MICHAEL ADDITION OF 1,3-CYCLOPENTANEDIONE, 1,3-CYCLOHEXANEDIONE AND 1,3-CYCLOHEPTANEDIONE TO 1-(X-PHENYL)-2-NITROETHYLENES

Pavel HRNČIAR and Igor ČULÁK

Department of Organic Chemistry, Comenius University, 842 15 Bratislava

Received June 17th, 1983

Michael addition of 1,3-cyclopentanedione, 1,3-cyclohexanedione and 1,3-cycloheptanedione to 1-(X-phenyl)-2-nitroethylenes was studied. 1,3-Cyclopentanedione afforded 2-(1-(X-phenyl)-2-nitroethyl)-1,3-cyclopentanediones (*I*), 1,3-cyclohexanedione gave 9-(X-phenyl)-8-hydroxyimino-7-oxabicyclo[4,3,0]-1-nonen-2-ones (*IIa*—*IIe*), whereas reaction with 1,3-cycloheptanedione led to 10-(X-phenyl)-8-oxabicyclo[5,3,0]-1-decen-2-ones (*IIg*—*IIj*) as well as 9,9′-hydroxyaminobis(10-(X-phenyl)-8-oxabicyclo[5,3,0]-1-decen-2-ones) (*III*). Products *I* were isolated also in the addition of 1,3-cyclohexanedione and 1,3-cycloheptanedione to 1-(X-phenyl)-2-nitroethylene when X = H or an electron accepting substituent and the reaction was performed at −5 to 0°C, and were converted into *II*. The structure of the compounds and mechanism of the conversion of *I* to *II* is discussed on the basis of IR, ^{1}H NMR and ^{13}C NMR spectra.

As found by Dornow and Boberg[1], 2,4-pentanedione or ethyl acetoacetate add to 1-phenyl-2-nitroethylene in the "classical" way. Also the addition of cyclic β-diketones to nitroalkenes proceeds normally[2-4]. On the other hand, other authors[5-7] reported that reaction of 1,3-cyclohexanedione with 1-phenyl-2-nitroethylene afforded a product containing one molecule of water less than the expected adduct, and suggested several, incorrect, structures for this product. The correct structure *IIa*, published by Ansell and coworkers[8,9], was determined on the basis of X-ray diffraction analysis and ^{1}H NMR and IR spectral studies. Analogous behaviour was found for the reaction of 5,5-dimethyl-1,3-cyclohexanedione with 1-phenyl-2-nitroethylene[10].

In the present communication we investigate the effect of the ring size and the substituent X on the character of the product in the addition of 1,3-cycloalkanediones to 1-(X-phenyl)-2-nitroethylenes. The addition was performed with 1,3-cyclopentanedione, 1,3-cyclohexanedione and 1,3-cycloheptanedione. Michael addition, of 1,3-cyclopentanedione and 1,3-cycloheptanedione with 1-(X-phenyl)-2-nitroethylene has not been hitherto described. Analysis of the reaction products revealed that under identical conditions the mentioned 1,3-cycloalkanediones afforded different products.

1,3-Cyclopentanedione reacted with 1-(X-phenyl)-2-nitroethylenes (where X = H, 4-F, 4-Cl, 4-Br, 3-Br, 4-CH_3, 4-OCH_3, 4-NO_2, 4-$NHCOCH_3$ and 4-$N(CH_3)_2$)

to give products of the "classical" Michael addition, *i.e.* 2-(1-(X-phenyl)-2-nitroethyl)-1,3-cyclopentanediones *Ia–Ik*. These compounds represented final products since they were isolated even when prolonged reaction time, higher reaction temperature or higher concentration of the catalyst were employed. It is known[8–10] that both 1,3-cyclohexanedione and 5,5-dimethyl-1,3-cyclohexanedione react with 1-phenyl-2-nitroethylene under the conditions described in procedure *A* in the Experimental part, affording products with one molecule of water less than expected. Since in 1,3-cyclopentanedione, similarly to 1,3-cyclohexanedione and their 2-monosubstituted derivatives, the keto-enol form is preferred, the reaction stops at the stage of the structure *I* probably because further transformation of compounds *I* into the derivatives *II* or *III* would be sterically demanding, leading to a structure with two five-membered rings linked by a double bond. The structure of the compounds *I* has been confirmed by their IR, ^{1}H NMR and ^{13}C NMR spectra (Tables I, II).

