NO$	81.1 (81.10)	8.35 (8.24)	4.85 (4.98)
(2c) [94.5—95.5]	(59)	3 100, 2 920, 2 850, 1 630, 1 510, 1 390, 1 330, 1 250, 840, 770	7.5—6.5 (m, 4 H), 5.08 (br s, 1 H), 4.48 (s, 1 H), 4.20 (s, 1 H), 3.78 (s, 3 H), 2.90 (br s, 1 H), 2.2—1.5 (m, 12 H)	$C_{19}H_{23}NO_2$	76.8 (76.73)	7.9 (7.80)	4.55 (4.71)
(2d) [90—91]	(87)	3 170, 2 930, 2 860, 1 640, 1 601, 1 520, 1 450, 1 400, 1 335, 1 241, 1 159, 870, 762	7.3—7.0 (m, 4 H), 5.05 (br s, 1 H), 4.55 (s, 1 H), 4.18 (s, 1 H), 2.85 (br s, 1 H), 2.39 (s, 3 H), 2.3—1.5 (m, 12 H)	$C_{19}H_{23}NO$	81.25 (81.10)	8.15 (8.24)	4.9 (4.98)
(2e) [54—55]	(83)	3 090, 2 910, 2 840, 1 640, 1 610, 1 400, 1 320, 1 310, 1 250, 1 235, 960, 785	6.82 (dd, J 9.0 and 17.0, 1 H), 6.26 (dd, J 17.0, and 3.0, 1 H), 5.50 (dd, J 3.0 and 9.0, 1 H), 5.00 (br s, 1 H), 4.94 (s, 1 H), 4.58 (s, 1 H), 2.95 (br s, 1 H), 2.5—1.1 (m, 12 H)	$C_{14}H_{19}NO$	77.35 (77.38)	8.85 (8.81)	6.45 (6.45)
(2f) [80—83]	(56)	3 090, 2 910, 2 850, 1 660, 1 635, 1 450, 1 435, 1 385, 1 330, 1 235, 1 200, 960, 885	6.70 (dq, J 16.0 and 17.0, 1 H), 6.32 (d, J 16.0, 1 H), 4.90 (br s, 1 H), 4.80 (s, 1 H), 4.48 (s, 1 H), 2.88 (br s, 1 H), 1.82 (d, J 6.0, 3 H), 2.2—1.4 (m, 12 H)	$C_{15}H_{21}NO$	77.88 (77.88)	9.25 (9.15)	5.95 (6.05)
(2g) [74—76]	(82)	3 080, 2 920, 2 895, 2 850, 1 625, 1 450, 1 435, 1 390, 1 340, 1 195, 880	5.25—4.80 (m, 2 H), 4.80 (br s, 1 H), 4.62 (s, 1 H), 4.54 (s, 1 H), 2.90 (br s, 1 H), 2.3—1.3 (m, 12 H), 1.90 (s, 3 H)	$C_{15}H_{21}NO$	77.79 (77.88)	9.15 (9.05)	6.13 (6.05)
(2h) [88—90]	(99)	3 060, 2 920, 2 840, 1 620, 1 580, 1 450, 1 395, 1 335, 870, 690	7.70—6.85 (m, 7 H), 5.20 (br s, 1 H), 4.90 (s, 1 H), 4.70 (s, 1 H), 2.98 (br s, 1 H), 2.2—1.5 (m, 12 H)	$C_{20}H_{23}NO$	81.88 (81.87)	8.00 (7.90)	4.67 (4.77)

^{a} Purified by chromatography (Woelm N alumina or Merck aluminium oxide 60PF-254, type E, CH$_2$Cl$_2$–hexane system) and recrystallized from CH$_2$Cl$_2$–hexane. ^{b} As KBr discs. ^{c} All ^{1}H n.m.r. spectra were measured in CCl$_4$ unless otherwise noted. Multiplicities and J values (Hz) are given in parentheses. ^{d} In CDCl$_3$.

