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Reaction of Conjugated Dienones with Hydrazoic Acid. II.[1]

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Reaction of bicyclic conjugated dienones (II, III, IV, V, and VI) with hydrazoic acid in PPA was carried out and the results were summarized in Table I. All products were probably formed by action of two molar equivalents of hydrazoic acid. From the substrates (I and III), the aldehyde-lactams (XI, XIX, and XX) were obtained whose formation is the first observation in this reaction.

It was reported in the previous paper[3] that 4a-methyl-4,4a,5,6-tetrahydro-2(3*H*)-naphthalenone (I) reacted with hydrazoic acid in polyphosphoric acid (PPA) to afford four kinds of keto-lactam (VII—X). This implied that the extended dienone (I) was attacked with two moles of hydrazoic acid on carbonyl group and a double bond. In order to further delineate the mode and the scope of this reaction, the behaviour of 4,4a,5,6-tetrahydro-1,4a-dimethyl-2(3*H*)-naphthalenone (II), 4,4a,5,6-tetrahydro-4a,8-dimethyl-2(3*H*)-naphthalenone (III), 4,4a,5,6-tetrahydro-4,4,7-trimethyl-2(3*H*)-naphthalenone (IV), 4,6,7,8-tetrahydro-2(3*H*)-naphthalenone (V), and 3,3a,4,5-tetrahydro-2-indenone (VI) to hydrazoic acid in PPA was studied.

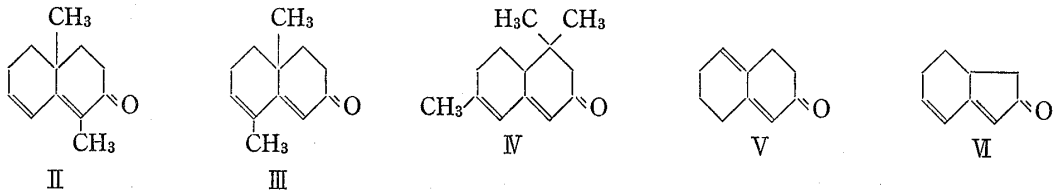

Chart 1

It was expected that the substituents attached to double bond would affect the mode of this reaction, because α,β-unsaturated ketones carrying substituent at α position such as 2-methyl-2-cyclohexenone gave an abnormal Schmidt reaction product, 2-amino-3-methyl-2-cyclohexenone.[4] Thus, the dienone (II) which have methyl group at α position was submitted to this reaction in PPA under the same condition as in the case of dienones previously examined.[3] When two and half molar equivalents of sodium azide was used, four products

1) This paper constitutes part VI in a series entitled "Reaction of Conjugated Ketones with Azides." Part V: K. Nomura, J. Adachi, Y. Namekawa, and K. Mitsuhashi, *Yakugaku Zasshi*, **93**, 931 (1973).
2) Location: *Gofuku, Toyama.*
3) K. Mitsuhashi, K. Nomura, and F. Miyoshi, *Chem. Pharm. Bull.* (Tokyo), **19**, 1983 (1971).
4) K. Mitsuhashi and K. Nomura, *Chem. Pharm. Bull.* (Tokyo), **13**, 951 (1965).

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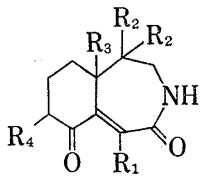
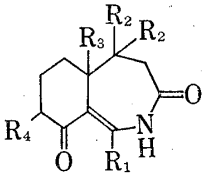
(XII, XIII, XIV, and XV) were obtained from reaction mixture after separation by column chromatography (see Table I). All these four compounds showed the same elemental analyses corresponding to the empirical formula of $C_{12}H_{17}O_2N$. These structures were assigned by infrared (IR), ultraviolet (UV) and nuclear magnetic resonance (NMR) spectra, taking into consideration the structures[3] of keto-lactams obtained from dienone (I). It seemed that this result resembled the reaction of the dienone (I) with hydrazoic acid in the point of formation of keto-lactam derivatives and methyl group at α position had not any particular influences.

