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Rearrangement in Dihydroresorcinol Derivatives. XI.[1] Photolysis and Thermolysis of 3-Azido-2-cyclohexen-1-ones and 2-Cyclopenten-1-ones

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Both photolysis and thermolysis of 2-alkylsubstituted 3-azido-2-cyclohexen-1-ones and -2-cyclopenten-1-ones in methanol gave mainly the α-aminoketal derivatives, although the corresponding 2-unsubstituted compounds gave the Curtius-type rearrangement products.

It has recently been shown that photolysis and thermolysis of 3-azido-2-cyclohexen-1-one (I) give only the Curtius–type rearrangement product, the azepinone (II), while the introduction of alkyl function at C-2 position of I makes azirine formation possible probably because of an increase in stability of the azirine ring.[1] We now describe the experimental details of the preliminary report and further the extention to the five-membered analogues, 3-azido-2-cyclopenten-1-ones (VII: R=H, VIII: R=CH_3).

Photolysis and Thermolysis of 3-Azido-2-cyclohexen-1-ones

The 2-alkyl-substituted 3-azido-2-cyclohexen-1-ones (IIIa—e) were prepared by the usual methods[3]; 2-Alkyl-3-chloro-2-cyclohexen-1-ones (IVa—e), prepared by treatment of 2-alkyl-cyclohexane-1,3-diones with phosphorous trichloride, thionyl chloride or oxalyl chloride, were reacted with sodium azide to give 2-alkyl-3-azido-2-cyclohexen-1-ones (IIIa—e).

Photolysis of the azides (IIIa—e) was performed by irradiation of a methanolic solution at 0—5° for 4—11 hr with a 450 W high pressure mercury lamp in a Pyrex vessel. Thermolysis was carried out by heating a methanolic solution of the azides (IIIa—e) in a sealed bomb at 140—150° for 3—20 hr.

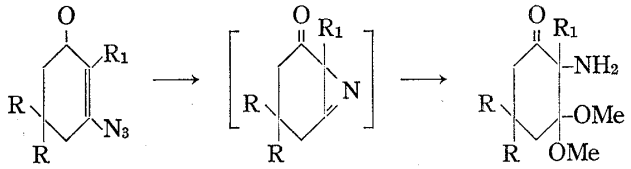
Photolysis of 2-benzyl-3-azido-2-cyclohexen-1-one (IIIa) followed by purification using column chromatography on alumina gave a 50% yield of colorless product of the molecular formula $C_{15}H_{21}O_3N$. The structure was assigned as 2-amino-2-benzoyl-3,3-dimethoxycyclohexanone (Va) on the basis of the following spectral evidence. Its infrared (IR) spectrum shows the existence of the primary amino (ν 3375 and 3300 cm^{-1}), ketal (ν 1180, 1150 and 1060 cm^{-1}) and six-membered unconjugated carbonyl function (ν 1710 cm^{-1}). The nuclear magnetic resonance (NMR) spectrum (in $CDCl_3$) exhibits a broad singlet at τ 8.72 (2H, NH_2, disappeared by addition of D_2O), a multiplet at τ 8.8—7.2 (6H, ring methylene), a quartet at τ 7.00 (J= 14 Hz, 2H, benzyl methylene), a multiplet at τ 3.2—2.6 (5H, aromatic proton) and two methoxy singlets at τ (6.84 and 6.46). Furthermore, the mass spectrum shows a characteristic base peak at m/e 101 ascribed to a fragment peak [CH_2=CH—C(OMe)=$\overset{+}{O}$Me].

Thermolysis of IIIa gave Va and methyl phenylpropionate in 52 and 8% yields, respectively. These compounds were identified with the authentic specimens by IR and NMR comparison.

1) Part X: Y. Tamura, Y. Yoshimura, T. Nishimura, S. Kato, and Y. Kita, *Tetrahedron Letters*, **1973**, 351.
2) Location: *6-1-1, Toneyama, Toyonaka, Osaka.*
3) Y. Tamura, Y. Yoshimura, and Y. Kita, *Chem. Pharm. Bull.* (Tokyo), **19**, 1068 (1971); *idem, ibid.*, **20**, 871 (1972).

