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125. **Kemmotsu Mitsuhashi and Keiichi Nomura :** The Reaction of α,β-Unsaturated Cycloalkenones with Azides. I. The Anomalous Products in the Schmidt Reaction.[*1]

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The Schmidt reaction of α,β-unsaturated cycloalkenones, in contrast with the Beckmann rearrangement reaction of their oximes, has not so far been reported in the literatures, except the reaction of α,β-unsaturated aliphatic ketones with hydrazoic acid to give dihydro β-azido ketones.[1)] In the view point that hydrazoic acid is able to react not only with carbonyl group but also with olefinic linkage, it is interesting to investigate the behavior of 2-cyclohexenones with hydrazoic acid in the presence of the acid catalyst.

The first compound selected for the study was 2-methyl-2-cyclohexenone (Ia). When Ia was treated with sodium azide in the presence of several acid catalysts (*i.e.* 70% sulfuric, trichloroacetic, concentrated hydrochloric and polyphosphoric acids), sole isolable basic product (IIa) was, in all cases, obtained in the yields shown in Table I. From the results of the Table, polyphosphoric acid (PPA) was recognized to be a more suitable catalyst for this reaction. The identification of IIa as 2-amino-3-methyl-2-cyclohexenone was established through the following verifications.

On heating with phthalic anhydride, IIa was converted to the phthalimido derivative (IVa), $C_{15}H_{13}O_3N$. From the nuclear magnetic resonance spectrum of IIa in deuteriochloroform, no olefinic proton signal was recognized, and a broad peak at $6.34\,\tau$ (NH_2) which disappeared in deuterio oxide, and a triplet at $8.60\,\tau$ ($J=1.0$ c.p.s.,[*3] $>C-CH_3$) were observed. The infrared spectrum of IIa showed a conjugated carbonyl at 1650 and 1600 cm^{-1} and N-H absorption at 3500 and 3430 cm^{-1}. The ultraviolet sepectrum exhibited absorption maxima at 235 and 290 mμ (α,β-unsaturatd carbonyl). From these results, it is considered that this base (IIa) would be either 2-amino-3-methyl-2-cyclohexenone or 2-methyl-3-amino-2-cyclohexenone. When IIa was refluxed with 10% hydrochloric acid, a nitrogen free compound was obtained as colorless crystals which is identical with an authentic specimen of 3-methyl-1,2-cyclohexanedione (IIIa) prepared

Table I. Reaction of 2-Methyl-2-cyclohexenone (Ia) with Sodium Azide in Various Acids

Acid	Addition of NaN_3		Stirring		Yield of IIa	Recovery of Ia
	Period (hr.)	Temp. (°C)	Period (hr.)	Temp. (°C)	(%)	(%)
conc. HCl	1	5	1	20~35	19	0
70% H_2SO_4	0.5	2~3	2	0~5	trace	40
CCl_3CO_2H	at once	60	4	60~65	6	15
PPA	1	11~13	6	13~40	38.6	0
〃	1	10	6	11~14	16	4

[*1] Reported at the 84th Annual Meeting of the Pharmaceutical Society of Japan, Tokyo, April, 1964.

[*2] Gofuku, Toyama (三橋監物, 野村敬一).

[*3] This coupling would be due to a long range coupling with C_4-protons.

1) J. H. Boyer : J. Am. Chem. Soc., 73, 5248 (1951).

by the method of Wallach.[2] Thus, it was assumed that IIa was 2-amino-3-methyl-2-cyclohexenone.

As a further chemical evidence, the phthalimide (IVa) was dehydrogenated by palladium on charcoal to afford the corresponding phenolic compound (Va) and in turn, methylated with diazomethane to the methyl ether (VIa), which was identified with 2-phthalimido-*m*-cresol methyl ether prepared from 6-methyl-*o*-anisidine and phthalic anhydride.

In connection with the above result, 2-phenyl analog (Ib) was subjected to the similar reaction. As was expected, only 2-amino-3-phenyl-2-cyclohexenone (IIb) was isolated as a product. The identity of IIb, as 2-amino-3-phenyl-2-cyclohexenone, was achieved by the same procedure as that for IIa : IIb was converted into the phthalimide (IVb) followed by the dehydrogenation to yield the corresponding phenol (Vb) and finally methylated to its methyl ether (VIb). This compound (VIb) was identified with a sample synthesized by the route outlined in Chart 1 (VIII→IX→VIb).