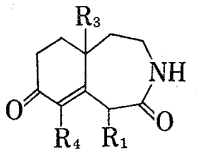
Table I. Reaction Products of Dienones with Hydrazoic Acid

Substrate	Products (yield %)					
	A	B	C	D	E	F
I	VII (26)	VIII (2)	IX (3.5)	X (3)	XI (5)	—
II	XII (0.3)	XIII (0.85)	XIV[a] (2.9)	XV[a] (5.9)	—	—
III	XVI[a] (1)	—	XVII (7.5)	XVIII (20)	XIX[a] (18.5)	XX[a] (5.5)
IV	XXII[a] (10)	XXIII[a] (4.5)	—	—	—	—
V	—	—	XXIV (27.7)	XXV (9.5)	—	—
VI	—	—	XXVI (13.1)	XXVII (16.4)	—	—

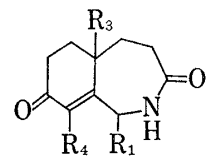
a) The conformation of methyl group was undefined.

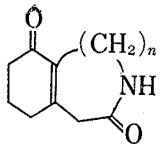


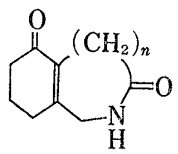




VII : $R_1=R_2=R_4=H$, $R_3=CH_3$ VIII : $R_1=R_2=R_4=H$, $R_3=CH_3$ IX : $R_1=R_4=H$, $R_3=CH_3$
XII : $R_2=R_4=H$, $R_1=R_3=CH_3$ XIII : $R_2=R_4=H$, $R_1=R_3=CH_3$ XIV : $R_4=H$, $R_1=R_3=CH_3$
XVI : $R_1=R_2=H$, $R_3=R_4=CH_3$ XXIII : $R_1=R_3=H$, $R_2=R_4=CH_3$ XVII : $R_1=H$, $R_3=R_4=CH_3$
XXII : $R_1=R_3=H$, $R_2=R_4=CH_3$







X : $R_1=R_4=H$, $R_3=CH_3$
XV : $R_4=H$, $R_1=R_3=CH_3$
XVIII : $R_1=H$, $R_3=R_4=CH_3$

XXIV : $n=2$
XXVI : $n=1$

XXV : $n=2$
XXVII : $n=1$

The same reaction was examined with the dienone (III) which has methyl group at γ position. The reaction products: XVI in 1%, XVII in 7.5%, XVIII in 20%, XIX in 18.5%, and XX in 5.5% yield, were obtained. All five compounds showed the same empirical formula of $C_{12}H_{17}O_2N$. The structures of keto-lactams (XVI, XVII, and XVIII) were confirmed by IR, UV, and NMR spectra referring to those data of keto-lactams (XII, XIV, and XV). The remaining products (XIX and XX) have not been observed in this reaction so far. Their IR spectra showed the presence of lactam (XIX: 3200, 3060, 1640 and XX: 3160, 3040, 1665 cm^{-1}) and aldehydic group (XIX: 2720, 1715 and XX: 2720, 1720 cm^{-1}). The presence of aldehydic group was confirmed by the conversion of XIX into the primary alcohol derivative (XXI) with sodium borohydride. The NMR spectrum of XIX showed an aldehyde proton

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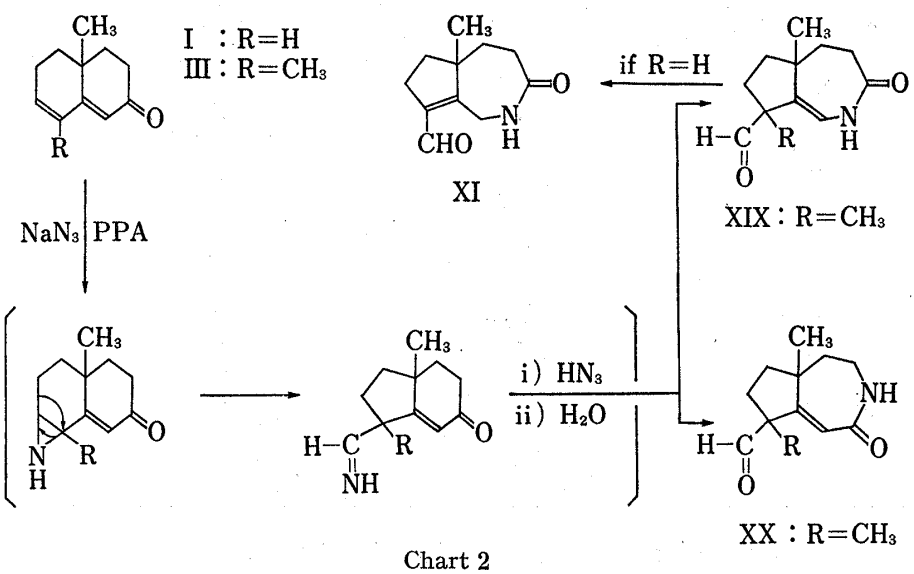