Similar behavior was observed on both photolysis and thermolysis of 2-methyl- (IIIb), 2-allyl-(IIIc), 2-ethoxycarbonylmethyl- (IIId) and 2-benzyl-5,5-dimethyl-3-azido-2-cyclohexen-1-one (IIIe). The corresponding α-aminoketals (Vb—e) were obtained in yields as shown in Table. The structures of Vb—e were deduced from the elemental analysis and spectral data referring to the data of Va, details of which are given in the experimental section. In the case of the pyrolysis of 2-allyl-3-azido-2-cyclohexen-1-one (IIIc), tetrahydroindole derivative (VI) was also obtained along with Vc. The formation of α-aminoketal (Va—e)

TABLE I



IIIa—e Va—e

No.	Starting azides R	R_1	Reaction conditions	Yiled of reaction products Azepinone II	α-Aminoketal Va—e	Indole VI
I	H	H	Δ in MeOH	36		
			hν MeOH	—	—	—[a]
IIIa	H	$CH_2C_6H_5$	Δ MeOH		52	[b]
			hν MeOH		50	
IIIb	H	CH_3	Δ MeOH		53	
			hν MeOH		71	
IIIc	H	$CH_2CH{=}CH_2$	Δ MeOH		30	4
			hν MeOH		27	trace
IIId	H	CH_2CO_2Et	Δ MeOH		19	
			hν MeOH		36	
IIIe	CH_3	$CH_2C_6H_5$	Δ MeOH		60	
			hν MeOH		69	

a) complex mixture
b) Methyl phenylpropionate was obtained as a minor product.

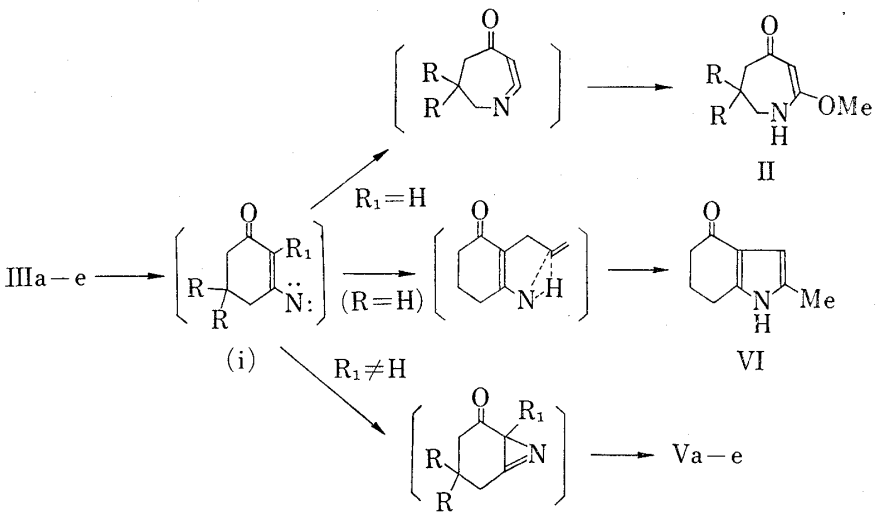


Chart 1

suggests the presence of the fused azirine as a reaction intermediate.[4] However, attempts to obtain the intermediate azirine were unsuccessful.

The results, summerized in Table, indicate that the alkyl group at C-2 position of 3-azido-2-cyclohexen-1-one has a dramatic effect on the reaction paths. As for the reaction mechanism of these reactions, it is speculated to proceed through the nitrene intermediate (i) as reported in the previous communication.[1]

Photolysis and Thermolysis of 3-Azido-2-cyclopenten-1-ones

To confirm the generality of the assumption that the introduction of alkyl function at C-2 position makes the azirine formation possible, we investigated both photolysis and thermolysis of 3-azido-2-cyclopenten-1-ones (VII: R=H, VIII: R=CH_3).

