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CARBOCYCLIZATION REACTIONS OF 1-NITROCYCLOALKENES AND CROSS-CONJUGATED DIENAMINES

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Abstract – Dodecahydro-8a-nitro-as-indacen-4(2H)-one, dodecahydro-9a-nitro-4H-benz|e|inden-4-one, dodecahydro-9b-nitro-5H-benz|e|inden-5-one and dodecahydro-4a-nitro-9(1H)-phenanthrenone of cis-anti-cis backbone are synthesized in quantitative yield by cycloaddition reaction of 1-nitro-cyclopent-1-ene and 1-nitro-cyclohex-1-ene with 1-(cyclopenten-1-yl)- and 1-(cyclohexen-1-yl)-1-(piperidin-1-yl)-ethenes respectively. The enamine intermediates are also isolated and characterized.

In connection with our studies on the reactivity of nitroolefins with enamines,[1] we have turned our attention to nitrocycloalkenes.[2] In this context we wish to report here on their behaviour as 2π-electron components in carbocyclization reactions with cross-conjugated dienamines, which behave as 4π-electron components.

RESULTS

Cross-conjugated dienamines 1[5] and 2[6] were reacted with 1-nitro-cyclopent-1-ene (3)[2] and 1-nitro-cyclohex-1-ene (4)[2] to afford in quantitative yield fused tricyclic systems 5 or 6, depending on the ring size of the parent dienamine (Scheme 1). When this was a six-membered one (m = 2), the tetrasubstituted enamines 5c and 5d were very stable and could be separated, whereas in the case of the five-membered ring (m = 1), the forms 5a and 5b rapidly isomerized into the corresponding double bond isomers 6a and 6b. All the reactions were carried out in the absence of solvent, at -30 °C. The presence of solvents however, such as ether, acetonitrile and benzene, did not modify substantially the reaction course, except for the rate and yield.

The tetrasubstituted enamines 5c and 5d also isomerized into their corresponding isomers 6c and 6d respectively, by standing either in chloroform or in methanol for a few days. An, as yet unidentified, acidic impurity appears to be responsible for this isomerization.[7] In fact, the equilibration rate could be enhanced by bubbling gaseous hydrochloric acid into the solution. The acid-catalysed isomerization of 5c and 5d into their isomers 6c and 6d respectively was fast, even in aqueous medium, in which enamines are known to undergo rapid hydrolysis.

Hydrolyses under kinetic control of compounds 5c and 5d were performed in methanol-water with the acid catalyst in ratio 1:1, to give the corresponding tricyclic ketones 7c and 7d in quantitative yield. The same ketones were obtained from hydro-

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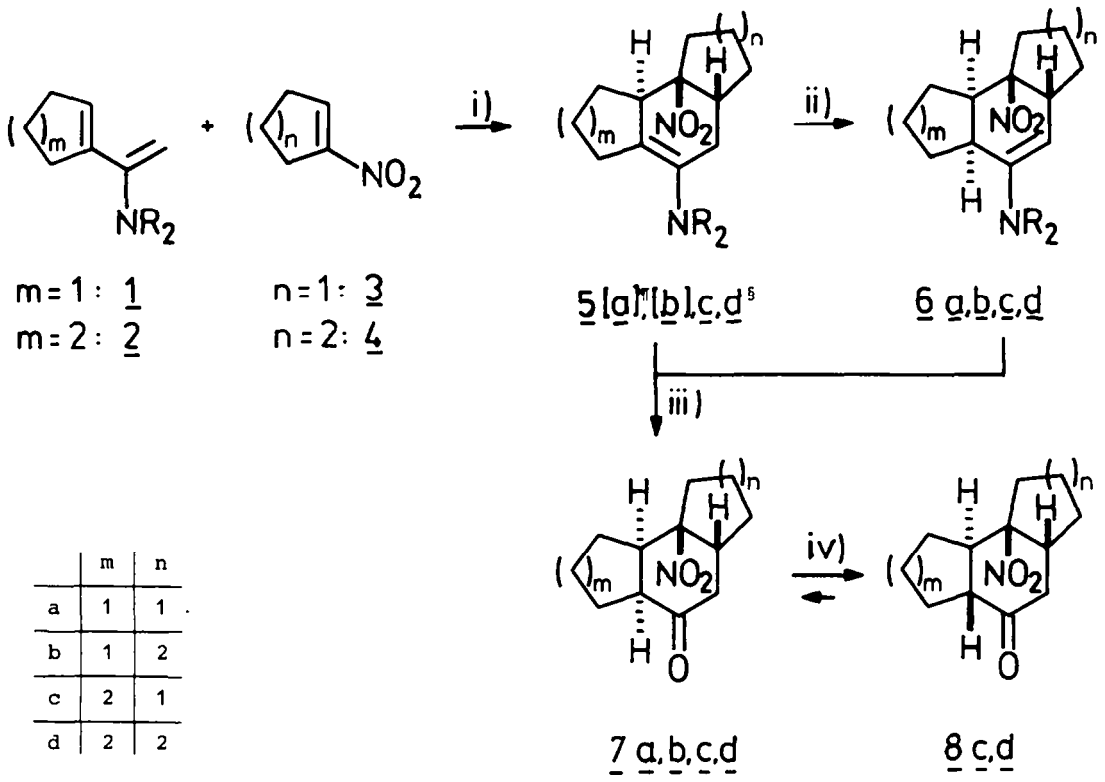
lyses of the trisubstituted enamines 6c and 6d, when carried out under non-equilibrating conditions. Hydrolyses of enamines 6a and 6b furnished the corresponding tricyclic ketones 7a and 7b in quantitative yield.

