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Reaction of Conjugated Dienones with Hydrazoic Acid[1]

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The reaction of conjugated dienones (V, XII, XV, and XVII) with hydrazoic acid was examined. From the substrates (V and XII), the keto-lactam derivatives (VI, VII, VIII, and IX) were formed by the action of two moles of hydrazoic acid. From the other substrate (XV), a lactam derivative, a normal Schmidt reaction product, was obtained. The cross-conjugated dienone (XVII) could not react with hydrazoic acid in PPA, but gave a dienone–phenol rearrangement product. A possible pathway to the formation of keto-lactam derivatives (VI—IX) from V was presented.

In previous publications,[1,3] we reported that α,β-unsaturated ketones reacted with hydrazoic acid in the presence of polyphosphoric acid (PPA) to afford enone type lactams and/or α,β-unsaturated α-aminoketones, or β-diketones, depending on the structure of α,β-unsaturated ketones. From these results, it was proposed that the attack of hydrazoic acid on each carbonyl-carbon atom of the α,β-unsaturated ketones would produce the enone type lactams and the attack on the β-position would produce the α,β-unsaturated α-aminoketones or β-diketones. It seemed of interest to extend this reaction to conjugated dienones with respect to the position of the reaction center and the mode of reaction.

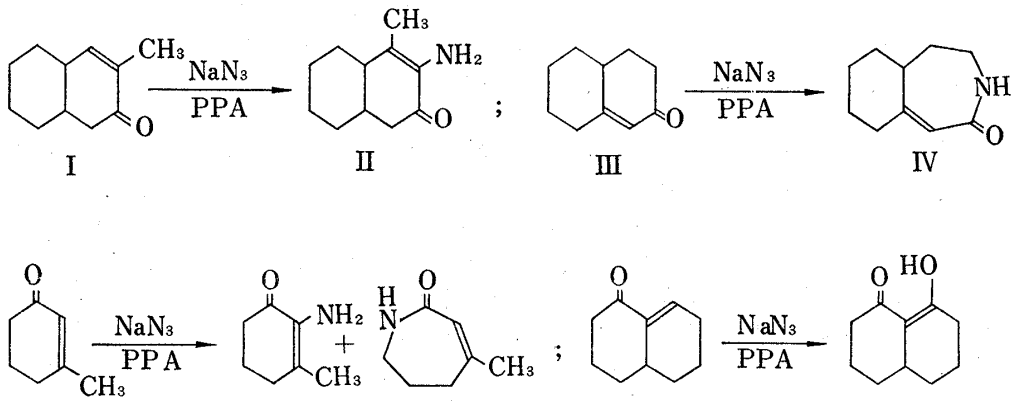


Chart 1

1) This paper constitutes part IV in a series entitled, "Reaction of Conjugated Ketones with Azides." Part III: K. Mitsuhashi, K. Nomura, N. Minami, and M. Matsuyama, *Chem. Pharm. Bull.* (Tokyo), **17**, 1578 (1969).
2) Location: *Gofuku, Toyama.*
3) *a*) K. Mitsuhashi and K. Nomura, *Chem. Pharm. Bull.* (Tokyo), **13**, 951 (1965); *b*) K. Mitsuhashi, K. Nomura, I. Watanabe, and N. Minami, *ibid.*, **17**, 1572 (1969).

In the present study, we chose 10-methyl-3,4,5,6-tetrahydro-2-naphthalenone (V), cholesta-3,5-dien-7-one (XII), cholesta-4,6-dien-3-one (XV), and 10-methyl-5,6,7,8-tetrahydro-2-naphthalenone (XVII) as the conjugated dienone substrate.

First, the dienone (V) was treated with one molar equivalent of sodium azide in PPA under the same condition as in the case of α,β-unsaturated ketones.[1,3] After working-up, a small amount (5%) of the compound (VI), a trace of the compound (IX), and 50% recovery of the unreacted dienone (V) were obtained. When this reaction was carried out with two molar equivalents of sodium azide, the compound (VI) was obtained as the major product in about 20% yield, and the compounds (VII, VIII, and IX) as minor products in small quantities (2—3.5%).