Chart 2

at 0.73 τ as a singlet and an olefinic proton at 4.35 τ as a doublet (J=2 Hz). On the other hand, the NMR spectrum of XX showed an aldehyde proton at 0.55 τ as a singlet and an olefinic proton at 4.33 τ as a doublet (J=7 Hz) which changed to a singlet on treatment with deuterium oxide. Thus, XIX was presumed to have an enamine lactam moiety and XX to have an enone lactam moiety. The appearance of aldehydic function implied that a contraction of ring would take place in addition to Schmidt rearrangement. Similar ring contraction was found in a fission-rearrangement of α,β-epoxyketone.[5] A pathway to the formation of aldehyde compounds (XIX and XX) is postulated as shown in Chart 2. The aziridine ring which would be produced by the reaction of hydrazoic acid to double bond, probably gave rise to the fission-rearrangement followed by hydrolysis, to generate these aldehydes (XIX and XX). Although the reaction of I with hydrazoic acid was explored in previous paper,[3] one minor product was remained as an unknown product. Now this structure was estimated by taking consideration of spectral data of aldehyde (XIX and XX), and elemental analysis to be aldehyde-lactam (XI). Although we could not get any definite evidence as a fused five-seven membered ring system for the compounds (XIX, XX, and XI), these structures were assigned on the consideration of pathway of this reaction. Among the keto-lactams obtained, XVI could be formed by the migration of γ methyl group to δ position. The related phenomenon could be seen in the reaction[4] of α,β-unsaturated ketone with hydrazoic acid.

4,4a,5,6-Tetrahydro-4,4,7-trimethyl-2(3*H*)-naphthalenone (IV) whose δ position is occupied by substituent was examined using two molar equivalents of sodium azide to give only two keto-lactam derivatives (XXII and XXIII) in 10% and 4.5% yield respectively.

As a bicyclic dienone in which both β and γ position form juncture, 4,6,7,8-tetrahydro-2(3*H*)-naphthalenone (V) was examined. The two keto-lactams (XXIV and XXV) were obtained in 27.7% and 9.5% yield respectively.

Finally the dienone (VI) which has a tetrahydro-2-indenone skeleton and is analogue to dienone (I) was submitted to this reaction. The two keto-lactams (XXVI and XXVII) were obtained in 13.1% and 16.4% yield respectively. The IR and UV spectra of XXVI and XXVII suggested the keto-lactam structure. Both structures were deduced by their NMR spectra (double resonance measurement) at 100 MHz (Table II): in the compound XXVI two homoallylic couplings (C_1-protons were splitted by C_4-protons (J=4 Hz) and C_5-protons (J=2 Hz)) were observed, while in the compound XXVII a homoallylic coupling (J=4 Hz) between C_1-protons and C_4-protons was observed.

5) H.O. House and R.L. Wasson, *J. Am. Chem. Soc.*, **79**, 1488 (1957).

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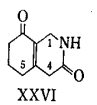
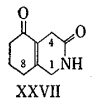
Table II. NMR Data of XXVI and XXVII in $CDCl_3$ at 100 MHz (in τ value) (single and double irradiation)

 XXVI	N–H	C_1–H	C_4–H	C_5–H
	3.03	5.86	6.90	7.70
	broad peak	multiplet	triplet $J=4$ Hz	multiplet
	(irradiation)	septet $J=2$ Hz	—	—
		(irradiation)	singlet	doublet $J=5.5$ Hz
		singlet	(irradiation)	—
		broad triplet	—	(irradiation)
 XXVII	N–H	C_1–H	C_4–H	C_8–H
	2.28	5.92	6.95	7.73
	broad peak	broad triplet	septet $J=2$ Hz	multiplet
	(irradiation)	triplet $J=4$ Hz	—	—
		(irradiation)	broad triplet	—
		singlet	(irradiation)	sharpened
		—	triplet $J=4$ Hz	(irradiation)

The data of these reactions were summerized in Table I where the classification of the products (A—F) were based on the direction of ring expansion for lactams and formation of ketonic function and also ring contraction. From these results, it was concluded that in each of these reactions, both carbonyl group and δ position of $\alpha,\beta,\gamma,\delta$-unsaturated ketone were suffered the attack of hydrazoic acid. These reactions were too variable to discuss the correlation between the structure of substrates and the reaction products. The formation of ketonic and aldehydic functions in any group of products could be explained in terms of cleavage of an aziridine intermediate.