Thermolysis of 2-unsubstituted azide (VII: R=H), prepared from 3-chloro-2-cyclopenten-1-one (IX: R=H) and sodium azide, gave a 43% yield of colorless product of the molecular formula $C_6H_9O_2N$. The structure was assigned as 2,3-dihydro-6-methoxy-4-pyridone (X) on the basis of the following spectral evidence. Its IR spectrum shows characteristic bands at 1620 and 1565 cm^{-1} ascribed to N-C(OR)=C-C=O system, which closely resembles that of 1-methyl-2,3-dihydro-6-methoxy-4-pyridone.[5] The NMR spectrum exhibits a triplet at τ 7.60 (J=7 Hz, 2H, CH_2CO), a triplet at τ 6.48 (J=7 Hz, CH_2N), a singlet at τ 6.25 (3H, OCH_3), a singlet at τ 5.27 (1H, CH=) and a broad singlet at τ 4.70—4.30 (1H, NH, disappeared by addition of D_2O). Although the seven-membered analogue of X, 4,5,6,7-tetrahydro-2-methoxy-1H-azepin-4-one exists in equilibrium of enamine-imine forms in chloroform solution,[3] compound (X) is shown to exist solely as the enamine form in chloroform.

Photolysis of VII afforded an unidentified complex mixture as observed in the six-membered analogues.

In contrast to the case of VII, the photoirradiation of a methanolic solution of VIII (R=CH_3), prepared from 3-chloro-2-methyl-3-cyclopenten-1-one (XI: R=CH_3) and sodium azide, under the same condition as employed to III gave 2-amino-2-methyl-3, 3-dimethoxy-cyclopentanone (XII) in 22% yield. The structure of XII was readily assigned by a comparison of its spectral data with those of Va. Thus, strong infrared absorption bands at 3400, 3350, 1750, 1145, 1090 and 1060 cm^{-1} suggest the presence of amino, five-membered carbonyl and ketal moieties. The NMR spectrum of XII is similar to that of Va except for the absence of a ring methylene signal. Thermolysis of VIII gave the same product, XII, in 10% yield.

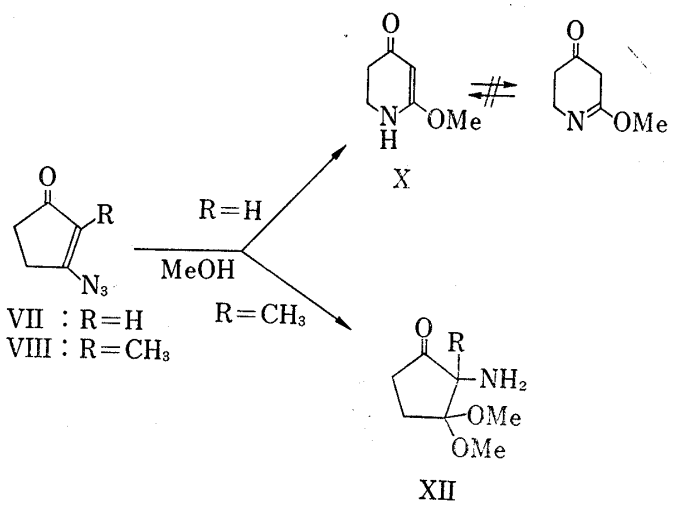


Chart 2

It is proved that the alkyl substituent at C-2 position of 3-azido-2-cyclopenten-1-one has also an important influence on the reaction pathway, as in the case of the cyclohexenone derivatives (IIIa—e).

4) A. Hassner and F.W. Fowler, *Tetrahedron Letters*, **1967**, 1545; *idem*, *J. Am. Chem. Soc.*, **90**, 2869 (1968); F.W. Fowler, *Adv. in Het. Chem.*, **13**, 54 (1971).

5 T. Oishi, M. Ochiai, T. Nakayama, and Y. Ban, *Chem. Pharm. Bull.* (Tokyo), **17**, 2314 (1969).

Experimental

All melting points are uncorrected. Thin-layer chromatography (TLC) was carried out using alumina GF_{258} (E. Merck). Ultraviolet (UV) spectra were determined with a Hitachi EPS-3T spectrophotometer, IR spectra with a Hitachi EPI-G2 spectrometer, NMR spectra (unless noted otherwise, TMS as internal standard) with a Hitachi R-20 instrument, and mass spectra with a Hitachi RMU-6D spectrometer at 70 eV.

