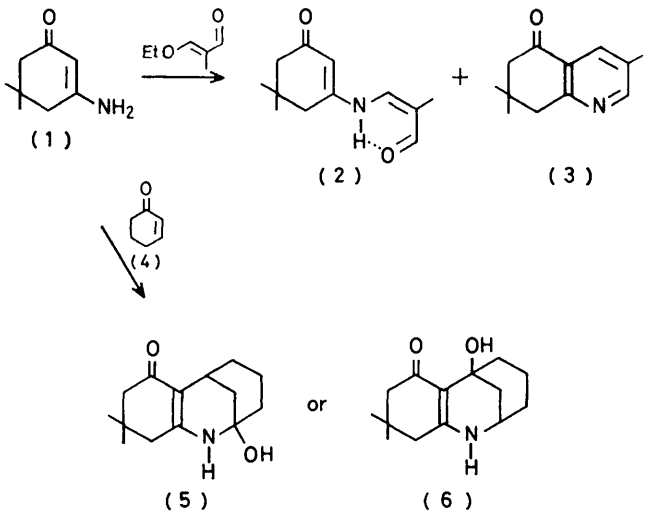
Reactions between Enaminones and Enones. Part 2.[1] *C versus N*-Alkylation with Cyclohex-2-enone. Structure Confirmation by Reduction of a Dienaminone Derivative of Dehydrated Dimedone Dimer

By **Ibrahim Chaaban, John V. Greenhill,*** and **Mohamed Ramli,** School of Pharmacy, University of Bradford, Bradford, West Yorks. BD7 1DP

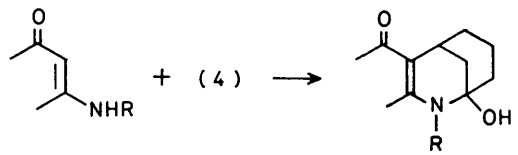
Primary and secondary enaminones derived from cyclohexane-1,3-dione, dimedone, and acetylacetone react with cyclohexenone to give exclusively *C*-alkylated derivatives. In every case the products form carbinolamines which exist as 1-hydroxy-2-azacyclo[3.3.1]nonenes. This was confirmed in some examples by formation of an extra ring between nitrogen and oxygen. A series of dienaminones were prepared from 2-(5,5-dimethyl-3-oxocyclohex-1-enyl)-5,5-dimethylcyclohexane-1,3-dione and one of these was reduced to give an azanonene identical with that from *C*-alkylation.

We have previously reported the *C*-alkylation of enaminones by methyl vinyl ketone.[1] Other workers have also generally observed *C*-alkylation of free enaminones.[2] *N*-Alkylation is normally only achieved after preliminary deprotonation.[3] That *C*-alkylation cannot be assumed to be the exclusive route is shown by our recent report [4] that 3-ethoxy-2-methylacrolein gives 25% of the *N*-alkyl derivative (2). The conditions of this reaction (110 °C in the presence of piperidine acetate) would not cause *N*-deprotonation. Also formed was the quinolinone (3) (57%), not reported in the previous paper.[4] We shall shortly publish our reason for thinking that this arises from *C*-alkylation.



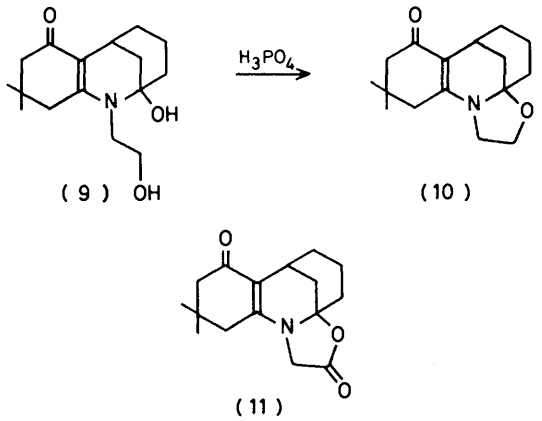
When the enaminone (1) reacted with cyclohex-2-enone (4) an adduct was obtained which corresponded to (5) or (6). No carbonyl band (i.r.) was observed. Initial *C*-alkylation would reasonably lead to the carbinolamine (5), but whether *N*-alkylation would proceed to the alcohol (6) is doubtful.

