

The Reaction of α,β -Unsaturated Ketones with Azides. III.¹⁾

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(Received November 14, 1968)

The reaction of seven kinds of conjugated bicycloalkenones (I, III, V, VII, IX, XV and XX) with hydrazoic acid were studied. From compounds (I, III, V and VII), enone type lactams were obtained and from compounds (IX, XV and XX), α,β -unsaturated α -aminoketones were obtained. The three types of reaction products (a) lactams, b) α,β -unsaturated α -aminoketones and c) β -diketones) were observed from present and previous results. The correlation between the structure of α,β -unsaturated ketone and the reaction product was discussed.

In preceding papers,^{1,3)} we reported that the reaction of α,β -unsaturated ketones and acylcyclohexenes with hydrazoic acid in the presence of acidic catalyst to give three types of reaction products: a) lactams, b) α,β -unsaturated α -aminoketones and c) β -diketones. In the view point of the concurrent reactivity of carbonyl group and olefinic linkage for hydrazoic acid, the complication of this reaction was supposed. We are interested in the correlation between the structure of α,β -unsaturated ketone and the type of reaction product for clarification of the pathway of this reaction and for further application to polycyclic compound. In this paper, we describe the reaction of bicycloalkenones (five octalones and two hexahydroindenones) with sodium azide in polyphosphoric acid (PPA) and discuss the correlation between the structure of the ketones and the products.

Among the bicycloalkenones, four compounds (4,4a,5,6,7,8-hexahydro-2(3*H*)-naphthalenone(I), 3,4,5,6,7,8-hexahydro-1(2*H*)-naphthalenone(III), 3,3a,4,5,6,7-hexahydroindenone-2 (V) and 4,5,6,7-tetrahydroindanone (VII)) having a common structural unit concerning with the position of double bond (β -position of α,β -unsaturated ketones are located at the juncture of bicyclic structures) were examined for the reaction with sodium azide in PPA. From these reaction, lactam derivatives (II, IV, VI and VIII) were obtained respectively as sole isolatable compound in each case. The structures of these products were confirmed by elemental analysis, ultraviolet (UV), infrared (IR) and nuclear magnetic resonance (NMR) spectra. The structure of II was also confirmed by chemical evidence obtaining oxalic acid (characterized as oxal-*p*-toluide) after ozonolysis followed by hydrolysis. From above results, it is found that these lactams obtained were exclusively enone type lactams which were distinguished from enamine type lactams by UV spectra.⁴⁾ Thus it shows that olefinic part has a lower migration aptitude than methylene part in the formation of lactam derivatives by the so-called Schmidt reaction of α,β -unsaturated cyclic ketones. This is consisted with the case⁵⁾ of benzalacetone by which the styryl group has a low migration aptitude.

Further, three α,β -unsaturated octalones (IX, XV, XX) of which double bond is located indifferently at the juncture respectively were selected as the substrate for the reaction with

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2) Location: Gofuku, Toyama.

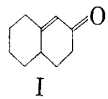
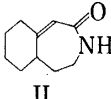
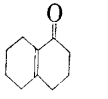
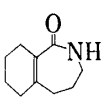
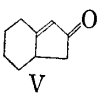
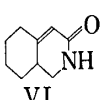
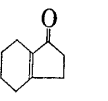
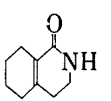
3) K. Mitsushashi and K. Nomura, *Chem. Pharm. Bull.* (Tokyo), **13**, 951 (1965).

4) R.H. Mazur, *J. Org. Chem.*, **26**, 1289 (1961); C.W. Shoppe, G. Kruger and R.N. Mirringtor, *J. Chem. Soc.*, **1962**, 1050.