Table 2. Photolysis of 5-methylene-4-aroyl- and -acryloyl-4-azatricyclo[4.3.1.1$^{3.8}$]undecanes (2a—h)

Compound	Irrad'n time (h)	c/mM^a	Products	% Yield^b
(2a)	0.5	(0.28)	(3a)	(66)
(2b)	0.5	(0.21)	(3b)	(75)
(2c)	0.5	(0.20)	(3c)	(83)
(2d)	1.0	(0.60)	(3d)	(29)^c
			(4d)	(36)^c
(2e)	1.5	(0.46)	(6a)	(40)
(2f)	0.7	(0.32)	(6b)	(44)
(2g)	1.5	(0.17)	(5)	(25)
(2h)	1.5	(0.48)	(6c)	(61)

^{a} An ethereal solution of (2) deoxygenated by bubbling argon through it for 0.5 h, was irradiated with a low-pressure mercury lamp (60 W) through a quartz filter at room temperature. ^{b} Isolated yields after preparative t.l.c. (Merck aluminium oxide PF-254, type E, CH$_2$Cl$_2$–hexane system). ^{c} The irradiation in hexane also afforded (3d) and (4d) in 37 and 26% yields respectively.

carbonyl group.[2b,6] The geometrical constraint of enamide molecules by hydrogen-bonding is also known to prohibit the photochemical cyclization[3b] or to control the regiochemistry of the photocyclizations.[5,7]

The observed photochemical behaviour of the acryloylen-

amines (2e—h) can be rationalized in terms of conformational factors, i.e. on the basis of a molecular model study and ^{1}H n.m.r. data [3-H appears at δ 5.20—4.80 and 5-CH$_2$ at δ 4.94—4.00 for (2a—h), Table 1]. Of the four possible conformations, the Z* isomers seem to be less important. Assuming, therefore, the presence of E isomers, the steric repulsion between the 5-methylene group and C=C group in the E-s-trans conformation disfavours the cyclization for R^4=H (2e,f,h), on the grounds of molecular geometry. In contrast, the presence of an α-methyl substituent (2g; R^4=Me) permits the E-s-cis conformation to equilibrate with the prerequisite E-s-trans geometry as a result of steric repulsion between the 5-methylene and R^4 (Me) groups, thus, leading to the photocyclization.† The 1,3-acyl shift, the major photochemical reaction of enamides, suffers, in general, no geometrical constraint[2a] and, therefore, the

* Concerning the amide bond.
† The calculated strain energies on a carbon analogue (i.e. a triene system) by molecular mechanics using the MMP$_2$ program[8] are 28.70 (for a corresponding geometry to E-s-trans in Scheme) and 22.83 (E-s-cis) kcal/mol for R^4 = R^5 = H, and 30.22 (E-s-trans) and 29.76 (E-s-cis) kcal/mol for R^4 = Me, R^5 = H, respectively. The results are in agreement with the above view: further details will be published in a future publication.