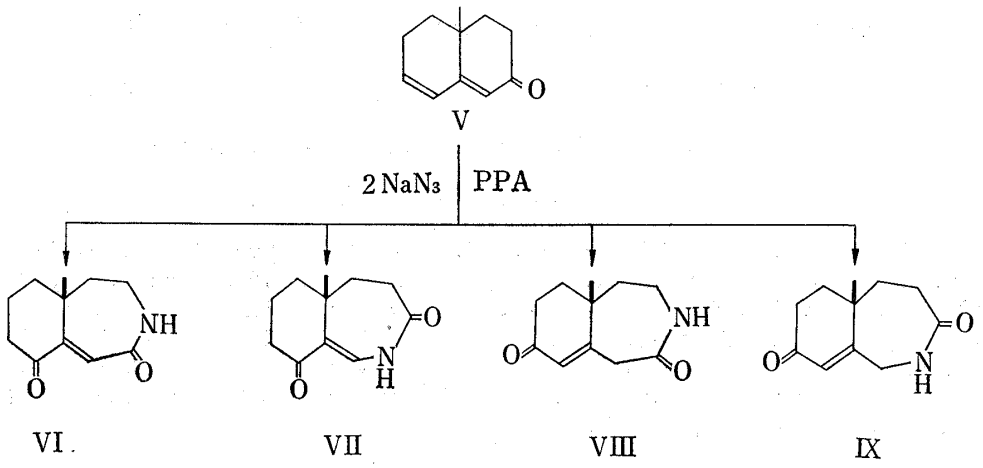


Chart 2

All these four products showed the same elemental analyses corresponding to the empirical formula of $C_{11}H_{15}O_2N$. These structures were assigned by infrared (IR), ultraviolet (UV), and nuclear magnetic resonance (NMR) spectra (Table I), taking into consideration the pathway of this reaction (see Chart 4). Their IR spectra (Table I) showed the presence of a lactam (3240—3180, 3100—3040, and 1670—1630 cm^{-1}) and another carbonyl group in all the compounds. The UV maxima at longer wavelength than 230 mμ suggested the presence of a conjugated carbonyl group. NMR spectra (Table I) before and after the addition of deuterium oxide (D_2O) provided detailed information about the structural features of the four compounds (VI,VII, VIII, and IX). The amide N-H proton appeared as a typical broad peak at 2.33 (VI), 2.17 (VII), 3.10 (VIII), and 3.10 τ (IX), which vanished on treatment with D_2O.

The NMR spectrum of VI showed an olefinic proton at 3.90 τ as a doublet (J=2 Hz) and two methylene protons in a lower field (6.50—6.95 τ) as a multiplet. After deuterium exchange, the olefinic signal was reduced to a singlet and the pattern of methylene signal changed. There were no noticeable changes in other regions of the spectrum. The small coupling constant (J=2 Hz) indicated a long-range interaction[4] between NH and CH=C protons. The signal at 6.50—6.95 τ must correspond to a methylene group adjacent to NH group. The structure of VI was consistent with these spectral features and was further supported by comparison of its IR, UV, and NMR spectra with those of 3-aza-A-homocholest-4a-ene-4,6-dione (X) reported by Singh[5] (see Table I).

The NMR spectrum of VII showed an olefinic proton at 3.22 τ as a doublet (J=7 Hz) and methylene protons at a higher field above 7.00 τ. After treatment with D_2O, the signal

4) N.S. Bhacca and D.H. Williams, "Application of NMR Spectroscopy in Organic Chemistry," Holden-Day Inc., San Francisco, 1964.
5) H. Singh and S. Padmanabhan, *Chem. Ind.* (London), **1967**, 118.