2-Benzyl-3-chloro-2-cyclohexen-1-one (IVa)——A solution of 2-benzylcyclohexane-1,3-dione (5.00 g), and PCl_3 (15.0 g) in abs. chloroform (50 ml) was refluxed for 4 hr. The reaction mixture was poured into 30 ml of H_2O and extracted with ether (3×50 ml). The extract was washed with 10% NaOH aq. and sat. NaCl, dried ($MgSO_4$), and concentrated *in vacuo* to give a pale yellow oil. The oil was distilled *in vacuo* to afford 4.31 g (70%) of colorless IVa, bp 170—171° (12 mmHg). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1670, 1615, 1490, 955 and 900. NMR ($CDCl_3$) τ: 8.3—7.8 (m, 2H, CH_2), 7.60 (t, $J=6$ Hz, 2H, CH_2CO), 7.28 (t, $J=6$ Hz, 2H, $CH_2C=$), 6.25 (s, 2H, $C\underline{H}_2C_6H_5$) and 2.80 (s, 5H, C_6H_5). *Anal.* Calcd. for $C_{13}H_{13}OCl$: C, 70.74; H, 5.95. Found: C, 70.71; H, 5.85.

The following 3-chloro-2-cyclohexen-1-ones (IVb,c) were synthesized according to the above method.

3-Chloro-2-methyl-2-cyclohexen-1-one (IVb), bp 92—93° (15 mmHg) [lit.[6] 83—84° (7 mmHg)], was obtained in 40% yield from 2-methylcyclohexane-1,3-dione. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1660, 1640, 1430, 980 and 900.

2-Allyl-3-chloro-2-cyclohexen-1-one (IVc), bp 96° (7 mmHg), was obtained in 50% yield from 2-allylcyclohexane-1,3-dione. IR $\nu_{max}^{CHCl_3}$ cm^{-1} :1665, 1640, 1620, 1420, 940, 920, and 900. *Anal.* Calcd. for $C_9H_{11}OCl$: C, 63.34; H, 6.51. Found: C, 62.73; H, 6.41.

3-Chloro-2-ethoxycarbonylmethyl-2-cyclohexen-1-one (IVd)——A solution of 2-ethoxycarbonylmethylcyclohexane-1,3-dione (3.24 g) and $SOCl_2$ (6 ml) in abs. benzene (40 ml) was refluxed for 2 hr. After concentration of the solution *in vacuo*, the residual oil was dissolved in benzene and washed with 10% Na_2CO_3 aq. and sat. NaCl, dried ($MgSO_4$), and concentrated *in vacuo* to give a pale yellow oil. The oil was distilled *in vacuo* to give 2.75 g (78%) of IVd as a colorless oil, bp 150—160° (8 mmHg) (bath temp.). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1720, 1670, 1620, 1340, 1300, 1170, 1020, and 960. *Anal.* Calcd. for $C_{10}H_{13}O_3Cl$; C, 55.43; H, 6.06. Found: C, 55.15; H, 5.90.

2-Benzyl-3-chloro-5,5-dimethyl-2-cyclohexen-1-one (IVe)——2-Benzyl-5,5-dimethylcyclohexane-1,3-dione (2.30 g) was added to ($COCl_2$) (7 ml) with cooling, and the mixture was allowed to stand at room temperature for 7 days until the solid was dissolved and then carefully evaporated *in vacuo*. The residual oil was distilled *in vacuo* to give 2.05 g (83%) of IVe as a colorless oil, bp 105—106° (0.02 mmHg). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1665 and 1615. NMR ($CDCl_3$) τ: 8.95 (s, 6H, $2\times CH_3$), 7.71 (s, 2H, $CH_2C=$), 7.68 (s, 2H, $COCH_2$), 6.22 (s, 2H, $CH_2C_6H_5$) and 2.70 (s, 5H, C_6H_5). *Anal.* Calcd. for $C_{15}H_{17}OCl$: C, 72.42; H, 6.68. Found: C, 72.03; H, 6.83.

This stuff was not obtained by treatment with PCl_3 in abs. chloroform.