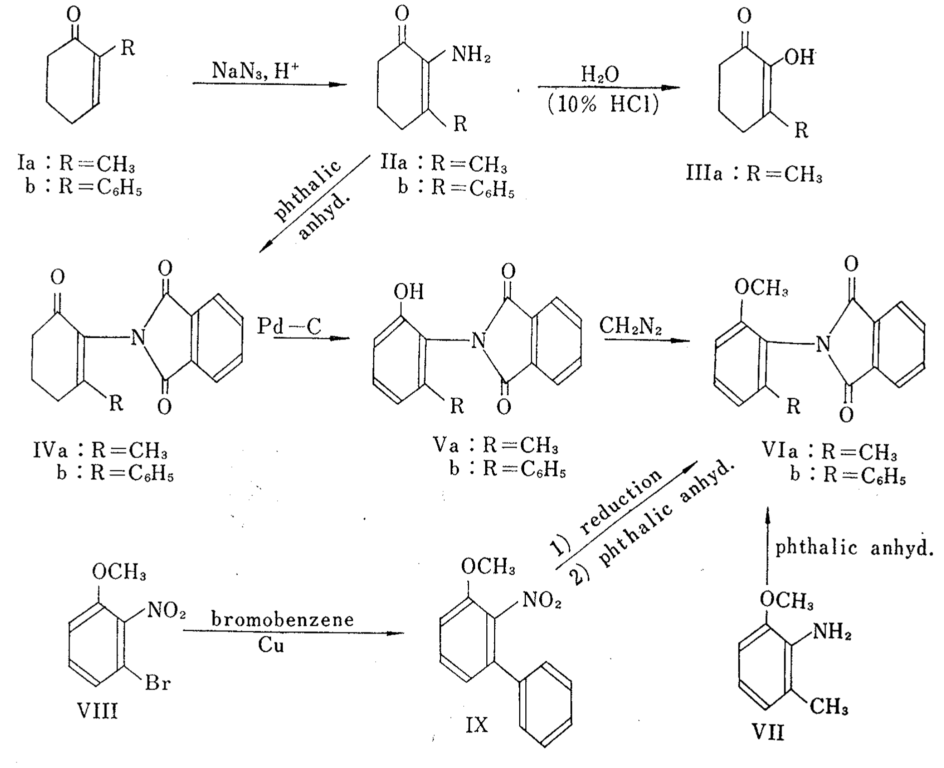

Chart 1.

It has been reported that several naphthoquinones reacted with hydrazoic acid in glacial acetic acid to afford aminonaphthoquinones,[3] but as far as 2-cycloalkenones are concerned, it is the first observation that an amino group was introduced to the α-position of carbonyl group accompanied by the simultaneous migration of the methyl or the phenyl group present at the α-position to the β-position.

On the other hand, the reaction of 3-methyl-2-cyclohexenone (Xa) with hydrazoic acid in polyphosphoric acid was examined. Two reaction products were isolated : 4-methyl-1,5,6,7-tetrahydro-2*H*-azepin-2-one (XIa, 23% yield) and 2-amino-3-methyl-2-cyclohexenone (IIa, 27% yield). These compounds were identified as following. The

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[2] O. Wallach : Ann., **414**, 314 (1916).

[3] Fieser and Hartwell : J. Am. Chem. Soc., **57**, 1482 (1935).

infrared spectrum of XIa showed the presence of lactam (3240, 3070, and 1650 cm^{-1}). The ultraviolet spectrum of XIa indicated the presence of α,β-unsaturated ε-lactam[4,5] ($\lambda_{\max}^{\text{EtOH}}$ 217.5 mμ, ε 15,500). The nuclear magnetic resonance spectrum of XIa was in agreement with the above conclusion. The hydrogenated product (XIIa) of XIa was identical with an authentic sample of 4-methylhexahydro-2*H*-azepin-2-one obtained from the Beckmann reaction of 3-methylcyclohexanone oxime by the method of Wallach.[6] Concerning of the basic product (IIa), its phthalimido derivative was identical with 2-phthalimido-3-methyl-2-cyclohexenone obtained by the conversion of the reaction product of Ia to the phthalimido derivative.

Table II. Nuclear Magnetic Resonance of the Products*4

No.	Position of peaks (τ-value)	Number of protons	Remarks
Ib	2.84	1	triplet (J=4.5 c.p.s.)
	7.26	4	multiplet
	7.65～8.20	2	〃
IVa	6.37	2	broad one peak
	7.44～7.85	4	multiplet
	7.88～8.13	2	〃
	8.20	3	triplet (J=1.0 c.p.s.)
VIIa	1.60～2.10	4	multiplet
	7.25～7.65	4	〃
	8.06	3	singlet
VIIIb	2.18～2.50	4	broad one peak
	2.78	5	one peak
	6.90～7.94	6	multiplet
XIIIa	1.47	1	one peak
	4.47	1	singlet
	6.85	2	multiplet
	7.50～7.90	2	〃
	7.90～8.50	2	〃
	8.14	3	singlet

In this case, a normal Schmidt reaction product (XIa) and an abnormal compound (IIa) resulting from the introduction of an amino group on position 2 of Xa were obtained.