Table I. Spectral Data

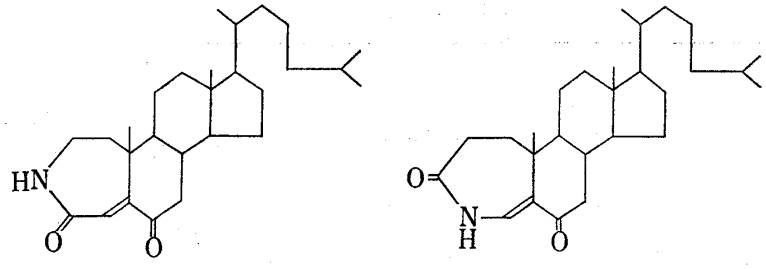
Compound No.	IR ν_{max}^{KBr} cm^{-1}		UV λ_{max}^{EtOH} mμ (log ε)	NMR τ-value	NMR Multiplicity[a]	NMR No. of protons	Remarks
VI	3240	1700	231 (3.95)	2.33[b]	br.p	1	-NH-CO-
	3040	1660		3.90[c]	d (J=2 Hz)	1	=CH-CO-N
		1605		6.50—6.95	m	2	-CH_2-N
VII	3200	1690	286 (4.17)	2.17[b]	br.p	1	-NH-CO-
	3100	1670		3.22[c]	d (J=7 Hz)	1	>C=CH-N
		1590					
VIII	3200	1665	240 (4.07)	3.10[b]	br.p	1	-NH-CO-
	3100	1630		4.06	s	1	>C=CH-CO-
		1615		6.40	d (J=14 Hz)	1	-HCH-CO-N
				6.20—7.20	m	2	-CH_2-N
				6.95[c]	br.p	1	-HCH-CO-N
IX	3180	1665	230 (4.29)	3.10[b]	br.p	1	-NH-CO-
	3080	1645		4.16	s	1	>C=CH-CO-
				5.88[c]	d-d (J=15Hz, J=4Hz)	1	=C-HCH-N
				6.50[c]	d-d (J=15Hz, J=7.5Hz)	1	=C-HCH-N
XIII	3280	1710	234 (3.93)	3.78[c]	d (J=2Hz)	1	=CH-CO-N
	3060	1670		4.05[b]	br.p	1	-NH-CO-
		1620		6.40—6.90	br.p	1	>CH-N
XIV	3260	1680	244 (3.88)	4.05	s	1	>C=CH-N
	3100	1610		6.33	d (J=14 Hz)	1	-HCH-CO-N
				6.20—7.00	br.p	1	>CH-N
				7.08[c]	br.d (J=14 Hz)	1	-HCH-CO-N
Spectral data reported by Singh[5]							
X		1695	234 (3.95)[d]	2.40[b,d]	br.p	1	-NH-CO-
		1670		4.06	d (J=1.5 Hz)	1	=CH-CO-N
				6.75	m	2	-CH_2-N
XI		1705	279 (4.19)	2.40[b]	br.p	1	-NH-CO-
		1675		3.45	d (J=7 Hz)	1	>C=CH-N

a) s: singlet, m: multiplet, d-d: doublet of doublet, br.p: broad peak, br.d: broad doublet.
b) These signals disappeared on addition of D_2O.
c) Pattern of these signals changed on addition of D_2O.
d) These value were estimated from Singh's data.[5]

of an olefinic proton changed to a singlet and the methylene proton region was not affected. The coupling constant (J=7 Hz) indicated that an olefinic proton must be vicinal to the NH group. On the basis of the spectral data of VII and those of 4-aza-A-homocholest-4a-ene-3,6-dione (XI) reported by Singh[5] (see Table I), the structure of VII was established.

The NMR spectrum of VIII showed an olefinec proton at 4.06 τ as a singlet and two methylene protons as an AB quartet centered at 6.68 τ (J=14 Hz) merged with a methylene multiplet representing two protons (6.30—7.00 τ). The contour of B side signals (6.90 τ) were changed by treatment with D_2O. This phenomenon indicated a long-range interaction[4] between a proton of methylene group adjacent to the carbonyl group of amide function and NH proton. The NMR spectum of IX showed an olefinic proton at 4.16 τ as a singlet and two methylene protons as an AB part of ABX pattern (centered at 6.19 τ, J_{AB}=15 Hz, J_{AX} =4 Hz, J_{BX}=7.5 Hz). The structures of VIII and IX were well explained by their spectral data and also by considering the reaction pathway.

A pathway to the formation of the products (VI, VII, VIII, and IX) from 10-methyl-3,4,5,6-tetrahydro-2-naphthalenone (V) is postulated as shown in Chart 4. In the same way as the reaction of α,β-unsaturated ketones with hydrazoic acid,[1,3] the dienone (V) would un-



X XI

Chart 3

dergo a nucleophilic attack by hydrazoic acid at δ-position and then form an aziridine ring at γ- and δ-positions accompanying elimination of nitrogen. For the next step, the cleavage of C-N bond of aziridine ring in two directions would occur. The resulting two intermediates would undergo a Schmidt rearrangement reaction by hydrazoic acid to yield two keto-lactam derivatives (VI, VII, VIII, and IX) from each. The formation of VI as a major product by the reaction of V with hydrazoic acid would be inferred from the fact that the reaction of α,β-unsaturated ketone (III) gave the enone-type lactam (IV) as a sole isolable product[3] and that of α,β-unsaturated ketone (I) gave the α-amino-α,β-unsaturated ketone (II) as a major product.[3]