SCHEME 1



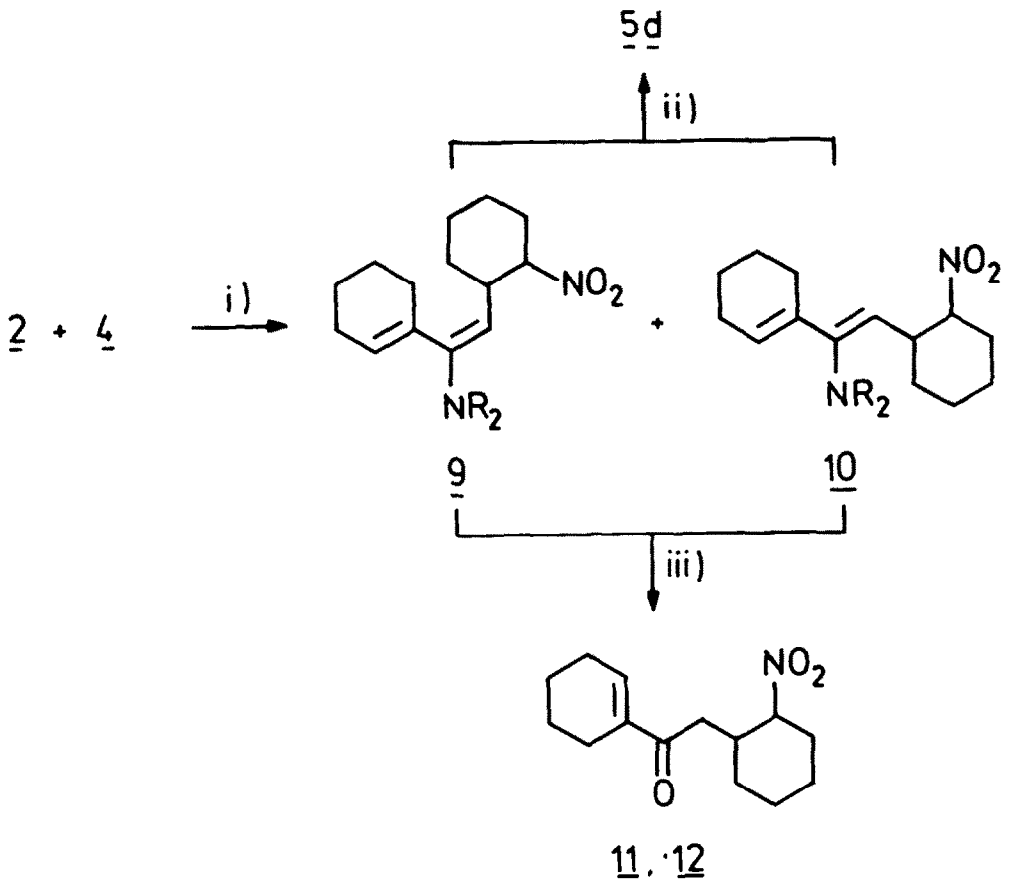
	m	n
a	1	1
b	1	2
c	2	1
d	2	2

¶ Compounds in brackets were not isolated.
§ All products are racemic.
NR_2 = piperidin-1-yl; i) -30 °C, no solvent; ii) $CHCl_3$, r.t., 72 h; iii) H_3O^+, r.t.; iv) TsOH, C_6H_6, 80 °C.

These latter ketones, for which m = 1, did not equilibrate significantly by prolonged heating in acidic medium, whereas ketones 7c and 7d, for which m = 2, underwent equilibration under the same conditions as above. The ketone 7c was completely converted into its diastereoisomer 8c, while compound 7d afforded a 65:35 mixture of 8d and itself.

The reaction between the enamine 2 and 1-nitro-cyclohex-1-ene (4) deserves further comments. Its course in fact was different from that of the other reactions, in as much as the products which were isolated firstly were the nitroalkylated open-chain enamines 9 and 10, as a 1:4 mixture of E and Z diastereoisomers[8] (Scheme 2). The Z isomer was more stable, as it could be crystallized from methanol, whereas the corresponding E isomer could not be heated without being modified. Both isomers however cyclized into the already cited enamine 5d, either by heating or by standing in a solvent for some period. Both systems 9 and 10 were also very sensitive to humidity and in fact they hydrolysed by simple standing in the air, to give a 7:3 mixture of the open-chain ketones 11 and 12, which differed in the configuration of the carbon atom bearing the nitro group, as demonstrated by an inspection of the proton NMR spectrum.

SCHEME 2



NR_2 = piperidin-1-yl; i) -30°C, no solvent; ii) MeOH, r.t., 96 h; iii) H_2O, r.t.