Experimental[6]

Reaction of 4,4a,5,6-Tetrahydro-1,4a-dimethyl-2(3*H*)-naphthalenone (II) with Sodium Azide in PPA—To a stirred suspension of 6 g of II[7] in 120 g of PPA[4] was added 5.5 g of NaN_3 (2.5 molar equivalents) at 25° during 3 hr in N_2 atmosphere. The reaction mixture was stirred at 25° for 5 hr and at 40—50° for 1 hr. The mixture was poured onto ice and extracted with ether. The extract was dried over Na_2SO_4 and evaporated to give 0.2 g of a pale yellow oil (fraction A). The acidic aqueous layer was neutralized with 50% KOH and extracted with $CHCl_3$. The extract was dried over Na_2SO_4 and evaporated to give 6.0 g of a brown viscous oil (fraction B). In the fraction A, only starting material was detected by gas-liquid chromatography (GLC). The fraction B which showed more than 4 spots on thin-layer chromatography (TLC) (SiO_2) was chromatographed on SiO_2 (600 g). After development with $CHCl_3$, the fraction eluted with $CHCl_3$–MeOH (99: 1) afforded 0.06 g (0.85%) of colorless prisms (XIII), mp 131—132° (AcOEt). *Anal.* Calcd. for $C_{12}H_{17}O_2N$: C, 69.54; H, 8.27; N, 6.76. Found: C, 69.33; H, 8.03; N, 6.94. IR ν_{max}^{KBr} cm^{-1}: 3200, 3100 (NH), 1685 (C=O), 1620 (C=C). UV λ_{max}^{EtOH} nm (log ε): 280 (3.92). NMR ($CDCl_3$) τ: 2.70 (1H, broad signal, –NH–CO–, disappeared on addition of D_2O), 7.10—7.70 (4H, m), 7.70—8.50 (6H, m), 8.05 (3H, s, $>C=\dot{C}-CH_3$), 8.85 (3H, s, $>C-CH_3$).

The second fraction eluted with $CHCl_3$–MeOH (49: 1) gave 0.02 g (0.3%) of colorless prisms (XII), mp 145—147° (AcOEt). *Anal.* Calcd. for $C_{12}H_{17}O_2N$: C, 69.54; H, 8.27; N, 6.76. Found: C, 69.44; H, 8.32; N, 7.01. IR ν_{max}^{KBr} cm^{-1}: 3400, 3280 (NH), 1690 (C=O), 1650 (lactam C=O), 1605 (C=C). UV λ_{max}^{EtOH} nm (log ε): 239 (3.87). NMR ($CDCl_3$) τ: 2.75 (1H, broad signal –NH–CO–, disappeared on addition of D_2O), 6.50—6.95 (2H, m, $-C\underline{H}_2-NH-$), 7.30—7.90 (4H, m), 8.00 (3H, s, $>C=\dot{C}-CH_3$), 8.00—8.60 (4H, m), 8.80 (3H, s, $>C-CH_3$).

Further elution with $CHCl_3$–MeOH (49: 1) afforded 0.60 g of a colorless solid which was a mixture of XIV and XV in ratio 1: 2 according to NMR measurement. Recrystallization of this mixture from acetone gave the compound XIV as colorless prisms, mp 216—219°. *Anal.* Calcd. for $C_{12}H_{17}O_2N$: C, 69.54; H, 8.27; N, 6.76. Found: C, 69.69; H, 8.40; N, 6.85. IR ν_{max}^{KBr} cm^{-1}: 3280 (NH), 1675 (C=O), 1650 (lactam C=O). UV λ_{max}^{EtOH} nm (log ε): 244 (4.06). NMR ($CDCl_3$) τ: 2.95 (1H, broad signal, –NH–CO–, disappeared on addition of D_2O), 4.05 (1H, s, $>C=CH-$), 6.20—6.85 (3H, m, $-C\underline{H}_2-NH-$, $>C=\dot{C}-\dot{C}H-CO-$), 7.35—7.85 (2H, m, $-CH_2-CO-$), 7.90—8.45 (4H, m), 8.70 (3H, d, $J=7$ Hz, $>CH-C\underline{H}_3$).

6) All melting points were measured on Yanagimoto micro-melting point apparatus and uncorrected. NMR spectra were taken on a JNM-C-60H spectrometer with tetramethylsilane as an internal standard. Abbreviation; s=singlet, d=doublet, t=triplet, m=multiplet.

7) D.K. Danejee and V.B. Angadi, *J. Org. Chem.*, **26**, 2988 (1961).