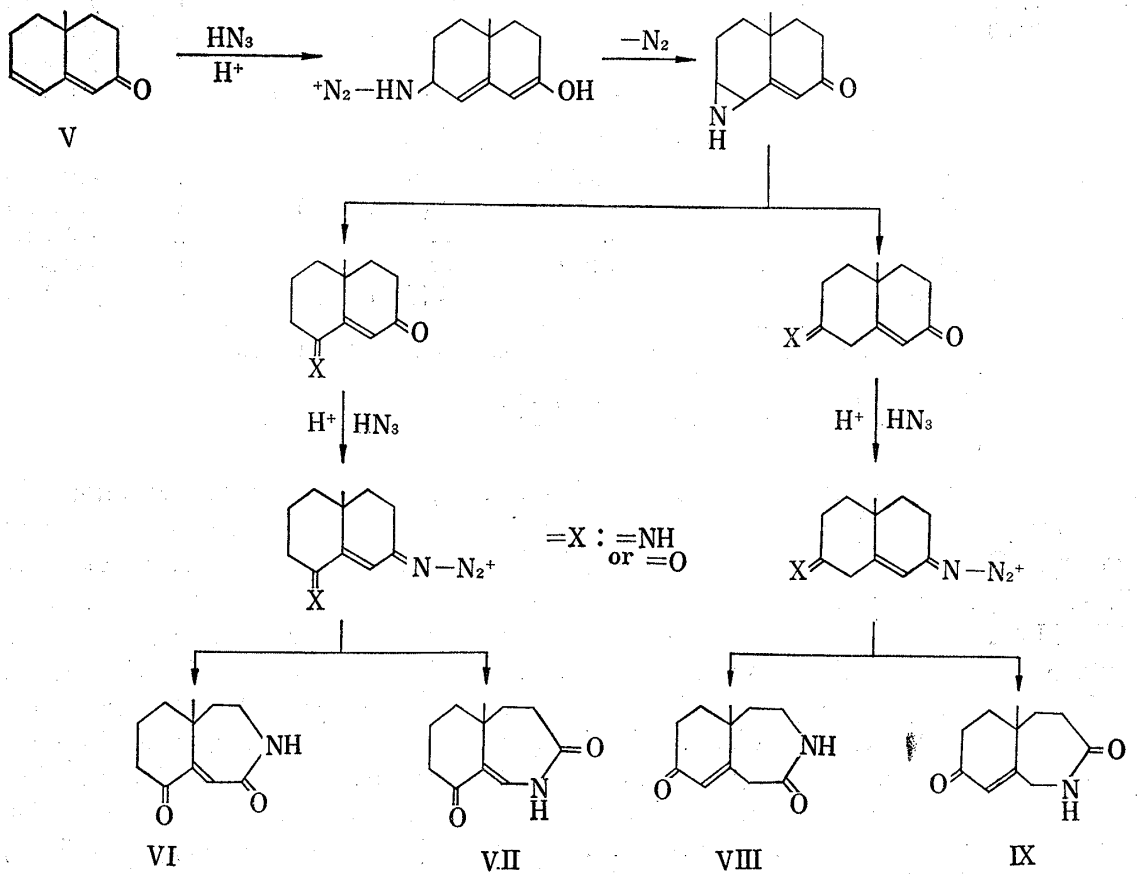


Chart 4

Next, the above reaction was examined with cholesta-3,5-dien-7-one (XII). When three molar equivalents of sodium azide was used, a reaction product (XIII) in 22% yield and the alternative product (XIV) in 12% yield were obtained. The structures of these

compounds (XIII and XIV) corresponding to the empirical formula of $C_{27}H_{43}O_2N$ were confirmed by IR, UV, and NMR spectral data referring to data of VI and VIII. Also the oxime of XIV was identified by the mixed melting point test and comparison of IR and UV spectra with a sample of 3-hydroximino-7a-aza-B-homocholest-4-en-7-one reported by Singh.[6] This result resembles the reaction of the dienone (V) with hydrazoic acid in the point of formation of keto-lactam derivatives.

Further, cholesta-4,6-dien-3-one (XV) was submitted to this reaction, using three molar equivalents of sodium azide. In this case, the dienone-type lactam (XVI) was obtained in 75% yield, in spite of the use of excess of sodium azide. This compound (XVI) showed an UV maximum at 267 mμ (log ε 4.36) and N-H band at 3220 and 3020 cm^{-1} and carbonyl band at 1665 cm^{-1} and two absorption bands at 1620 and 1585 cm^{-1} due to double bonds in its IR spectrum. The NMR spectrum of XVI indicated the presence of an amide N-H proton at 2.85 τ which disappeared on addition of D_2O, and two olefinic protons at 4.06 τ as a broad singlet and another olefinic proton at 4.36 τ as a broad singlet whose width narrowed on addition of D_2O. This phenomenon indicated that the olefinic proton (4.36 τ) was affected by a long-range coupling with an amide N-H proton through carbonyl. On the basis of these data, this compound (XVI) was presumed to be 3-aza-A-homocholesta-4a,6-dien-4-one. In contrast to the reaction of the dienones (V and XII) with hydrazoic acid, the above result indicates that a normal Schmidt reaction progressed to give the dienone-type lactam (XVI).