When above reaction was carried out in concentrated hydrochloric acid, instead of polyphosphoric acid, a normal Schmidt reaction product (XIa) was obtained in the quantitative yield.

Furthermore, 2-cyclohexenone (Xc) was submitted to the Schmidt reaction in polyphosphoric acid; 1,5,6,7-tetrahydro-2*H*-azepin-2-one (XIc) in about 0.5% yield and 2-amino-2-cyclohexenone (IIc) in about 3.5% yield were detected. The reaction products were separated to the basic and the neutral fractions. An attempt to isolate pure compounds was unsuccessful owing to the tendency of them to polymerize. After hydrolysis of the crude basic fraction, 1,2-cyclohexanedione (IIIc) was yielded. This compound was identified with an authentic sample[7] and by the comparison of both oximes. Also, after catalytic reduction of the crude neutral fraction, caprolactam was

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*4 Measured at 60 Mc. by Varian A-60 and by J.M.N.-3H-60.

4) R.H. Mazur: J. Org. Chem., **26**, 1289 (1961).

5) C.W. Shoppee, G. Kauger, R.W. Minnington: J. Chem. Soc., **1962**, 1050.

6) O. Wallach: Ann., **309**, 1 (1899).

7) C.C. Hach, C.V. Banks, H.D. Diehl: Org. Syntheses, **32**, 35 (1952).

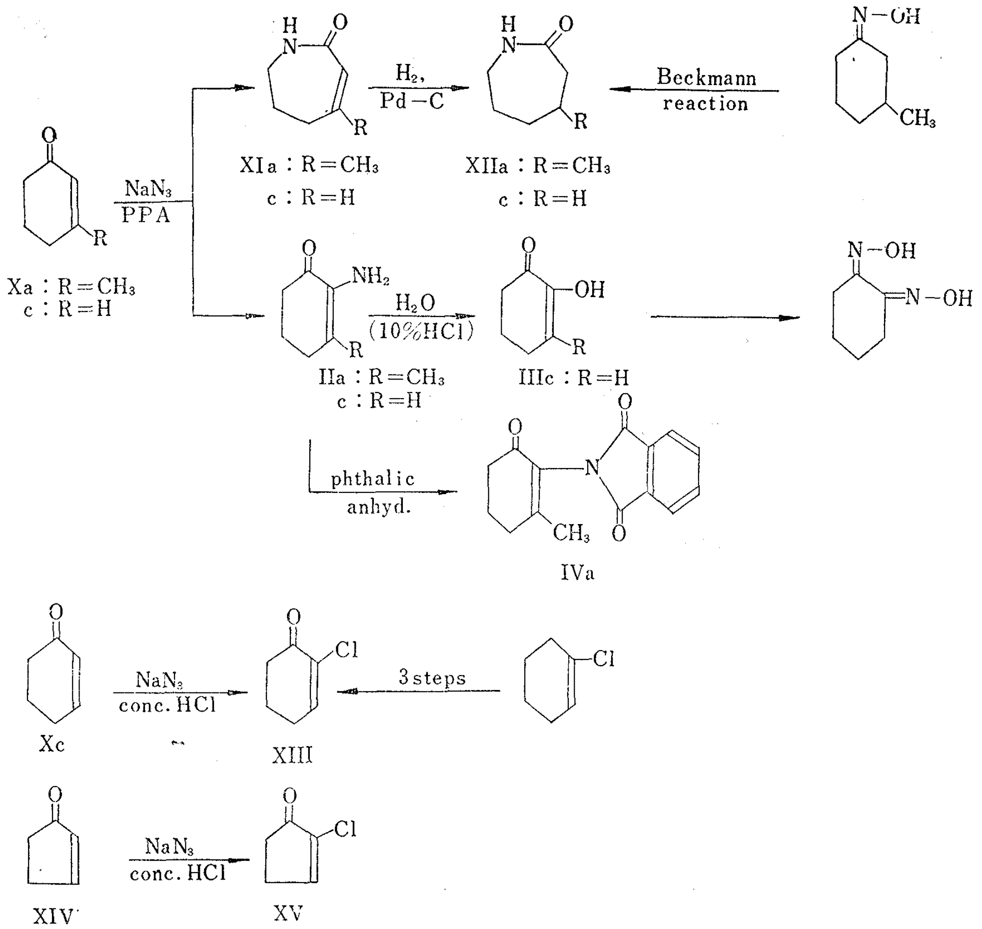

Chart2.

obtained which was identical with an authentic sample. Thus, as inferred from the results that the compound (IIa) was obtained from 2-methyl-2-cyclohexenone and also XIa and IIa were obtained from 3-methyl-2-cyclohexenone on the reactions with hydrazoic acid, it would be concluded that the compounds (XIc) and (IIc) were achieved on this Schmidt reaction in low yields.