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The mother liquor from which the compound XIV was removed as extensively as possible, was recrystallized from AcOEt afforded the compound XV as colorless prisms, mp 211.5—212.5°. *Anal.* Calcd. for $C_{12}H_{17}O_2N$: C, 69.54; H, 8.27; N, 6.76. Found: C, 69.40; H, 8.20; N, 6.71. IR ν_{max}^{KBr} cm^{-1}: 3400, 3280, 3200, 3080 (NH), 1665 (C=O). UV λ_{max}^{EtOH} nm (log ε): 230 (4.01). NMR ($CDCl_3$) τ: 2.75 (1H, broad signal, –NH–CO–, disappeared on addition of D_2O), 4.05 (1H, s, >C=CH–), 5.50—5.90 (1H, m, >C=C–CH–NH–, quartet (J= 7 Hz) on addition of D_2O), 7.00—7.75 (4H, m), 7.75—8.45 (4H, m), 8.62 (3H, d, J=7 Hz, >CH–CH_3), 8.70 (3H, s, >C–CH_3).

Reaction of 4,4a,5,6-Tetrahydro-4a,8-dimethyl-2(3*H*)-naphthalenone (III) with Sodium Azide in PPA——To a stirred suspension of 5.3 g of III[8] in 100 g of PPA was added 4.55 g of NaN_3 at 12—17° during 2 hr in N_2 atmosphere. The reaction mixture was stirred at 20—30° for 7.5 hr and at 45—50° for 30 min. The mixture was poured onto ice and extracted with ether. The extract was dried over Na_2SO_4 and evaporated to give 0.5 g of a brown solid (fraction A). The acidic aqueous layer was neutralized with 50% KOH and extracted with $CHCl_3$. The extract was dried over Na_2SO_4 and evaporated to give 5.4 g of a viscous oil (fraction B). From fraction A, 0.44 g of colorless needles (XIX) (7%) was obtained by recrystallization (acetone), mp 150—152°. *Anal.* Calcd. for $C_{12}H_{17}O_2N$: C, 69.54; H, 8.27; N, 6.76. Found: C, 69.32; H, 8.35; N, 6.94. IR ν_{max}^{KBr} cm^{-1}: 3200, 3060 (NH), 2720 (CHO), 1715 (C=O), 1640 (lactam C=O). UV λ_{max}^{EtOH} nm (log ε): 251 (4.02). NMR ($CDCl_3$) τ: 0.55 (1H, s, –CHO), 1.60 (1H, broad signal, –NH–CO–, disappeared on addition of D_2O), 4.33 (1H, d, J=7 Hz, >C=CH–NH–, singlet on addition of D_2O), 7.15—7.45 (2H, m, –CH_2–CO–), 7.55—8.50 (6H, m), 8.75 (3H, s, >C–CH_3), 8.80 (3H, s, >C–CH_3). 2,4-Dinitrophenylhydrazone of XIX: mp 208—211° (EtOH–H_2O). *Anal.* Calcd. for $C_{18}H_{21}O_5N_5$: C, 55.80; H, 5.46; N, 18.08. Found: C, 55.53; H, 5.50; N, 17.87. The fraction B which showed more than 5 spots on TLC (SiO_2) was chromatographed on SiO_2 (300 g). The first fraction eluted with $CHCl_3$ afforded 0.71 g of XIX (11.5%). The second fraction eluted with $CHCl_3$ afforded 0.34 g of colorless prisms (XX) (5.5%), mp 152—155° (AcOEt). *Anal.* Calcd. for $C_{12}H_{17}O_2N$: C, 69.54; H, 8.27; N, 6.76. Found: C, 69.35; H, 8.16; N, 6.74. IR ν_{max}^{KBr} cm^{-1}: 3160, 3040 (NH), 2720 (CHO), 1720 (C=O), 1665 (lactam C=O), 1620 (C=C). UV λ_{max}^{EtOH} nm (log ε): 223 (3.96). NMR ($CDCl_3$) τ: 0.73 (1H, s, –CHO), 2.60 (1H, broad signal, –NH–CO–, disappeared on addition of D_2O), 4.35 (1H, d, J=2 Hz, –C=CH–CO–NH–, singlet on addition of D_2O), 6.40—6.90 (2H, m, –CH_2–NH–), 7.55—8.55 (6H, m), 8.70 (3H, s, >C–CH_3), 8.80 (3H, s, >C–CH_3). The third fraction eluted with $CHCl_3$ afforded 0.07 g of colorless prisms (XVI) (1.1%), mp 164—167° (AcOEt–ether). *Anal.* Calcd. for $C_{12}H_{17}O_2N$: C, 69.54; H, 8.27; N, 6.76. Found: C, 69.31; H, 8.07; N, 6.80. IR ν_{max}^{KBr} cm^{-1}: 3200, 3040 (NH), 1690 (C=O), 1655 (lactam C=O), 1610 (C=C). UV λ_{max}^{EtOH} nm (log ε): 230 (4.01). NMR ($CDCl_3$) τ: 2.70 (1H, broad signal, –NH–CO–, disappeared on addition of D_2O), 4.05 (1H, d, J=2 Hz, >C=CH–CO–, singlet on addition of D_2O), 6.70 (2H, m, –CH_2–NH–), 7.90—8.40 (7H, m), 8.85 (3H, d, J=6 Hz, >CH–CH_3), 8.90 (3H, s, >C–CH_3). The fourth fraction eluted with $CHCl_3$–MeOH (99: 1) afforded 0.47 g of colorless needles (XVII) (7.5%), mp 183—185° (acetone). *Anal.* Calcd. for $C_{12}H_{17}O_2N$: C, 69.54; H, 8.27; N, 6.76. Found: C, 69.31; H, 8.20; N, 6.80. IR ν_{max}^{KBr} cm^{-1}: 3160, 3040 (NH), 1660 (C=O). UV λ_{max}^{EtOH} nm (log ε): 248 (4.09). NMR ($CDCl_3$) τ: 3.20 (1H, broad signal, –NH–CO–, disappeared on addition of D_2O), 6.50—6.85 (4H, m, –CH_2–NH– and >C=C–CH_2–CO–), 7.30—7.85 (2H, m, –CH_2–CO–), 7.90—8.50 (4H, m), 8.20 (3H, s, >C=C–CH_3), 8.70 (3H, s, >C–CH_3). Further elution with the same solvent afforded 1.2 g of colorless prisms (XVIII) (20%), mp 171—173° (AcOEt). *Anal.* Calcd. for $C_{12}H_{17}O_2N$: C, 69.54; H, 8.27; N, 6.76. Found: C, 69.30; H, 8.30; N, 6.63. IR ν_{max}^{KBr} cm^{-1}: 3160, 3040 (NH), 1650 (C=O), 1620 (C=C). UV λ_{max}^{EtOH} nm (log ε): 242 (4.08). NMR ($CDCl_3$) τ: 2.40 (1H, broad signal, –NH–CO–, disappeared on addition of D_2O), 6.00—6.20 (2H, m, >C=C–CH_2–NH–), 7.25—7.70 (4H, m, 2×CH_2–CO–), 7.70—8.45 (4H, m), 8.20 (3H, s, >C=C–CH_3), 8.70 (3H, s, >C–CH_3).

