$\nu_{max}^{CHCl_3}$ $cm^{-1}$ : 1730 (OAc), 1668, 1622 ($\Delta^4$-3-ketone). *Anal.* Calcd. for $C_{22}H_{32}O_3S$ : C, 70.17; H, 8.57; S, 8.52. Found : C, 69.95; H, 8.61; S, 8.76.

The authors are grateful to Messrs. Y. Matsui, I. Tanaka, and A. Takasuka for spectral measurements, to Mr. H. Iwata for rotation measurement, and to the members of Analysis Room of this Laboratory for elemental analyses.

## Summary

Some 16$\beta$-acetylthio and 16$\beta$-alkylthio estrones were prepared by substitution of 16-bromo-17-ketosteroids with sulfur nucleophiles. Both 16$\alpha$- and 16$\beta$-bromoestrone methyl ether gave the same 16$\beta$-substituted product. Transformation of these alkylthio estrones into 19-norsteroid derivatives by lithium-ammonium reduction was studied.

(Received May 4, 1964)

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[Chem. Pharm. Bull. 12 (8) 910 ~ 916]

*UDC 547.445.07*

## 128. Tetsuzo Kato, Hiroshi Yamanaka, Takuitsu Niitsuma, Kokichi Wagatsuma, and Masako Oizumi : Studies on Ketene and its Derivatives. VI*1. Reaction of Diketene with Aminopyridines and their N-Oxides.

(*Pharmaceutical Institute, Tohoku University School of Medicine**2)

Diketene reacts easily with aromatic primary amine *e.g.* aniline, to give acetoacetanilide in a good yield.[1~3] It has been also reported that aminoheterocycles such as 2-aminopyridine or 2-aminobenzthiazole react with diketene to yield their acetoacetates.[4,5]

On the other hand in the previous papers*1,6 of this series we reported that pyridine and quinoline reacted with diketene to give their diketene adducts, $C_{13}H_{11}O_3N$ and $C_{17}H_{13}O_3N$, which were identified with so-called Wollenberg type compound[7,8] and that the reaction of quinoline 1-oxide with diketene was more complicated resulting in the formation of 2-methyl-6-[(2-quinolyl)methyl]-4*H*-pyran-4-one.

Interest in this laboratory has been focused on the reaction of aminopyridines and their N-oxides as to whether diketene reacts toward the amino function of pyridine according to the usual reaction reported as above[1~5] or toward C=N double bond in the pyridine ring as described in our previous papers.*1,6

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*1 Part V. T. Kato, H. Yamanaka : This Bulletin, **12**, 18 (1964).
*2 Kita-4, Sendai, Miyagi-ken (加藤鉄三, 山中 宏, 新妻卓逸, 我妻光吉, 大泉雅子).
1) N. Wilsmore, F. Chick : J. Chem. Soc., **93**~**94**, 77 (1908); *Ibid.*, **97**~**98**, 1978 (1910).
2) G. Law : U. S. Pat., 1,982,675 (1934).
3) A. Boese : Ind. Eng. Chem., **32**, 16 (1940).
4) C. Allen, J. Allen, C. Wilson : J. Am. Chem. Soc., **66**, 1805 (1944).
5) E. Kodak : U. S. Pat., 2,108,602 (1938).
6) T. Kato, T. Kitagawa, Y. Yamamoto : Yakugaku Zasshi, **83**, 267 (1963).
7) O. Wollenberg : Ber., **67**, 1675 (1934).
8) J. Berson, W. Jones : J. Am. Chem. Soc., **78**, 1624 (1956).

The present paper deals with the reactions of three kinds of aminopyridines and their N-oxides with diketene, and describes that the difference of the position of amino group in the pyridine ring or the existence of N-oxide function resulted respectively in the formations of different products.