In accord with the literature[6–10], the addition of 1,3-cyclohexanedione to 1-(X-phenyl)-2-nitroethylenes (procedure *A*) affords products having one molecule of water less than the expected classical Michael addition products, the outcome of the reaction being independent of the substituent X. On the basis of the IR, ^{1}H NMR and ^{13}C NMR spectra we conclude that the obtained products are 9-(X-phenyl)-8-hydroxyimino-7-oxabicyclo[4.3.0]-1-nonen-2-ones *IIa–IIe*. Their IR spectra contain two characteristic bands in the region 1 600–1 700 cm^{-1}. Comparison of the spectra of compounds *I–III* (Table I) indicates that the band at 1 655–1 658 cm^{-1} is due to the C=O stretching vibration of the carbonyl, conjugated with the C=C double bond, whereas the band at 1 695–1 700 cm^{-1} belongs to the C=N stretching vibration. The ^{1}H NMR spectra of compounds *II* (Table I) exhibit two triplets at 4·73–4·85 ppm ($J \sim 1$ Hz) and 4·85–5·00 ppm ($J \sim 1$ Hz), corresponding to one proton, and two singlets at 10·08–10·15 ppm and 10·38 ppm, also corresponding to one proton. It follows that two geometric isomers (*E*,*Z*) of the oximes are present. Also the ^{13}C NMR spectrum of compound *IIa* (Table II) confirms the structure *II*. The double signals of atoms $C_{(8)}$, $C_{(9)}$, $C_{(6)}$, $C_{(1)}$ as well as the $C_{(2)}$ (carbonyl) and aromatic $C_{(1)}$, $C_{(2)}$, $C_{(3)}$ and $C_{(4)}$ atoms, prove that the *E*,*Z*-isomerism at the C=N oxime bond affects the character of carbon atoms in a large part of the molecule. We found that the ratio of the *E*- and *Z*-isomers varies, depending on the solvent from which the compounds are crystallized: this is also reflected by their melting points.

Also the Michael addition of 1,3-cycloheptanedione to 1-(X-phenyl)-2-nitroethylene (procedure *A*) afforded products analogous to those from 1,3-cyclohexanedione, *i.e.* 10-(X-phenyl)-9-hydroxyimino-8-oxabicyclo[5.3.0]-1-decen-2-ones *IIg–IIk*. The IR, ^{1}H NMR and ^{13}C NMR spectra of compound *IIg* resemble those of compounds obtained by reaction with 1,3-cyclohexanedione (Tables I and II). The ^{1}H NMR spectra of compounds *IIg–IIk* as well the ^{13}C NMR spectrum of the compound *IIg* also show the formation of *E*,*Z*-isomeric oximes. Contrary to 1,3-cyclohexane-

