dioxane was added, and again hydrogenated. After the reaction, the catalyst was removed by filtration, the filtrate was poured into water, and the solution was extracted with Et_2O. The extract was washed with water, dried, and distilled, affording 0.45 g. of a colorless liquid, b.p. 60~62°. Yield, 21.03%.

Summary

The methyl derivatives of 2-, 3-, and 4-methylpyridine, 2-methylthiophene, and 2-methylfuran were synthesized from the corresponding primary alcohol by way of its phenylurethan by treating the alcohol with phenyl isocyanate and catalytic hydrogenation of the urethan formed, in the presence of palladium-black and sodium hydroxide.

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90. Keizo Kitahonoki: Azaditerpenoid. V.[1] Syntheses of 8-Azaperhydrophenanthrene Derivatives from Agathenedicarboxylic Acid.

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Ruzicka and his co-workers[2,3] obtained a diketo-ester (II) by the ozonolysis of dimethyl agathenedicarboxylate (I) during determination of the structure of this resin acid. In the present paper the syntheses of 8-azaperhydrophenanthrene derivatives from the diketo-ester (II) are described.

When the diketo-ester (II) was treated with methanolic ammonia, pyridine derivative (III), m.p. 145~146°, was obtained in 67% yield. The ultraviolet and infrared absorption spectra of this substance indicated the presence of a pyridine ring (U. V. $\lambda_{max}^{95\%EtOH}$ 272 mμ (log ε 3.78)[4]; I. R. λ_{max}^{Nujol} 6.28, 6.38 μ). In this reaction, presumably an intermediate dihydropyridine ring was first formed and then dehydrogenated to the pyridine derivative.[4]

The pyridine ring in (III) resists catalytic reduction[5] and is neither reduced in acetic acid over Adams' platinum-catalyst at atmospheric pressure nor at 3 atm. using Skita's apparatus. When the pyridine derivative (III) was reduced with sodium and ethanol, it was observed that the pyridine ring was reduced to the piperidine ring, partially with the concomitant reduction of the ester group at C-1 to the alcohol group to give several different reduction products. By chromatography and fractional crystallizations of the basic reduction mixture or its benzoates, four isomeric imino-esters and two isomeric imino-alcohols, corresponding to the formulae (IVa) and (Va), respectively, were obtained in a pure state as a free base or benzoate, as shown in Table I. These isomers are considered to be stereoisomers differing in their spatial configurations about the new asymmetric carbon atoms at 7-, 13-, and 14-positions.

Table I.

Reduction product		m. p. (°C)		
		Free base (IVa)	Benzoate (IVb)	
Imino-ester isomers	A	97~97.5	oil	
	B		113~115	
	C		153~156	
	D		154~156	
		Free base (Va)	O-Benzoate (Vc)	Dibenzoate (Vb)
Imino-alcohol isomers	A	153~155		157~158
	B		146~147	182~183

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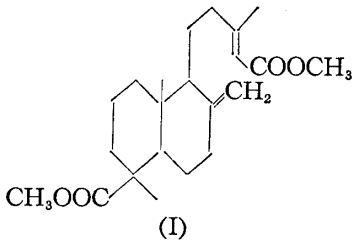
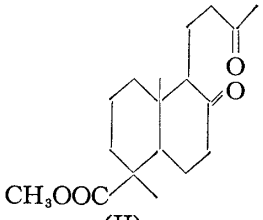
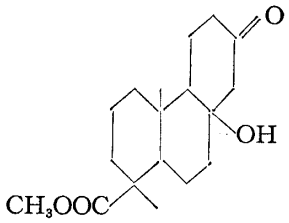
1) Part IV. M. Ohta: This Bulletin, **4**, 273(1956).
2) L. Ruzicka, E. Bernold, A. Tallichet: Helv. Chim. Acta, **24**, 223(1941).
3) cf. R. Zwicky: Dissertation, Eidg. Tech. Hochschule, Zürich(1950).
4) cf. L. Ruzicka, L. Sternbach, O. Jeger: Helv. Chim. Acta, **24**, 504(1941).
5) cf. E. Ochiai: Yakugaku Zasshi, **61**, 298(1941).