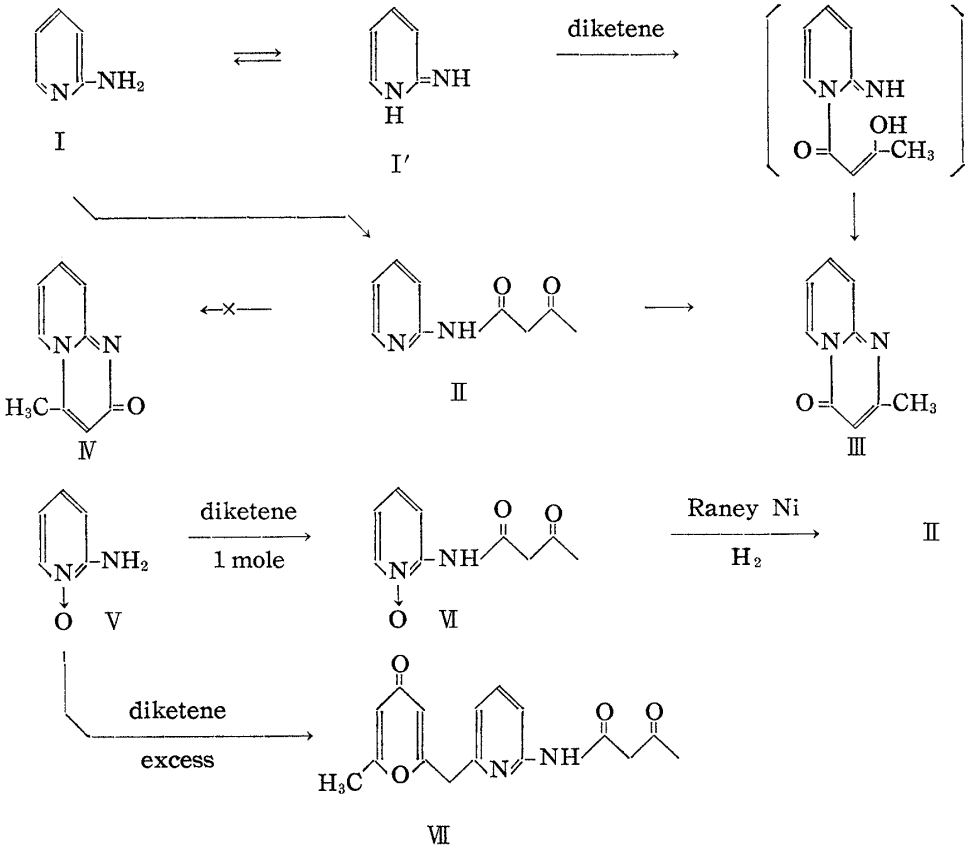


Chart 1.

2-Aminopyridine (I) reacted readily with diketene to give 2-acetoacetamidopyridine (II) as described by Allen,[4] but we found that white needles of m.p. 120°, $C_9H_8ON_2$, were also obtainable as a by-product which was identical with 2-methyl-4*H*-pyrido-[1,2-*a*]pyrimidin-4-one (III).[9] Although 4-methyl-2*H*-pyrido[1,2-*a*]pyrimidin-2-one (IV) would be expected to prepare by its intramolecular ring closure, Adams[9] reported that the reaction of II with conc. sulfuric acid caused the rearrangement to result in the formation of III only.

In considering this rearrangement, we assumed that the acetoacetate (II) was the first product in this reaction and then transfered to III by the rearrangement as described above. However, we confirmed that II was indifferent to further treatment with diketene in the same solvent even under forcing conditions. This fact shows that diketene did not react merely toward the amino function at 2-position of pyridine ring giving II but also toward the ring nitrogen which exists as the imino form (I′) to give III as illustrated in Chart 1.

2-Aminopyridine 1-oxide (V) reacted with an equimolar quantity of diketene to give 2-acetoacetamidopyridine 1-oxide (VI) in a good yield, but the reaction with an excess of diketene afforded white crystals of m.p. 190° which were also obtainable from the reaction of VI with another mole of diketene. Elemental analysis and the molecular weight determination provided the formula $C_{16}H_{16}O_4N_2$, and the infrared absorption spectrum

9) R. Adams: J. Am. Chem. Soc., **74**, 5491 (1952).