Scheme.
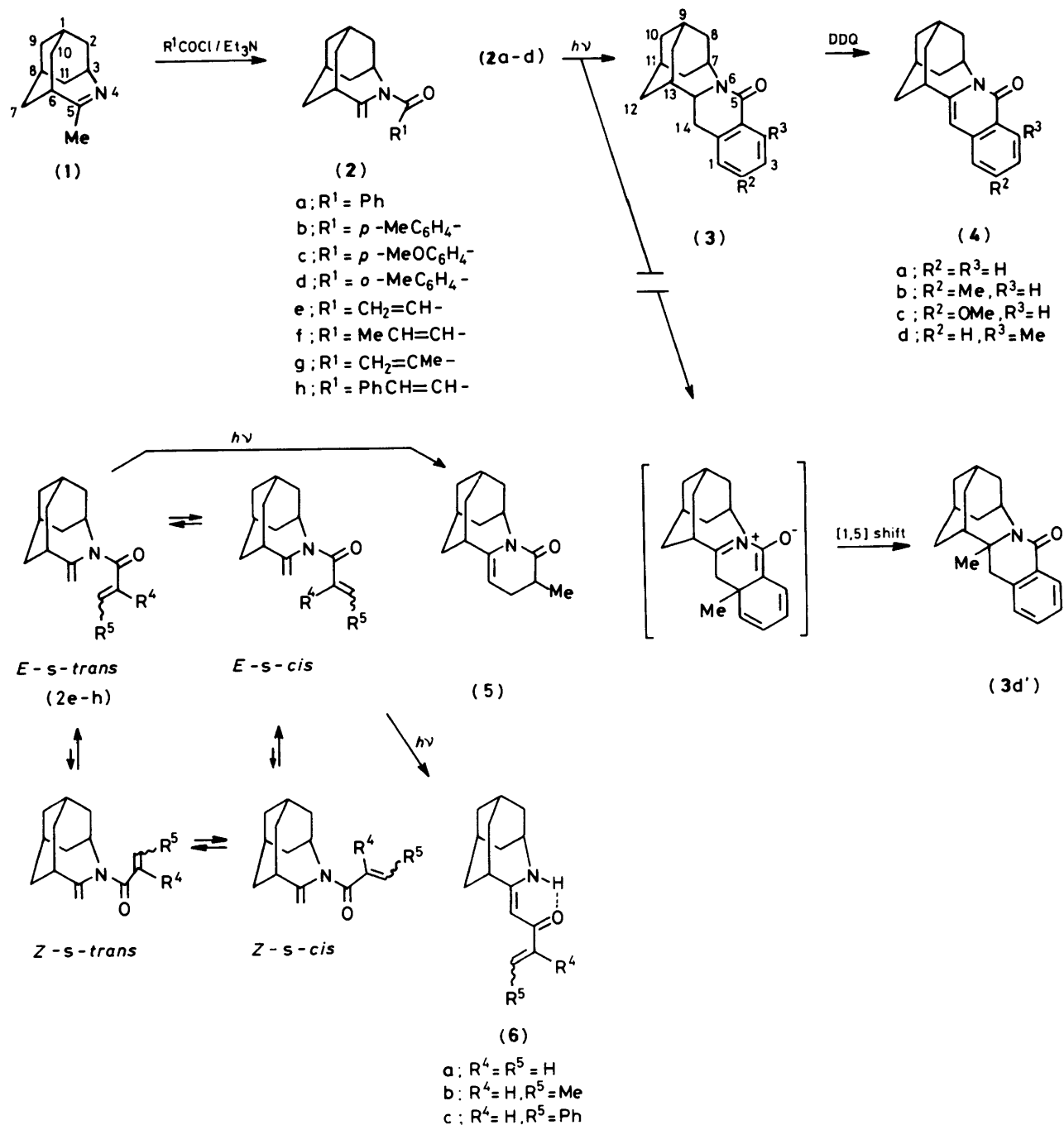
acryloylenamines (2e,f,h) afford the vinylogous amides (6a—c) upon irradiation.

Experimental

M.p.s were taken in a sealed tube on a Yanagimoto micro-melting point apparatus and are uncorrected. Microanalyses were performed with a Perkin-Elmer 240B elemental analyzer. ^{1}H n.m.r. spectra were taken at 25 °C with a JEOL JMN-C-60HL instrument at 60 MHz using Me$_4$Si as internal standard. I.r. spectra were recorded on a JASCO A-100 spectrometer.

4-Benzoyl-5-methylene-4-azatricyclo[4.3.1.1 ^{3,8}]*undecane* (2a).—Benzoyl chloride (106 mg, 0.75 mmol) in ether (1 ml) was

added to an ice-cooled and stirred mixture of 5-methyl-4-tricyclo[4.3.1.1 ^{3,8}]undec-4-ene (1)[4] (81 mg, 0.50 mmol) and triethylamine (76 mg, 0.75 mmol) in anhydrous ether (3 ml), and the stirring was continued for 3 h at room temperature. The mixture was filtered and the filtrate evaporated under reduced pressure to give a residue which was chromatographed on an alumina (Woelm N) column by elution with CH$_2$Cl$_2$ to afford the benzoyl derivative (2a) as crystals (110 mg, 82%); for the physical and analytical data, see Table 1.