DISCUSSION

|4 + 2| Carbocyclization reactions of acyclic nitroolefins were already known[5,6] but all of them lacked the extremely high stereoselectivity observed for the cyclic ones. To give an idea, it will be sufficient to say that the ^{13}C NMR spectrum of the crude reaction mixture of 1a with 1-nitro-cyclopent-1-ene showed no other peaks but those of the product 6a.

The stereochemistry of the tricyclic compounds of kinetic formation, with the obvious exception of enamines 5, is cis-anti-cis, as demonstrated by the single crystal X-ray diffraction analysis of the ketone 7c, which was identified as dodecahydro-9b-nitro-5H-benz|e|inden-5-one |3aR*-(3aα,5aβ,9aβ,9bα)| (Figure).

With the structure of the ketone 7c unambiguously settled and those of the other ketones 7a, 7b and 7d assignable as cis-anti-cis and those of compounds 8c and 8d as trans-anti-cis, we can consider the stereochemical aspects of the reactions by which they are produced.

The question whether these cycloaddition reactions are concerted or not may arise once more. Although the cyclization reaction between enamine 2 and 1-nitrocyclohex-1-ene clearly proceeds in a non-concerted manner, as proved by the initial formation of the enamines 9 and 10, the same cannot be said with certainty for the other reactions. This also because the cis addition of the nitroolefin and the exclusive formation of the anti products would keep with the general preference for endo orientation in the Diels-Alder reactions.[9] In any case, whatever the

mechanism, the nitro group assumes the endo conformation, which on the other hand is also the less sterically hindered arrangement, thus determining the anti configuration observed.

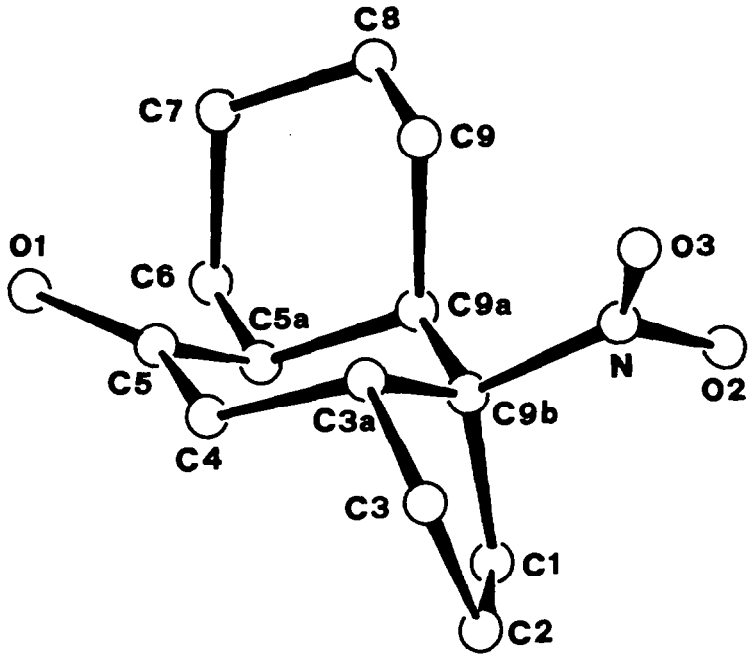
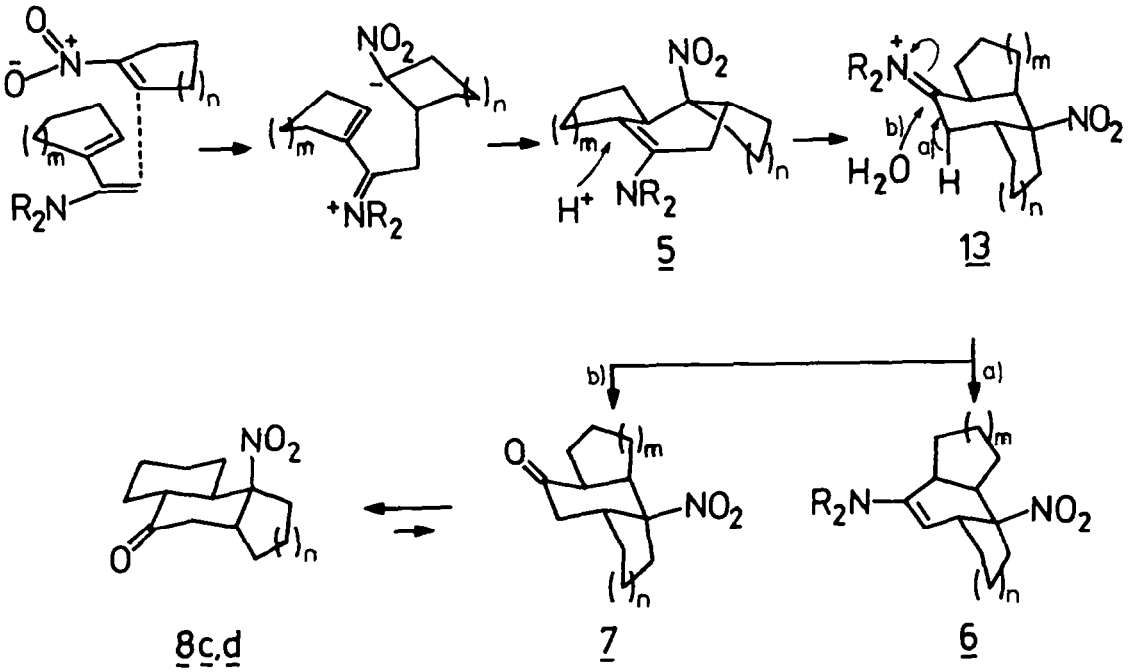


Figure †

†For reason of consistency the benz|e|indene numbering was also used in the structure.