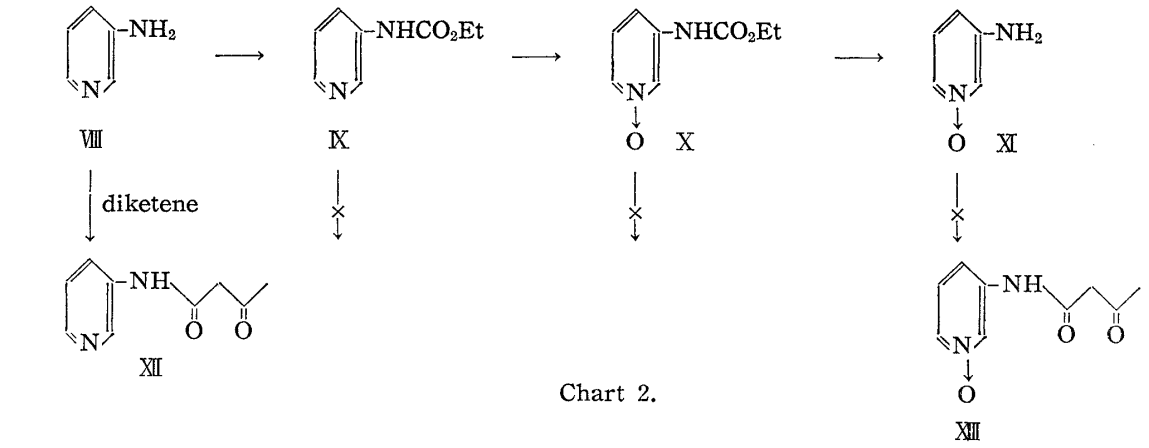


Chart 2.