3-Azido-2-benzyl-2-cyclohexen-1-one (IIIa)——Freshly distilled IVa (5.47 g) was added dropwise to a stirred solution of NaN_3 (5.47 g) in MeOH (40 ml) and H_2O (10 ml) with ice-cooling, and after addition stirring was continued at room temperature for 2 days. The reaction mixture was poured into 20 ml of H_2O and extracted with ether (3×50 ml). The extract was dried ($MgSO_4$) and concentrated *in vacuo* to give 945 mg of IIIa as a pale yellow oil, which was used for the next reactions without purification. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2100, 1655 and 1610. NMR ($CDCl_3$) τ: 8.2—7.25 [m, 6H, $-(CH_2)_3-$], 6.42 (s, 2H, $C\underline{H}_2C_6H_5$) and 2.82 (s, 5H, C_6H_5).

3-Azido-2-methyl-2-cyclohexen-1-one (IIIb)——Prepared from IVb (4.48 g) and NaN_3 (3.00 g) in MeOH (20 ml) and H_2O (10 ml) as described for IIIa. Compound (IIIb, 2.00 g) was obtained as a yellow oil, which was used for the next reactions without purification. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2100, 1655 and 1620. NMR ($CDCl_3$) τ: 8.31 (t, $J=1$ Hz, CH_3), 8.2—7.2 [m, 6H, $-(CH_2)_3-$].

3-Azido-2-allyl-2-cyclohexen-1-one (IIIc)——Prepared from IVc (4.50 g) and NaN_3 (3.54 g) in MeOH (40 ml) and H_2O (10 ml). Compound (IIIc, 1.59 g) was obtained as a yellow oil, which was used for the next reactions without purification. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3075, 2100, 1650 and 1605.

3-Azido-2-ethoxycarbonylmethyl-2-cyclohexen-1-one (IIId)——Prepared from IVd (636 mg) and NaN_3 (246 mg) in dimethylformamide (DMF) (3 ml) was stirred at room temperature for 36 hr. The mixture was poured into 10 ml of H_2O and extracted with ether (30 ml). The extract was dried ($MgSO_4$) and concentrated *in vacuo* to give 453 mg of IIId as yellow crystals, which was used for the next reactions without purification. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2100, 1720, 1650, 1620, 1280 and 1080.

3-Azido-2-benzyl-5,5-dimethyl-2-cyclohexen-1-one (IIIe)——Prepared from IVe (1.00 g) and NaN_3 (0.53 g) in DMF (4 ml) as described for IIId. Compound (IIIe, 1.05 g) was obtained as yellow crystals and used for the next reactions without purification. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2100, 1660 and 1610.

Photolysis of IIIa——A solution of IIIa (446 mg) in MeOH (7 ml) was irradiated with a 450 W high pressure mercury lamp in a Pyrex vessel at 0—5° for 10.5 hr. After concentration of the mixture *in vacuo*, the residual solid was purified by passing through a short column of alumina with benzene: chloroform=

6) S.I. Zav'yalov and G.V. Kondrat'eva, *Zh. Obsch. Khim.*, 30, 3987 (1961).

9: 1. Concentration of the fraction followed by distillation under reduced pressure gave 252 mg (50%) of colorless crystals Va, bp 120—160° (0.03—0.05 mmHg) (bath temp.). *Anal.* Calcd. for $C_{15}H_{21}O_3N$: C, 68.44; H, 7.98; N, 5.32. Found: C, 68.26; H, 8.07; N, 5.50.

Thermolysis of IIIa——After heating a solution of IIIa (679 mg) in abs. MeOH (20 ml) at 140° for 3 hr in a sealed bomb, the solution was concentrated *in vacuo* and the residue was chromatographed on alumina. The column was treated successively with petr. ether (50 ml), benzene (50 ml) and benzene: chloroform=10: 1 (200 ml). Concentration of the benzene fraction followed by distillation *in vacuo* gave 40.3 mg (8%) of methyl phenylpropionate, bp 50—60° (0.07—0.08 mmHg) (bath temp.), which was identified with the authentic specimen by IR and NMR comparison. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1730, 1600 and 1490. NMR (CCl_4) τ: 7.35 [m, 4H, $-(CH_2)_2-$], 6.41 (s, 3H, CCH_3) and 2.88 (s, 5H, C_6H_5). Concentration of the fraction of benzene: chloroform=10: 1 followed by distillation *in vacuo* gave 410 mg (52%) of Va as colorless crystals, bp 120—140° (0.04—0.05 mmHg) (bath temp.), mp 52—53°, which was identified with the authentic sample by mixed melting point and TLC determination and comparison of IR spectra.