TABLE I

Spectral parameters of the synthesized compounds

Compound	λ_{max}, nm log ε	$\nu(NO_2)$	ν(CO), ν(C=N)	^{1}H NMR, δ ppm		
Ia	247 4·13	1 542 1 375	1 633	2·35 (4 H, s), 4·43 (1 H, t),	5·1 (2 H, d) 7·23 (5 H, s)	—
Ib	249 4·12	1 545 1 380	1 632	2·35 (4 H, s), 4·43 (1 H, t),	5·1 (2 H, d) 7—7·36 (4 H, m)	—
Ic	246 4·10	1 548 1 380	1 632	2·35 (4 H, s), 4·43 (1 H, t),	5·1 (2 H, d) 7·3 (4 H, s)	—
Id	246 4·18	1 544 1 382	1 632	2·35 (4 H, s), 4·43 (1 H, t),	5·1 (2 H, d) 7·15—7·48 (4 H, q)	
Ie	245 4·0	1 542 1 380	1 628	2·35 (4 H, s), 4·43 (1 H, t),	5·1 (2 H, d) 7·23—7·5 (4 H, m)	—
If	250 4·12	1 542 1 382	1 625	2·2 (3 H, s), 2·35 (4 H, s),	4·38 (1 H, t), 5·05 (2 H, d)	6·95—7·23 (4 H, q)
Ig	252	1 542	1 634	2·35 (4 H, s),	4·38 (1 H, t),	6·75; 7·2 (4 H, 2 d)
Ih	257 4·18	1 515, 1 545 1 382	1 632	2·35 (4 H, s), 4·6 (1 H, t)	5·08 (2 H, t) 8·18 (4 H, m)	—
Ii	250 4·17	1 520, 1 544 1 370, 1 382	1 630	2·35 (4 H, s), 4·62 (1 H, t)	5·2 (2 H, d) 7·75—8·25 (4 H, m),	—
Ij	249 4·137	1 540 1 380	1 629	2 (3 H, s), 2·35 (4 H, s),	4·4 (1 H, t), 5·1 (2 H, t),	7·25—7·63 (4 H, m) 10·1 (1 H, s)

TABLE I
(*Continued*)

Compound	λ_{max}, nm log ε	$\nu(NO_2)$	ν(CO), ν(C=N)	^{1}H NMR, δ ppm		
Ik	253 4·142	1 543 1 382	1 624	2·35 (4 H, s), 3·1 (6 H, s),	4·5 (1 H, t), 5·15 (2 H, d),	7·38—7·75 (4 H, m)
Il	258 4·102	1 540 1 368	1 620, 1 700	1·65—1·9 (2 H, m), 2·2—2·4 (4 H, m),	4·75—5·25 (3 H, m) 7·23 (5 H, s)	—
Im	259 4·108	1 542 1 370	1 620, 1 700	1·65—1·9 (2 H, m), 2·2—2·4 (4 H, m),	4·75—5·25 (3 H, m) 7·25 (4 H, s)	—
IIa	268 4·062	—	1 655, 1 695	1·98—2·3 (4 H, m), 2·25—2·75 (2 H, m),	4·8; 4·95 (1 H, 2 t), 7·2 (5 H, s)	10·13; 10·38 (1 H, 2 s)
IIb	269 4·071	—	1 655, 1 695 2·25—2·75	1·98—2·3 (4 H, m), 2·25—2·75 (2 H, m),	4·78; 5 (1 H, 2 t), 7·23 (4 H, s),	10·15; 10·38 (1 H, 2s)
IIc	267 4·111	—	1 675, 1 695	1·98—2·3 (4 H, m), 2·25—2·75 (2 H, m),	4·85; 4·95 (1 H, 2t), 7—7·5 (4 H, 2 d)	10·11; 10·33 (1 H, 2 s)
IId	270 4·026	—	1 657, 1 700	1·98—2·3 (7 H, m), 2·25—2·75 (2 H, m),	4·75; 4·9 (1 H, 2 t), 6·88—7·28 (4 H, k)	10·11; 10·35 (1 H, 2 s)
IIe	271 4·082	—	1 658, 1 695	1·98—2·3 (4 H, m) 2·25—2·75 (2 H, m),	3·65 (3 H, s) 4·73; 4·85 (1 H, 2 t),	6·7—7·15 (4 H, 2 d) 10·08; 10·35 (1 H, s)
IIf	271 4·011	—	1 653, 1 698	1·03 (6 H, s), 2·13 (2 H, t)	5·1 (2 H, s), 4·85; 4·96 (1 H, 2t),	7·19 (5 H, s) 10·15; 10·43 (1 H, 2 s)
In	264 3·221	1 543 1 368	1 690, 1 720	1·25—1·75 (4 H, m), 2·08—2·38 (4 H, m),	4·1 (1 H, t), 4·63 (2 H, d),	5·03 (1 H, m) 7·2 (5 H, s)