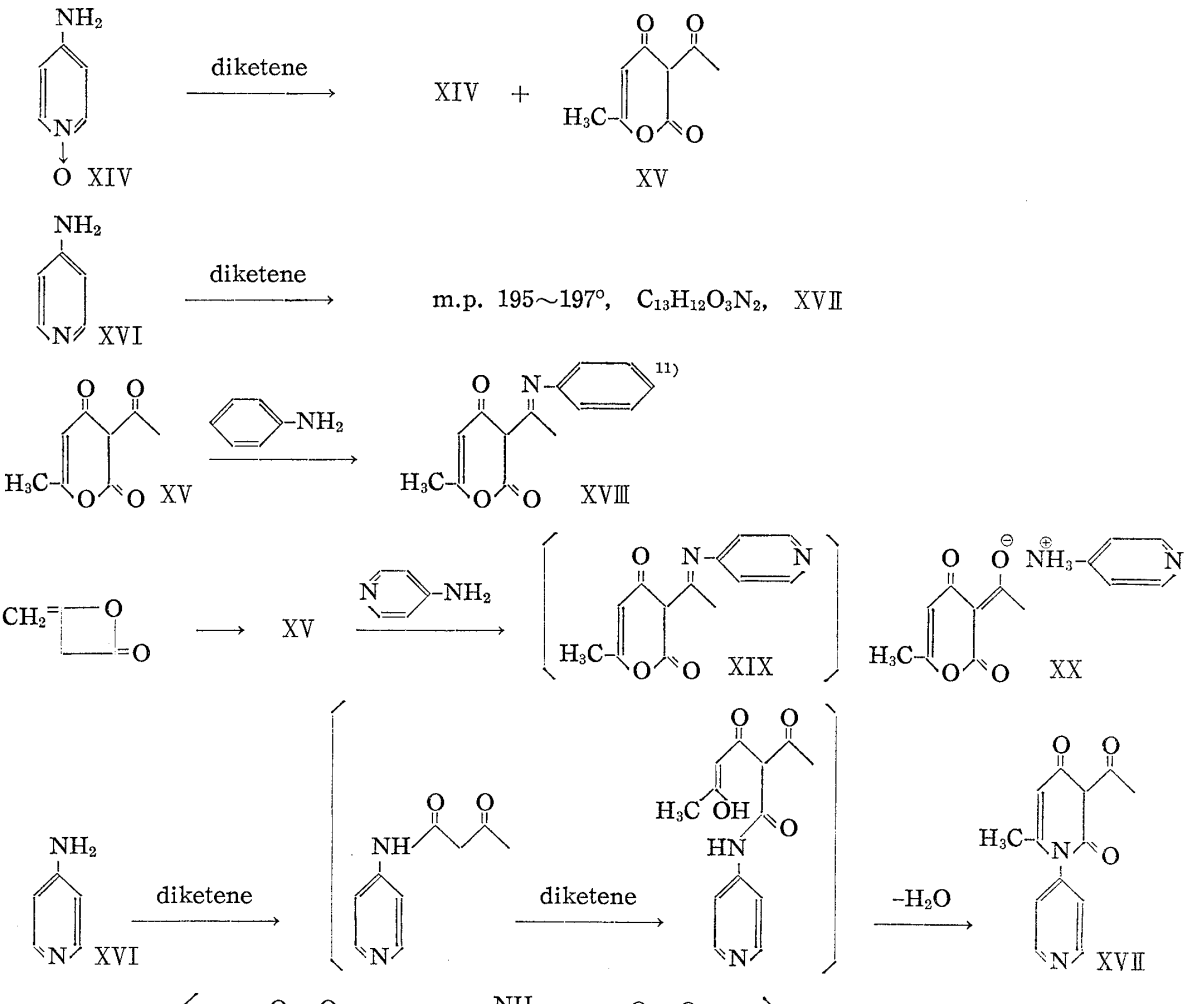


Chart 3.

indicated the presence of 4-pyrone and the absence of N-oxide function. In our previous paper*[1] we stated that quinoline 1-oxide reacted with diketene to give 2-[(2-quinolyl)methyl]-4*H*-pyran-4-one. Accordingly, we have lead to the conclusion that the structure of m.p. 190° is presumably represented as 2-[(6-acetoacetamido-2-pyridyl)-methyl]-6-methyl-4*H*-pyran-4-one (Ⅶ).

Upon catalytic reduction with Raney nickel Ⅵ was reduced to Ⅱ. As illustrated in Chart 2. 3-aminopyridine (Ⅷ) was converted to the urethane (Ⅸ), next to its N-oxide (X) and finally to 3-aminopyridine 1-oxide (Ⅺ). Although Ⅸ and X did not react with diketene, Ⅷ and Ⅺ were converted to their acetoacetates (Ⅻ and XIII) similarly as in the case of aniline. The acetoacetates thus obtained did not react with another mole of diketene, and atempts to prepare the naphthyridine ring system by their intramolecular ring closure reaction with concentrated sulfuric acid failed.

It is of interest to know the result of the reaction of 4-amino derivatives. Although 4-aminopyridine 1-oxide (XIV) did not react with diketene in chloroform or acetonitrile resulting in the recovery of XIV and in the formation of dehydracetic acid (XV). 4-aminopyridine (XVI) was converted into white needles of m.p. 195.5~197°.*[3] Elemental analysis and molecular weight determination provided the empirical formula $C_{13}H_{12}O_3N_2$, which shows one mole of XVI reacted with two moles of diketene and one mole of water was eliminated. Both of ferric chloride reaction for enolic compound and diazo color test for primary amine were negative. The infrared absorption spectrum of this compound contradicted the existences of NH and 4-pyrone. Hydrolyses with 10% hydrochloric acid afforded 4-aminopyridine and 2,6-dimethyl-4*H*-pyran-4-one (XXI).

Therefore, neither Wollenberg type compound nor naphthyridine ring system could be given for this structure.

On the other hand, it has been already reported that primary amine such as aniline reacts with dehydracetic acid (XV) to give the anil such as 3-(1-phenyliminoethyl)-6-methyl-2*H*-pyran-2,4(3*H*)-dione (XVIII).[10] In consequence, we first assumed that dehydracetic acid, which was formed by the dimerization of diketene as an intermediate, reacted with 4-aminopyridine (XVI) giving the anil (XIX). However, the reaction of XV

Table I. Proton Magnetic Resonance Spectra[a]

| Compd. | τ-Value | Multiplicity[b] | Assignment |
|---|---|---|---|
| XVII[c] | 1.50 | q ($J_1$=5.0 c.p.s., $J_2$=1.5 c.p.s.) | proton of pyridine |
| | 2.40 | q ($J_1$=5.0 c.p.s., $J_2$=1.5 c.p.s.) | 〃 |
| | 3.70 | s | vinyl protone |
| | 7.15 | s | $CH_3CO$- |
| | 7.68 | s | $CH_3$- |
| XV[c] | 4.05 | s | vinyl protone |
| | 7.35 | s | $CH_3CO$- |
| | 7.73 | s | $CH_3$- |
| XXI | 3.96 | s | vinyl protone |
| | 7.77 | s | $CH_3$- |

*a*) Spectra were obtained on a Varian A-60 spectrometer using $CDCl_3$ as solvent and tetramethylsilane as internal standard.
*b*) s=singlet, q=quartet.
*c*) Protone at 3-position (or 4-OH proton) was not assigned.