However, when 2-cyclohexenone was reacted with hydrazoic acid in concentrated hydrochloric acid, a nitrogen free colorless product, C_6H_7OCl, was obtained in 13% yield and none of the other products could be isolated. The structure of this compound was assigned to 2-chloro-2-cyclohexenone (XIII) by elemental analysis, infrared, ultraviolet and nuclear magnetic resonance spectra and confirmed by the mixed melting point measurement and the comparison of infrared spectrum with an authentic sample prepared by the method of Braude.[8] Similarly, when 2-cyclopentenone (XIV) was treated with hydrazoic acid in hydrochloric acid, 2-chloro-2-cyclopentenone (XV) was obtained. Since the evolution of chlorine from the mixture of hydrazoic acid and concentrated hydrochloric acid at 0~10° was noticed, it is considered that these compounds (XIII and XV) would be yielded by the elimination of hydrogen chloride from the dichloro intermediate which would be formed by the addition of chlorine to Xc and XIV.

In the view of the results of our experiments, it is considered that either carbonyl group or olefinic linkage would be reacted with hydrazoic acid in acid catalyst. The formation of 2-amino-2-cyclohexenones could be understood in a sense of aziridine

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[8] E. A. Braude, J. A. Coles: J. Chem. Soc., **1950**, 2017.

intermediate which could be formed by attacking of hydrazoic acid on the double bond. The production of dihydro-2-azepinones can explain according to the normal Schmidt reaction which is the attack on the carbonyl group.

Experiments concerning of the mechanism of this rearrangement and the reaction with 2-octalones are in progress.

Experimental*5

Polyphosphoric acid (PPA) used in these reactions was prepared by dissolving 92 g. of P_2O_5 in 88 ml. of 85% H_3PO_4 ($d=1.7$) under warming on water bath in a vessel equipped with $CaCl_2$-drying tube.

Reaction of 2-Methyl-2-cyclohexenone (Ia) with Sodium Azide in Polyphosphoric Acid——To a stirred suspension of 5 g. of Ia in PPA (75 g.), NaN_3 (3.2 g.) was added at 11~13° for 1 hr. After stirring at 13~40° for 6 hr., the reaction mixture was poured onto ice and made alkaline with 50% NaOH and extracted with $CHCl_3$, and then the $CHCl_3$ solution was extracted with 10% HCl (basic fraction). The HCl layer was neutralized with powdered Na_2CO_3 and extracted with $CHCl_3$, dried over anhydrous Na_2SO_4, removed $CHCl_3$ to afford brown oily residue (2.8 g.). The $CHCl_3$ solution which could not be extracted with 10% HCl was dried over anhydrous Na_2SO_4, and removed the solvent to give dark brown tar which could not further investigate owing to polymerization. The distillation of the basic fraction gave colorless oil (IIa), b.p$_{0.4}$ 83~100°, 2.2 g., 38.6% yield. UV λ_{max}^{EtOH} mμ (ε): 235 (2250), 290 (4250). IR $\nu_{max}^{liq.}$ cm^{-1}: 3500, 3430 (NH_2), 1650 (conjugated C=O), 1585 (C=C). This ppoduct (IIa) was unstable on long standing to be converted partially into 3-methyl-1,2-cyclohexanedione (IIIa).

The same reaction of Ia using other acid catalysts was performed in similar procedure as that of the case with PPA (see Table I).

Conversion of IIa into Phthalimido Derivative (IVa)——A mixture of 1.0 g. of IIa and 1.0 g. of phthalic anhydride was heated at 180±5° for 16 hr. After cooling, the solid obtained was extracted with hot acetone, treated with active charcoal and removed acetone to give colorless prisms, m.p. 148~150° (IVa) (from benzene-hexane), yield 0.5 g. IR ν_{max}^{KBr} cm^{-1}: 1692, 1657 (-CONCO-), 1625 (C=C). *Anal.* Calcd. for $C_{15}H_{13}O_3N$: C, 70.58; H, 5.13; N, 5.49. Found: C, 70.42; H, 5.17; N, 5.46.