Sodium Borohydride Reduction of XIX——To a solution of 53 mg of XIX in 10 ml of MeOH was added 50 mg of $NaBH_4$ and stirred at 18° for 1 hr. The reaction mixture was worked up as usual to give 54 mg of colorless solid (XXI) which showed only one spot on TLC (SiO_2). Recrystallization from acetone gave colorless needles, mp 180—182°. *Anal.* Calcd. for $C_{12}H_{19}O_2N$: C, 68.86; H, 9.15; N, 6.69. Found: C, 68.71; H, 9.25; N, 6.48. IR ν_{max}^{KBr} cm^{-1}: 3400, 3160 (OH, NH), 1640 (lactam C=O). NMR (C_5D_5N) τ: 3.90 (1H, d, J=5 Hz, >C=CH–NH–), 6.30, 6.38 (2H, two peaks, –CH_2–OH), 7.00—7.45 (2H, m, –CH_2–CO–), 7.75—8.55 (6H, m), 8.20 (1H, s, –OH, disappeared on addition of D_2O), 8.70 (3H, s, >C–CH_3), 8.80 (3H, s, >C–CH_3).

Reaction of 4,4a,5,6-Tetrahydro-4,4,7-trimethyl-2(3*H*)-naphthalenone (IV) with Sodium Azide in PPA——To a stirred suspension of 2.5 g of IV[9] in 50 g of PPA was added 2.5 g of NaN_3 at 12—14° during 1.5 hr. The reaction mixture was stirred at 25—30° for 6.5 hr and at 32—35° for 6 hr. The mixture was poured onto ice and extracted with ether. The extract was dried over Na_2SO_4 and concentrated to give 0.23 g of the starting material (IV) (9% recovery). The aqueous layer was neutralized with 50% KOH and extracted with $CHCl_3$. The extract was dried over Na_2SO_4 and evaporated to give 2.58 g of a brown oily residue. This residue which showed more than 6 spots on TLC (SiO_2) was chromatographed on SiO_2 (130 g). Elution with $CHCl_3$ afforded 0.07 g (2.3%) of colorless prisms (XXIII), mp 138—140° (AcOEt). *Anal.* Calcd. for $C_{13}H_{19}O_2N$: C, 70.55; H, 8.65; N, 6.33. Found: C, 70.80; H, 8.43; N, 6.43. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3440, 3240, 3120