*[3] White needles of m.p. 252~253° and pale yellow needles of m.p. 286~287° were obtained as by-products. However, because of their low yields the structural determinations have not been completed yet.

10) A. Oppenheim, H. Precht: Ber., 9, 1100 (1876). lit. m.p. 115°. Our sample was prepared according to the method of S. Garrat (J. Org. Chem., 28, 1886 (1963). m.p. 120°).

with XVI afforded none of the same crystal of m.p. 195.5~197° nor the anil (XIX), but gave white crystals of m.p. 141~142° (decomp.), $C_{13}H_{14}O_4N_2$ (XX). XX was chromatographed on alumina to give the starting 4-aminopyridine (XVI), and thermal analysis showed XX is uniquely represented as a molecular compound between 4-aminopyridine (XIV) and dehydracetic acid (XV).

The nuclear magnetic resonance spectrum of m.p. 195.5~197° shows a complex multiplet at $\tau$ 2.38, 2.47 (pyridine), and singlets at $\tau$ 3.70 (vinyl proton), $\tau$ 7.15 ($CH_3CO$) and $\tau$ 7.68 ($CH_3$). This assignment would be reasonably given comparing with the spectra of dehydracetic acid (XV) and 2,6-dimethyl-4*H*-pyran-4-one (XXI) as shown in Table I.

In view of the above facts among some considerable structures for this empirical formula, $C_{13}H_{12}O_3N_2$, the most reasonable structure to be drawn from available data is given as 1-(4-pyridyl)-3-acetyl-6-methyl-2,4(1*H*,3*H*)-pyridinedione (XVII), and the details of the mechanism of the formation of XVII remain obscure for the present, a likely mechanism is shown in Chart 3.

## Experimental

**Reaction of Diketene with 2-Aminopyridine (I)**——To a solution of 2-aminopyridine (1.6 g., 0.017 mole) in 10 ml. of benzene was added 2 g. (0.024 mole) of diketene in 5 ml. of benzene by drops. After heating on a steam bath for 5 min., the reaction mixture was allowed to stand at a room temperature. White prisms separated in a pure state were collected by filtration, m.p. 110°, 1.94 g. Recrystallization from benzene gave white prisms of m.p. 110~112°, undepressed on admixture with 2-acetoacetamidopyridine (II).[4] The filtrate was condensed to give 1.5 g. of pale yellow solid (m.p. ca. 100°), which was purified by alumina chromatography to give 0.88 g. of m.p. 120~121° (white needles from benzene, m.p. 121~122°), undepressed on admixture with an authentic sample (III) prepared according to the method of Adams.[9] Yield, 28%.

The eluted fraction, followed to III, was condensed to yield 0.2 g. of II. Total yield of II was 2.14 g. (61%).

**Reaction of 2-Aminopyridine 1-Oxide (V) with Diketene**——1) with an equimolar quantity of diketene: To 0.55 g. (0.005 mole) of 2-aminopyridine 1-oxide (V)[11] was added 0.42 g. (0.005 mole) of diketene. After 15 min. of reflux on a steam bath, the solvent was removed. The residual solid (m.p. ca. 120°, 0.97 g.) was recrystallized from MeOH to give white crystals of m.p. 126~128°. Yield, 0.78 g. (80%). *Anal.* Calcd. for $C_9H_{10}O_3N_2$ (VI): C, 55.66; H, 5.19; N, 14.43. Found: C, 56.13; H, 5.31; N, 14.76. IR $\nu^{KBr}$ $cm^{-1}$: 1713, 1695, 1361, 1212.

2) with an excess of diketene: To a solution of 0.55 g. (0.005 mole) of V in 30 ml. of $CHCl_3$ was added 2.3 g. (0.025 mole) of diketene. After 30 min. of reflux and removal of the solvent, a residual semi-solid was washed with 10 ml. of cold benzene to give 0.55 g. of an orange crystalline solid which was recrystallized from hot benzene to give white needles of m.p. 190° (decomp.). Yield, 0.4 g. (27%). $FeCl_3$ color test was positive (purple). *Anal.* Calcd. for $C_{16}H_{16}O_4N_2$ (VII): C, 63.99; H, 5.37; N, 9.33. Found: C, 63.35; H, 5.17; N, 9.34. IR $\nu^{KBr}$ $cm^{-1}$: 3440, 1700 (shoulder), 1680, 1635, 1368.