A series of similar compounds was prepared (see Table 1). In every case only one product was obtained and the i.r. and u.v. spectra suggested that all products were of the same molecular type. The reaction also succeeded with two acyclic enaminones (7a and b) to give the azabicyclononenes (8a and b). That *C*-alkylation occurred to give the molecular type (5) was established in three examples. Compound (9), when heated in phosphoric acid, gave a product which could only be a cyclic ether (10). When the dimedone derivative of ethyl glycine reacted with cyclohexenone, spontaneous ring closure



a; R = H
b; R = Me

gave a product (11) which showed a strong band at $\nu_{max.}$ 1 800 cm^{-1}, typical for a five-membered ring lactone. The third method establishing the carbinolamine structure involved some further developments of our work on dienaminediones.[5]

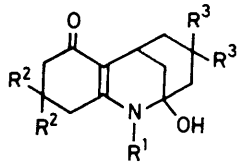


We first sought to improve the yield of the dehydrated dimer of the dimedone (12). This was achieved in refluxing xylene with a catalytic amount of toluene-*p*-sulphonic acid. In improving the yield of (12) from 26% (ref. 6) to 65% we were surprised to obtain a second, neutral product (13), the structure of which was solved by *X*-ray crystallography.[7] A reasonable mechanism for the formation of this dehydrated tetramer is shown in the Scheme.

As reported previously,[5] the dimer (12) reacts with primary or secondary amines to give dienaminediones of

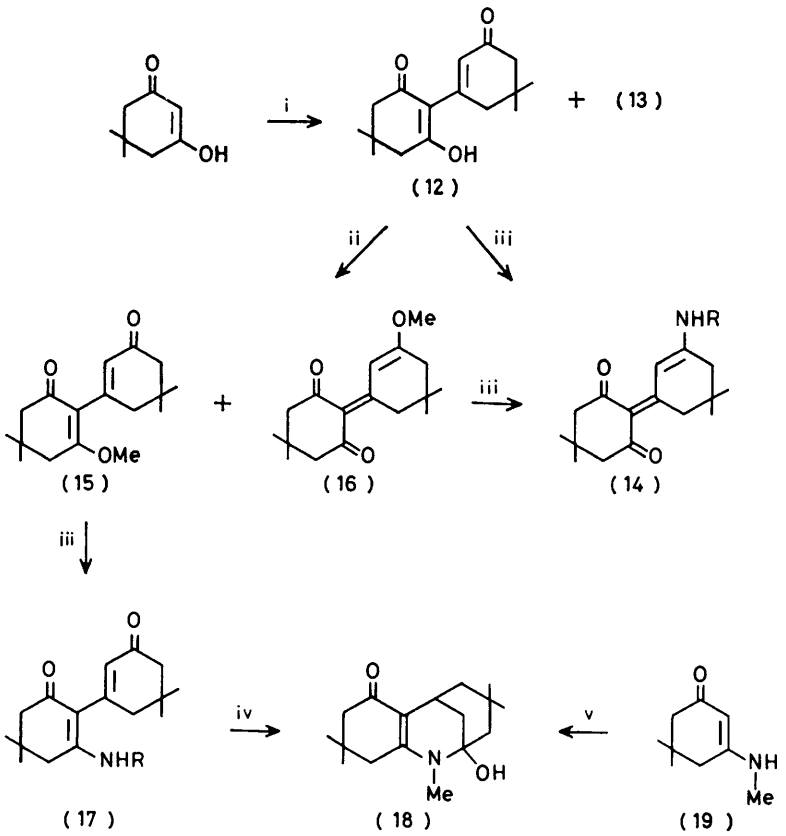
TABLE 1

1-Hydroxy-2-azatricyclo[7.3.1.0^{3,8}]tridec-3(8)-en-7-ones



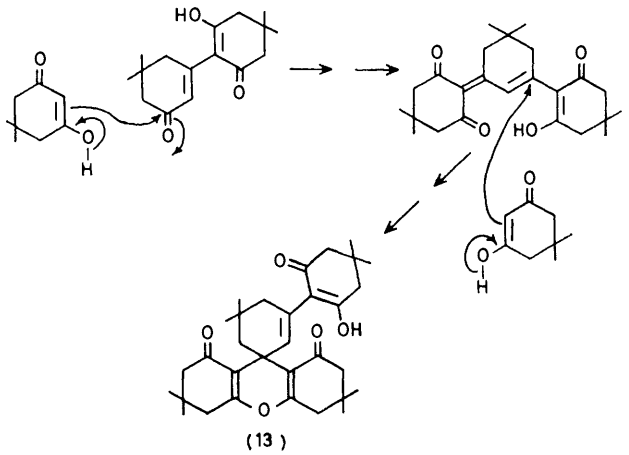
Comp.	R^1	R^2	R^3	Form	Method	Yield (%)	M.p. (°C) [a]	Calc. (%) C	H	N	Cl	Found (%) C	H	N	Cl
(20)	H	H	H	base	1	10	248 (d)	69.6	8.2	6.8		69.6	8.2	6.9	
					2	15									
(21)	Ph	H	H	base	2	28	232—233	76.3	7.4	4.9		76.7	7.0	5.2	
(22)	$PhCH_2CH_2$	H	H	base	3	69	197—198	88.2	8.0	4.5		77.3	7.8	4.5	
(23)	$PhCH_2CH_2$	H	H	HCl			219—220	69.1	7.5	4.0	10.2	69.1	7.5	8.1	10.3
(5)	H	Me	H	base	1	26	246—247	71.5	8.9	6.9		71.5	8.9	6.0	
					2	30									
(24)	Me	Me	H	base	2	40	170—171	72.3	9.2	5.6		72.1	9.4	5.7	
					3	48									
(25)	Me	Me	H	HCl			218—220	63.1	8.4	4.9	12.4	62.9	8.6	4.9	12.3
(26)	Ph	Me	H	base	2	55	206—207	77.2	8.0	4.5		77.1	8.1	4.6	
(9)	CH_2CH_2OH	Me	H	HCl	3	13	262—263	60.9	8.2	4.4	11.3	61.4	8.7	4.6	11.3
(27)	H	Me	Me	base	1	11	233—234	73.0	95.			73.4	9.3		
(28)	H	Me	Me	HCl			214 (d)	64.1	8.7	4.7	11.9	64.1	8.4	4.8	11.8
(18)	Me	Me	Me	base	1	2	196—197	73.6	9.8	5.1		73.8	9.4	5.1	