The cis fusion between the ring of the substrate and the newly formed six-membered ring, both in the enamines 6 and in the corresponding ketones 7, is a consequence of the type of protonation of the tetrasubstituted enamines 5 from which they derive. The protonation is highly stereoselective, occurring exclusively

SCHEME 3



from the β side of the molecule, resulting in the formation of the immonium intermediate 13 (Scheme 3).

Equilibration of the systems 5 into the corresponding isomers 6 would involve abstraction of a proton from the methylene carbon atom adjacent to the iminium carbon atom (route a), while the formation of the ketones 7 would derive from the attack of one molecule of water onto the iminium carbon atom of 13 (route b). This latter reaction seems more difficult than the former, probably owing to the highly hindered steric situation of the cis-anti-cis geometry in the intermediate itself.

Equilibration of the cis-anti-cis backbone into the corresponding trans-anti-cis does not occur for the ketones 7a and 7b, in which the confiqurational change would involve a five-membered ring. This is in accordance with the preferite cis ring junction of the five-membered rings.[6] Of the remaining tricyclic ketones of kinetic formation, i.e. 7c and 7d, only the former undergoes complete equilibration into its trans-anti-cis diastereoisomer 8c, whereas the dodecahydro-phenanthrenone system 7d converts only partially into 8d. This is rather strange, as no evident steric reason is present in the diastereoisomer 8d when compared with 8c, which could account for this result, also if one consider that the trans-anti-cis geometry of perhydrophenanthrene is more stable than the cis-anti-cis geometry by 1.44 Kcal/mole.[10]

EXPERIMENTAL

The ^{1}HNMR spectra were run on either a JNM-60-HL Jeol or on a Bruker WP-80 spectrometer. The ^{13}CNMR spectra were run on a Bruker WP-80 spectrometer at 20.1 MHz. The solvent for both ^{1}HNMR and ^{13}CNMR spectra was $CDCl_3$ with tetramethylsilane as internal standard. IR spectra were recorded on a Perkin-Elmer 297 spectrophotometer. Flash chromatography was performed on Merck Kieselgel (40-63 μm). M.ps were measured on a Büchi 510 apparatus.

Materials. Enamines 1 and 2 were prepared from piperidine and (cyclopenten-1-yl)-methyl ketone[11] and (cyclohexen-1-yl)-methyl ketone respectively, by the White and Weingarten method.[12]

1-(Cyclopenten-1-yl)-1-(piperidin-1-yl)-ethene (1). B.p.$_{1mmHg}$ 73°C. IR (neat): 1620, 1575 cm^{-1}; ^{1}H NMR: δ 5.9 (m, 1H, C=CH), 4.3, 4.1 (2s, 2H, C=CH_2), 2.8 (m, 4H, CH_2NCH_2), 2.6-2.1 (m, 4H, CH_2C=CHCH_2), 2.1-1.75 (m, 2H, CH_2CH_2C=CH), 1.5 (m, 6H, $NCH_2(CH_2)_3$).

1-(Cyclohexen-1-yl)-1-(piperidin-1-yl)-ethene (2). B.p.$_{3mmHg}$ 98°C. IR (neat): 1630, 1585 cm^{-1}; ^{1}H NMR: δ 6.0 (m, 1H, C=CH), 4.1, 3.9 (2s, 2H, C=CH_2), 2.7 (m, 4H, CH_2NCH_2), 2.1 (m, 4H, CH_2C=CHCH_2), 1.5 (m, 10H, $NCH_2(CH_2)_3$ and CH_2CH_2C=CH).

1-Nitro-cyclopent-1-ene (3) and 1-nitro-cyclohex-1-ene (4) were prepared in accordance with E.J.Corey.[2]

General Procedure for the reactions between enamines 1 and 2 and 1-nitro-cycloolefins 3 and 4.

A) Conditions in solution. A solution of the nitro-cycloolefin (10 mmoles) in dry ether (10 ml) was added dropwise to a solution of the appropriate enamine (10 mmoles) in dry ether (20 ml) cooled to 0°C. The mixture was kept at 5°C for 48 h. If after that period a crystalline product was formed, it was filtered off, otherwise, the solvent was evaporated and the crude reaction mixture was kept at -30°C for further 24 h, until it solidified. The solid was filtered off with the aid of a small amount of methanol.

B) Conditions without solvent. The nitro-cycloolefin (10 mmoles) was added dropwise to the enamine (10 mmoles), both cooled to -30°C, and kept at the same temperature for 48 h. The solid product was then washed with cold methanol and filtered off. In the case of enamine 2 and nitroolefin 4, the reaction mixture solidified in methanol, by scratching.

Reaction of 1-(cyclopenten-1-yl)-1-(piperidin-1-yl)-ethene (1) with 1-nitro-cyclopent-1-ene (3).