Dehydrogenation of IVa——A solution of 0.13 g. of IVa and 5%-Pd/C (0.135 g.) in *p*-cymene (4 ml.) was heated at 180±10° for 4.5 hr. under stirring. After extracting the reaction mixture with hot benzene, the catalyst was filtered off. The filtrate was extracted with 5% NaOH and the extract was acidified with 10% HCl, salting out with NaCl, extracted with ether, dried over anhydrous Na_2SO_4 and removed ether to give light brown residue (Va) (40 mg.) which was methylated without further purification.

Methylation of Va——To a solution of crude Va (40 mg.) in MeOH (1 ml.). the ether solution of CH_2N_2 prepared from nitrosomethylurea (7 g.) was added and kept to stand for 3 days. After standing, CH_2N_2 and the solvent were distilled off and the residue obtained was purified by column chromatography on basic Al_2O_3. Elution of the column with benzene gave colorless crystals (m.p. 125~138°) which was recrystallized from ether-hexane to afford colorless rhombic plates, m.p. 137~141°. *Anal.* Calcd. for $C_{16}H_{13}O_3N$: C, 71.90; H, 4.90. Found: C, 72.68; H, 5.37.

Synthesis of VIa——To a well mixed mixture of phthalic anhydride (1.0 g.) and 2-amino-*m*-cresol methyl ether (VII) (1.0 g.) synthesized by the Haworth's method,9) was heated at 175~185° for 25 min. After extracting with hot benzene, the solvent was distilled off to give light red solid mass. This was passed through basic Al_2O_3 with benzene as the elutant to give colorless crystals (1.7 g.). The recrystallization gave colorless prisms (from MeOH), m.p. 145~145.5°. *Anal.* Calcd. for $C_{16}H_{13}O_3N$: C, 71.90; H, 4.90. Found: C, 72.11; H, 5.44. This compound, 2-phthalimido-*m*-cresol methyl ether, showed no depression of the melting point on admixture with the product of m.p. 137~141° (VIa), derived from the reaction product of Ia and their IR spectra were completely identical.

Hydrolysis of IIa——A solution of 1 g. of IIa in 10 ml. of 10% HCl was heated on water bath for 1 hr. After cooling, colorless crystals were precipitated and the crystals filtered were recrystallized from hexane to give easily volatile colorless needles, m.p. 59~60° (IIIa), yield 0.2 g. From the filtrate, this compound was also obtained by extracting with ether. UV λ_{max}^{EtOH} mμ (ε): 272 (1240). IR ν_{max}^{KBr} cm^{-1}: 3355 (OH), 1653, 1633 (C=O).

This compound is identical with an authentic sample prepared by the method of Wallach2) by mixed melting point measurement and IR spectral comparison.

Reaction of 2-Phenyl-2-cyclohexenone (Ib) with Sodium Azide in Polyphosphoric Acid——2-Phenyl-

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*5 All melting points are uncorrected.

9) *a*) R. D. Haworth, A. Lapworth: J. Chem. Soc., **123**, 2982 (1923). *b*) G. P. Gibson: *Ibid.*, **123**, 1269 (1923).

2-cyclohexenone (Ib), m.p. 90~93° (lit.[10] m.p. 94~96°) was synthesized from 1-phenylcyclohexene *via* its nitrosochloride, over-all yield about 30%. The reaction of 2-phenyl-2-cyclohexenone (Ib) with HN_3 was carried out as the procedure described for 2-methyl analog (Ia) using 5 g. of Ib, 2.3 g. of NaN_3 and 75 g. of PPA. The basic fraction obtained was a dark brown crystalline mass (1.5 g.), 27.4% yield, and recrystallized from petr. ether, to give colorless plates, m.p. 71~73.5° (IIb). IR ν_{max}^{KBr} cm^{-1}: 3510, 3440 (NH_2), 1650 (conjugated C=O), 1615 (C=C). *Anal.* Calcd. for $C_{12}H_{13}ON$: C, 76.97; H, 7.00; N, 7.48. Found: C, 77.06; H, 7.17; N, 7.53.

Conversion of IIb into Phthalimido Derivative——A mixture of IIb (0.5 g.) and phthalic anhydride (0.5 g.) was heated at 170~180° for 10 min. After working up in a similar way as for IVa, the reaction product obtained was recrystallized from hexane-acetone; colorless plates, m.p. 183~185° (IVb), yield 0.62 g. (67.5%). IR ν_{max}^{KBr} cm^{-1}: 1700, 1665 (-CO-N-CO-), 1620 (C=C). *Anal.* Calcd. for $C_{20}H_{15}O_3N$: C, 75.69; H, 4.76; N, 4.41. Found: C, 75.86; H, 4.62; N, 4.75.