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(NH), 1680 (C=O), 1590 (C=C). UV λ_{max}^{EtOH} nm (log ε): 283 (4.07). NMR ($CDCl_3$) τ: 1.65 (1H, broad signal, –NH–CO–, disappeared on addition of D_2O), 2.95 (1H, m, >C=C<u>H</u>–NH–, sharpened on addition of D_2O), 7.15—8.75 (6H, m), 7.62 (2H, m), 8.83 (3H, s, >C–CH_3), 8.86 (3H, d, J=6 Hz, >CH–C<u>H</u>$_3$), 9.08 (3H, broad peak, >C–CH_3). Further elution with the same solvent furnished 0.22 g of a colorless solid which was a mixture of XXII and XXIII in ratio 2: 1 according to NMR measurement. Next fraction eluted with $CHCl_3$–MeOH (99: 1) gave 0.15 g (5%) of colorless prisms (XXII), mp 155—157° (AcOEt). *Anal.* Calcd. for $C_{13}H_{19}O_2N$: C, 70.55; H, 8.65; N, 6.33. Found: C, 70.80; H, 8.43; N, 6.43. IR ν_{max}^{KBr} cm^{-1}: 3440, 3200 (NH), 1695 (C=O), 1660 (lactam C=O), 1600 (C=C). UV λ_{max}^{EtOH} nm (log ε): 239 (3.86). NMR ($CDCl_3$) τ: 2.55 (1H, broad signal, –NH–CO–, disappeared on addition of D_2O), 3.55 (1H, m, >C=CH–CO–, doublet (J=2 Hz) on addition of D_2O), 7.10 (2H, m), 7.20—8.70 (6H, m), 8.85 (3H, d, J=7 Hz, >CH–C<u>H</u>$_3$), 8.90 (3H, s, >C–CH_3), 9.20 (3H, s, >C–CH_3).

Reaction of 4,6,7,8-Tetrahydro-2(3*H*)-naphthalenone (V) with Sodium Azide in PPA——To a stirred suspension of 2 g of V[10] in 30 g of PPA was added 1 g of NaN_3 at 15—20° during 1.3 hr in N_2 stream. After stirring at 30—45° for 3 hr, additional NaN_3 (0.5 g) was added to the reaction mixture at 15—20° during 20 min. The mixture was stirred at 30—45° for 5.5 hr and then poured onto ice, neutralized with 50% KOH, and extracted with $CHCl_3$. The extract was dried over Na_2SO_4 and concentrated *in vacuo* to give a brown viscous residue (2.5 g). The benzene-soluble part (1.89 g) of this residue was chromatographed on SiO_2 (30 g). The first fraction eluted with $CHCl_3$–MeOH (99: 1) was a colorless oil (0.25 g) which showed 3 spots on TLC (Al_2O_3). The second fraction eluted with $CHCl_3$–MeOH (19: 1) was a solid mass (1.09 g) which showed 2 spots on TLC (Al_2O_3). The third fraction eluted with $CHCl_3$–MeOH (19: 1) was a colorless oil (0.26 g).

The first fraction (0.25 g) was further chromatographed on neutral Al_2O_3 (50 g). Elution with $CHCl_3$ afforded 0.2 g (9%) of colorless needles (XXIV), mp 157—158.5° (benzene–cyclohexane). *Anal.* Calcd. for $C_{10}H_{13}O_2N$: C, 67.02; H, 7.31; N, 7.82. Found: C, 67.31; H, 7.45; N, 7.74. IR ν_{max}^{KBr} cm^{-1}: 3170, 3060 (NH), 1690 (C=O), 1655 (lactam C=O), 1625 (C=C). UV λ_{max}^{EtOH} nm (log ε): 245 (4.05). NMR ($CDCl_3$) τ: 2.75 (1H, broad signal, –NH–CO–, disappeared on addition of D_2O), 6.55 (4H, m), 7.55 (6H, m), 8.20 (2H, m). Elution with the same solvent afforded 0.03 g of colorless needles (XXV), mp 147—150° (benzene–cyclohexane). *Anal.* Calcd. for $C_{10}H_{13}O_2N$: C, 67.02; H, 7.31; N, 7.82. Found: C, 66.82; H, 7.39; N, 7.60. IR ν_{max}^{KBr} cm^{-1}: 3150, 3020 (NH), 1680 (C=O), 1665 (lactam C=O), 1640 (C=C). UV λ_{max}^{EtOH} nm (log ε): 241 (4.13). NMR ($CDCl_3$) τ: 2.45 (1H, broad signal, –NH–CO–, disappeared on addition of D_2O), 6.05 (2H, d, J=5 Hz, >C=C–C<u>H</u>$_2$–NH–, singlet on addition of D_2O), 7.35 (4H, m), 7.60 (4H, m), 8.00 (2H, m).