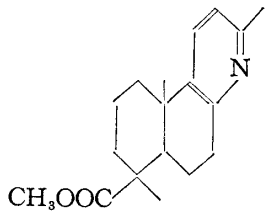
(I)



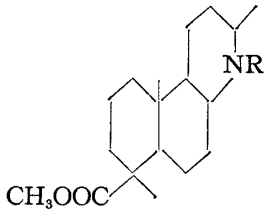
(II)



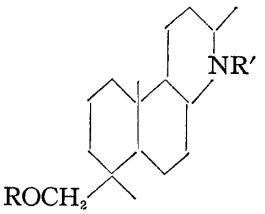
(II')



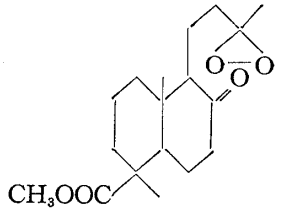
(III)



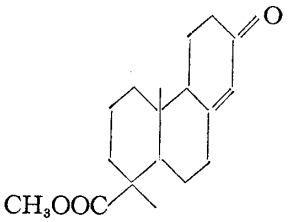
(IVa) R=H
(IVb) R=COC_6H_5
(IVc) R=CH_3



(Va) R=R'=H
(Vb) R=R'=COC_6H_5
(Vc) R=COC_6H_5, R'=H



(VI)



(VII)

The carboxyl group attached to C-1 of agathenedicarboxylic acid is far more hindered than that of abietic acid, and the ester group at C-1 of dimethyl agathenedicarboxylate is difficult to reduce to the alcohol group.[6] Similarly in the case of (III), the ester group should be sterically hindered and resistant to sodium-and-alcohol reduction.

The dibenzoate (Vb), m.p. 157~158°, was hydrolyzed with hydrochloric acid to the imino-alcohol (Va).

As described above, various 8-azaperhydrophenanthrene derivatives were formed by sodium-and-alcohol reduction of (III). An attempt was made to synthesize directly the piperidine ring by catalytic reduction of (II) in methanolic ammonia. The diketo-ester (II), dissolved in 10% methanolic ammonia, gradually absorbed about 2 moles of hydrogen during catalytic reduction over Adams' catalyst. A crystalline product, m.p. 97.0~97.5°, was obtained in 48.7% yield. From the analytical values, infrared absorption spectra, and other characteristics, this compound was found to be the desired 8-azaperhydrophenanthrene derivative (IVa) and identical with the imino-ester A in Table I, obtained by sodium-and-alcohol reduction of (III). This imino-ester was converted to an oily benzoate (IVb) and to an N-methyl derivative (IVc), m.p. 86.5~87°, by methylation with formic acid and formaldehyde solution.

The yield of the diketo-ester (II) from the ozonization of dimethyl agathenedicarboxylate (I) was rather low by Ruzicka's procedure,[2,3] but it was obtained in much better yields (70~80%) by carrying out the ozonization at −40° and decomposing the ozonide with zinc and acetic acid. By-product, such as the peroxide (VI) or the α,β-unsaturated ketone (VII),[2] was not found by this method. Moreover, the diketo-ester, m.p. 217~219°, exhibited a sharp absorption band at 2.85 μ in its infrared spectrum, which is characteristic of tertiary hydroxyl groups.[7] Therefore, this substance should have the isomeric ketol structure (II'), first formed by treatment of the oily diketone (II) with methanolic sodium hydroxide.[8] When the ketol (II') is dissolved in methanolic ammonia, it is considered to open to the diketo-ester (II) and react with ammonia to give a dihydropyridine derivative.[7]

The author expresses his deep gratitude to Prof. E. Ochiai of the University of Tokyo for his kind guidance. He is also grateful to Dr. K. Takeda, Director of this Laboratory, for granting leave of absence in order to carry out this work at the University of Tokyo. The infrared spectra were taken by Mr.