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hydrazoic acid. In the case of 4a,5,6,7,8,8a-hexahydro-1(4H)-naphthalenone(IX), α -amino derivative (X) was obtained from the basic fraction of the crude reaction product in 26% yield and α -diketone derivative (XII) from the acidic fraction in 1.3% yield. Their structures were identified by following methods. On heating with phthalic anhydride, the α -amino derivative(X) gave phthalimido derivative (XI), $C_{18}H_{17}O_3N$. The IR and NMR spectra of XI suggested for the structure to be 4a,5,6,7,8,8a-hexahydro-2-phthalimido-1(4H)-naphthalenone. For another evidence, the hydrolysis of X by 10% hydrochloric acid was carried out to give α -diketone derivative (XII) which was identified with the sample obtained from the acidic fraction and that derived from 1-decalone by oxidation with selenium dioxide by mixed melting point measurement and comparison of IR spectra. From the neutral fraction, two compounds were isolated in a small amount which were proposed to be XIII and XIV by elemental analysis and spectral data.

TABLE I

Starting material	Product	UV $\lambda_{\text{max}}^{\text{EtOH}}$ $m\mu$ (ϵ)	IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1}	(τ -value)	NMR Remarks ^{a)}	No. of protons
		219 (17600)	3260 3070 1665 1615	7.5—9.0 6.8—7.3 4.58 1.55 ^{b)}	m m s br. s	11 2 1 1
		222 (13040)	3200 3020 1640 1630	7.5—8.5 6.85 ^{c)} 3.1 ^{b)}	m t-d($J=6$, 6 cps) br. s	12 2 1
		217.5 (14400)	3200 3020 1650 1610	7.3—8.8 6.3—7.15 4.35 3.2 ^{b)}	m m br. s br. s	9 2 1 1
		215.5 (12150)	3200 3020 1650 1620	7.5—8.5 6.15 ^{c)} 3.5 ^{b)}	m t-d($J=7.5$, 3 cps) br. s	10 2 1

a) m: multiplet, s: singlet, br. s: broad signal, t-d: triplet of doublet

b) These signals were disappeared by adding D_2O .

c) These signals were changed to triplet by adding D_2O .

In extension of this reaction, 4a,5,6,7,8,8a-hexahydro-2(1H)-naphthalenone (XV) was examined. 4a,5,6,7,8,8a-Hexahydro-3-amino-2(1H)-naphthalenone(XVI) was obtained from the basic fraction of the crude reaction product in 21% yield and 2,3-decalindione(XVIII) from the non basic fraction in 1.2% yield. The structure of XVI was confirmed by derivation of XVI to 4a,5,6,7,8,8a-hexahydro-3-phthalimido-2(1H)-naphthalenone(XVII) and by hydrolysis to 2,3-decalindione (XVIII). A trace of the compound proposed to be XIX was detected from the non basic fraction. This result resembles to the case of IX and also is analogous with the case of 2-cyclohexenone and 2-methyl-2-cyclohexenone in the point of producing α -amino derivative as a main product.

In connection with the reaction³⁾ of 2-methyl- and 2-phenyl-2-cyclohexenone, the migration of methyl or phenyl group from α -position to β -position was expected in the case of octalone derivatives. Thus 4a,5,6,7,8,8a-hexahydro-3-methyl-2(1H)-naphthalenone(XX) was selected for this research. As was expected, XX gave 4a,5,6,7,8,8a-hexahydro-3-amino-4-methyl-2(1H)-naphthalenone(XXI) in 55% yield from the basic fraction of this reaction product. No product was isolated from the non basic fraction. The structure of XXI was confirmed