[a] d = decomposes.



Reagents: i, TsOH; ii, MeOH–BF_3; iii, RNH_2; iv, Ni–H_2; v, 5,5-dimethylcyclohex-2-enone, H^+

type (14) which are characterised by their yellow colour ($\lambda_{max.}$ 400—440 nm) and the unusually high chemical shift of the vinyl proton. Further examples of this reaction are given in the Experimental section. Treatment of the dimer (12) with diazomethane has been reported [6] to give a 6 : 4 mixture of the ethers (15) and



(13)

SCHEME

(16). We allowed the crude mixture to react with t-butylamine in refluxing ethanol and obtained a mixture of the previously prepared dienaminedione (14; R = Bu^t) (20%) and a colourless compound (17; R = Bu^t) (67%). The new derivative (17; R = Bu^t) showed a normal chemical shift (τ 3.83) for the vinyl proton and u.v. absorption expected for a 2-substituted enaminone [$\lambda_{max.}$(H_2O) 290 nm (ε 17 800); $\lambda_{max.}$ (0.1M-HCl) 268 nm (ε 14 200)]. Additionally there was a shoulder at 235 nm due to the cyclohexenone ring and a weak long-wavelength band [$\lambda_{max.}$ (H_2O) 352 nm (ε 4 800)] suggesting a small contribution from the dienaminone system. This pattern of behaviour was shown by all dienaminediones of types (14) and (17) prepared. Clearly the two rings of structure (14) lie in the same plane while those of (17) are twisted relative to each other.

We found it more convenient to prepare the ether mixture using BF_3–methanol when the ratio of (15) to (16) was determined (n.m.r.) as *ca.* 4 : 1. Reactions with several bases were performed on this mixture and the products were separated by fractional recrystallisation or chromatography. Later it was found possible to isolate the required ether (15).

Reduction of the dienaminone (17; R = Me) over Raney nickel gave a product (18) identical with that from reaction of the dimedone derivative (19) and 5,5-dimethylcyclohex-2-enone.

EXPERIMENTAL

1-Hydroxy-5,5-dimethyl-2-azatricyclo[7.3.1.$0^{3,8}$]*tridec-3(8)-en-7-one* (5).—*Method* 1. A solution of 3-amino-5,5-dimethylcyclohex-2-enone (1.39 g, 10 mmol) and cyclohex-2-enone (0.96 g, 10 mmol) in ethanol (40 ml) was saturated with hydrogen chloride and refluxed for 2 h. After removal of the solvent, the basic products were released with NaOH and then extracted into EtOAc (3 × 100 ml). The organic solution was washed with H_2O (50 ml), dried ($MgSO_4$), and evaporated to give the *tricyclotridecenone* (0.6 g, 26%), m.p. 246—247 °C (from butan-2-one); τ ([$^2H_6$]-DMSO, 60 MHz) 2.90 (1 H, s, NH), 4.21 (1 H, s, OH), 6.97 (1 H, m, 9-H), 7.78 (2 H, s, 4-CH_2), 8.02 (2 H, s, 6-CH_2), 8.2—8.7 (8 H, m, 4 × CH_2), and 9.04 (6 H, s, 2 × CH_3).

Method 2. The same reagents as in Method 1 were dissolved in propionic acid (20 ml) and the mixture was refluxed for 1 h. The solvent was evaporated off and the base extracted and worked up as in Method 1 to give the same product (0.7 g, 30%).