Photolysis of IIIb——A solution of IIIb (461 mg) in abs. MeOH (25 ml) was irradiated for 4 hr under the same condition as employed for IIIa. After concentration of the solution *in vacuo*, the residue was distilled *in vacuo* to give 410 mg (71%) of Vb as a pale yellow oil, bp 75—85° (0.045 mmHg) (bath temp.). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3375, 3300, 2825, 1715, 1590, 1180, 1150, 1090, 1080 and 1040. NMR ($CDCl_3$) τ: 8.88 (s, 3H, CH_3), 8.55 (bs, 2H, NH_2, disappeared by addition of D_2O), 8.6—8.0 (m, 4H), 7.9—7.5 (m, 2H, CH_2CO), 6.88 (s, 3H, OCH_3) and 6.60 (s, 3H, OCH_3). Mass Spectrum *m/e*: 187 (M^+), 156, 144, 124, 112, 101 (base peak), 86, 70, 69, 57, 55 and 43. *Anal.* Calcd. for $C_9H_{17}O_3N$: C, 57.72; H, 9.17; N, 7.48. Found: C, 58.15; H, 9.47; N, 7.33.

Thermolysis of IIIb——A solution of IIIb (1.45 g) in abs. MeOH (10 ml) was heated at 80° for 20 hr. Working up as described for IIIa gave 723 mg (53%) of Vb as a yellow oil, bp 80—90° (0.07 mmHg) (bath temp.), which was identified with the authentic specimen in all respects.

Photolysis of IIIc——A solution of IIIc (718 mg) in abs. MeOH (120 ml) was irradiated for 3 hr under the same condition as employed for IIIa. After concentration of the solution *in vacuo*, the residual oil was submitted to the prep. TLC (alumina/$CHCl_3$) to give two bands. Extraction of the band of higher *Rf* value with $CHCl_3$ gave crude Vc, which was distilled *in vacuo* to give 234 mg (27%) of Vc as a pale yellow oil, bp 115—120° (0.4 mmHg) (bath temp.). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3380, 3305, 3075, 2830, 1715, 1625, 1590, 1180, 1150, 1090 and 1060. NMR (CCl_4) τ: 8.55 (bs, 2H, NH_2, disappeared by addition of D_2O), 8.5—7.5 (m, 8H, $4\times CH_2$), 6.88 (s, 3H, $CH=CH_2$). Mass Spectrum *m/e*: 213 (M^+), 182 ($M-OCH_3$), 175, 170, 149, 138, 112, 101 (base peak), 96, 84, 71, 57, and 55. *Anal.* Calcd. for $C_{11}H_{19}O_3N$: C, 61.70; H, 8.98; N, 6.37. Found: C, 61.94; H, 8.98; N, 6.57. From the band of lower *Rf* value, 0.015 g of VI was obtained. This stuff was identified with the authentic specimen prepared from the thermolysis of IIIc by IR comparison.

Thermolysis of IIIc——After heating a solution of IIIc (1.29 g) in abs. MeOH (30 ml) at 140° for 3 hr in a sealed bomb, the solution was evaporated *in vacuo* and the residue was chromatographed on alumina. The column was treated successively with benzene (50 ml), benzene: chloroform=10: 1 (300 ml) and chloroform (100 ml). Concentration of the benzene: chloroform=10: 1 fraction followed by distillation *in vacuo* gave 428 mg (30%) of Vc, bp 100—120° (0.08 mmHg) (bath temp.). The chloroform fraction was concentrated *in vacuo* to give 37.4 mg (4%) of VI. Recrystallization from benzene–*n*-hexane gave colorless crystals of VI, mp 204° (lit. 208°). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3450 and 1640. NMR ($CDCl_3$) τ: 8.05—7.35 (m, 4H, $2\times CH_2$), 7.76 (s, 3H, CH_3), 7.20 (t, J=6 Hz, 2H, $CH_2C=$), 3.9—3.7 (m, 1H, CH=) and 0.9—0.7 (bs, 1H, NH). This stuff was identified with the authentic specimen[7] by IR and NMR comparison.