**Reaction of 2-Acetoacetamidopyridine 1-Oxide (VI) with Diketene**——To a solution of 0.2 g. of VI in 10 ml. of $CHCl_3$ was added 0.9 g. of diketene. After 30 min. of reflux on a steam bath, the solvent was evaporated *in vacuo* to give a tarrish residue to which was added ca. 2 ml. of of benzene and allowed to stand in a refrigerator overnight.

The separating crystalline solid was collected, washed with $Et_2O$, recrystallized from benzene to give white needles of m.p. 190° (decomp.). The IR absorption spectrum was identical in every respect with that of VII obtained in the above run.

**Reduction of 2-Acetoacetamidopyridine 1-Oxide (VI)**——A mixture of 0.2 g. of Raney Ni and 0.2 g. of VI in 5 ml. of MeOH was shaken in $H_2$ according to the general method reported by Hayashi and Yamanaka.[12] $H_2$ 18 ml. was absorbed (theoretical amount; 23 ml.). After removal of the catalyst by filtration, the filtrate was condensed to dryness. Recrystallization from benzene afforded white crystals of m.p. 110~112°, undepressed on admixture with II.

**3-Ethoxycarbonylaminopyridine 1-Oxide (X)**——A mixture of 10 g. of 3-ethoxycarbonylaminopyridine (IX),[13] 9 g. of 30% $H_2O_2$ and 20 ml. of AcOH was warmed on a steam bath for 9 hr., condensed under

11) R. Katritzky, *et al.*: J. Chem. Soc., **1957**, 191.
12) E. Hayashi, H. Yamanaka, K. Shimizu: This Bulletin, **7**, 141 (1959).
13) T. Curtius, E. Mohr: Ber., **31**, 2994 (1898).

reduced pressure, and the resulted residue was extracted with $CHCl_3$, dried with $K_2CO_3$. From the $CHCl_3$ extract a crystalline solid was obtained. Recrystallization from $Me_2CO$ gave 9.9 g. of white needles, m.p. 197° (decomp.). Yield, 90%. *Anal.* Calcd. for $C_8H_{10}O_3N_2$ (X): C, 52.74; H, 5.53; N, 15.38. Found: C, 52.88; H, 5.68; N, 15.76. IR $\nu^{KBr}$ $cm^{-1}$: 1730, 1631, 1587, 1502, 1250.

**3-Aminopyridine 1-Oxide (XI)**——A solution of 2 g. of 3-ethoxycarbonylaminopyridine 1-oxide (X) and 3 ml. of conc. HCl was heated for 10 hr. After evaporation of HCl on a steam bath under reduced pressure, the residue was neutralized by use of Amberlite IR-A 400. From the MeOH eluted solution hygroscopic white crystals were obtained. Recrystallization from $Me_2CO$ afforded 0.63 g. (53%) of m.p. 119~120°.[14] HCl salt, m.p. 148°.[15] Picrate, m.p. 175°. *Anal.* Calcd. for $C_5H_6ON_2$–$C_6H_3O_7N_3$ (XI-picrate): C, 38.95; H, 2.67; N, 20.65. Found: C, 39.38; H, 3.08; N, 21.28.

**Reaction of 3-Aminopyridine (VIII) with Diketene**——To a solution of 1 g. of VIII in 20 ml. of benzene, was added 1.96 g. of diketene. After allowing to stand at a room temperature until the exothermic reaction ceased, the mixture was warmed on a steam bath for 30 min. under reflux, cooled in an ice-bath. Pale yellow crystals separated were collected by filtration, 1.34 g., m.p. 137~140°. Recrystallization from benzene afforded white needles of m.p. 142~142.5°.[16] *Anal.* Calcd. for $C_9H_{10}O_2N_2$ (XII): C, 60.66; H, 5.66; N, 15.72. Found: C, 61.06; H, 5.76; N, 15.63. IR $\nu^{KBr}$ $cm^{-1}$: 1730, 1695, 1613, 1592, 1558, 1479.

The filtrate was washed with 2*N* $Na_2CO_3$, condensed to dryness to give reddish crude crystals which were recrystallized from benzene giving 0.03 g. of XII, m.p. 142°. Total yield of XII was 1.37 g. (72.6%). From the $Na_2CO_3$ washing 0.04 g. of dehydracetic acid (XV) was obtained.