6) L. Ruzicka, J. R. Hosking: Helv. Chim. Acta, **14**, 203(1931); L. Ruzicka, H. Jacobs: Rec. trav. chim., **57**, 509(1938).
7) cf. F. J. McQuillin: J. Chem. Soc., **1955**, 528.
8) Zwicky assumed that the oily diketo-ester was enolized with NaOH solution and transformed to the crystalline substance; see Footnote (3).

Y. Matsui of this Laboratory and the elemental analyses were carried out by the members of the Central Analysis Room of the Faculty of Pharmaceutical Sciences, University of Tokyo, the Analysis Room of Kowa Chemical Laboratories, and the Analysis Room of the Shionogi Research Laboratory, to all of whom the author's thanks are expressed.

Experimental[9]

Agathenedicarboxylic Acid—This resin acid was extracted from Manila-copal with 6% $(NH_4)_2CO_3$ solution according to the procedure of Ruzicka and Hosking.[10] Recrystallization of the crude acid from MeOH gave colorless prisms, m.p. 194~199°. *Anal.* Calcd. for $C_{20}H_{30}O_4$: C, 71.82; H, 9.04. Found: C, 72.10; H, 9.20. $[\alpha]_D^{25}$ +58.9° (l=1, c=4.418, 95% EtOH). The yield differed depending upon the kind of copal used (in one case, 10.7%; in another case, 2.1~2.3%).

Dimethyl Agathenedicarboxylate[2] **(I)**—This was obtained by methylation of the above acid with CH_2N_2 in the usual manner. Colorless oil, $b.p._{0.22}$ 172~174°.

Diketo-ester (II) and Ketol (II')—The above dimethyl ester (3.0 g.) was dissolved in AcOEt (30 cc.) and AcOH (10 cc.). Oxygen containing O_3 (2.5%, v/v) was passed through the solution at −35° to −40° (bath temp.) for 7.3 hrs. at a rate of ca. 100 cc./min. until a Br_2-AcOH solution was no longer decolorized. Zn powder (3.5 g.) and AcOH (10 cc.) were added, the mixture was stirred for 2 hrs. at −5° to −10°, and kept cold overnight. On testing with a Zn-I-starch test paper it showed no color or only a slightly yellow spot. After removal of the remaining Zn powder, the solvent was evaporated *in vacuo* and the residual oil dissolved in ether was washed with 5% Na_2CO_3 and water. Evaporation of the solvent left a yellow oil (2.6 g.), which was distilled to give the diketo-ester (II) as pale yellow oil (2.37 g.), $b.p._{0.003}$ 165~190° (bath temp.). To a solution of the oil in MeOH (25 cc.), 2*N* NaOH solution (25 cc.) was added. Soon crystalline precipitate appeared which was extracted with ether, washed with water, and dried over Na_2SO_4. Evaporation of the solvent gave crystals (2.03 g.), m.p. 211~214°, sparingly soluble in ether and an ether-soluble oil (0.24 g.). The crystals were washed with ether and recrystallized from acetone to colorless prisms, m.p. 217~219°. *Anal.* Calcd. for $C_{18}H_{28}O_4$ (ketol (II')): C, 70.10; H, 9.15. Found: C, 70.04; H, 9.26. $[\alpha]_D^{26}$ +77.7° (l=1, c=5.147, $CHCl_3$). U.V. λ_{max}^{EtOH} 278~282 mμ (ε 23.3). I.R. λ_{max}^{Nujol} μ: 2.85 (OH), 5.82 (C=O, $COOCH_3$).