1-Hydroxy-2,5,5-trimethyl-2-azatricyclo[7.3.1.$0^{3,8}$]*tridec-3(8)-en-7-one* (24) *as an example of Method* 3. A mixture of 5,5-dimethyl-3-methylaminocyclohex-2-enone (1 g), cyclohex-2-enone (1 g), and diglyme (20 ml) was saturated with hydrogen chloride when the solid dissolved. The solution was refluxed for ¼ h, cooled, and the product collected to give the *tricyclotridecenone hydrochloride* (0.9 g, 48%), m.p. 218—220 °C (from ethanol–ethyl acetate). The *base* was released with sodium hydroxide and extracted with chloroform, m.p. 170—171 °C (from toluene); τ ($CDCl_3$) 5.60 (1 H, br, OH), 6.78 (1 H, m, 9-CH), 7.05 (3 H, s, NCH_3), 7.68 (2 H, s, 4-CH_2), 7.90 (2 H, s, 6-CH_2), 8.18 (2 H, d, 13-CH_2) 8.3—8.8 (6 H, m, 3 × CH_2), and 8.97 (6 H, s, 2 × CH_3).

8,8-Dimethyl-2-oxa-5-azatetracyclo[10.3.1.$0^{1,5}$.$0^{6,11}$]*hexadec-6(11)-en-10-one* (10).—A solution of 1-hydroxy-2-(2-hydroxyethyl)-5,5-dimethyl-2-azatricyclo[7.3.1.$0^{3,8}$]tridec-3(8)-en-7-one hydrochloride (9) (1.75 g) in phosphoric acid (5 ml) was boiled for 5 min, cooled, and poured into water (50 ml). The solution was made alkaline with aqueous sodium hydroxide and extracted with chloroform (3 × 20 ml). The organic solution was washed with H_2O (20 ml) and evaporated to give the *tetracyclohexadecenone* (1.1 g, 76%), m.p. 122—123 °C (from ethyl acetate) (Found: C, 73.7; H, 8.5; N, 5.6. $C_{16}H_{23}NO_2$ requires C, 73.6; H, 8.8; N, 5.4%); $\nu_{max.}$ (KBr) 1 550, 1 605 (enaminone system), and

TABLE 2

U.v. and i.r. data for tricyclotridecenones

	0.1M-HCl		H_2O		0.1M-NaOH		
Compd.	$\lambda_{max.}$/nm	ϵ	$\lambda_{max.}$/nm	ϵ	$\lambda_{max.}$/nm	ϵ	$\nu_{max.}$ (KBr)/cm^{-1}
(20)	293	21 400	304	25 900	306	26 100	3 250, 1 560, 1 500
(21)	305	27 700	315	33 100	316	33 100	3 350, 1 600, 1 550
(22)	305	24 000	319	31 600	320	32 200	3 350, 1 590, 1 535
(5)	295	20 100	306	26 000	307	25 000	3 250, 1 560, 1 510
(24)	303	22 000	320	28 000	321	29 400	3 350, 1 580, 1 530
(26)	307	26 500	317	31 500	318	31 500	3 250, 1 590, 1 550
(9)	302	20 400	315	26 400	315	26 100	3 450, 1 610, 1 570
(27)	297	20 400	307	25 400	308	25 100	3 220, 1 565, 1 515
(18)	305	20 700	320	25 400	320	27 200	3 200, 1 590, 1 550

1 145 cm^{-1} (–O–); $\lambda_{max.}$ (H_2O) 314 nm (ε 26 000); $\lambda_{max.}$ (0.1M-HCl) 302 nm (ε 20 100). The *hydrobromide* had m.p. 300 °C (decomp.) (from ethanol) (Found: C, 56.1; H, 7.0; Br, 23.5; N, 4.1. $C_{16}H_{24}BrNO_2$ requires C, 56.1; H, 7.0; Br, 23.4; N, 4.1%).

Methyl N-(5,5-*Dimethyl*-3-*oxocyclohexenyl*)*glycinate*.—A mixture of dimedone (2.8 g, 20 mmol), methylglycine hydrochloride (2.52 g, 20 mmol), *N*-ethylpiperidine (2.5 g, 24 mmol) and toluene was stirred and refluxed for 1¼ h during which water (0.32 ml) was collected in a Dean–Stark separator. The cooled solution was rapidly washed with 1% aqueous sodium hydroxide and water, dried ($MgSO_4$), and evaporated to give the *enaminone ester* (2.3 g, 55%), m.p. 112—113° (from toluene) (Found: C, 62.5; H, 8.1; N, 6.7. $C_{11}H_{17}NO_3$ requires C, 62.6; H, 8.1; N, 6.6%); $\nu_{max.}$ (KBr) 1 550 (br) (enaminone) and 1 740 cm^{-1} (ester C=O); $\lambda_{max.}$ (H_2O) 289 nm (ε 27 100); $\lambda_{max.}$ (0.1M-HCl) 285 nm (ε 25 200). Similarly was prepared *ethyl* N-(5,5-*dimethyl*-3-*oxocyclohexenyl*)*glycinate* (69%), m.p. 95—96 °C (from toluene) (Found: C, 63.9; H, 8.5. $C_{12}H_{19}NO_3$ requires C, 64.0; H, 8.4%); τ ($CDCl_3$) 4.6 (1 H, br, NH), 5.00 (1 H, s, =CH), 5.75 (2 H, q, CH_2), 6.17 (2 H, d, $NHCH_2$-CO), 7.73 (2 H, s, CH_2), 7.82 (2 H, s, CH_2), 8.70 (3 H, t, CH_3), and 8.94 (6 H, s, 2 × CH_3).