1,2,3,3a,5a,6,7,8,8a,8b-decahydro-8a-nitro-4-(piperidin-1-yl)-as-indacene [3aS*-(3aα,5aβ,8aβ,8bα)] (6a) (100% yield). M.p. 62-3°C, from methanol (Found: C, 70.30; H, 8.88; N, 9.56. Calc for $C_{17}H_{26}N_2O_2$: C, 70.31; H, 9.02; N, 9.65%). IR (nujol): 1633 (N-C=C), 1534 cm^{-1} (NO_2); ^{1}H NMR: δ 4.3 (d J 2.5 Hz, 1H, H-5), 3.6 (m, 1H, H-3a), 2.9 (m, 4H, CH_2NCH_2), 2.70-1.25 (m, 20H), 1.55 (m, 6H, $NCH_2(CH_2)_3$); ^{13}C NMR (multiplicity): 144.8 (s), 102.6(d), 100.0 (s), 48.2 (2C, t), 44.7 (d), 37.5 (d), 37.1 (d), 35.2 (t), 30.1 (t), 28.4 (t), 26.2 (t), 24.4 (2C, t), 23.1 (t), 21.5 (t), 20.0 ppm (t).

This is another example of deviation[5] from the general behaviour of the tetrasubstituted enamines towards protonation.[7]

Dodecahydro-8a-nitro-as-indacen-4(2H)-one |3aS*-(3aα,5aβ,8aβ,8bα)| (7a). Hydrolysis of enamine 6a (5 mmoles), carried out in acetone, water and hydrochloric acid (5 mmoles), furnished the ketone 7a in quantitative yield. M.p. 36-7°C (Found: C, 64.30; H, 7.81; N, 6.30. Calc for $C_{12}H_{17}NO_3$: C, 64.55; H, 7.67; N, 6.27%). IR ($CHCl_3$): 1710 (C=O), 1530 cm^{-1} (NO_2); ^1H NMR: δ 3.4 (m, 1H, H-3a), 3.15-1.0 (m, 16H). ^{13}C NMR (multiplicity): 209.3 (s), 100.7 (s), 50.0 (d), 49.2 (d), 43.4 (t), 40.9 (d), 36.4 (t), 31.0 (t), 28.6 (t), 25.0 (t), 21.6 (t), 20.4 ppm (t).

Reaction of 1-(cyclopenten-1-yl)-1-(piperidin-1-yl)-ethene (1) with 1-nitro-cyclohex-1-ene (4).

2,3,3a,5a,6,7,8,9,9a,9b-decahydro-9a-nitro-4-(piperidin-1-yl)-1H-benz|e|indene |3aS*-(3aα,5aβ,9aβ,9bα)| (6b) (100% yield). M.p. 100°C, from methanol (Found: C, 71.30; H, 9.14; N, 9.15. Calc for $C_{18}H_{28}N_2O_2$: C, 71.02; H, 9.27; N, 9.20%). IR (nujol): 1630 (N-C=C), 1530 cm^{-1} (NO_2); ^1H NMR: δ 4.3 (d J 1.0 Hz, 1H, H-5), 3.4 (bm, 1H, H-3a), 3.1-2.1 (m, 6H), 2.1-0.8 (m, 20H); ^{13}C NMR (multiplicity): 148.2 (s), 103.2 (d), 93.0 (s), 50.2 (d), 49.5 (2C, t), 39.2 (d), 32.0 (t), 31.7 (t), 30.4 (t), 28.7 (t), 26.2 (t), 25.8 (2C, t), 24.7 (t), 23.4 (t), 22.5 (t), 20.3 ppm (t).

Dodecahydro-9a-nitro-4H-benz|e|inden-4-one |3aS*-(3aα,5aβ,9aβ,9bα)| (7b). Hydrolysis of enamine 6b, carried out in a mixture acetone-water, with hydrochloric acid in ratio 1:1, furnished the ketone 7b, m.p. 86-8°C, from methanol (Found: C, 65.92; H, 7.85; N, 5.95. Calc for $C_{13}H_{19}NO_3$: C, 65.80; H, 8.07; N, 5.90%). IR (nujol): 1700 (C=O), 1530 cm^{-1} (NO_2); ^1H NMR: δ 3.2 (m, 1H, H-3a), 3.0-2.0 (m, 6H), 2.0-1.0 (m, 12H); ^{13}C NMR (multiplicity): 209.3 (s), 92.3 (s), 53.3 (d), 50.6 (d), 42.6 (t), 34.1 (t), 31.6 (t), 27.0 (t), 26.3 (t), 24.1 (t), 22.5 (t), 20.8 (t), 18.9 ppm (t).

Reaction of 1-(cyclohexen-1-yl)-1-(piperidin-1-yl)-ethene (2) with 1-nitro-cyclopent-1-ene (3).