Pyridine Derivative (III)—The above ketol (2.7 g.) was dissolved in MeOH-NH_3 (MeOH 600 cc., NH_3 89 g.) and the solution was allowed to stand at room temp. for 1 month. The yellow solution was warmed at 50° for 12 hrs. and then evaporated. Ether was added to the brown residue and insoluble substance was removed. The ether solution was extracted with 5% HCl, the aqueous layer was basified with Na_2CO_3, and extracted with ether. This ether solution was washed with water, dried over Na_2SO_4, and evaporated. The residual brown crystals were washed with a small amount of ether to remove the colored material and the pale yellow substance (1.69 g.) was recrystallized twice from ether to colorless prisms, m.p. 145~146°. *Anal.* Calcd. for $C_{18}H_{25}O_2N$: C, 75.23; H, 8.77; N, 4.87. Found: C, 74.99; H, 8.82; N, 5.08. $[\alpha]_D^{23}$ +135.5° (l=1, c=2.181, $CHCl_3$). U.V. $\lambda_{max}^{95\%EtOH}$ 272, 280 mμ (log ε 3.78, 3.67). I.R. λ_{max}^{Nujol} μ: 6.28, 6.38 (pyridine ring), 5.82 ($COOCH_3$).

Reduction of the Pyridine Derivative (III) with Na and EtOH—i) A solution of the pyridine derivative (III) (1.58 g.) in dehyd. EtOH (40 cc.) was heated under reflux in an oil bath (bath temp., 110~120°). To the solution Na (16.2 g.) was added in several portions and some amount of EtOH was also added to dissolve EtONa. After 4 hrs., all amount of Na dissolved and heating was continued for another 1 hr. After cool, the brown solution was poured into water and extracted with ether. The ethereal solution was shaken with 10% HCl, the aqueous layer was basified with Na_2CO_3, and extracted again with ether. The ether solution was washed with water, dried over Na_2SO_4, and evaporated to give a brown oil (1.27 g.). Pyridine (4 cc.) and BzCl (1.5 g.) were added to the oil, the mixture was allowed to stand overnight, and heated in a water bath for 8 hrs. Pyridine was distilled off, ether and water added to the residue, and the insoluble substance (0.25 g.) was collected by filtration. This was recrystallized from acetone to colorless needles, m.p. 279~280°. *Anal.* Calcd. for $C_{24}H_{36}O_2NCl \cdot H_2O$ [HCl-salt of (Vc)]: C, 67.98; H, 9.03; N, 3.30; Cl, 8.36. Found: C, 68.02; H, 9.01; N, 3.35; Cl, 8.38.

A suspension of the HCl-salt (60 mg.) in water was basified with Na_2CO_3 and extracted with ether. The ether solution was washed with water, dried over Na_2SO_4, and evaporated to give a crystalline residue (50 mg.), which was recrystallized from petr. ether-ether to colorless prisms (Vc), m.p. 146~147°. *Anal.* Calcd. for $C_{24}H_{35}O_2N$: C, 78.00; H, 9.55; N, 3.79. Found: C, 77.69; H, 9.58; N, 3.74. $[\alpha]_D^{21}$ +14.0° (l=1, c=1.463, $CHCl_3$). I. R. λ_{max}^{Nujol} 5.83 μ (-OCO-).

Dibenzoate: The above monobenzoate (50 mg.) was benzoylated and the crude oily dibenzoate was chromatographed on alumina (Merck product), yielding almost pure material (50 mg.), which was recrystallized from petr. ether-ether to give colorless needles, m.p. 182~183° (Vb). *Anal.* Calcd. for

9) Melting points were determined in soft-glass capillary tubes and are uncorrected. Infrared spectra were measured with a Perkin-Elmer Single-beam Infrared Spectrophotometer, Model 12C, and the ultraviolet spectra were taken with a Beckman Model DU Spectrophotometer.

10) L. Ruzicka, J. R. Hosking: Ann., **469**, 147 (1929).

$C_{31}H_{39}O_3N$: C, 78.61; H, 8.30; N, 2.96. Found: C, 78.43; H, 8.39; N, 3.39. $[\alpha]_D^{19}$ −76.3° (l=1, c=1.159, $CHCl_3$). I.R. $\lambda_{max}^{Nujol}\mu$: 5.82 (-OCO-), 6.17 (>NCO-).