8,8-*Dimethyl*-2-*oxa*-5-*azatetracyclo*[10.3.1.$0^{1,5}$.$0^{6,11}$]*hexadec*-6(11)-*en*-10-*one* (11).—From the ethylglycine enaminone (1.13 g, 5 mmol) and cyclohex-2-enone (0.53 g, 0.55 mmol) by Method 3 above was obtained the *tetracyclohexadecenedione hydrochloride* (0.55 g, 35%), m.p. 252 °C (decomp.) (from methanol–ether) (Found: C, 61.9; H, 7.1; Cl, 11.4; N, 4.5. $C_{16}H_{22}ClNO_3$ requires C, 61.6; H, 7.1; Cl, 11.4; N, 4.5%); $\nu_{max.}$ (KBr) 1 570, 1 610 (enaminone), and 1 810 cm^{-1} (ester C=O); $\lambda_{max.}$ (H_2O) 310 (ε 26 200); $\lambda_{max.}$ (0.1M-HCl) 308 (ε 25 200); $\lambda_{max.}$ (0.1M-NaOH) 320 nm (ε 30 000). It gave a *hydrobromide* having m.p. 319 °C (decomp.) (from methanol–ethyl acetate) (Found: C, 54.0; H, 6.2. $C_{16}H_{22}BrNO_3$ requires C, 53.9; H, 6.2%). Careful treatment with aqueous sodium hydrogen carbonate (1 mol equiv.) and extraction with chloroform gave the free *base*, $\nu_{max.}$ 1 565, 1 610, and 1 800 cm^{-1}.

4-*Acetyl*-1-*hydroxy*-3-*methyl*-2-*azabicyclo*[3.3.1]*non*-3-*ene* (8a).—A solution of 4-aminopent-3-en-2-one (0.99 g, 10 mmol) and cyclohex-2-enone (0.96 g, 10 mmol) in ethanol (50 ml) was acidified with hydrogen chloride and refluxed for 7 h. Evaporation gave the *bicyclononene hydrochloride* (0.8 g, 35%) m.p. 201 °C (decomp.) (from ethanol–ether) (Found: C, 57.3; H, 7.6; N, 6.4. $C_{11}H_{18}ClNO_2$ requires C, 57.0; H, 7.8; N, 6.1%); $\lambda_{max.}$ (H_2O) 316 (ε 15 800); $\lambda_{max.}$ (0.1M-HCl) 302 nm (ε 10 000); τ ([$^2H_4$]MeOH) 6.85 (1 H, m, 5-CH), 7.39 (3 H, s, CH_3), 7.68 (3 H, s, $COCH_3$), and 8.0—8.5 (8 H, m, 4 × CH_2).

4-*Acetyl*-1-*hydroxy*-2,3-*dimethyl*-2-*azabicyclo*[3.3.1]*non*-3-*ene* (8b).—A solution of 4-methylaminopent-3-en-2-one (2.26 g, 20 mmol) and cyclohex-2-enone (1.84 g, 20 mmol) in ethanol (50 ml) was saturated with hydrogen chloride and refluxed for 2 h. After removal of the solvent, the residue was treated with dilute ammonium hydroxide and extracted with ethyl acetate to give the *bicyclononene* (0.5 g, 12%), m.p. 133—134 °C (from toluene–light petroleum) (Found: C, 69.0; H, 9.2; N, 6.8. $C_{12}H_{19}NO_2$ requires C, 68.9; H, 9.1; N, 6.7%); $\nu_{max.}$ (KBr) 1 520, 1 600 (enaminone), and 3 300 cm^{-1} (OH); $\lambda_{max.}$ (H_2O) 333 nm (ε 21 100); τ ($CDCl_3$) 5.95 (1 H, m, 5-CH), 7.07 (3 H, s, NCH_3), 7.55 (3 H, s, CH_3), 7.88 (3 H, s, $COCH_3$), 8.08 (2 H, d, 9-CH_2), and 8.2—8.7 (6 H, m, 3 × CH_2).