Photolysis of IIId——A solution of IIId (1.69 g) in abs. MeOH (100 ml) was irradiated for 2.5 hr under the same condition as employed for IIIa. After concentration of the solution *in vacuo*, the residue was chromatographed on alumina. The column was treated successively with petr. ether (50 ml), benzene (100 ml) and benzene: EtOAc=10: 1 (350 ml). Concentration of the benzene: EtOAc=10: 1 fraction followed by distillation *in vacuo* gave 706 mg (36%) of Vd as a yellow oil, bp 158—163° (0.1 mmHg) (bath temp.). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3450, 3350, 1720, 1660, 1590, 1150, 1090, 1050 and 1020. NMR ($CDCl_3$) τ: 8.78 (t, J=7 Hz, 3H, $CH_2C\underline{H}_3$), 8.5—7.0 [m, 6H, $(CH_2)_3$], 7.72 (bs, 2H, NH_2), 6.79 (s, 3H, OCH_3), 6.58 (s, 3H, OCH_3), 6.36 (d, J=2 Hz, 2H, CH_2CO) and 5.94 (q, J=7 Hz, 2H, OCH_2). Mass Spectrum *m/e*: 259 (M^+), 158, 154, 122, 112 and 101 (base peak). *Anal.* Calcd. for $C_{12}H_{21}O_5N$: C, 55.58; H, 8.16; N, 5.49. Found: C, 55.70; H, 8.23; N, 5.50.

Thermolysis of IIId——After heating a solution of IIId (230 mg) in abs. MeOH (5 ml) at 80° for 11 hr in a sealed bomb, the solution was evaporated *in vacuo* and the residue was purified by prep. TLC (alumina/benzene: EtOAc=2: 1) to give 49.2 mg (19%) of Vd as a yellow oil, which was identified with the authentic specimen in all respects.

Photolysis of IIIe——A solution of IIIe (250 mg) in abs. MeOH (15 ml) was irradiated for 4 hr as employed for IIIa. After concentration of the solution *in vacuo*, the residue was chromatographed on alumina. The column was treated successively with petr. ether (50 ml), benzene (150 ml) and benzene: EtOAc=10: 1 (150 ml). Concentration of the benzene: EtOAc=10 :1 fraction followed by distillation *in vacuo* gave 112 mg

7) H. Stetter and R. Lanterbach, *Ann.*, **655**, 20 (1962).

(69%) of Ve as a yellow viscous oil, bp 150—155° (0.1 mmHg) (bath temp.). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3400—3350, 1710, 1600, 1180, 1140, 1090, 1080 and 1050. NMR ($CDCl_3$) τ: 8.50 (s, 3H, CH_3), 8.35 (s, 3H, CH_3), 8.0 (bs, 2H, NH_2), 6.80 (s, 3H, OCH_3), 6.47 (s, 3H, OCH_3) and 2.85—2.75 (m, 5H, C_6H_5). Mass Spectrum *m/e*: 287 (M^+), 168, 129 (base peak) and 91. *Anal.* Calcd. for $C_{17}H_{25}O_3N$: C, 71.04; H, 8.77; N, 14.62. Found: C, 71.25; H, 8.88; N, 14.81.

Thermolysis of IIIe——After heating a solution of IIIe (60.0 mg) in abs. MeOH (3 ml) at 80° for 4 hr in a sealed bomb, the solution was evaporated *in vacuo* and the residual oil was purified by prep. TLC (alumina/benzene: EtOAc=2: 1) to give 41.1 mg (60%) of Ve, which was identified with the authentic specimen in all respects.

3-Chloro-2-cyclopenten-1-one (IX)——i) A solution of cyclopentane-1,3-dione (797 mg) and PCl_3 (1 ml) in abs. chloroform (20 ml) was refluxed for 4 hr. Working up as described for the preparation of IVa gave 232 mg (24%) of IX as a colorless oil, bp 95° (20 mmHg) (bath temp.). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1710 and 1600, which was used for the next reaction without further purification.

ii) IX was also obtained by the reaction of cyclopentane-1,3-dione (1.82 g) and $(COCl)_2$ (3.67 g) at room temperature for 5 hr in 23% yield.