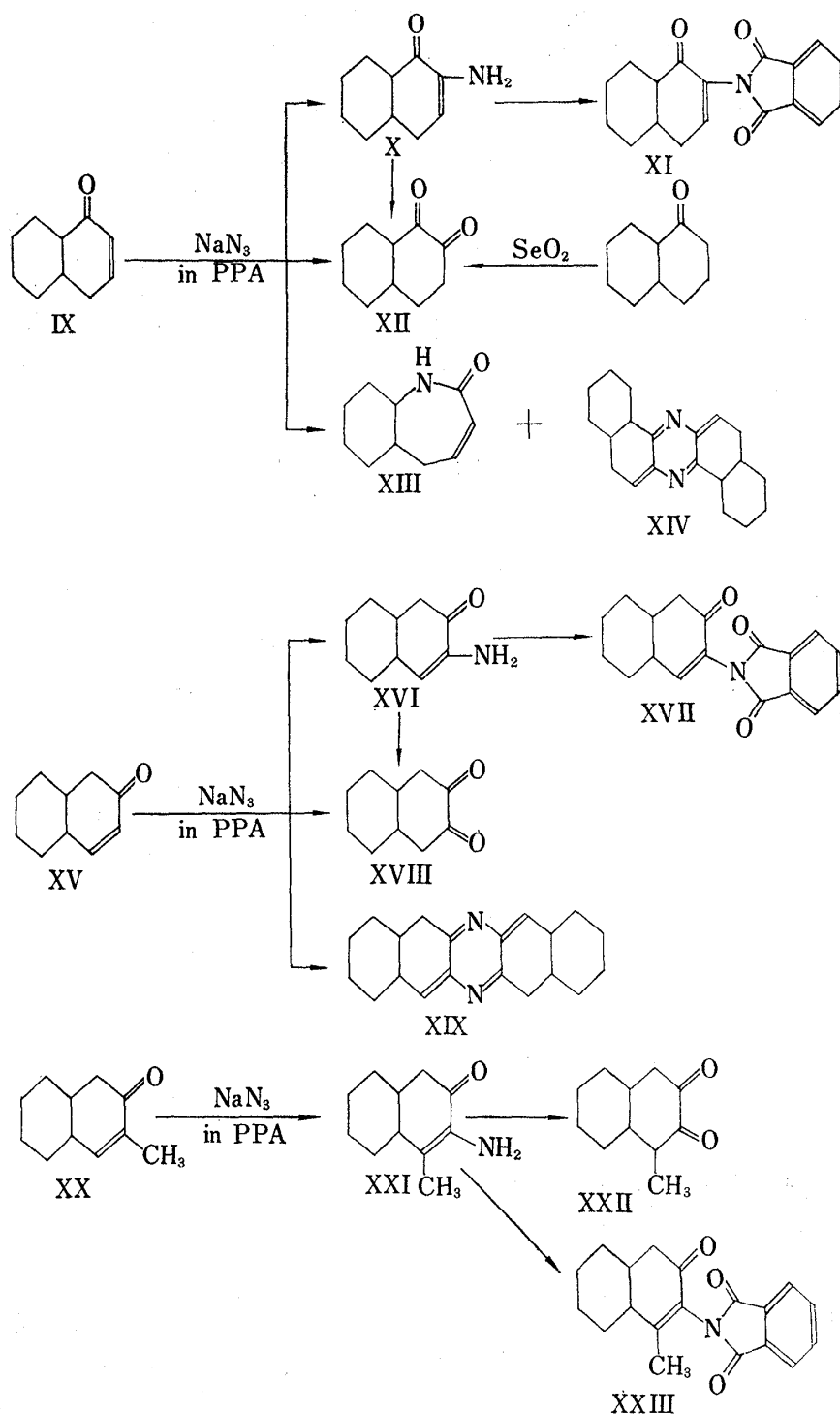


Chart 1

by conversion to phthalimido derivative (XXIII) and hydrolysis to α -diketone derivative (XXII).