5,5-*Dimethyl*-2-(5,5-*dimethyl*-3-*oxocyclohex*-1-*enyl*)*cyclohexane*-1,3-*dione* (12).—A solution of dimedone (28 g) and toluene-*p*-sulphonic acid (2.5 g) in xylene (250 ml) was refluxed and stirred under a Dean–Stark water separator for 6 h (2.1 ml of water was collected). The cooled reaction mixture was washed with dilute ammonium hydroxide solution (4 × 200 ml). The combined ammoniacal extract was washed with ethyl acetate which was separated and added to the xylene solution. The organic solution was washed with water (3 × 100 ml), dried ($MgSO_4$), and evaporated to give 3′-(2-*hydroxy*-4,4-*dimethyl*-6-*oxocyclohex*-1-*enyl*)-3,3,5′,5′,6,6-*hexamethyl*-3,4,5,6-*tetrahydroxanthen*-9-*spirocyclohex*-2′-*ene*-1(2H),8(7H)-*dione* (4.0 g, 15.8%), m.p. 251—252 °C (from acetone–water) (Found: C, 75.6; H, 8.3. $C_{32}H_{42}O_5$ requires C, 75.9; H, 8.3%); $\nu_{max.}$ (mull) 3 250, 1 680, 1 650, and 1 610 cm^{-1}; $\lambda_{max.}$ (EtOH) 232 (ε 18 900) and 267 nm (ε 8 000); $\lambda_{max.}$ (0.1M-NaOH) 297 nm (ε 22 000). The combined ammoniacal extracts were acidified (aq. HCl) and extracted with ethyl acetate (4 × 300 ml). The extracts were washed (H_2O, 100 ml) and dried ($MgSO_4$), and the solvent was removed to give the dehydrated dimer (12) (17.0 g, 65%), m.p. 158 °C (from acetone) (lit.,[6] 158 °C).

5,5-*Dimethyl*-2-(5,5-*dimethyl*-3-*benzylaminocyclohex*-2-*enylidene*)*cyclohexane*-1,3-*dione* (14; R = $PhCH_2$).—A solution of dimedone dehydrated dimer (2.6 g, 10 mmol) and benzylamine (1.1 g, 10 mmol) in toluene was refluxed for 6 h under a Dean–Stark water separator (0.18 ml, 10 mmol of water collected). Addition of light petroleum (b.p. 40—60 °C) to the cooled solution gave a solid which was recrystallised to give the *dienaminedione* (3.2 g, 93%), m.p. 175—176 °C (from toluene–light petroleum) (Found: C, 78.9; H, 8.3; N, 4.0. $C_{23}H_{29}NO_2$ requires C, 78.6; H, 8.3; N, 4.0%). $\nu_{max.}$ (KBr) 3 400 (NH), and 1 540 cm^{-1} (broad, dienaminedione system); $\lambda_{max.}$ (EtOH) 411 (ε 47 100), 287 (11 000), and 255 (7 300); $\lambda_{max.}$ (H_2O) 406 (ε 22 600), 285 (9 700), and 257 (8 900); $\lambda_{max.}$ (0.1M-HCl) 260 (ε 11 300); $\lambda_{max.}$ (0.1M-NaOH) 295 (ε 22 600) and 237 nm (15 700). Similarly were obtained (a) 2-(3-*anilino*-5,5-*dimethylcyclohex*-2-*enylidene*)-5,5-*dimethylcyclohexane*-1,3-*dione* (14; R = Ph) (57%), m.p. 191—192 °C (from toluene) (Found: C, 78.4; H, 8.2; N, 4.1. $C_{22}H_{27}NO_2$ requires C, 78.3; H, 8.0; N, 4.2%); $\nu_{max.}$ (mull) 3 200, 1 550, and 1 610 cm^{-1}; $\lambda_{max.}$ (EtOH) 440 (ε 32 300) and 278 (8 700); $\lambda_{max.}$ (H_2O) 430 (ε 26 000) and 287 (11 100); $\lambda_{max.}$ (0.1M-HCl) 270 (ε 12 500); $\lambda_{max.}$ (0.1M-NaOH) 293 nm (ε 16 900); (b) 2-(3-*amino*-5,5-*dimethylcyclohex*-2-*enylidene*)-5,5-*dimethylcyclohexane*-1,3-*dione* (14; R = H) (ammonia was passed through the solution during a 2 h reflux) (88%), m.p. 260—261 °C (from toluene) (Found: C, 73.2; H, 9.2; N, 5.5. $C_{16}H_{23}NO_2$ requires C, 73.6; H, 8.8; N, 5.4%); $\nu_{max.}$ (mull) 3 200, 1 530, and 1 610 cm^{-1}; $\lambda_{max.}$ (EtOH) 407 (ε 42 700), 288 (7 100), and 255 (6 400); $\lambda_{max.}$ (H_2O) 400 (ε 16 700), 289 (13 200) and 255 (7 800); $\lambda_{max.}$ (0.1M-HCl) 260 (ε 7 800); $\lambda_{max.}$ (0.1M-NaOH) 294 (ε 21 300) and 230 nm (14 200); and (c) 5,5-*dimethyl*-2-(5,5-*dimethyl*-3-*methylaminocyclohex*-2-*enylidene*)*cyclohexane*-1,3-*dione* (14; R = Me) (by refluxing for 8 h with an excess of 3% methylamine–ethanol) (76%), m.p. 211—212 °C (from toluene) (Found: C, 74.2; H, 9.1; N, 4.8. $C_{17}H_{25}NO_2$ requires C, 74.2; H, 9.1; N, 5.1%); $\lambda_{max.}$ (EtOH) 407 (ε 38 000), 285 (6 100), and 257 (4 000); $\lambda_{max.}$ (H_2O) 403 (ε 18 600), 293 (9 700), and 257 (6 100); $\lambda_{max.}$ (0.1M-HCl) 260 (ε 16 200); $\lambda_{max.}$ (0.1M-NaOH) 293 nm (ε 16 200); τ ($CDCl_3$) 2.1 (1 H, s, =CH).