TABLE I
(*Continued*)

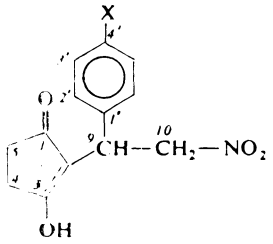
Compound	λ_{max}, nm log ε	$\nu(NO_2)$	ν(CO), ν(C=N)	^{1}H NMR, δ ppm		
IIg	273 4·044	—	1 620, 1 695	1·5—2 (6 H, m), 2·68—2·88 (2 H, m),	4·83; 4·95 (1 H, 2 t), 7·18 (5 H, s)	10·05; 10·3 (1 H, 2 s)
IIh	274 4·121	—	1 620, 1 695	1·5—2 (6 H, m), 2·68—3 (2 H, m),	4·85; 4·95 (1 H, 2 t), 7·23 (5 H, s)	9·98; 10·2 (1 H, 2 s)
IIi	272 4·146	—	1 620, 1 695	1·5—2 (6 H, m), 2·68—3 (2 H, m),	4·85; 4·95 (1 H, 2 t), 7—7·45 (4 H, 2 d)	9·98; 10·2 (1 H, 2 s)
IIj	274 4·181	—	1 620, 1 690	1·5—2 (6 H, m), 2·68—3 (2 H, m),	3·68 (3 H, s), 4·75; 4·88 (1 H, 2 t),	6·68—7·18 (4 H, 2d) 10·1—10·33 (1 H, 2 s)
IIk	271 4·076	1 520 1 370	1 620, 1 695	1·5—2 (6 H, m), 2·68—3 (2 H, m),	4·9; 4·98 (1 H, 2 t), 9·78—10·38 (4 H, m)	9·95; 10·1 (1 H, 2 s)
IIIa	272 4·367	—	1 600	1·75 (12 H, s), 2·45—2·7 (4 H, m),	4·33 (2 H, t), 5·18 (2 H, t),	7·13 (10 H, s) 8·63 (1 H, s)
IIIb	272 4·370		1 600	1·75 (12 H, s), 2·45—2·7 (4 H, m),	4·33 (D H, t), 5·18 (2 H, t),	7—7·35 (2 H, q) 8·76(1 H, s)

dione, 1,3-cycloheptanedione reacts with 1-(X-phenyl)-2-nitroethylenes (X = H, Cl) at higher concentration of the methoxide and reactants (procedure *B*) to give products different from compounds *II*. On the basis of elemental analysis and IR, ^{1}H NMR, ^{13}C NMR and mass spectra we assume that these products are 9,9'--hydroxyaminobis(20-(X-phenyl)-8-oxabicyclo[5.3.0]-1-decen-2-ones) *IIIa* and *IIIb*. In the carbonyl region, the IR spectra of compounds *IIIa* and *IIIb* exhibit one band at 1 600 cm^{-1} due to carbonyl group conjugated with a C=C double bond. Their ^{1}H NMR spectra display two doublets at 4·30–4·40 ppm ($J \sim 1$ Hz; 2 H) due to protons at the $C_{(9)}$, $C_{(9')}$, $C_{(10)}$ and $C_{(10')}$ atoms and two singlets of the hydroxyamino group proton at 8·7–8·9 ppm, showing thus that compounds *IIIa* and *IIIb* represent mixtures of geometric isomers (Table I). The suggested structure *III* is confirmed also by the ^{13}C NMR spectrum of *IIIa* (Table II).