2,3,3a,4,6,7,8,9,9a,9b-decahydro-9b-nitro-5-(piperidin-1-yl)-1H-benz|e|indene |3aR*-(3aα,9aβ,9bα)| (5c) (100% yield). M.p. 108-9°C, from methanol (Found: C, 71.19; H, 9.49; N, 9.01. Calc for $C_{18}H_{28}N_2O_2$: C, 71.02; H, 9.27; N, 9.20%). IR (nujol): 1668 (N-C=C), 1532 cm^{-1} (NO_2); ^1H NMR (C_6D_6): δ 3.4 (dt J_1 9.0 Hz, J_2 2.0 Hz, 1H, H-9a), 3.1-2.0 (m, 9H), 2.0-0.95 (m, 18H); ^{13}C NMR (multiplicity): 137.4 (s), 126.4 (s), 116.6 (s), 51.8 (2C, t), 42.8 (d), 38.3 (d), 34.5 (t), 31.0 (t), 29.8 (t), 28.5 (t), 27.4 (t), 26.8 (t), 26.6 (2C, t), 25.5 (t), 24.6 (t), 21.9 (t), 18.8 ppm (t).

2,3,3a,5a,6,7,8,9,9a,9b-decahydro-9b-nitro-5-(piperidin-1-yl)-1H-benz|e|indene |3aR*-(3aα,5aβ,9aβ,9bα)| (6c). By standing in chloroform for four days, the enamine 5c equilibrates into enamine 6c, m.p. 123-4°C, from methanol (Found: C, 71.32; H, 9.04; N, 9.19. Calc for $C_{18}H_{28}N_2O_2$: C, 71.02; H, 9.27; N, 9.20%). IR (nujol): 1630 (N-C=C), 1530 cm^{-1} (NO_2); ^1H NMR: δ 4.5 (dd J_1 2.0 Hz, J_2 2.5 Hz, 1H, C=CH), 3.65 (m, 1H, H-5a), 3.0-1.95 (m, 10H), 1.95-1.0 (m, 16H); ^{13}C NMR (multiplicity): 130.0 (s), 109.3 (d), 103.7 (s), 100.5 (s), 51.8 (2C, t), 42.1 (d), 39.4 (d), 35.3 (t), 33.4 (d), 30.9 (t), 28.2 (t), 26.6 (t), 26.3 (2C, t), 25.5 (t), 24.8 (t), 21.9 ppm (t).

Dodecahydro-9b-nitro-5H-benz|e|inden-5-one |3aR*-(3aα,5aβ,9aβ,9bα)| (7c). Hydrolyses of enamines 5c and 6c, carried out under the same conditions, namely acetone-water and hydrochloric acid in equimolar amount, led to the ketone 7c, m.p. 102-3°C, from methanol (Found: C, 65.80; H, 8.21; N, 5.78. Calc for $C_{13}H_{19}NO_3$: C, 65.80; H, 8.07; N, 5.90%). IR ($CHCl_3$): 1710 (C=O), 1535 cm^{-1} (NO_2); ^1H NMR: δ 3.4 (m, 1H, H-5a), 3.15-0.95 (m, 18H); ^{13}C NMR (multiplicity): 209.5 (s), 103.0 (s), 45.1 (d), 45.0 (d), 43.3 (t), 39.5 (d), 35.4 (t), 31.8 (t), 26.9 (t), 25.7 (t), 25.1 (t), 21.5 (t), 20.9 ppm (t).

Dodecahydro-9b-nitro-5H-benz|e|inden-5-one |3aR*-(3aα,5aα,9aβ,9bα)| (8c). Equilibration of compound 7c in refluxing benzene with paratoluensulphonic acid as a catalyst, furnished the diastereoisomer 8c, oil, purified by chromatography (Found: C, 64.54; H, 7.88; N, 5.96. Calc for $C_{13}H_{19}NO_3$: C, 65.80; H, 8.07; N, 5.90%). IR ($CHCl_3$): 1705 (C=O), 1525 cm^{-1} (NO_2); ^1H NMR: δ 3.1-2.7 (m, 3H), 2.7-0.8 (m, 16H); ^{13}C NMR (multiplicity): 199.3 (s), 129.8 (s), 47.3 (d), 46.8 (d), 44.8 (d), 42.4 (t), 35.4 (t), 32.1 (t), 27.4 (t), 27.3 (t), 26.0 (t), 25.1 (t), 21.9 ppm (t).

Reaction of 1-(cyclohexen-1-yl)-1-(piperidin-1-yl)-ethene (2) with 1-nitro-cyclohex-1-ene (4). The reaction leads to the formation of two diastereoisomeric enamines 9 and 10, in ratio 1:4, which were separated by fractional crystallization from methanol, at -30°C.

(E)-1-(cyclohexen-1-yl)-2-(2-nitro-cyclohex-1-yl)-1-(piperidin-1-yl)-ethene (9). M.p. 62-4°C. IR (nujol): 1610 (N-C=C), 1540 cm^{-1} (NO_2); ^1H NMR: δ 5.6 (m, 1H, C=CH), 4.7-3.9 (m, d, 2H, $CHNO_2$ and N-C=CH), 4.0 (d J 9.5 Hz, N-C=CH), 2.7 (m, 5H, CH_2NCH_2 and $CHCHNO_2$), 2.4-0.85 (m, 22H); ^{13}C NMR (multiplicity): 134.8 (s), 127.8 (d), 101.0 (d), 92.7 (d), 52.1 (2C, t), 42.6 (d), 34.2 (t), 31.2 (t), 29.1 (t), 28.2 (t), 26.6 (2C, t), 25.0 (t), 24.3 (t), 22.3 (t), 19.5 ppm (t).