Methylation of 5,5-*Dimethyl*-2-(5,5-*dimethyl*-3-*oxocyclohex*-1-*enyl*)*cyclohexane*-1,3-*dione* (12).—A solution of dimedone

dehydrated dimer (5.2 g) in methanol (150 ml) was treated with 14% boron trifluoride–methanol (10 ml) and refluxed for 4 h. The cooled product was poured into a solution of sodium hydrogen carbonate (20 g) in water (200 ml), stirred for 10 min, and the product was extracted with ethyl acetate (5 × 200 ml). The organic solution was washed with H_2O (2 × 200 ml), dried ($MgSO_4$), and evaporated to give a yellow oil (4.8 g, 88%) shown [n.m.r. ($CDCl_3$)] to be a mixture of the two *O*-methyl ethers (15) and (16). *O*-Methyl peaks occurred at τ 6.2 and 6.3 in a ratio of *ca.* 4 : 1. Recrystallisation gave pure *5,5-dimethyl-2-(5,5-dimethyl-3-oxocyclohex-1-enyl)-3-methoxycyclohex-2-enone* (15) (59%), m.p. 76 °C [from light petroleum (b.p. 80—100 °C)] (Found: C, 74.1; H, 9.1. $C_{17}H_{24}O_3$ requires C, 73.9; H, 8.7%); $\nu_{max.}$ (KBr) 1 660 and 1 600 cm^{-1}; $\lambda_{max.}$ (H_2O) 274 nm (ε 16 400); τ ($CDCl_3$) 4.20 (1 H, t, *J* 1.5 Hz, =CH), 6.17 (3 H, s, OMe), 7.44 (2 H, s, 4-CH_2), 7.74br (6 H, s, 3 × CH_2), and 8.88 and 8.93 (6 H, 2 s, 4 × CH_3).