Dehydrogenation of Phthalimido Derivative (IVb)——A solution of 0.9 g. of IVb in *p*-cymene (25 ml.) was heated with 0.9 g. of 5%-Pd/C at 175~183° for 3.5 hr. under stirring. After working up in a similar procedure as for Va, the crude aromatized phenolic compound was obtained as brown solid (0.040 g.) and recrystallized from MeOH-benzene to give colorless needles, m.p. 158~161°, yield 25 mg. (VIIIb). IR ν_{max}^{KBr} cm^{-1}: 3350, 3200 (OH), 1685, 1640 (CO-N-CO). *Anal.* Calcd. for $C_{20}H_{13}O_3N \cdot 1\frac{1}{4}H_2O$: C, 71.11; H, 4.62. Found: C, 71.27; H, 4.64.

Methylation of Vb——To a solution of 35 mg. of Vb in MeOH (1 ml.) was added the ethereal solution of CH_2N_2 prepaped from 7 g. of nitrosomethylurea. After standing for a week, CH_2N_2 and ether were distilled off and the residue was dissolved in benzene and washed with 15% NaOH and then with H_2O, dried (Na_2SO_4) and removed the solvent to give light yellow solid residue (35 mg.) which was recrystallized twice from MeOH, m.p. 146~150° (VIb). *Anal.* Calcd. for $C_{21}H_{15}O_3N$: C, 76.58; H, 4.59. Found: C, 76.66; H, 4.32. No depression of melting point was observed when mixed with 2-phthalimido-3-methoxybiphenyl synthesized by the following route, and the IR spectra of both compounds were completely identical.

Synthesis of 2-Phthalimido-3-methoxybiphenyl (VIb)——A solution of 2-nitro-3-bromoanisol (3 g.) and bromobenzene (6 g.) in dimethylformamide (6 ml.) was refluxed with copper powder (6 g.) at 160~170° for 11 hr. under stirring. The reaction mixture was extracted with hot benzene exhaustively. On concentrating the benzene solution, colorless granular crystals were precipitated, m.p. >300° (from MeOH). It seems to be 2,2′-dinitro-3,3′-dimethoxybiphenyl according to the result of elemental analysis. *Anal.* Calcd. for $C_{14}H_{12}O_6N_2$: C, 55.26; H, 3.98. Found: C, 55.01; H, 3.86.

After separation of the precipitate, the solvent was removed under reduced pressure from the mother liquid and then the viscous residue obtained was distilled into two fractions: small amount of $b.p_{0.3}$ 120~135° (bath temperature) and $b.p_{0.35}$ 135~150° (bath temperature) (1 g.) as the main fraction which showed 2 spots at thin-layer chromatography (TLC) (silica gel, $CHCl_3$). In spite of several efforts for isolation by fractional distillation or column chromatography, separation did not succeed. By the reason mentioned above, further procedure was undertaken with the mixture of the nitro-compounds. A solution of this mixture (0.7 g.) in 15 ml. of AcOEt was catalytically hydrogenated with Raney Ni under shaking. After absorption of H_2 (165 ml.) for 2 hr., the crude amino compounds were obtained by usual treatment, of which TLC (silica gel, $CHCl_3$ (50 ml.): MeOH (4 drops)) showed two spots. The mixture of amino compounds (3 g.) was heated with 0.3 g. of phthalic anhydride at 170~185° for 20 min. The reaction mixture was extracted with hot benzene, washed with 2% HCl, 3% NaOH and H_2O, dried (Na_2SO_4) and removed the solvent to give dark brown viscous oil (0.20 g.). The mixture of phthalimide derivatives was separated by passing through basic Al_2O_3 using benzene to yield 43 mg. of a compound, m.p. 150.5~152° (from MeOH), as the first fraction and a trace of a compound, m.p. 158~160° (from MeOH), as the second fraction. The former compound was confirmed to be 2-phthalimido-3-methoxybiphenyl by IR and elemental analysis. *Anal.* Calcd. for $C_{21}H_{15}O_3N$: C, 76.58; H, 4.59; N, 4.25. Found: C, 76.79; H, 4.47; N, 4.34.

Reaction of 3-Methyl-2-cyclohexenone (Xa) with Sodium Azide in Polyphosphoric Acid——In a similar procedure as that for Ia, Xa (5 g.) was reacted with NaN_3 (3.5 g.) in PPA (77 g.). The reaction mixture was poured onto ice and adjusted to pH 7.5 with 50% NaOH, extracted with $CHCl_3$, dried (Na_2SO_4), removed the solvent to give oily residue containing fine granular crystals. The crystalline material has the melting point of 77~81.5°, and the recrystallization from hexane gave colorless rhombic plates, m.p. 81~82°, which is hygroscopic and easily soluble in H_2O, MeOH, EtOH, $CHCl_3$, hot hexane and soluble in benzene and sparingly soluble in cold hexane. UV λ_{max}^{EtOH} mμ (ε): 217.5 (15,500); IR ν_{max}^{KBr} cm^{-1}: 3240, 3070, 1650 (NH-CO-) and showed no amide band II at 1550~1530. *Anal.* Calcd. for $C_7H_{11}ON$: C, 67.17; H, 8.86; N, 11.19. Found: C, 67.33; H, 8.97; N, 11.41, This compound was characterized as a lactam (XIa).