(Z)-1-(cyclohexen-1-yl)-2-(2-nitro-cyclohex-1-yl)-1-(piperidin-1-yl)-ethene (10). M.p. 89-90°C, from methanol (Found: C, 71.70; H, 9.10; N, 8.74. Calc for $C_{19}H_{30}N_2O_2$ C, 71.66; H, 9.50; N, 8.80%). IR (nujol): 1605 (N-C=C), 1538 cm^{-1} (NO_2); ^1H NMR: δ 5.6 (m, 1H, C=CH), 4.65-4.20 (m, d, 2H, $CHNO_2$ and N-C=CH), 4.4 (d J 10 Hz, N-C=CH), 3.3 (bd, 1H, $CHCHNO_2$), 2.6 (m, 4H, CH_2NCH_2), 2.3-0.8 (m, 22H); ^{13}C NMR (multiplicity): 155.8 (s), 135.2 (s), 128.0 (d), 96.2 (d), 88.1 (d), 49.2 (2C, t), 38.6 (d), 32.1 (t), 29.0 (t), 26.0 (2C, t), 25.3 (t), 24.6 (t), 23.2 (t), 22.9 (t), 22.3 (t), 21.2 ppm (t).

1,2,3,4,4a,4b,5,6,7,8,10,10a-Dodecahydro-4a-nitro-9-(piperidin-1-yl)-phenanthrene |4aS*-(4aα,4bβ,10aα)| (5d). Both enamines 9 and 10 cyclize either in chloroform at room temp or in methanol at reflux to give the compound 5d in quantitative yield. M.p. 104-6°C, from methanol (Found: C, 71.76; H, 9.41; N, 8.75. Calc for $C_{19}H_{30}N_2O_2$: C, 71.66; H, 9.50; N, 8.80%). IR (nujol): 1672 (C=O), 1530 cm^{-1} (NO_2); ^1H NMR: δ 3.3 (bdt J_1 10.0 Hz, J_2 2.0 Hz, 1H, H-4b), 2.95-0.9 (m, 28H); ^{13}C NMR (multiplicity): 128.0 (s), 104.9 (s), 52.1 (2C, t), 48.7 (d), 31.5 (d), 31.2 (t), 31.0 (t), 29.3 (t), 28.2 (t), 27.1 (t), 26.6 (2C, t), 25.0 (t), 24.6 (t), 22.5 (t), 22.3 (t), 19.5 ppm (t).

1,2,3,4,4a,5,6,7,8,8a,10a-Dodecahydro-4a-nitro-9-(piperidin-1-yl)-phenanthrene |4aS*-(4aα,4bβ,8aβ,10aα)| (6d). Enamine 5d was equilibrated into its double bond isomer 6d in chloroform with gaseous hydrochloric acid. M.p. 71-3°C, from methanol (Found: C, 71.50; H, 9.46; N, 8.77. Calc for $C_{19}H_{30}N_2O_2$: C, 71.66; H, 9.50; N, 8.80%). IR ($CHCl_3$): 1625 (N-C=C), 1525 cm^{-1} (NO_2); ^1H NMR: δ 4.55 (bs, 1H, C=CH), 3.5 (m, 1H, H-8a), 3.1-0.8 (m, 28H); ^{13}C NMR (multiplicity): 148.2 (s), 108.8 (d), 95.1 (s), 51.7 (2C, t), 45.5 (d), 34.5 (d), 33.1 (d), 30.7 (t), 28.6 (t), 28.2 (t), 26.3 (2C, t), 25.4 (t), 24.8 (t), 23.3 (t), 22.2 (2C, t), 21.1 ppm (t).

Dodecahydro-4a-nitro-9(1H)-phenanthrenone |4aS*-(4aα,4bβ,8aβ,10aα)| (7d). Hydrolyses of enamines 5d and 6d, carried out in acetone-water with hydrochloric acid in equimolar ratio, led to the formation of ketone 7d in quantitative yield. M.p. 171-3°C, from acetone (Found: C, 67.12; H, 8.37; N, 5.56. Calc for $C_{14}H_{21}NO_3$: C, 66.91; H, 8.42; N, 5.57%). IR (nujol): 1705 (C=O), 1530 cm^{-1} (NO_2); ^1H NMR: δ 3.1 (m, 1H, H-8a), 2.9-2.0 (m, 8H), 2.0-0.8 (m, 12H); ^{13}C NMR (multiplicity): 209.5 (s), 95.2 (s), 49.6 (d), 46.3 (d), 42.8 (t), 33.2 (d), 30.1 (t), 26.7 (t), 25.8 (t), 25.0 (t), 22.5 (t), 21.5 (t), 19.0 ppm (t).

Dodecahydro-4a-nitro-9(1H)-phenanthrenone |4aS*-(4aα,4bβ,8aα,10aα)| (8d). Equilibration of the ketone 7d, carried out in refluxing benzene with paratoluensulphonic acid in traces, led to a 35:65 mixture of 7d and 8d, from which 8d was separated by flash chromatography. M.p. 66-7°C (Found: C, 66.80; H, 8.37; N, 5.61. Calc for $C_{14}H_{21}NO_3$: C, 66.91, H, 8.42; N, 5.57%). IR (nujol): 1710 (C=O), 1535, 1525 cm^{-1} (NO_2); ^1H NMR: δ 3.4-2.7 (m, 2H), 2.7-0.85 (m, 12H); ^{13}C NMR (multiplicity): 210.2 (s), 93.8 (s), 48.3 (d), 44.2 (t), 42.9 (d), 42.5 (d), 32.8 (t), 30.4 (t), 26.3 (2C, t), 26.1 (t), 24.8 (t), 24.3 (t), 22.2 ppm (t).