**Reaction of 3-Aminopyridine 1-Oxide (XI) with Diketene**——A mixture of 0.6 g. of XI and 0.96 g. of diketene in 40 ml. of $CHCl_3$ was allowed to stand at a room temperature for 2 hr. The solvent was evaporated under reduced pressure to give a crystalline solid. Recrystallization from $Me_2CO$ afforded white needles of m.p. 162°. $FeCl_3$ color test was positive. Yield, 0.82 g. (93%). *Anal.* Calcd. for $C_9H_{10}O_3N_2$ (XIII): C, 55.66; H, 5.19; N, 14.43. Found: C, 55.54; H, 5.17; N, 14.73. IR $\nu^{KBr}$ $cm^{-1}$: 1724, 1685, 1621. 1580, 1493, 1269.

**Reaction of 3-Ethoxycarbonylaminopyridine (IX), 3-Acetoacetamidopyridine (XII) and their N-Oxides (X, XIII) with Diketene**——To a solution of 0.5 g. (0.003 mole) of IX in 30 ml. of $CHCl_3$ was added 0.3 g. (0.003 mole) of diketene. After 2 hr. of reflux and removal of the solvent under reduced pressure, the residual solid was recrystallized from petr. ether to recover 0.38 g. (76%) of the starting material (IX).

Similar treatment of X, XII and XIII as above resulted in the recovery of the corresponding starting materials in the yield of 84%, 31% and 75% respectively.

**Reaction of 3-Acetoacetamidopyridine 1-Oxide (XIII) with conc. Sulfuric Acid**——XIII (0.3 g.) was dissolved in 0.2 ml. of conc. $H_2SO_4$. After 30 min. of heating on a steam bath, the reaction mixture was poured onto 20 ml. of ice-water. The solution was passed over a column of Amberlite IR-A 400 and after absorbance of the acidic substance the eluted solution was condensed to yield a crystalline solid which was identical with 3-aminopyridine 1-oxide (XI) by admixture of its picrate with an authentic sample. Yield, 0.06 g. (37%).

**Reaction of 4-Aminopyridine 1-Oxide (XIV) with Diketene**——A solution of 1.1 g. of XIV and 1.1 g. of diketene in $CHCl_3$ was treated similarly as described above. The starting XIV (0.8 g.) was recovered (73%) with 0.31 g. (38%) of dehydracetic acid (XV).

**Reaction of 4-Aminopyridine (XVI) with Diketene**——To a solution of 9.5 g. of XVI in 50 ml. of $CHCl_3$ was added 18.5 g. of diketene in 10 ml. of diketene dropwise with constant stirring. The reaction mixture was warmed on a steam bath at 70~75° for 1 hr. After evaporation of the solvent under reduced pressure, a pale yellow residual solid was obtained, which was washed with petr. ether then with $H_2O$. From the petr. ether washing a small amount of dehydracetic acid (XV) was obtained. The water insoluble residue, which was a crystalline solid, was recrystallized from MeOH to give white needles of m.p. 195.5~197°. Yield, 8.9 g. *Anal.* Calcd. for $C_{13}H_{12}O_3N_2$ (XVII): C, 63.92; H, 4.95; N, 11.47. Found: C, 63.67; H, 5.06; N, 11.18. IR $\nu^{KBr}$ $cm^{-1}$: 1704, 1658, 1575, 1531, 1395, 1163, 854, 834.

Diazo color test and $FeCl_3$ reaction were negative. Iodoform reaction was positive.

The water soluble fraction was condensed under reduced pressure to give a tarrish solid which was purified by chromatography to give a small amount of white needles of m.p. 252~253° and pale yellow needles of m.p. 286~287°.*3

**Reaction of 4-Aminopyridine (XVI) with Dehydroacetic Acid (XV)**——A solution of 0.12 g. of XVI and 0.2 g. of XV in 5 ml. of $CHCl_3$ was warmed on a steam bath for 2 hr. After cooling, separating crystals were collected by filtration. Recrystallization from $Me_2CO$ afforded white prisms of m.p. 142~143° (decomp.). Yield, 0.25 g. (81%). *Anal.* Calcd. for $C_{13}H_{14}O_4N_2$ (XX): C, 59.53; H, 5.38; N, 10.68. Found: C, 59.69; H, 5.43; N, 10.50.