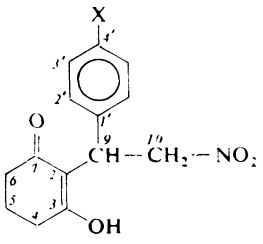
TABLE II
^{13}C NMR Spectral data

Compound	$C_{(1)}$	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(5)}$	$C_{(6)}$	$C_{(7)}$
Ia	194·5	114·2	138·7	30·1	38·1	—	—
Il	185·1	113·4	140·7	32·9	20·5	37·8	—
In	206·2	67·1	204·2	44·3	22·9	24·0	45·1
IIa	116·8 117·7	128·2 128·4	21·0	22·5	36·5	173·6 173·7	—
IIj	117·0 117·8	192·4 193·03	35·3	22·5	21·0	30·7	173·4 173·5
IIIa	111·6	195·0	43·6	23·8	22·4	29·5	171·3

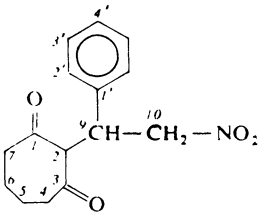
Compound	$C_{(8)}$	$C_{(9)}$	$C_{(10)}$	$C_{(1')}$	$C_{(2')}$	$C_{(3')}$	$C_{(4')}$
Ia	—	39·1	76·6	139·7	128·5	127·6	127·0
Il	—	38·1	77·7	140·7	128·3	127·7	126·4
In	—	41·0	79·0	138·1	128·5	128·3	127·4
IIa	156·2 138·9	44·4 44·8	—	136·4 138·9	128·2 128·5	127·5 127·9	126·8 127·9
IIj	—	158·3 165·2	44·1 43·7	129·0 130·9	128·3 128·6	113·6 113·7	156·4 158·1
IIIa	—	102·3	51·9	142·9	128·3	127·3	126·4



Ia, X = H
Ib, X = *p*-F
Ic, X = *p*-Cl
Id, X = *p*-Br
Ie, X = *m*-Br

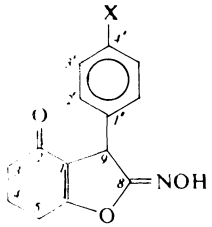


If, X = *p*-CH_3
Ig, X = *p*-OCH_3
Ih, X = *p*-NO_2
Ii, X = *m*-NO_2
Ij, X = *p*-$NHCOCH_3$
Ik, X = *p*-$N(CH_3)_2$