3-Azido-2-cyclopenten-1-one (VII)——i) Prepared from IX (232 mg) and NaN_3 (106 mg) in MeOH (2 ml) and H_2O (0.5 ml) as described for IIIa. Compound (VII, 106 mg) was obtained as a yellow oil, which was used for the next reactions without purification. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2100, 1700 and 1590.

ii) To a solution of IX (185 mg) in DMF (5 ml) at room temperature was added NaN_3 (150 mg) in portions, and the reaction mixture was allowed to stand for 5 hr. The mixture was worked up in the usual manner to give 83.0 mg of VII.

Photolysis of VII——A solution of VII (150 mg) in abs. MeOH (15 ml) was irradiated for 6 hr as described for IIIa. The solution was evaporated *in vacuo* to give a complex mixture, which could not be purified in spite of every effort.

Thermolysis of VII——After heating a solution of VII (106 mg) in abs. MeOH (20 ml) at 80° for 4 hr in a sealed bomb, the solution was evaporated *in vacuo* and the residue was sublimated *in vacuo* to give 47.0 mg (43%) of X, bp 135—140° (0.09 mmHg) (bath temp.), mp 109—110°. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3430, 1620 and 1565. UV λ_{max}^{EtOH} nm (log ε): 289 (4.69). NMR ($CDCl_3$) τ: 7.60 (t, J=7 Hz, 2H, CH_2CO), 6.48 (t, J=7 Hz, CH_2N), 6.25 (s, 3H, OCH_3), 5.27 (s, 1H, CH=) and 4.70—4.30, (bs, 1H, NH). *Anal.* Calcd. for $C_6H_9O_2N$: C, 56.68; H, 7.14; N, 11.02. Found: C, 56.73; H, 7.08; N, 11.02.

3-Chloro-2-methyl-2-cyclopenten-1-one (XI)——A solution of 2-methylcyclopentane-1,3-dione (14.1 g) and PCl_3 (11.6 g) in abs. chloroform (100 ml) was refluxed for 4 hr. Working up as described for IVa gave 10.4 g (63%) of XI as a colorless oil, bp 80° (23 mmHg). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1700 and 1640. *Anal.* Calcd. for C_6H_7OCl: C, 55.18; H, 5.41. Found: C, 54.96; H, 5.44.

3-Azido-2-methyl-2-cyclopenten-1-one (VIII)——Prepared from IX (3.20 g) and NaN_3 (2.07 g) in MeOH (15 ml) and H_2O (5 ml) as described for IIIa. Compound (VIII, 1.55 g) was obtained as yellow crystals, mp 34°, which was used for the next reactions without purification. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2100, 1690 and 1630.

Photolysis of VIII——A solution of VIII (164 mg) in abs. MeOH (15 ml) was irradiated for 6 hr as described for IIIa. After concentration of the solution *in vacuo* followed by distillation *in vacuo* to give 45.0 mg (22%) of XII as a colorless viscous oil, bp 125—130° (0.08 mmHg) (bath temp.), which crystallized on standing, mp 45°. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3400, 3350, 1750, 1145, 1090 and 1060. NMR ($CDCl_3$) τ: 8.93 (s, 3H, CCH_3), 8.22 (s, 2H, NH_2), 8.14—7.58 [m, 6H, $-(CH_2)_3-$], 6.80 (s, 3H, OCH_3) and 6.62 (s, 3H, OCH_3). UV λ_{max}^{EtOH} nm (log ε): 263.5 (2.28) and 298 (1.88). *Anal.* Calcd. for $C_8H_{15}O_3N$: C, 55.47; H, 8.73; N, 8.09. Found: C, 55.32; H, 8.60; N, 7.82.

Thermolysis of VIII——After heating a solution of VIII (1.41 g) in abs. MeOH (10 ml) at 80° for 6 hr, the solution was concentrated *in vacuo* and the residue was purified by prep. TLC (alumina/benzene: EtOAc=1: 1) to give a colorless oil, which was distilled *in vacuo* to give 161 mg (10%) of XII, bp 120—125° (0.06 mmHg) (bath temp.), which crystallized on standing, mp 45°. This stuff was identified with the authentic specimen by comparison with IR and NMR spectra.