14) T. Murray, C. Hauser: J. Org. Chem., **19**, 2013 (1954); lit. m.p. 124~125°.
15) F. Leonard, A. Wajngurt: *Ibid.*, **21**, 1077 (1956); lit. m.p. 149~150°.
16) C. Hauser, G. Reynolds: *Ibid.*, **15**, 1224 (1950).

XX was chromatographed on alumina to give XVI in a almost quantitative amount. Hydrolyses of XX with 20% HCl resulted in the formation of the starting materials, XV and XVI.

We thank Misses E. Sugawara and N. Nanjo for the elemental analyses and Miss S. Oizumi for the spectral data. Thanks are also due to the Ministry of Education for Grant-in-Aid for Fundamental Scientific Research (Studies on Amine N-Oxide, Representative : Prof. E. Ochiai) of 1960～1962.

## Summary

Reaction of diketene with three of aminopyridine and their N-oxides was examined. 2-Aminopyridine (I) afforded its acetoacetate (II) and 2-methyl-4*H*-pyrido[1,2-*a*]pyrimidin-4-one (III) as a by-product. N-oxide of I (V) afforded its acetoacetate (VI) and 2-[(6-acetoacetamido-2-pyridyl)methyl]-6-methyl-4*H*-pyran-4-one (VII). 3-Amino isomers (VIII and XI) underwent their acetoacetates (XII and XVIII) respectively. Although 4-aminopyridine 1-oxide (XIV) did not react with diketene, 4-aminopyridine (XVI) afforded 1-(4-pyridyl-3-acetyl-6-methyl-2,4-(1*H*,3*H*)-pyridinedione (XVII).

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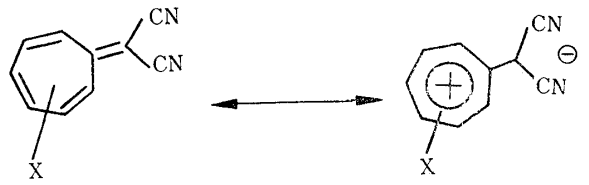
[Chem. Pharm. Bull. 12 (8) 916 ~ 924]

*UDC 547.517*

# 129. Yoshio Kitahara and Tadahiro Kato : Heptafulvenes. IV.*1 Mass Spectra of 8,8-Dicyanoheptafulvene Derivatives.

(*Chemical Research Institute of Non-Aqueous Solutions, Tohoku University**2)

8,8-Dicyanoheptafulvene and a number of its derivatives (I) have been synthesized recently. The ionic structure (Ib) makes a major contribution to the structure of these of derivatives which are considered*1,1,2) to belong to a stable type of aromatic compound possessing a 6$\pi$-electron structure.



I Ib

X=H, alkyl, phenyl, $OCH_3$

Rapid progress has been made[3] in the investigation of the structure of organic compounds and their fragment ions through analysis of the cation mass spectra obtained by electron impact of these compounds.

In this paper, we discuss the mass spectra of the twelve heptafulvene derivatives*3 and two other compounds shown below;

8,8-dicyanoheptafulvene (II), dicyanostyrene (III), phenylpropiolonitrile (IV), 1-methyl-8,8-dicyanoheptafulvene (V), 1-isopropyl-8,8-dicyanoheptafulvene (VI), 2-methyl-8,8-dicyanoheptafulvene (VII), 2-isopropyl-8,8-dicyanoheptafulvene (VIII), 3-methyl-8,8-dicyano-

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*1 part III. Y. Kitahara, K. Doi, T. Kato : Bull. Chem. Soc. Japan, to be published.

*2 Katahira-cho 75, Sendai (北原喜男, 加藤忠弘).

*3 The measured 8,8-dicyanoheptafulvene derivatives were all synthesized in the author's laboratory.

1) T. Nozoe, T. Mukai, K. Osaka, N. Shishido : Bull. Chem. Soc. Japan, 34, 1384 (1961).

2) Tadahiro Kato : Ph. D. Thesis, Tohoku University 1962.

3) For examples. *a*) H. Budzikiewicz, C. Djerassi, D. H. Williams : "Interpretation of Mass Spectra of Organic Compounds," Holden-Day, Inc., San Francisco, 1964. *b*) K. Biemann : "Mass Spectrometry, Organic Chemical Applications," McGraw-Hill Book Company, Inc., New York, 1962.