By column chromatography (SiO_2) of the second fraction (1.09 g), a colorless crystal (0.66 g) was obtained and was a mixture of XXIV and XXV in ratio 5: 1 which was estimated by NMR measurement.

The third fraction (0.26 g) was passed through a column of SiO_2 to give 0.05 g of XXV.

3,3a,4,5-Tetrahydro-2-indenone (VI)——A solution of 5 g of 3,3a,4,5,6,7-hexahydro-2-indenone,[11] 13.5 g of chloranil, and 5.5 ml of AcOH in 300 ml of dioxane was refluxed for 4 hr with stirring. After concentration *in vacuo*, the residue was triturated with $CHCl_3$ and filtered. The filtrate was washed with 5% NaOH and dried over Na_2SO_4. After evaporation of the solvent, distillation gave 1.07 g (21%) of a colorless oil (VI), bp 110° (5 mmHg). IR ν_{max}^{film} cm^{-1}: 1700 (C=O), 1620, 1580 (C=C). UV λ_{max}^{EtOH} nm (log ε): 282 (4.23). 2,4-Dinitrophenylhydrazone of VI: mp 210—212° (AcOEt). *Anal.* Calcd. for $C_{15}H_{14}O_4N_4$: C, 57.32; H, 4.49; N, 17.83. Found: C, 57.12; H, 4.32; N, 17.96.

Reaction of 3,3a,4,5-Tetrahydro-2-indenone (VI) with Sodium Azide in PPA——To a stirred suspension of 2.0 g of VI in 30 g of PPA was added 2.4 g of NaN_3 at 15—20° during 1.5 hr. After stirring at 20—30° for 7 hr, the reaction mixture was poured onto ice, neutralized with 50% KOH, and extracted with $CHCl_3$. The extract was dried over Na_2SO_4 and evaporated to give 1.9 g of a brown solid which showed 2 spots on TLC (SiO_2). This solid was chromatographed on SiO_2 (90 g). Elution with $CHCl_3$–MeOH (98: 2) gave 0.32 g (13.1%) of pale yellow needles (XXVI), mp 243—245° (benzene). *Anal.* Calcd. for $C_9H_{11}O_2N$: C, 65.44; H, 6.71; N, 8.48. Found: C, 65.60; H, 6.72; N, 8.47. IR ν_{max}^{KBr} cm^{-1}: 3160, 3030 (NH), 1665 (C=O). UV λ_{max}^{EtOH} nm (log ε): 239 (4.00). NMR ($CDCl_3$) τ: 3.0 (1H, broad signal, –NH–CO–, disappeared on addition of D_2O), 5.8 (2H, m, –C<u>H</u>$_2$–NH–), 6.9 (2H, m, –CH_2–CO–, triplet (J=4 Hz) on addition of D_2O), 7.4—8.1 (6H, m). Next elution with $CHCl_3$–MeOH (24: 1) gave 0.40 g (16.4%) of pale yellow needles (XXVII), mp 228—232° (benzene). *Anal.* Calcd. for $C_9H_{11}O_2N$: C, 65.44; H, 6.71; N, 8.48. Found: C, 65.51; H, 6.86; N, 8.46. IR ν_{max}^{KBr} cm^{-1}: 3160, 3010 (N<u>H</u>), 1660 (C=O), 1610 (C=C). UV λ_{max}^{EtOH} nm (log ε): 241 (3.96). NMR ($CDCl_3$) τ: 2.28 (1H, broad signal, –NH–CO–, disappeared on addition of D_2O), 5.92 (2H, m, –C<u>H</u>$_2$–NH–, triplet (J=4 Hz) on addition of D_2O), 6.95 (2H, m, –CH_2–CO–), 7.4—8.1 (6H, m).

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