3-Benzylamino-5,5-dimethyl-2-(5,5-dimethyl-3-oxocyclohex-1-enyl)cyclohex-2-enone (17; R = $PhCH_2$).—The methoxy-ether mixture above (2.6 g) and benzylamine (2 g) were dissolved in ethanol (50 ml) and refluxed for 6 h. Removal of the solvent and trituration with ether gave *3-benzylamino-5,5-dimethyl-2-(5,5-dimethyl-3-oxocyclohex-1-enyl)cyclohex-2-enone* (0.9 g, 27%), m.p. 143—144 °C (from toluene) (Found: C, 78.6; H, 8.3; N, 4.0. $C_{23}H_{29}NO_2$ requires C, 78.6; H, 8.3; N, 4.0%); $\nu_{max.}$ (KBr) 3 300 (NH) 1 640 (conjugated C=O) 1 570, and 1 540 cm^{-1} (enaminone system); $\lambda_{max.}$ (H_2O) 305 (ε 34 600) and 234 (10 900); $\lambda_{max.}$ (0.1M-HCl) 301 (ε 30 500) and 233 (11 500); $\lambda_{max.}$ (0.1M-NaOH) 305 nm (ε 32 200); τ ($CDCl_3$) 2.70 (5 H, s, C_6H_5), 3.5 (1 H, br, NH), 4.14 (1 H, s, =CH), 5.56 (2 H, d, $PhCH_2$), and 8.97 and 9.01 (12 H, 2 s, 4 × CH_3). Evaporation of the ether triturates gave the dienaminedione (14; R = $PhCH_2$) (0.2 g, 6%), m.p. 175—176 °C, identical (mixed m.p., i.r.) with the sample prepared above. Similarly were prepared (a) *2-(5,5-dimethyl-3-oxycyclohex-1-enyl)-5,5-dimethyl-3-methylaminocyclohex-2-enone* (17; R = Me), isolated by column chromatography (silica eluted with 7.5% ethanol–toluene) (76%) m.p. 185—186 °C (from toluene) (Found: C, 73.7; H, 9.1; N, 5.3. $C_{17}H_{25}NO_2$ requires C, 74.2; H, 9.1; N, 5.1%); $\nu_{max.}$ (KBr) 3 330, 1 650, 1 615, and 1 560 cm^{-1}; $\lambda_{max.}$ (H_2O) 305 (ε 34 500) and 234 (10 900); $\lambda_{max.}$ (0.1M-HCl) 301 (ε 30 500) and 233 (11 500); $\lambda_{max.}$ (0.1M-NaOH) 305 nm (ε 32 200); τ ($CDCl_3$) 4.05 (1 H, s, =CH), 7.01 (3 H, d, NCH_3), 7.50, 7.56, and 7.71 (8 H, 3 s, 4 × CH_2), and 8.84 (12 H, s, 4 × CH_3). A second (yellow) eluate proved to be the *dienaminedione* (14; R = Me) (13%), m.p. 211—212 °C, identical (mixed m.p., i.r.) with the sample prepared above; (b) *2-(5,5-dimethyl-3-oxocyclohex-1-enyl)-5,5-dimethyl-3-t-butylaminocyclohex-2-enone* (17; R = Bu^t), isolated by fractional recrystallisation (66%), m.p. 186—187 °C (from ethanol–ether) (Found: C, 75.7; H, 9.4; N, 4.2. $C_{20}H_{31}NO_2$ requires C, 75.7; H, 9.8; N, 4.4%); $\lambda_{max.}$ (H_2O) 352 (ε 4 800), 290 (17 800), and 235 (sh); $\lambda_{max.}$ (0.1M-HCl) 268 (ε 14 200); $\lambda_{max.}$ (0.1M-NaOH) 352 (ε 5 500), 291 (18 500), and 235 nm (sh); τ ($CDCl_3$) 3.83 (1 H, s, =CH). A second fraction proved to be the dienaminedione (14; R = Bu^t) (19%), m.p. 248—249 °C, identical (mixed m.p., i.r.) with the material previously reported.[5]

1-Hydroxy-2,5,5,11,11-pentamethyl-2-azatricyclo[7.3.1.$0^{3,8}$]-*tridec-3(8)-en-7-one* (18).—A solution of 2-(5,5-dimethyl-3-oxocyclohex-1-enyl)-5,5-dimethyl-3-methylaminocyclohex-2-enone (0.5 g) in methanol (50 ml) containing Raney nickel (W7) was hydrogenated at room temperature and atmospheric pressure until 1 mol equiv. of hydrogen had been absorbed (*ca.* ½ h). The solution was filtered and the filtrate evaporated to give the tricyclotridecenone (0.45 g, 90%), m.p. 196—197 °C, identical (t.l.c., mixed m.p., i.r.) with the sample prepared by Method 1 above; τ ($CDCl_3$) 5.1 (1 H, br, OH), 6.78 (1 H, m, 9-CH), 7.00 (3 H, s, NCH_3), 7.78 (2 H, s, 4-CH_2), 7.86 (2 H, s, 6-CH_2), 8.0—8.6 (6 H, m, 3 × CH_2), and 8.82, 8.86, 9.08, and 9.20 (12 H, 4 s, 4 × CH_3).

[1/587 *Received*, 13*th April*, 1981]

REFERENCES

[1] Part 1, J. V. Greenhill and M. I. Mohamed, *J. Chem. Soc., Perkin Trans. 1*, 1979, 1411.
[2] (*a*) H. Möhrle and J. Herbke, *Pharmazie*, 1980, **35**, 288; (*b*) G. B. Bennett, W. R. J. Simpson, R. B. Mason, R. J. Strohschein, and R. Mansukhani, *J. Org. Chem.*, 1977, **42**, 221 and references cited therein.
[3] J. V. Greenhill, *Chem. Soc. Rev.*, 1977, **6**, 277.
[4] J. V. Greenhill, M. A. Moten, R. Hanke, and E. Breitmaier, *J. Chem. Research*, 1981, (*S*), 66; (*M*) 821.
[5] J. V. Greenhill, *J. Chem. Soc. C*, 1970, 1002.
[6] N. Schamp, E. De Bundel and E. Delarue, *Bull. Soc. Chim. Belg.*, 1965, **75**, 230.
[7] J. P. Declerg, N. De Kimpe, and J. V. Greenhill, *Cryst. Struct. Commun.*, in the press.