The above and previous^{1,3)} results are summarized in Table III. Under consideration of correlation between the structure of α,β -unsaturated ketones and their reaction products, these reactions are classified to three types: Type A in which starting ketones afford lactam derivatives considered to be ordinary Schmidt reaction products and the characteristic feature of starting ketone is designated that β -position of α,β -unsaturated ketone is located at the juncture in octalones or substituted with alkyl group (examined only methyl group) in cyclohexenones, Type B in which α,β -unsaturated ketone give α,β -unsaturated α -aminoketones and


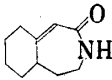



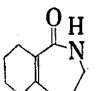

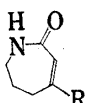

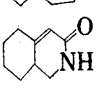



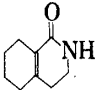





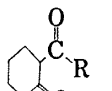

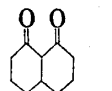
TABLE II. The Nuclear Magnetic Resonance Data (in CDCl_3 , τ -value)

Compound	Position of peaks	Remarks	Compound	Position of peaks	Remarks
XII	4.05	1H br. s	XI	2.0 — 2.4	4H m
	6.8 — 9.15	2H m ($-\text{CH}_2-\text{CO}-$)		2.9	1H m ($-\text{CH}_2-\text{CH}=$)
	7.4 — 8.8	11H m		7.3 — 8.9	14H m
XXII	4.0	1H br. s	XVII	2.15 — 2.35	4H m
	8.1	3H s ($-\text{CH}_3$)		3.2	1H br. d ($>\text{CH}-\text{CH}=$)
	7.5 — 8.9	12H m			$J=3$ cps
XIII	3.05	1H br. s ($-\text{NH}-\text{CO}-$)	XXIII	7.2 — 9.0	14H m
	3.70	1H t-d ($-\text{CH}_2-\text{CH}=\text{CH}-$) $J=12, 4.5$ cps		2.1 — 2.5	4H m ($-\text{CH}_2-\text{CO}-$)
				7.4 — 7.6	2H m ($-\text{CH}_2-\text{CO}-$)
	4.15	1H br. d ($-\text{CH}=\text{CH}-$) $J=12$ cps		8.1	3H s ($-\text{CH}_3$)
				7.6 — 8.9	10H m
	6.5 — 7.3	1H m ($>\text{CH}-\text{N}$)			
	7.3 — 9.0	11H m			

s: singlet, d: doublet, m: multiplet, t-d: triplet of doublet, br. s: broad signal, br. d: broad doublet

the double bond of the starting compound is positioned indifferently at the juncture in octalones or β -position of 2-cyclohexenones is not substituted and Type C in which β -diketones are obtained and concerning the structure of α,β -unsaturated ketones, carbonyl group and double bond are not located in the same ring.

TABLE III. Main Products of Reaction^{a)} of α,β -Unsaturated Ketones with NaN_3 in PPA

A			B		
Starting material	Product	Yield %	Starting material	Product	Yield %
		15.4			R=H 3.5 R=CH ₃ 27
		16.8			R=H 0.5 R=CH ₃ 23
		94.3			R=CH ₃ 38.6 R=C ₆ H ₅ 27.4
		49.1			26
C					R=H 20.8 R=CH ₃ 55.3
Starting material	Product	Yield %			
		R=CH ₃ 30 R=C ₆ H ₅ 69.3			
		14.9			

^{a)} including previous results^{1,2)}

It is shown that there is a correlation between the structures of α,β -unsaturated ketones and reaction products. Lactam derivatives would be formed by attack of hydrazoic acid at carbonyl carbon and proceeding as generally accepted pathway⁶⁾ for so-called Schmidt reaction (type A). For the formation of abnormal Schmidt reaction products (type B and C), following pathway would be assumed. The aziridine derivative would be suggested as an intermediate which would be formed by attack of hydrazoic acid to β -position of α,β -unsaturated ketones followed by cyclization accompanying elimination of nitrogen. Two direction for the cleavage of aziridine ring at C-N bond would derive to different types of reaction product (type B or C). As α,β -unsaturated ketone having no hydrogen at β -position to carbonyl group gave abnormal product (type B and C), we supposed that the steric factor for reaction of α,β -unsaturated ketones with hydrazoic acid controls their reactivity. Thus, in the reaction at β -position of α,β -unsaturated ketone, more hindered ketones gave lactams and less hindered ketones gave abnormal products. Further, it seems that 4,4a,5,6,7,8-hexahydro-2(3*H*)-naphthalenone (I) and 3-methyl-2-cyclohexenone resemble to each other according above consideration. But the difference was observed in reaction products (see Table III); instead that I gave lactam as a sole product, 3-methyl-2-cyclohexenone gave α,β -unsaturated α -amino-ketone and also lactam derivative. It implies that β -position of 3-methyl-2-cyclohexenone could react with hydrazoic acid. The difference of reactivity of β -position at 3-methyl-2-cyclohexenone and compound (I) would be explained in a sense of the rigidity of cyclo-alkenones.