(Cyclohexen-1-yl)- |1-(2-nitro-cyclohex-1-yl)|methyl ketone (11) and (12). Hydrolyses of enamines 9 and 10, carried out in water with hydrochloric acid in traces, furnished an oily mixture of the ketones 11 and 12 |2,4-Dinitrophenylhydrazone derivatives, m.p. 173-4°C, from methanol (Found: C, 55.7, H, 5.64; N, 16.43. Calc for $C_{20}H_{25}N_5O_6$: C, 55.7; H, 5.84; N, 16.23)|. IR (neat): 1660 (C=O), 1630 (C=C), 1530 cm^{-1} (NO_2): ^1H NMR: δ 6.9 (m, 1H, C=CH), 4.8 (bm W_H 10 Hz, 0.5H, $CHNO_2$), 4.4 (dt W_H 28 Hz, 0.5H, $CHNO_2$), 2.6 (m, 3H), 2.45-1.0 (m, 16H); ^{13}C NMR (multiplicity): 198.9 (s), 140.6 (d), 139.7 (s), 90.5 (d), 85.7 (d), 39.7 (t), 37.8 (d), 34.8 (d), 32.0 (t), 30.5 (t), 28.6 (t), 27.3 (t), 26.0 (t), 24.7 (t), 24.4 (t), 23.0 (t), 21.9 (t), 21.5 (t), 21.2 ppm (t).

X-Ray structure determination of dodecahydro-9b-nitro-5H-benz|e|inden-5-one |3aR*-(3aα,5aβ,9aβ,9bα)| (7c).

Crystal Data. Formula $C_{13}H_{19}NO_3$; M = 237.3. The crystals are monoclinic and belong to the space group $P2_1/c$, with Z = 8. The cell parameters are a = 11.056(1), b = 6.512(7), c = 17.670(4) Å, β = 101.99(1) , V = 1224.3 $Å^3$.

Intensity measurements. The intensity data collection was carried out on an Enraf Nonius CAD4 diffractometer. 3360 reflections were collected in the range $2.5° < \theta < 28°$, using monochromatized Mo-K_α radiation, λ = 0.71069 Å, with variable ω/2θ scan and a maximum measuring time of 100 s for reflection.

The intensity of four standard reflections, monitored every 3000 s exposure time, did not change significantly during data collection. After correction for Lorentz and polarization factors, a total of 1785 independent reflections were used in the subsequent calculations.

Structure determination and refinement. The structure was solved using Multan 11/82.[13] All non hydrogen atoms appeared on the E-map, except the carbon atoms of the five-membered ring, which were located by a subsequent Fourier map. Refinement was carried out by means of full-matrix least squares techniques, using anisotropic temperature factors. In the last cycles, hydrogen atoms were located at calculated positions, and the Killean and Lawrence weighting method was used. The final R index was 0.047. Calculations were performed by the Enraf-Nonius SDP programs.[13]

Supplementary Material Available. A listing of observed and calculated structure factors including tables of positional and thermal parameters, temperature factors and bond lengths and angles.

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REFERENCES

1. G.Barbarella, S.Brückner, G.Pitacco and E.Valentin, Tetrahedron 40, 2441 (1984).
2. E.J.Corey and H.Estreichen, J.Am.Chem.Soc. 100, 6294 (1978). The first reaction between an acyclic tertiary enamine and 1-nitro-cyclohex-1-ene was performed by D.Seebach and J.Golinski,[3] while an analogous reaction with a secondary enamine was performed by H.Meyer.[4]
3. D.Seebach and J.Golinski, Helv.Chim.Acta 64, 1413 (1981).
4. H.Meyer, Liebigs Ann.Chem. 1534 (1981).
5. G.Pitacco, A.Risaliti, M.L.Trevisan and E.Valentin, Tetrahedron 33, 3145 (1977).

6. F.Benedetti, G.Pitacco and E.Valentin, Tetrahedron 35, 2293 (1979).
7. F.Johnson, L.G.Duquette, A.Whitehead and L.C.Dorman, Tetrahedron 30, 3241(1974).
8. S.Patai, The Chemistry of Functional Group, Suppl.F, Chapter 15, J. Wiley & Sons, 1982.
9. D.Ginsburg, Tetrahedron 39, 2095 (1983).
10. N.L.Allinger, B.J.Gorden, I.J.Tyminski and M.T.Wuesthoff, J.Org.Chem. 36, 739 (1971).
11. P.F.Casals, Bull.Soc.Chim.Fr., 253 (1963).
12. W.A.White and H.Weingarten, J.Org.Chem. 32, 213 (1967).
13. B.A.Frenz and Y.Okaya, "Enraf-Nonius Structure Determination Package", Enraf-Nonius, Delft, Holland (1980).