The acylation of (1) with p-methyl-, p-methoxy-, and o-methyl-benzoyl chlorides, and acryloyl-, crotonyl-, methacroyl-, and cinnamoyl chlorides was carried out similarly to afford the corresponding 5-methylene-4-aroyl- and -acryloyl-compounds (2b—h) (see Table 1).

Table 3. Physical and analytical data for the photoproducts (3a—d), (5), (6a—c) and some related derivatives (4a—d)

Compound (M.p., °C)[a]	$\nu_{max}./cm^{-1}$ [b]	δ_H		% Found (requires)		
				C	H	N
(3a) (144.5—146.5)	2 910, 2 845, 1 635, 1 600, 1 580, 740, 735, 695	8.1—6.8 (m, 4 H), 5.42 (br s, 1 H), 3.78 (dd, J 13.5 and 3.0, 1 H), 3.10 (dd, J 13.5 and 15.0, 1 H), 2.50 (dd, J 3.0 and 15.0, 1 H), 2.5—1.3 (m, 13 H)	$C_{18}H_{21}NO$	80.85 (80.86)	8.05 (7.92)	5.1 (5.24)
(3b) (143.5—145.5)	2 910, 2 845, 1 625, 1 580, 835, 775, 700	7.95—6.70 (m, 3 H), 5.35 (br s, 1 H), 3.78 (dd, J 13.5 and 3.0, 1 H), 3.07 (dd, J 13.5 and 15.0, 1 H), 2.42 (dd, J 15.0 and 3.0, 1 H), 2.33 (s, 3 H), 2.4—1.3 (m, 13 H)	$C_{19}H_{23}NO$	81.1 (81.10)	8.45 (8.24)	4.8 (4.98)
(3c) (156.5—158.5)	2 900, 2 840, 1 625, 1 608, 1 580, 1 440, 1 400, 1 335, 1 260, 1 022, 840, 777, 700	8.0—6.4 (m, 3 H), 5.36 (br s, 1 H), 3.80 (s, 3 H), 3.77 (dd, J 13.5 and 3.0, 1 H), 3.08 (dd, J 15.0 and 13.5, 1 H), 2.48 (dd, J 15.0 and 3.0, 1 H), 2.4—1.3 (m, 13 H)	$C_{19}H_{23}NO_2$	76.7 (76.73)	8.0 (7.80)	4.55 (4.71)
(3d) (151—153)	3 070, 3 020, 2 925, 2 850, 1 650, 1 640, 1 605, 1 445, 1 405, 1 330, 1 302, 1 260, 1 102, 1 055, 960, 780, 760, 700	7.5—6.6 (m, 3 H), 5.38 (br s, 1 H), 3.79 (dd, J 13.5 and 3.0, 1 H), 3.16 (dd, J 13.5 and 15.0, 1 H), 2.60 (s, 3 H), 2.50 (dd, J 15.0 and 3.0, 1 H), 2.3—1.4 (m, 13 H)	$C_{19}H_{25}NO$	81.15 (81.10)	8.4 (8.24)	4.7 (4.98)
(4a)[e] (152—154)	2 920, 2 850, 1 640, 1 620, 1 595, 1 440, 1 160, 825, 760	8.5—7.1 (m, 4 H), 6.12 (s, 1 H), 5.95 (br s, 1 H), 3.02 (br s, 1 H), 2.50—1.52 (m, 14 H)	$C_{18}H_{19}NO$	81.5 (81.47)	6.95 (7.22)	5.2 (5.28)
(4b)[e] (170—172)	2 920, 2 850, 1 640, 1 620, 1 600, 1 440, 815, 780	8.25—6.75 (m, 3 H), 6.00 (s, 1 H), 5.92 (br s, 1 H), 3.00 (br s, 1 H), 3.00 (br s, 1 H), 2.42 (s, 3 H), 2.50—1.42 (m, 12 H)	$C_{19}H_{21}NO$	81.57 (81.68)	7.73 (7.58)	4.98 (5.01)