Experimental⁷⁾

General Procedure for Reaction of α,β -Unsaturated Ketones with Hydrazoic Acid in Polyphosphoric Acid (PPA)—To PPA (about fifteen times the weight of ketones) in a three necked flask equipped with a mechanical stirrer and a thermometer was added 0.02 moles of α,β -unsaturated ketones. The viscous suspension was stirred for 30 min and then 0.024–0.030 moles of NaN_3 was added in three equal portions over 3 hr at 20–25°. The reaction mixture was stirred for 2–5 hr at 30–35° depending on how long the starting material was remained by checking on TLC. The reaction mixture was poured into ice and neutralized (pH 6.8) with 50% KOH and extracted with CHCl_3 or ether. The extract was dried over Na_2SO_4 and removed solvent. The residue was separated to dil. hydrochloric acid soluble fraction (basic fraction) and insoluble fraction (non basic fraction). For the two fractions, isolation of the reaction products was undertaken.

Reaction of 4,4a,5,6,7,8-Hexahydro-2(3*H*)-naphthalenone (I) with Sodium Azide in PPA—Using 5.05 g of I⁸⁾, 2.6 g of NaN_3 and 85 g of PPA, this reaction was carried out by the same way described in the general procedure. From the non basic fraction, 0.854 g of lactam derivative (II), mp 111–112° (ether) (bp 100–120° (0.65 mmHg)), was obtained. From the basic fraction, any product could not be isolated. *Anal.* Calcd. for $\text{C}_{10}\text{H}_{15}\text{ON}$: C, 72.69; H, 9.15; N, 8.48. Found: C, 72.72; H, 9.57; N, 8.15.

Ozonolysis of II—To a solution of 40 mg of II in 50 ml of CCl_4 , ozone was introduced at –30––25° for about 30 min, until starting material was disappeared on TLC. The reaction mixture was treated with 3% H_2O_2 (20 ml) and allowed to stand over night. The carbon tetrachloride layer was evaporated to give viscous oil (56 mg). A solution of this oil (56 mg) in 10% HCl (1.5 ml) was refluxed for 1 hr, extracted with ether, dried over Na_2SO_4 and removed solvent to give colorless crystals (28 mg), mp 140–148°, which was converted to oxal-*p*-toluide (mp 266–268°) by heating with *p*-toluidine as usual. The toluidine was identical with an authentic sample of oxal-*p*-toluide by mixed melting point measurement and IR spectral comparison.

Reaction of 3,4,5,6,7,8-Hexahydro-1(2*H*)-naphthalenone (III) with Sodium Azide in PPA—III⁹⁾ (3.3 g) was reacted with 2.15 g of NaN_3 in 46.2 g of PPA. The reaction mixture was stirred for 5 hr at 30–40° and worked up to give 3.16 g of brown oily product which was divided to two fractions by extracting with 2.5% HCl. The non basic fraction (2.3 g) showed 6 spots on TLC and was chromatographed on silica gel (100 g) with CHCl_3 as elutant to give 0.28 g of crystals (IV) of mp 159–160° (ether–hexane) as the sole isolatable product. *Anal.* Calcd. for $\text{C}_{10}\text{H}_{15}\text{ON}$: C, 72.69; H, 9.15; N, 8.48. Found: C, 72.72; H, 9.15; N, 8.62.

6) P. de Mayo, "Molecular Rearrangement," Interscience Publishers, Inc., New York, N. Y., 1963, pp.509–510.