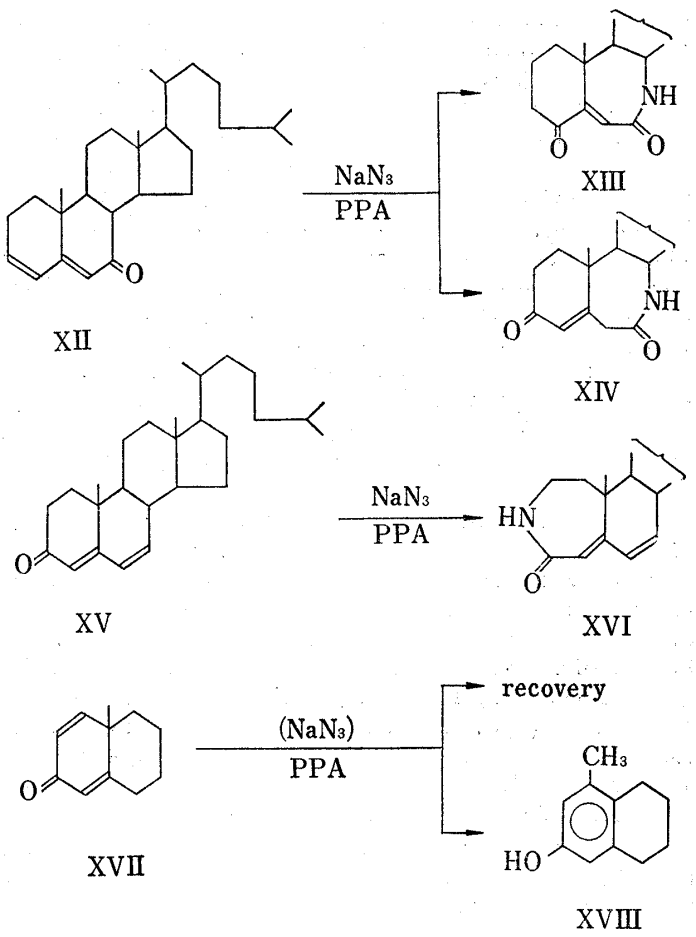


Chart 5

Differing from the extended dienones mentioned above, 10-methyl-5,6,7,8-tetrahydro-2-naphthalenone (XVII) was submitted to this reaction as a substrate of cross-conjugated dienones. This reaction was unsuccessful under our ordinary condition, and the starting material (XVII) was recovered in 22% yield and 4-methyl-5,6,7,8-tetrahydro-2-naphthol (XVIII) was isolated in 3% yield, which was probably formed by a dienone-phenol rearrangement.[7] It is found that this reaction is inapplicable to cross-conjugated dienones.

Among the reactions of extended dienones with hydrazoic acid, those of the substrates (V and XII) gave interesting abnormal products (VI—IX, XIII and XIV). On the other hand, XV gave a normal product (XVI). This different behavior would be attributable to the steric hindrance at C-7 position of cholesta-4,6-dien-3-one (XV).

6) H. Singh and S. Padamanabhan, *Tetrahedron Letters*, **1967**, 3689.
7) R.B. Woodward and T. Singh, *J. Am. Chem. Soc.*, **72**, 494 (1950).

Experimental[8]