(4c)[e] (189—191)	3 060, 2 990, 2 910, 2 850, 1 645, 1 620, 1 595, 1 370, 1 250, 1 175, 1 038, 878, 830, 770, 685	8.25—6.50 (m, 3 H), 6.08 (s, 1 H), 5.87 (br s, 1 H), 3.85 (s, 3 H), 2.96 (br s, 1 H), 2.4—1.45 (m, 12 H)	$C_{19}H_{21}NO_2$	77.27 (77.26)	7.29 (7.17)	4.61 (4.74)
(4d)[e] (204—207)	3 050, 2 910, 2 845, 1 660, 1 640, 1 595, 1 480, 1 440, 1 380, 1 315, 1 260, 1 200, 1 035, 1 000, 898, 890, 780, 700, 682	7.5—6.9 (m, 3 H), 6.04 (s, 1 H), 5.90 (br s, 1 H), 2.95 (br s, 1 H), 2.83 (s, 3 H), 2.5—1.5 (m, 12 H)	$C_{19}H_{21}NO$	81.9 (81.68)	7.61 (7.58)	4.85 (5.01)
(5) (73—76)	2 910, 2 840, 1 660, 1 590, 1 545, 1 300, 1 105, 800, 735	5.55 (br s, 1 H), 5.15 (br s, 1 H), 3.65 (br s, 1 H), 2.45 (br s, 1 H), 2.3—1.5 (14 H), 1.12 (d, J 6.0, 3 H)	$C_{15}H_{21}NO$	78.15 (77.88)	8.95 (9.15)	5.95 (6.05)
(6a) (oil)	3 300—2 600, 2 910, 2 840, 1 595, 1 560, 1 300, 1 115, 810, 735, 695	11.75 (br s, 1 H)[d], 6.23 (dd, J 18.0 and 8.0, 1 H), 5.90 (dd, J 18.0 and 4.0, 1 H), 5.31 (dd, J 8.0 and 4.0, 1 H), 4.88 (s, 1 H), 3.68 (br s, 1 H), 2.40 (br s, 1 H), 2.4—1.4 (m, 12 H)	$C_{14}H_{19}NO$	77.3 (77.38)	9.05 (8.81)	6.25 (6.45)
(6b) (73—75)	3 300—2 600, 2 920, 2 850, 1 595, 1 560, 1 295, 1 220, 1 115, 1 058, 865, 835, 765	11.60 (br s, 1 H)[d], 6.56 (dq, J 16.0 and 7.0, 1 H), 5.82 (dd, J 16.0 and 1.5, 1 H), 4.80 (s, 1 H), 3.65 (br s, 1 H), 2.35 (br s, 1 H), 1.82 (dd, J 7.0 and 1.5, 3 H), 2.2—1.4 (m, 12 H)	$C_{15}H_{21}NO$	77.9 (77.88)	9.3 (9.15)	5.9 (6.05)
(6c) (Oil)	3 300—2 600, 2 970, 2 920, 2 850, 1 660, 1 650, 1 590, 1 335, 1 290, 1 110, 765, 695	11.80 (br s, 1 H)[d], 7.8—5.6 (m, 7 H), 4.97 (s, 1 H), 3.60 (br s, 1 H), 2.5—1.4 (m, 13 H)	$C_{20}H_{23}NO$	81.6 (81.87)	7.7 (7.90)	4.8 (4.77)

[a] For isolation, see Table 2 and Experimental section. [b] Solid compounds were scanned as KBr discs and oils were scanned as neat films. [c] All [1]H n.m.r. spectra were measured CCl₄. Multiplicities and J values (Hz) are given in parentheses. [d] D_2O exchangeable. [e] For the yields, see Experimental section.