7) All melting points are uncorrected.

8) C. Mannich, W. Koch and F. Borkowsky, *Chem. Ber.*, **70**, 355 (1937).

9) W.P. Campbell and G.C. Harris, *J. Am. Chem. Soc.*, **63**, 2721 (1941).

Reaction of 3,3a,4,5,6,7-Hexahydroindenone-2 (V) with Sodium Azide in PPA—The reaction was carried out using 3.0 g of V,¹⁰ 1.9 g of NaN₃ and 45 g of PPA. The crude reaction product (3.2 g) was chromatographed on silica gel (96 g). The fraction eluted with CHCl₃–MeOH (9:1) gave 1.64 g of VI, colorless needles (ether) of mp 134–134.5°. *Anal.* Calcd. for C₉H₁₃ON: C, 71.49; H, 8.67; N, 9.26. Found: C, 71.45; H, 8.73; N, 9.51.

Reaction of 4,5,6,7-Tetrahydroindanone-1(VII) with Sodium Azide in PPA—VII¹¹ (4 g) was reacted with 2.9 g of NaN₃ in 60 g of PPA. The reaction mixture was stirred at 30–40° for 5 hr and worked up as usual to give a brown viscous oily residue (4.3 g). The oily residue was triturated with hexane to give solid mass (1.16 g). Recrystallization from ether–hexane gave colorless needles (VIII), mp 146.5–147°. *Anal.* Calcd. for C₉H₁₃ON: C, 71.49; H, 8.67; N, 9.26. Found: C, 71.36; H, 9.02; N, 9.52.

The remaining liquid fraction was distilled to recover starting material (1.15 g), bp 127–130° (20 mmHg). The residue of the distillation was recrystallized from ether–hexane to give colorless needles, mp 146–147° (0.12 g), which was identical with VIII.

Reaction of 4a,5,6,7,8,8a-Hexahydro-1(4H)-naphthalenone (IX) with Sodium Azide in PPA—By the same way described above, 3 g of IX¹² was reacted with 1.95 g of NaN₃ in 42 g of PPA. After working up as usual, the reaction product (3.3 g) was dissolved in benzene and extracted with 5% HCl. The hydrochloric acid layer was neutralized with powdered Na₂CO₃, extracted with ether dried over Na₂SO₄ and removed ether to afford reddish viscous oil (0.86 g, 26%) (basic fraction) which showed one spot on TLC (Al₂O₃). The benzene layer was extracted with 10% NaOH. The sodium hydroxide layer was acidified with 10% HCl, extracted with ether, dried over Na₂SO₄ and removed solvent to give brown oil (0.10 g) (acidic fraction). The benzene solution (neutral fraction) was dried over Na₂SO₄ and removed solvent to give oily residue (0.94 g). The acidic fraction (0.10 g) was chromatographed on silica gel with benzene to give 0.04 g of 1,2-decalindione (XII), mp 88.7–89.7° (ether–hexane). *Anal.* Calcd. for C₁₀H₁₄O₂: C, 72.26; H, 8.49. Found: C, 72.62; H, 8.51. IR $\nu_{\text{max}}^{\text{KBr}}$ cm⁻¹: 3380, 1640, 1630, 1380, 1175. UV $\lambda_{\text{max}}^{\text{EtOH}}$ m μ (ϵ): 276.5 (12140). The neutral fraction (0.90 g) was chromatographed on silica gel (27 g). The fraction eluted with benzene gave crystals (0.052 g) of mp 87–89°, which was identical with the compound (XII). The fraction eluted with benzene–CHCl₃ (10:1) gave colorless needles (ether–hexane) of mp 169–172° (XIV), 4 mg. *Anal.* Calcd. for C₂₀H₂₈N₂: C, 81.58; H, 8.90; N, 9.52. Found: C, 81.55; H, 8.80; N, 9.57. IR $\nu_{\text{max}}^{\text{KBr}}$ cm⁻¹: 1600, 1480, 1320. UV $\lambda_{\text{max}}^{\text{EtOH}}$ m μ : 249, 252, 330, 340. The fraction (87 mg) eluted with CHCl₃ was sublimed (bp 80–90° bath (0.035 mmHg)) and recrystallized from ether–hexane to give colorless needles (XIII), mp 125–138° (10 mg). *Anal.* Calcd. for C₁₀H₁₅ON: C, 72.69; H, 9.15; N, 8.48. Found: C, 72.49; H, 8.98; N, 8.34. IR $\nu_{\text{max}}^{\text{KBr}}$ cm⁻¹: 3160, 3000, 1640, 1600, 1420, 800.