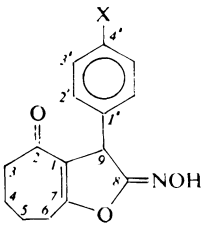


Il, X = H
Im, X = *p*-Cl

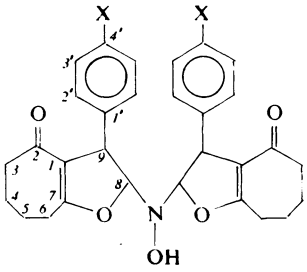
In, X = H



IIa, X = H
IIb, X = *p*-Cl
IIc, X = *p*-Br
IId, X = *p*-CH_3
IIe, X = *p*-OCH_3



IIg, X = H
IIh, X = *p*-Cl
IIi, X = *p*-Br
IIj, X = *p*-OCH_3
IIk, X = *p*-NO_2

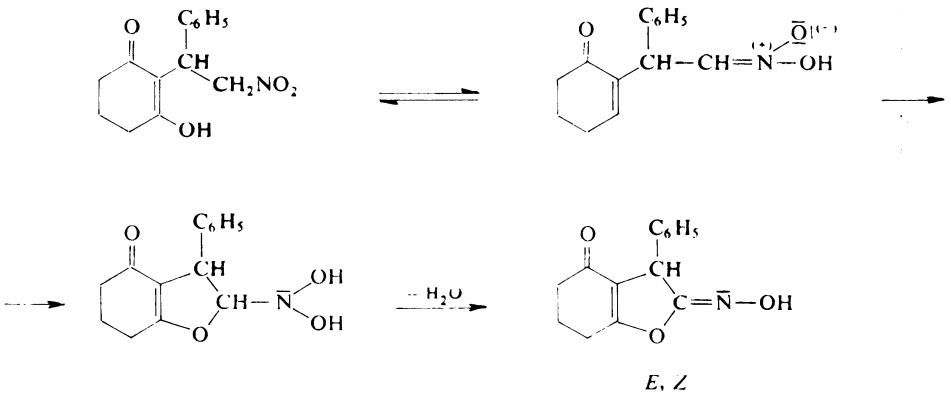


IIIa, X = H
IIIb, X = *p*-Cl

Mass spectrum of compound *IIIa* shows molecular weight 485, a marked loss of water and formation of fragments of 228 and 257 mass units. A similar structure for the products of Michael addition of 2,4-pentanedione and ethyl acetylacetate to 1-phenyl-2-nitroethylene has been assumed by Spanish authors[11].

In order to find out whether the compounds *II* and *III* arise as products of subsequent elimination of water from the classical Michael addition products *I*, we performed the reaction of 1,3-cyclohexanedione and 1,3-cycloheptanedione with 1-(X-phenyl)-2-nitroethylenes at −2°C (procedure *C*) and found that under these conditions 2-(2-(X-phenyl)-2-nitroethyl)-1,3-cyclohexanediones *Ie*–*Im* or 2-(1-(X-phenyl)-2-nitroethyl)-1,3-cycloheptanedione *In* can be isolated, albeit only when X is H or an electron-accepting substituent. According to kinetic measurements of the Michael addition of 1,3-cyclopentanedione to 1-(X-phenyl)-2-nitroethylenes, the

reaction rate is substantially reduced by electron-donating substituents[12]. Since the conversion of compound *I* into *II* does not depend on the substituent X, we were not able to isolate the reaction products *I* with electron-donating substituents on the phenyl group. Reaction of *I* in methanol, catalyzed by sodium methoxide, afforded compounds *II*. The same conversion, although much slower, took place in methanol in the absence of methoxide (reflux for 24 h) and its mechanism can be described by Scheme 1.



SCHEME 1

EXPERIMENTAL

The UV spectra were recorded in methanol on a Perkin–Elmer 450 instrument, IR spectra were measured on a Perkin–Elmer 180 spectrometer in chloroform. ^{1}H NMR Spectra were taken on a Tesla BS 482 (80 MHz) instrument and ^{13}H NMR spectra on a Jeol FX-60 (15·03 MHz) spectrometer; all in hexadeuteriodimethyl sulfoxide with hexamethyldisiloxane as internal standard. The mass spectra were measured on an MS 902 S (AEI) spectrometer (70 eV). Melting points were determined on a Kofler block.

Reaction of 1,3-Cyclopentanedione, 1,3-Cyclohexanedione and 1,3-Cycloheptanedione with 1-(X-Phenyl)-2-nitroethylenes

A) A solution of 1,3-cycloalkanedione (50 mmol) in a solution of sodium (0·25 g) in methanol (15 ml) was added during 10 min with exclusion of moisture to a stirred saturated solution of 1-(X-phenyl)-2-nitroethylene (50 mmol) in methanol (15—45 ml; according to solubility of the ethylenic component). After stirring at 30—40°C for 30 min, the mixture was left aside at 0°C for 12 h and the separated product was crystallized (Table III). Thus, 1,3-cyclopentanedione afforded 2-(1-(X-phenyl)-2-nitroethyl)-1,3-cyclopentanediones *Ia—Ik* (X = H, 4-F, 4-Cl, 4-Br, 3-Br, 4-OCH_3, 4-NO_2, 4-$NHCOCH_3$, 4-$N(CH_3)_2$), 1,3-cyclohexanedione gave 9-(X-phenyl)--8-hydroxyimino-7-oxabicyclo[3.4.0]-1-nonen-2-ones *IIa—IIe* (X = H, 4-Cl, 4-Br, 4-CH_3, 4-OCH_3), and reaction of 1,3-cycloheptanedione led to 10-(X-phenyl)-9-hydroxyimino-8-oxabicyclo[5.3.0]-1-decen-2-ones *IIg—IIk* (X = H, 4-Cl, 4-Br, 4-OCH_3, 4-NO_2). The spectral and analytical data of all the products are given in Table I—III.