The above ether solution of the mixture of benzoates was washed successively with 10% Na_2CO_3, 5% HCl, and water, dried over Na_2SO_4, and evaporated. To the residue a small amount of ether was added, crystals (0.27 g.), m. p. 153~156°, which were obtained were chromatographed on alumina in petr. ether-ether (100 : 4), and recrystallized from petr. ether to colorless needles (Vb), m.p. 157~158°. *Anal.* Calcd. for $C_{31}H_{39}O_3N$: C, 78.61; H, 8.30; N, 2.96. Found: C, 78.64; H, 8.02; N, 3.02. $[\alpha]_D^{22}$ +21.4°(l=1, c=1.409, $CHCl_3$). I. R. $\lambda_{max}^{Nujol}\mu$: 5.82 (-OCO-), 6.07 (>NCO-).

Concentration of the filtrate of the above crystals, m.p. 153~156°, gave a second crop of crystals (70 mg.), m.p. 150~153°, which were recrystallized from ether to colorless rods (IVb), m.p. 154~156°. *Anal.* Calcd. for $C_{25}H_{35}O_3N$: C, 75.53; H, 8.87; N, 3.52. Found: C, 75.16; H, 8.64; N, 3.50. I. R. $\lambda_{max}^{Nujol}\mu$: 5.82 ($COOCH_3$), 6.06 (>NCO-). The noncrystallized oil (0.82 g.) from the filtrate of the second crystal, m.p. 150~153°, was separated into four fractions by chromatography on alumina (20 g.) Petr. ether-ether (20 : 1) fraction gave colorless prisms (IVb) (from petr. ether), m.p. 113~115°. *Anal.* Calcd. for $C_{25}H_{35}O_3N$: C, 75.53; H, 8.87; N, 3.52. Found: C, 75.38; H, 9.07; N, 3.87. I.R. $\lambda_{max}^{Nujol}\mu$: 5.815 ($COOCH_3$), 6.075 (>NCO-).

Petr. ether-ether (10 : 1) fraction gave (a) colorless rods (from ether), m. p. 154~156° (IVb), identical with the above benzoate, and (b) colorless needles (50 mg.), m.p. 157~158° (from petr. ether), identical with the above dibenzoate, m.p. 157~158° (Vb).

ii) Pyridine derivative (III) (2.44 g.) was reduced by Na+EtOH as in i). Trituration of the basic reduction product (2.02 g.) with ether and petr. ether afforded crystals (0.32 g.), m. p. 144~151°, which were recrystallized twice from ether to colorless prisms (Va), m. p. 153~155°. *Anal.* Calcd. for $C_{17}H_{31}ON$: C, 76.92; H, 11.77; N, 5.28. Found: C, 76.72; H, 11.74; N, 5.16. $[\alpha]_D^{18}$ +9.8° (l=1, c=1.324, $CHCl_3$). I. R. λ_{max}^{Nujol}: 3.16 μ (OH).

Dibenzoate: Colorless needles, m.p. 157~158° (from ether), identical with the dibenzoate, m.p. 157~158°, from i) (admixture and infrared spectra). *Anal.* Calcd. for $C_{31}H_{39}O_3N$: C, 78.61; H, 8.30; N. 2.96. Found: C, 78.54; H, 8.46; N, 2.93.

The residual oil (1.68 g.) from the filtrate of the above crystals, m.p. 144~151°, was carefully chromatographed on alumina (80 g.) and the following five fractions from the 11 fractions were treated further. Fract. 1. From petr. ether-benzene (10 : 4~10 : 5) : The crystals (50 mg.), after three recrystallizations from petr. ether, gave colorless rods, m.p. 94~97°. This substance showed no depression of m. p. on admixture with the imino-ester (IVa), m.p. 97~97.5°, described below and the infrared spectra of the two samples were identical.