To the mother liquid was added 10 ml. of 5% HCl, saturated with NaCl and extracted with ether (non-basic fraction) and the HCl layer was made alkaline to pH 9~10 with 10% NaOH, after salting out

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10) W. E. Bachmann, L. B. Wick: J. Am. Chem. Soc., 72, 3382 (1950).

with NaCl, extracted with ether (basic fraction) and then extracted with $CHCl_3$. These three fractions were dried (Na_2SO_4) and removed the solvent respectively. The fraction extracted with $CHCl_3$ was brown solid (0.95 g.) which was identical with XIa by IR comparison and mixed melting point measurement and TLC. The basic fraction was dark brown oil (1.56 g.), and 104 mg. of this product was heated with 230 mg. of phthalic anhydride at 180° for 35 min. and the reaction mixture was worked up in a similar way as for IIa to give small amount of fine plates, m.p. 153~154° (from MeOH). This phthalimido derivative was identical with 2-phthalimido-3-methyl-2-cyclohexenone (IVa) obtained in the reaction of Ia with NaN_3 by IR spectral comparison and mixed melting point measurement.

The non-basic fraction was shown to be a mixture of five species of components by thin-layer chromatography containing small amount of XIa, so no further research was made.

Hydrogenation of 4-Methyl-1,5,6,7-tetrahydro-2*H*-azepin-2-one(XIa)——A solution of 500 mg. of XIa in 30 ml. of EtOH was shaken with Raney Ni. After 82.55 ml. of H_2 was absorbed during 8 hr., the reaction mixture was filtered and washed the catalyst with EtOH. The filtrate was concentrated under reduced pressure to give colorless solid (386 mg.) which was purified by Al_2O_3-column chromatography, sublimation and recrystallization from hexane to give colorless rhombic plates, m.p. 99.5~100.7° (XIIa). *Anal.* Calcd. for $C_7H_{13}ON$: C, 66.10; H, 10.30; N, 11.01. Found: C, 66.15; H, 10.38; N, 10.94.

On admixing with the authentic 4-methylhexahydro-2*H*-azepin-2-one, m.p. 98~98.5°, prepared by the method of Wallach,[*6] showed no depression in melting point and IR spectra of both compounds were identical.

Reaction of 3-Methyl-2-cyclohexenone (Xa) in Conc. Hydrochloric Acid——To a suspension of 5.0 g. of Xb in conc. HCl (18 ml.), NaN_3 (3.5 g.) was added during 1.5 hr. under stirring. After stirring for 30 min., 18 ml. of conc. HCl was added to the reaction mixture and again stirred at room temperature (13°) for 2 hr. This mixture was poured onto ice (90 g.) and neutralized with powdered $NaHCO_3$ and extracted with $CHCl_3$, dried (Na_2SO_4) and distilled off the solvent to give pale yellow solid (5.5 g.) and recrystallized from hexane to afford colorless rhombic plates which is identical with XIIa obtained from the reaction of XIa with NaN_3 in PPA.

Reaction of 2-Cyclohexenone (Xc) with Sodium Azide in Polyphosphoric Acid——To a well stirred suspension of 14 g. of Xc in PPA (22.4 g.), NaN_3 (13.4 g.) was added at 17~18° during 1.5 hr. After stirring at 40~45° for 6 hr., the reaction mixture was poured into ice water and extracted with $CHCl_3$ (non-basic fraction). The diluted acidic layer was made alkaline to pH 7.5 with 50% NaOH and then extracted exhaustively with $CHCl_3$ (basic fraction). Both extracts were dried (Na_2SO_4) and removed $CHCl_3$ to obtain brown oily product (0.74 g.) from the non-basic fraction and dark brown oily product (12.2 g.) from the basic fraction.

Hydrolysis of the Basic Fraction——The basic fraction (12.2 g.) was hydrolyzed with 10% HCl (60 ml.) by heating on water bath for 1 hr., after cooling the hydrolyzed product was extracted with ether, washed with saturated aqueous NaCl, dried (Na_2SO_4) and removed ether to give red viscous oily residue (1.63 g.). The distillation of this residue under reduced pressure gave a colorless oil (0.576 g.), b.p_{15} 74~77° which was identical with an authentic sample of 1,2-cyclohexanedione (IIIc) prepared by the method of Hach, *et al.*7) by IR spectrum.