Conversion of the Basic Fraction (X) to 4a,5,6,7,8,8a-Hexahydro-2-phthalimido-1(4H)-naphthalenone (XI)—A mixture of 0.43 g of X and 0.6 g of phthalic anhydride was heated at 170–180° for 30 min. After cooling, the mixture was dissolved in CHCl₃, washed with 5% NaOH and dried over Na₂SO₄. After removal of CHCl₃, brown oily residue (0.54 g) was chromatographed on Al₂O₃. Elution with benzene gave colorless plates (XI) of mp 145–147° (ether–hexane), 90 mg. *Anal.* Calcd. for C₁₆H₁₇O₃N: C, 73.20; H, 5.80; N, 4.74. Found: C, 73.00; H, 5.95; N, 4.86. IR $\nu_{\text{max}}^{\text{KBr}}$ cm⁻¹: 1750, 1700, 1670, 1630, 1390, 1120.

Hydrolysis of the Basic Fraction (X)—A solution of 0.16 g of X in 3 ml of 10% HCl was heated on water bath for 1.5 hr. After cooling, the solution was diluted with H₂O, extracted with ether and dried over Na₂SO₄. After removal of ether, the solid residue (0.020 g) was sublimed *in vacuo* to give crystals (1,2-decalindione (XII)) of mp 87–88° (bp 60–70° (1.0 mmHg)).

Synthesis of 1,2-Decalindione (XII)—To a solution of 1.5 g of 1-decalone in 15 ml of EtOH was added 2 g of SeO₂ and refluxed for 9 hr. After removal of Se by filtration, the filtrate was evaporated to give oily residue. The residue was dissolved in ether and extracted with 5% NaOH. The sodium hydroxide layer was acidified with 10% HCl, extracted with ether, dried over Na₂SO₄ and removed the solvent to give brown oily residue (0.659 g). The benzene solution of the residue was passed through the column of silica gel to give XII, mp 89.5–90° (ether–hexane), 60 mg. *Anal.* Calcd. for C₁₀H₁₄O₂: C, 72.26; H, 8.49. Found: C, 72.69; H, 8.50.

Reaction of 4a,5,6,7,8,8a-Hexahydro-2(1H)-naphthalenone (XV) with Sodium Azide in PPA—This reaction was carried out using 1.5 g of XV,¹³ 0.975 g of NaN₃ and 21 g of PPA. The crude reaction product (1.59 g) was dissolved in benzene and extracted with 5% HCl. The acidic layer was neutralized with 10% NaOH, extracted with ether dried over Na₂SO₄ and evaporated *in vacuo* to give brown viscous oil (basic fraction (XVI)), (0.344 g), which showed one spot on TLC. The benzene solution was dried over Na₂SO₄ and removed benzene to give brown residue (non basic fraction) (0.616 g). The non basic fraction (0.615 g) was chromatographed on silica gel (40 g). The fraction eluted with benzene gave 2,3-decalindione (XVIII), mp 97–98° (ether–hexane), 36 mg. *Anal.* Calcd. for C₁₀H₁₄O₂: C, 72.26; H, 8.49. Found: C, 72.12; H, 8.53. IR $\nu_{\text{max}}^{\text{KBr}}$ cm⁻¹: 3400, 1640, 1620, 1210, 1190. The fraction eluted with benzene–CHCl₃ (2:1) gave XIX,

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15 mg, mp 225—227° (ether-acetone) as pale yellow needles. *Anal.* Calcd. for $C_{30}H_{26}N_2$: C, 81.58; H, 8.16; N, 9.52. Found: C, 81.68; H, 8.37; N, 9.35. IR ν_{\max}^{KBr} cm^{-1} : 2900, 2840, 1600, 1480, 1420, 1300. UV λ_{\max}^{EtOH} $m\mu$: 246, 249, 330, 345.