Reaction of 10-Methyl-3,4,5,6-tetrahydro-2-naphthalenone (V) with Sodium Azide in PPA——Run-1 (Use of 1 Molar Equivalent of NaN_3): To a stirred suspension of 2.5 g of V[9] in 35 g of PPA[3] was added 1.3 g of NaN_3 at 15—20° during 3 hr in N_2 atmosphere. The reaction mixture was stirred at 20—30° for 3 hr and at 30—50° for 5 hr. When cooled, the reaction mixture was poured on ice and extracted with $CHCl_3$. The extract was dried over Na_2SO_4 and evaporated to afford a brown oily residue (1.27 g), whose distillation gave a colorless oil (V) of bp 90° (0.3 mmHg), 0.5 g (25%). 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 afford a viscous oily residue (1.27 g), which showed more than 3 spots on thin-layer chromatography (TLC) (SiO_2). This residue was chromatographed on silica gel (50 g). After development with benzene, the fraction eluted by $CHCl_3$ afforded 0.14 g of a colorless solid which was purified by recrystallization ($CHCl_3$–cyclohexane) and sublimation (100—140°/0.06 mmHg) to give colorless prisms (VI), mp 135—137°. *Anal.* Calcd. for $C_{11}H_{15}O_2N$ (VI): C, 68.37; H, 7.82; N, 7.25. Found: C, 68.29; H, 7.59; N, 7.25. NMR ($CDCl_3$) τ: 2.33 (1H, broad singal, -NH-CO-, disappeared on addition of D_2O), 3.90 (1H, d, $J=2$ Hz, =C<u>H</u>-CO-NH-, singlet on addition of D_2O), 6.50—6.95 (2H, m, -C<u>H</u>$_2$-NH-, sharpened on addition of D_2O), 7.20—7.70 (2H, m, -CH_2-CO-), 7.70—8.60 (6H, m), 8.87 (3H, s, >C-CH_3). The second fraction eluted with $CHCl_3$–MeOH (49:1) gave 25 mg of coloress needles (IX), mp 207—210° ($CHCl_3$–cyclohexane). *Anal.* Calcd. for $C_{11}H_{15}O_2N$: C, 68.37; H, 7.82; N, 7.25. Found: C, 68.43; H, 7.71; N, 7.03. NMR ($CDCl_3$) τ: 3.10 (1H, broad singal, -NH-CO-, disappeared on addition of D_2O), 4.16 (1H, s, >C=CH-), 5.88 (1H, d, of d, $J=15$ Hz, $J'=4$ Hz, -HC<u>H</u>-NH-, doublet ($J=15$ Hz) on addition of D_2O), 6.50 (1H, d, of d, $J=15$ Hz, $J'=7.5$ Hz, -HC<u>H</u>-NH-, doublet ($J=15$ Hz) on addition of D_2O), 7.00 (4H, m, 2×-CH_2-CO), 7.85—8.40 (4H, m), 8.68 (3H, s, >C-CH_3).

Run-2 (Use of 2 Molar Equivalents of NaN_3): To a stirred suspension of 5.4 g of V in 83 g of PPA was added 4.86 g of NaN_3 at 15—20° during 4 hr in N_2 atmosphere. The reaction mixture was stirred at 20—25° for 3 hr and at 25—45° for 2 hr. The mixture was poured on ice and extracted with $CHCl_3$. The extract was dried over Na_2SO_4 and evaporated to give 1.29 g of a viscous 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 4.39 g of a viscous oil (fraction B). No isolable product was obtained from fraction A in spite of various efforts. The fraction B which showed more than 3 spots on TLC (SiO_2) was chromatographed on silica gel (150 g). Elution with $CHCl_3$ afforded coloress prisms (VII), mp 163—165° (acetone). Yield, 0.13 g (2%). *Anal.* Calcd. for $C_{11}H_{15}O_2N$: C, 68.37; H, 7.82; N, 7.25. Found: C, 68.52; H, 7.58; N, 7.41. NMR ($CDCl_3$) τ: 2.17 (1H, broad signal, -NH-CO-, disappeared on addition of D_2O), 3.22 (1H, d, $J=7$ Hz, =C<u>H</u>-NH-, singlet on addition of D_2O), 7.02—7.33 (2H, m, -CH_2-CO-), 7.33—7.75 (2H, m, -CH_2-CO-), 7.75—8.67 (6H, m), 8.88 (3H, s, >C-CH_3).

Further elution with the same solvent afforded 1.32 g (20%) of colorless prisms (VI), mp 136—140° (AcOEt). Next fraction (1.32 g) eluted with $CHCl_3$ was a mixture which showed 3 spots on TLC. From the benzene-insoluble part of this mixture, IX (0.19 g, 3%) was obtained as colorless pillars (acetone–MeOH), mp 205—210°. The benzene-soluble part (0.97 g) was chromatographed on silica gel (50 g). The first fraction eluted with $CHCl_3$ gave an undefined product as colorless prisms (AcOEt–MeOH), mp 156—157.5°. The second fraction eluted with $CHCl_3$ gave 0.22 g (3.5%) of colorless plates (VIII), mp 185—195° (acetone). *Anal.* Calcd. for $C_{11}H_{15}O_2N$: C, 68.37; H, 7.82; N, 7.25. Found: C, 68.48; H, 7.77; N, 7.23. NMR ($CDCl_3$) τ: 3.10 (1H, broad signal, -NH-CO-, disappeared on addition of D_2O), 4.06 (1H, s, >C=CH-), 6.40 (1H, d, $J=14$ Hz, -HC<u>H</u>-CO-NH-), 6.20—7.20 (2H, m, -C<u>H</u>$_2$-NH-), 6.95 (1H, broad d, $J=14$ Hz, -HC<u>H</u>-CO-NH-, sharpened on addition of D_2O), 7.30—7.80 (2H, m, -CH_2-CO-), 7.80—8.40 (4H, m), 8.68 (3H, s, >C-CH_3). The third fraction eluted with $CHCl_3$ gave a trace of IX.