Fract. 2. From petr. ether-benzene (10 : 10~0 : 10) : Crystals (0.14 g.), m.p. 80~95° (unsharp). This was converted to benozoate and chromatographed on alumina. The crystals from the middle fraction (petr. ether-ether) were recrystallized from ether-petr. ether to colorless prisms, m. p. 153~156°, which depressed to 120~131° on admixture with the benzoate (IVb), m. p. 154~156°, from method i). *Anal.* Calcd. for $C_{25}H_{35}O_3N$: C, 75.53; H, 8.87; N, 3.52. Found: C, 75.65; H, 9.02; N, 3.53. I. R. $\lambda_{max}^{Nujol}\mu$: 5.80 ($COOCH_3$), 6.18 (>NCO-).

Fract. 3. From benzene-Et_2O (10 : 0~10 : 2) : Oil (0.14 g.). The benzoate of this oil was chromatographed on alumina and the resulting crystalline substance was recrystallized from petr. ether-ether to give colorless prisms (IVb), m.p. 114~116°. *Anal.* Calcd. for $C_{25}H_{35}O_3N$: C, 75.53; H, 8.87; N, 3.52. Found: C, 75.79; H, 9.16; N, 3.99. I. R.: Almost identical with that of the benzoate (IVb), m. p. 113~115°, from method i); I.R. $\lambda_{max}^{Nujol}\mu$: 5.79 (-OCO-), 6.05 (>NCO-).

Fract. 4. From benzene-Et_2O (10 : 4~0 : 10) : Oil (0.34 g.). The residue was crystallized from petr. ether to scales (0.19 g.), m.p. 40~51° (unsharp). I. R. λ_{max}^{Nujol}: 2.74 μ(OH). This substance (0.18 g.) was converted to benzoate, thereby obtaining a hydrochloride (0.2 g.), sparingly soluble in water, as in i). This was recrystallized from acetone to colorless needles, m. p. 279~282°, identical with the HCl-salt of (Vc), m.p. 279~280°, by admixture and infrared spectra.

Fract. 5. From Et_2O-MeOH (10 : 1~10 : 2) : Crystals (0.18 g.), identical with the above imino-alcohol, m.p. 153~155° (Va).

Hydrolysis of the Dibenzoate (Vb)—A mixture of the dibenzoate (0.21 g.), m. p. 157~158°, conc. HCl (24 cc.), water (9 cc.), and EtOH (6 cc.) was heated in a water bath for 24 hrs. The solution was diluted with water, washed with ether, made alkaline with Na_2CO_3, and extracted with ether. Evaporation of the ether and trituration of the residue with a small amount of ether gave crystals, m. p. 152~156° (40 mg.), which were recrystallized from ether to colorless prisms (Va), m. p. 154~155.5°. This substance showed no depression in m. p. on admixture with the imino-alcohol (Va), m. p. 153~155°, and the infrared spectrum in Nujol differed from that of the latter presumably due to crystal water, but the infrared spectra of the two samples in $CHCl_3$ were identical. *Anal.* Calcd. for $C_{17}H_{31}ON\cdot{}^1/_4H_2O$: C, 75.63; H, 11.76; N, 5.19. Found: C, 76.05; H, 11.63: N, 5.25. I. R. $\lambda_{max}^{Nujol}\mu$: 2.90(OH), 3.06 (NH); $\lambda_{max}^{CHCl_3}$: 2.75 μ (OH).

Catalytic Reduction of the Ketol (II') in Methanolic Ammonia—A solution of the ketol (II') (0.8 g.) in methanolic ammonia (MeOH, 60 cc.; NH_3, 6 g.) was catalytically reduced over Adams' Pt-catalyst