General Procedure for Photolysis of 5-Methylene-4-aroyl- and -acryloyl-4-azatricyclo[4.3.1.1 ^{3,8}]*undecanes* (2a—h).—An ethereal solution of the appropriate compound (2) was deoxygenated by bubbling argon through the solution for 0.5 h and irradiated with a low-pressure mercury lamp (60 W) through a quartz filter at room temperature for 0.5—1.5 h. Removal of the solvent under reduced pressure gave a solid residue which was purified by preparative t.l.c. (Merck aluminium oxide 60PF-254, type E) by eluting with CH_2Cl_2-hexane to afford either the photocyclization or 1,3-acyl shift product. The results are summarized in Tables 2 and 3.

8,9,10,11,12,13-Hexahydro-7,11; 9,13-dimethanoazonino-[1,2b]*isoquinolin-5(7H)-one* (4a).—A mixture of the octahydro derivative (3a) (36 mg, 0.14 mmol) and DDQ (46 mg, 0.20 mmol) in anhydrous benzene (2 ml) was heated to reflux for 26 h. After removal of the solvent, a solid residue was purified on a preparative t.l.c. (Merck aluminium oxide 60PF-254, type E) by elution with CH_2Cl_2 to give the hexahydro derivative (4a) as crystals (24 mg, 77%). The oxidation of (3b), (3c), and (3d) was carried out similarly to afford (4b), (4c), and (4d) in 80, 65, and 60% yields, respectively. The physical and analytical data of (4a—d) are also summarized in Table 3.

References

1 Synthesis of Novel Carbo- and Hetero-polycycles. Part 3. For Part 2, see S. Eguchi, K. Asai, and T. Sasaki, *Heterocycles*, 1986, **24**, 737. For Part 1. see S. Eguchi, T. Ikemoto, Y. Kobayakawa, and T. Sasaki, *J. Chem. Soc., Chem. Commun.*, 1985, 958.

2 For recent reviews, see (*a*) G. R. Lenz, *Synthesis*, 1979, 489; (*b*) I. Ninomiya and T. Naito, *Heterocycles*, 1981, **15**, 1433.

3 For some recent applications, see (*a*) J.-C. Gramain, Y. Troin, and D. Vallee, *J. Chem. Soc., Chem. Commun.*, 1981, 832; (*b*) M. Hutchins, M. Sainsbury, and D. Scopes, *Tetrahedron*, 1984, **40**, 1511; (*c*) A. Couture, R. Dubiez, and A. L. -Combier, *ibid.*, 1984, **40**, 1835; (*d*) I. Ninomiya, C. Hashimoto, T. Kiguchi, and T. Naito, *J. Chem. Soc., Perkin Trans. 1*, 1985, 941.

4 T. Sasaki, S. Eguchi, and N. Toi, *J. Org. Chem.*, 1978, **43**, 3810.

5 (*a*) I. Ninomiya, T. Kiguchi, O. Yamamoto, and T. Naito, *J. Chem. Soc., Perkin Trans. 1*, 1979, 1723; (*b*) I. Ninomiya, T. Kiguchi, and T. Naito, *J. Chem. Soc., Chem. Commun.*, 1974, 81; (*c*) See also, T. Kametani, T. Sugai, Y. Shoji, T. Honda, F. Satoh, and K. Fukumoto, *J. Chem. Soc., Perkin Trans. 1*, 1977, 1151.

6 Y. Ogata, K. Takagi, and I. Ishino, *J. Org. Chem.*, 1971, **36**, 3975.

7 I. Ninomiya, T. Kiguchi, S. Yamauchi, and T. Naito, *J. Chem. Soc., Perkin Trans. 1*, 1980, 197.

8 A modified Allinger's MM2 program by E. Osawa (Hokkaido University); MM2: N. L. Allinger, *J. Am. Chem. Soc.*, 1977, **99**, 8127.