The hydrolyzed product was converted into its dioxime which had m.p. 178~181.5° and identified with an authentic specimen.7)

The non-basic fraction (0.74 g.) was distilled *in vacuo* to give light yellow oil (0.143 g.), b.p_8 90~130°. This product showed three spots at thin-layer chromatography on silica gel ($CHCl_3$-MeOH (3:1)) but was used in the subsequent experiment without further purification.

Hydrogenation of the Non-basic Fraction——A solution of the distillate (0.143 g.) in EtOH (15 ml.) was catalytically hydrogenated with PtO_2 (60 mg.) under shaking. After 10 hr's shaking, when 20 ml. of H_2 was absorbed, the catalyst was filtered off and the solvent was evaporated under reduced pressure. The residue obtained was purified by column chromatography on silica gel eluting at first with benzene and then the mixed solvent of benzene and $CHCl_3$, whereby the ratio of the mixture was gradually changed to increase $CHCl_3$-portion. The material eluted by benzene-$CHCl_3$ (3:1) was recrystallized from pet. ether to afford colorless prisms, m.p. 69~70°, yield 55 mg.

The reduced product was identified with hexahydro-2*H*-azepin-2-one (caprolactam) by IR and mixture melting point.

Reaction of 2-Cyclohexenone (Xc) with Sodium Azide in Conc. Hydrochloric Acid——To a stirred suspension of Xc (5.7 g.) in conc. HCl (50 ml.) was added NaN_3 (4.6 g.) at 0~10° during 2 hr. After stirring for additional 2 hr. at room temperature, the reaction mixture was poured onto ice and basified with powdered Na_2CO_3, extracted with $CHCl_3$, washed with saturated aqueous NaCl, dried (Na_2SO_4) and evaporated $CHCl_3$ to give dark brown oil (2.6 g.). This oily product was distilled under reduced pressure to give colorless oil (1.0 g.), b.$p_{0.3}$ 70~80° (bath temp.), yield 13%, which crystallized on long standing, m.p. 67~72°. IR ν_{max}^{KBr} cm^{-1}: 1685 (conjugated C=O), 1605 (C=C). *Anal.* Calcd. for C_6H_7OCl: C, 55.01; H,

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[*6] In ref. 6) the melting point is 104~105°, but our result showed the data described here.

5.39; Cl. 27.28. Found : C, 55.23; H, 5.45; Cl, 27.03.

This reaction product was assigned to be 2-chloro-2-cyclohexenone (XIII) and was identified with an authentic specimen prepared by the method of Braude, *et al.*,[8] by IR and mixture melting point measurement.

No other compound except tar which contained nitrogen element was isolated.

Reaction of 2-Cyclopentenone (XIV) with Sodium Azide in Conc. Hydrochloric Acid——This reaction was carried out at the same condition as the case of Xc using XIV (5.0 g.), NaN_3 (4.0 g.) and conc. HCl (50 ml.) and worked up in the same manner as for Xc to give dark brown tar, yield 3.5 g. (Beilstein test: positive). It was purified by distillation, $b.p_{10}$ 80～88°, colorless oil (XV), yield 1.2 g. (17%). IR $\nu_{\max}^{\text{liq.}}$ cm^{-1}: 1705 (C=O), 1600 (C=C). The IR of this compound was identical with an authentic sample of 2-chloro-2-cyclopentenone (XV) prepared by the method of Hans-Werner, *et al.*[11]

The Evolution of Chlorine from Sodium Azide and Conc. Hydrochloric Acid——To conc. HCl (10 ml.) was added NaN_3 (1 g.) portionwise at 5° during 1 hr. and then this solution was tested by KI-starch aqueous solution to show purple color. The evolution of chlorine from NaN_3 and conc. HCl at lower temperature was demonstrated distinctly.

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Summary

2-Methyl- (Ia), 2-phenyl- (Ib), 3-methyl-2-cyclohexenone (Xa) and 2-cyclohexenone (Xc) were reacted with equivalent mole of sodium azide in polyphosphoric acid.

In all cases, 2-amino-2-cyclohexenone derivatives were yielded as abnormal reaction products. In the cases of Ia and Ib, migration of the methyl and the phenyl group to the position 3 was observed accompanied by the simultaneous introduction of an amino group at the position 2, respectively.

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[11] Hans-Werner, Wanzlick-Gottfried Gollmer : Chem. Ber., 88, 69 (1955)