Reaction of Cholesta-3,5-diene-7-one (XII) with Sodium Azide in PPA——To a stirred suspension of 5 g of XII[10] in 75 g of PPA was added 1.1 g of NaN_3 at 15—20° during 2 hr in N_2 stream. This mixture was stirred at 20—27° for 2 hr. Then 2.54 g of NaN_3 was added to the mixture at 20—30° during 2.5 hr. After stirring at 20—30° for 2 hr and then at 30—40° for 2 hr, the reaction mixture was poured on ice and extracted with $CHCl_3$. The extract was dried over $NaSO_4$ and evaporated to afford a brown resinous residue (5.52 g) (fraction A). 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 a brown resin (0.11 g) (fraction B). Fraction A which showed more than 2 spots on TLC (SiO_2) was chromatographed on silica gel (60 g). After development with benzene, the fraction eluted with benzene–$CHCl_3$ (7:3) afforded 1.19 g (22%) of colorless needles (XIII), (MeOH), mp 184—186°. *Anal.* Calcd. for $C_{27}H_{43}O_2N$: C, 78.40; H, 10.48; N, 3.39. Found: C, 78.20; H, 10.58; N, 3.18. NMR ($CDCl_3$) τ: 3.78 (1H, d, $J=2$ Hz, =C<u>H</u>-CO-NH-, singlet on addition of D_2O), 4.05

8) All melting points were measured on a Yanagimoto micro-melting point apparatus and are not corrected. NMR spectra were taken on a JNM-C-60H spectrometer with Me_4Si as internal standard.
9) J.A. Marshall and H. Roebke, *J. Org. Chem.*, **31**, 3109 (1966).
10) G.J. Kent and E.S. Wallis, *J. Org. Chem.*, **24**, 1235 (1957).

(1H, broad singal, -CO-NH-, disappeared on addition of D_2O), 6.40—6.90 (1H, broad signal, >CH-NH-), 7.30—7.70 (2H, m, $-CH_2-CO-$). $[\alpha]_D^{20}$ −18.6° (c=1.02, $CHCl_3$). Oxime of XIII: Prepared as usual and recrystallized from EtOH to colorless needles, mp 213—215°. *Anal.* Calcd. for $C_{27}H_{44}O_2N_2$: C, 75.65; H, 10.35; N, 6.54. Found: C, 75.47; H, 10.43; N, 6.25. IR cm^{-1} (KBr): $\nu_{O-H,N-H}$ 3240, 3170, 3020; $\nu_{C=O}$, $_{C=C}$ 1660; $\nu_{C=N}$ 1620. The second elution with $CHCl_3$ gave 0.66 g (2%) of an amorphous solid (XIV). *Anal.* Calcd. for $C_{27}H_{43}O_2N$: C, 78.40; H, 10.48; N, 3.39. Found: C, 78.30; H, 10.28; N, 3.55. NMR ($CDCl_3$) τ: 4.05 (1H, s, >C=CH-), 6.33 (1H, d, J=14 Hz, -HCH-CO-NH-), 6.20—7.00 (1H, broad signal, >CH-NH-), 7.08 (1H, broad d, J=14 Hz, -HCH-CO-NH-, sharpened on addition of D_2O). Oxime of XIV: Prepared as usual and recrystallized from AcOEt to colorless fine prisms, mp 237—245°. *Anal.* Calcd. for $C_{27}H_{44}O_2N_2$: C, 75.65; H, 10.35; N, 6.54. Found: C, 75.43; H, 10.46; N, 6.41. IR cm^{-1} ($CHCl_3$): $\nu_{O-H,N-H}$ 3570, 3380, 3080; $\nu_{C=O,C=N}$ 1660. UV λ_{max}^{EtOH} mμ (log ε): 246 (4.22). This oxime was identified with the sample of Singh[6] by the mixed melting point measurement and the comparison of IR spectra. Fraction B did not afford any isolable product.