(0.1 g.), gradually absorbing about 2 moles of H_2 (131 cc., 20°) during 40 hrs. After removal of the catalyst, the solution was evaporated to leave a residue, about one-half of which crystallized. The crystals were collected, washed with MeOH, dissolved in dil. HCl, washed with ether, basified with Na_2CO_3, and extracted with ether. Evaporation of the ether left a crystalline residue (0.37 g.), m.p. 93~96°, which was recrystallized from petr. ether to colorless rods, m.p. 97~97.5°. This substance showed a brown yellow color with $C(NO_2)_4$, but did not decolorize a Br_2-AcOH solution or $KMnO_4$-acetone solution, and absorbed no more H_2 in AcOH over Adams' Pt-catalyst. It did not give carbonyl derivatives and carbonyl absorption in its ultraviolet spectrum. *Anal.* Calcd. for $C_{18}H_{31}O_2N$: C, 73.67: H, 10.65: N, 4.77. Found: C, 73.68; H, 10.72; N, 4.81. $[\alpha]_D^{13}$ +42.0° (l=1, c=2.407, 95% EtOH). I.R. $\lambda_{max}^{Nujol}\mu$: 5.85 ($COOCH_3$), 2.94, 3.02(NH).

Benzoate: Oil. $[\alpha]_D^{23}$ −22.6° (l=1, c=3.235, $CHCl_3$). I.R. $\lambda_{max}^{Nujol}\mu$: 5.795 ($COOCH_3$), 6.11(>NCO-), no NH.

N-Methylpiperidine Derivative (IVc)—The above piperidine derivative (0.38 g.), m.p. 97.0~97.5°, was dissolved in a mixture of HCO_2H (90%, 2.8 cc.) and HCHO (30%, 1 cc.), and the solution was heated on a water bath for 6 hrs. After addition of dil. HCl, the solution was evaporated, the residue was dissolved in water, washed with ether, basified with Na_2CO_3, extracted with ether, and dried over Na_2SO_4. The crystalline residue (m.p. 76~79°) was recrystallized from petr. ether to colorless prisms, m.p. 86.5~87.0°. *Anal.* Calcd. for $C_{19}H_{33}O_2N$: C, 74.22; H, 10.81; N, 4.56. Found: C, 74.49; H, 10.96; N, 4.45.

Summary

The ketol (II'), obtained by ozonolysis of dimethyl agathenedicarboxylate, was converted to the pyridine derivative (III), which was reduced with sodium and ethanol to several stereoisomeric imino-esters (IVa) and imino-alcohols (Va). One of the imino-esters was obtained directly by catalytic reduction of the ketol (II') in methanolic ammonia.

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UCD 547.854.4

91. Shigeo Senda and Akio Suzui: Uracil Derivatives and Related Compounds. I. Condensation of Monosubstituted Urea and Ethyl Acetoacetate.

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Synthesis of 6-methyluracil by the condensation of urea and ethyl acetoacetate[1] is well known. Such ring closure reaction of uracil derivatives using monosubstituted ureas (substituents: phenyl, cyclohexyl, and methyl) instead of urea was examined in the present series of work.

For the condensation of phenylurea with ethyl acetoacetate, a mixture of the two compounds was stored over sulfuric acid in a vacuum desiccator until the mixture became dry and powdered, the mixture was dissolved in hot aqueous solution of sodium hydroxide, and the solution was acidified with hydrochloric acid, affording crystals of m.p. 203° in a good yield. This product was not the anticipated uracil compounds but a condensate product of 1 mole of ethyl acetoacetate with 2 moles of phenylurea, indicated by the elemental analysis. Same treatment of a mixture of phenylurea and ethyl 3-(3-phenylureido)-crotonate (I),[2] prepared from ethyl 3-aminocrotonate and phenyl isocyanate, and hydrolysis of its product gave 1-[3-(3-phenylureido)crotonoyl]-3'-phenylurea (II). The above-mentioned product of m.p. 203° was found to be identical with (II). Methylation of (II) with dimethyl sulfate gave 1,6-dimethyl-3-phenyluracil (III), liberating phenylurea which combined with carboxyl group and undergoing ring closure.

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1) Org. Syntheses, Coll. Vol. II, 422(1948).

2) A. Michaelis: Ann., **366**, 377(1909); R. Behrend, F. C. Meyer: Ber., **33**, 622(1900).