TABLE III

Analytical data for compounds *Ia—In*, *IIa—IIk* and *IIIa,b*

Compound	M.p., °C[a] yield, %	Formula (mol.wt.)	Calculated/Found %C	% H	% N
Ia	235—237	$C_{13}H_{13}NO_4$	63·15	5·30	5·67
	85	(265·2)	63·08	5·29	5·68
Ib	227—230	$C_{13}H_{12}FNO_4$	58·87	4·56	5·28
	80	(265·2)	58·63	4·73	5·13
Ic	230—232	$C_{13}H_{12}ClNO_4$	55·43	4·29	4·97
	85	(281·7)	56·07	4·24	5·19
Id	232—235	$C_{13}H_{12}BrNO_4$	47·88	3·71	4·29
	83	(326·1)	47·84	3·67	4·30
Ie	225—228	$C_{13}H_{12}BrNO_4$	47·88	3·71	4·29
	75	(326·1)	47·86	3·76	4·24
If	250—252	$C_{14}H_{15}NO_4$	64·26	5·79	5·36
	80	(261·3)	64·15	5·85	5·55
Ig	238—240	$C_{14}H_{15}NO_5$	60·64	5·45	5·50
	82	(277·3)	60·44	5·52	5·15
Ih	253—258	$C_{13}H_{12}N_2O_6$	53·43	4·14	9·59
	55	(292·2)	53·85	4·22	9·94
Ii	242—245	$C_{13}H_{12}N_2O_6$	53·43	4·14	9·59
	60	(292·3)	53·40	4·18	9·49
Ij	300 dec.	$C_{15}H_{16}N_2O_5$	59·21	5·30	9·21
	45	(304·3)	60·39	5·42	8·98
Ik	261—263[b]	$C_{15}H_{18}N_2O_4$	62·06	6·25	9·65
	50	(290·3)	61·83	6·08	9·87
Il	144—146	$C_{14}H_{15}NO_4$	64·36	5·79	5·36
	68	(261·3)	64·22	5·88	5·47
Im	148—150	$C_{14}H_{14}ClNO_4$	56·86	4·77	4·74
	70	(295·7)	57·06	4·75	4·81
In	149—152	$C_{15}H_{17}NO_4$	65·44	6·22	5·09
	70	(275·2)	65·63	6·28	5·11
IIa	174—178[c]	$C_{14}H_{13}NO_3$	69·12	5·39	5·76
	A-70	(243·3)	69·16	5·42	5·90
IIb	184—187	$C_{14}H_{12}ClNO_3$	60·57	4·36	5·05
	70	(277·6)	60·09	4·33	4·89
IIc	182—185	$C_{14}H_{12}BrNO_3$	52·20	3·75	4·35
	65	(322·2)	52·36	3·72	4·28

TABLE III
(*Continued*)