Conversion of the Basic Fraction (XVI) into 4a,5,6,7,8,8a-Hexahydro-3-phthalimido-2(1H)-naphthalenone (XVII)—A mixture of 0.100 g of the basic fraction and 0.155 g of phthalic anhydride was heated at 110—120° for 1 hr and at 170—180° for 30 min. After cooling, the mixture was dissolved in $CHCl_3$, washed with 5% NaOH, dried over Na_2SO_4 and removed $CHCl_3$ to give 112 mg of residue and passed through a column of Al_2O_3 (2 g) with benzene and again passed through a column of silica gel (1 g) with benzene to give colorless plates (XVII), mp 131.5—133° (ether-hexane), 8 mg. *Anal.* Calcd. for $C_{18}H_{17}O_3N$: C, 73.20; H, 5.80; N, 4.74. Found: C, 73.09; H, 5.53; N, 4.64. IR ν_{\max}^{KBr} cm^{-1} : 1750, 1700, 1640, 1380, 1110.

Hydrolysis of the Basic Fraction—A solution of 100 mg of XVI in 2 ml of 10% HCl was heated for 1.5 hr on water bath. The reaction mixture was extracted with ether, dried over Na_2SO_4 and removed ether to give 2,3-decalindione (XVIII), mp 98—99° (ether-hexane), (bp 70—80° (1.0 mmHg)).

Reaction of 4a,5,6,7,8,8a-Hexahydro-3-methyl-2(1H)-naphthalenone (XX) with Sodium Azide in PPA—Using 1.5 g of XX,¹³ 0.891 g of NaN_3 and 21 g of PPA, this reaction was carried out. The crude reaction product was dissolved in ether and divided to basic fraction and non basic fraction by extraction with 5% HCl. The basic fraction was reddish oil (0.905 g) and showed almost one spot on TLC. The non basic fraction was brown viscous oil (0.323 g) and showed more than 5 spots on TLC. From the non basic fraction, any product could not be isolated.

The basic fraction was mainly composed of the compound (XXII).

Conversion of the Compound (XXII) to 4a,5,6,7,8,8a-Hexahydro-4-methyl-3-phthalimido-2(1H)-naphthalenone (XXIII)—A mixture of 0.20 g of the basic fraction and 0.20 g of phthalic anhydride was heated at 130° for 1 hr and worked up as usual to afford colorless plates (XXIII) of mp 148—150° (ether-hexane), 132 mg. *Anal.* Calcd. for $C_{19}H_{19}O_3N$: C, 73.76; H, 6.19; N, 4.53. Found: C, 73.49; H, 6.03; N, 4.42. IR ν_{\max}^{KBr} cm^{-1} : 1770, 1700, 1650, 1630, 1380.

Hydrolysis of the Compound (XXII)—A solution of 0.20 g of the basic fraction in 4 ml of 10% HCl was heated on water bath for 7.5 hr. The reaction mixture was worked up as usual to give 32 mg of XXII, colorless needles, mp 97—99°. *Anal.* Calcd. for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.46; H, 8.90. IR ν_{\max}^{KBr} cm^{-1} : 3400, 1640, 1620, 1390, 1175, 1155. UV λ_{\max}^{EtOH} $m\mu$ (ϵ): 273 (9890).

Acknowledgement The authors are grateful to Mr. Masahiro Morikoshi of this Faculty for NMR spectral measurement and Mr. Haruo Takami of this Faculty for the elemental analyses.