Reaction of Cholesta-4,6-dien-3-one (XV) with Sodium Azide in PPA——This reaction was carried out under the same condition as in the case of V and XII, using 2.96 g of XV,[11] 1.50 g of NaN_3 and 42 g of PPA. The reaction mixture was poured on ice and extracted with $CHCl_3$. The extract was dried over Na_2SO_4 and evaporated to give 2.29 g of colorless scales (XVI), mp 245—246°. *Anal.* Calcd. for $C_{27}H_{43}ON$: C, 81.55; H, 10.90; N, 3.52. Found: C, 81.39; H, 11.10; N, 3.55. IR cm^{-1} (KBr): ν_{N-H} 3220, 3020; $\nu_{C=O}$ 1665; $\nu_{C=C}$ 1620, 1585. UV λ_{max}^{EtOH} mμ (log ε): 267 (4.36). NMR ($CDCl_3$) τ: 2.85 (1H, broad signal, -NH-CO-, disappeared on addition of D_2O), 4.08 (2H, s, -CH=CH-), 6.40—6.90 (2H, m, $-CH_2-NH-$). $[\alpha]_D^{19.5}$ −14.5° (c=1.38, $CHCl_3$). The aqueous layer was neutralized with 50% KOH, extracted with $CHCl_3$, the extract was dried over Na_2SO_4, and evaporated to give 0.41 g of a brown resin from which any product was not isolated.

10-Methyl-5,6,7,8-tetrahydro-2-naphthalenone (XVII)——A solution of 5.8 g of 10-methyl-3,4,5,6,7,8-hexahydro-2-naphthalenone[12] and 11 g of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone in 100 ml of dioxane was refluxed for 1.5 hr under stirring. When cooled, the resulting precipitate (2,3-dichloro-5,6-dicyanohydroquinone) was filtered. The filtrate was evaporated to give an oily residue. The ether solution of this residue was washed with 5% NaOH and water, dried over Na_2SO_4, and evaporated to give an oily residue. Distillation of this residue gave the colorless oil (XVII) of bp 115—116° (3 mmHg), 3.13 g (55%). IR cm^{-1} (film): $\nu_{C=O}$ 1640; $\nu_{C=C}$ 1620, 1605. UV λ_{max}^{EtOH} mμ: 243, 290 (shoulder). NMR (CCl_4) τ: 3.77 (2H, AB q, J=10 Hz), 4.14 (1H, s), 7.40—9.00 (8H, m), 8.79 (3H, s). 2,4-Dinitrophenylhydrazone of XVII: Prepared as usual and recrystallized from EtOH, mp 117—120° (reported[7] mp 127—129°). *Anal.* Calcd. for $C_{17}H_{18}O_4N_4$: C, 59.70; H, 5.27; N, 16.37. Found: C, 59.83; H, 5.09; N, 16.25.

Reaction of 10-Methyl-5,6,7,8-tetrahydro-2-naphthalenone (XVII) with Sodium Azide in PPA——To a stirred suspension of 2.9 g of XVII in 42 g of PPA was added 1.52 g of NaN_3 at 15—20° during 3 hr in N_2 stream. After stirring at 20—40° for 7 hr, only the starting material was detected on TLC (Al_2O_3). Further amount of NaN_3 (1.17 g) was added to the reaction mixture at 15—20° during 2.5 hr. The mixture was stirred at 20—25° for 3 hr and 25—40° for 4 hr. As a new spot did not increase on TLC (Al_2O_3), the reaction mixture was poured on ice and extracted with $CHCl_3$. The extract was dried over Na_2SO_4 and evaporated to afford 1.93 g of an oily residue. The residue which showed 3 spots on TLC (Al_2O_3) was chromatographed on Al_2O_3. From the fraction eluted with benzene, the starting material (XVII) was obtained as a colorless oil (0.64 g) in 22% recovery rate. The second fraction eluted with benzene–$CHCl_3$ (9:1) gave 4-methyl-5,6,7,8-tetrahydro-2-naphthol (XVIII) as colorless needles (hexane) of mp 104—106° (reported[7] mp 104—105°), 0.11 g (3%). *Anal.* Calcd. for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.59; H, 8.70. NMR ($CDCl_3$) τ: 3.50—3.80 (2H, m, aromatic protons), 5.40 (1H, s, phenolic proton), 7.10—7.75 (2H, m), 7.78 (3H, s, Ar-CH_3), 8.00—8.50 (2H, m).

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11) L. Mandell, *J. Am. Chem. Soc.*, **78**, 3199 (1956).
12) E.C. duFeu, F.J. Quillin, and R. Robinson, *J. Chem. Soc.*, **1937**, 53.