Compound	M.p., °C[a] yield, %	Formula (mol.wt.)	Calculated/Found		
			% C	% H	% N
IId	185—187	$C_{15}H_{15}NO_3$	70·02	5·88	5·44
	68	(257·3)	69·04	5·91	5·06
IIe	177—178	$C_{15}H_{15}NO_4$	65·92	5·53	5·13
	65	(273·3)	65·81	5·50	5·18
IIg	163—164[c]	$C_{15}H_{15}NO_3$	70·06	5·88	5·45
	75	(257·2)	69·39	6·01	5·14
IIh	177—179[c]	$C_{15}H_{14}ClNO_3$	61·77	4·84	4·80
	70	(291·7)	61·13	4·92	4·78
IIi	169—171[c]	$C_{15}H_{14}BrNO_3$	53·59	4·19	4·17
	68	(336·2)	52·76	4·25	3·99
IIj	178—181[c]	$C_{16}H_{17}NO_4$	66·89	5·96	4·88
	75	(287·3)	66·15	5·74	5·04
IIk	174—179[c]	$C_{15}H_{14}N_2O_5$	59·60	4·67	9·27
	55	(302·3)	59·36	4·81	9·61
IIIa	181·5—183·4[c]	$C_{30}H_{31}NO_5$	74·21	6·44	2·88
	54	(485·6)	73·61	6·39	2·94
IIIb	200—203[c]	$C_{20}H_{29}Cl_2NO_5$	64·99	5·27	2·53
	50	(554·5)	63·77	5·23	2·29

[a] Crystallized from methanol; [b] from chloroform; [c] from ethanol.

B) 1,3-Cycloalkanedione (50 mmol) was added to a solution of sodium (0·25 g) in methanol (15 ml). To this solution 1-(X-phenyl)-2-nitroethylene (50 mmol) was added and the reaction mixture was worked up as described in procedure *A*. With 1,3-cyclopentanedione and 1,3-cyclohexanedione the same products as in procedure *A* were isolated whereas 1,3-cycloheptanedione afforded 9,9'-hydroxyaminobis((10-X-phenyl)-8-oxabicyclo[5.3.0]-1-decen-2-ones) *IIIa*—*IIIb* (X = = H, Cl). For analytical and spectral data see Tables I—III.

C) 1,3-Cyclohexanedione or 1,3-cycloheptanedione (50 mmol) was added to a solution of sodium (0·25 g) in methanol (15 ml). A saturated solution of 1-(X-phenyl)-2-nitroethylene (50 mmol) in methanol (15—25 ml) was then added at −2°C under stirring. After stirring at −2°C for 1·5 h, the mixture was poured into an ice-water mixture, neutralized with 10% HCl and the precipitated product was crystallized from methanol. 1,3-Cyclohexanedione afforded 2[(1-X-phenyl)--2-nitroethyl]-1,3-cyclohexanediones *Ie*—*Im* (X = H, 4-Cl) and 1,3-cycloheptanedione reacted to give 2-(1-phenyl-2-nitroethyl)-1,3-cycloheptanedione (*In*). For analytical and spectral data of the products see Tables I—III.

REFERENCES

1. Dornow A., Boberg F.: Justus Liebigs Ann. Chem. *578*, 101 (1952).
2. Perekalin V. V., Parfenova K. S.: Zh. Prikl. Khim. *30*, 1279 (1957).
3. Danilova E. M., Perekalin V. V.: Zh. Org. Khim. *1*, 1708 (1965).
4. Danilova E. M., Perekalin V. V., Paperno T. J.: Zh. Org. Khim. *3*, 1860 (1967).
5. Stetter H., Höhne K.: Chem. Ber. *91*, 1344 (1958).
6. Larsen H. O., Ooi T. C., Sui A. K. Q., Hollenbeak K. H., Cue F. L.: Tetrahedron *25*, 4005 (1969).
7. Nielsen A. T., Archibald T. G.: Tetrahedron *25*, 2393 (1969).
8. Ansell G. B., Moore D. W., Nielsen A. T.: Chem. Commun. *1970*, 1602.
9. Ansell G. B., Moore D. W., Nielsen A. T.: J. Chem. Soc. B, *1971*, 2376.
10. Dominiani S. J., Chaney M. O., Jones N. D.: Tetrahedron Lett. *1970*, 4753.
11. Goméz-Sánchez A. S., Stiefel B. M., Fernández-Fernández R., Pacsul C., Beliana Ch.: J. Chem. Soc., Perkin Trans. *1*, 1982, 441.
12. Hrnčiar P., Čulák I., Gáplovský A.: Unpublished results.

Translated by M. Tichý.