[Chem. Pharm. Bull. 13(8) 942~947 (1965)]
UDC 547.91.07 : 547.517.07

123. Ken'ichi Takeda, Hitoshi Minato, Tadao Terasawa, and Chizuko Yanaihara*1 : Studies on Seven-membered Ring Derivatives. IV.*2 6,10-Dimethylbicyclo[5.3.0]decanones obtained from Guaiol.

(*Shionogi Research Laboratory, Shionogi & Co., Ltd.**3)

The structure of guaiol (I) was established by Plattner and his coworkers1) and its stereochemistry has been completely elucidated by us.2)

1) 6,10-Dimethylbicyclo[5.3.0]decan-3-ones

Plattner and Lemay1b) obtained a crystalline *levorotatory* dihydroguaiol (IIa), m.p. 78~79°, $[\alpha]_D$ −54.6°, and an oily *dextrorctatory* dihydroguaiol (IIb), $[\alpha]_D$ +40°, by the catalytic hydrogenation of guaiol (I) with Raney nickel under high pressure; and the Djerassi group3) also obtained the *levorotatory* dihydroguaiol and the impure *dextrorotatory* isomer, $[\alpha]_D$ +21.6°, under similar conditions, and confirmed these structures to be IIa and IIb respectively.

We reinvestigated the catalytic hydrogenation of guaiol according to the method of Plattner1b) and furnished the crystalline dihydroguaiol (IIa) predominating. From the mother liquor, IIa was removed by cooling with dryice-acetone, and the residue was purified by fractional distillation to give almost pure IIb as a colorless oil, b.p. 133~136°/6 mm., $[\alpha]_D$ +46.2°.

When each isomeric dihydroguaiol was oxidized with chromium trioxide in acetic acid solution following the method of Swiss workers,1d) *levorotatory* 6,10-dimethylbicyclo[5.3.0]decan-3-one (IIIa)*4 and the *dextrorotatory* isomer (IIIb)3) were isolated, respectively.

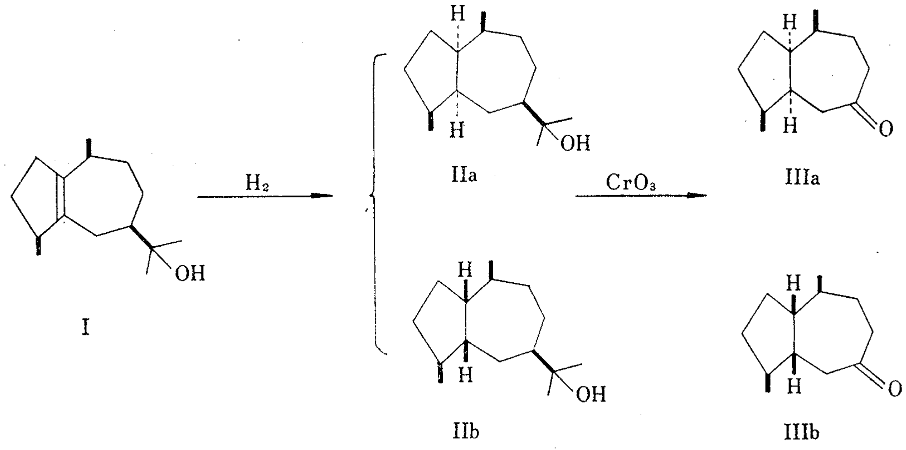

Chart 1.

[*1] Present address : Ojika, Shizuoka, Shizuoka College of Pharmacy.
[*2] Part III. K. Takeda, T. Kubota, W. Nagata : This Bulletin, 1, 241 (1953).
[*3] Fukushima-ku, Osaka (武田健一, 湊　均, 寺沢唯夫, 矢内原千鶴子).
[*4] 2,8-Dimethylbicyclo[0.3.5]decan-5-one according to Plattner.

1) *a*) A. St. Pfau, Pl. A. Plattner : Helv. Chim. Acta, **19**, 858 (1936). *b*) Pl. A. Plattner, L. Lemay : *Ibid.*, **23**, 897 (1940). *c*) Pl. A. Plattner, G. Magyar : *Ibid.*, **24**, 191 (1941). *d*) *Idem* : *Ibid.*, **25**, 581 (1942). *e*) Pl. A. Plattner : *Ibid.*, **24**, 283E (1941).
2) K. Takeda, H. Minato : Tetrahedron Letters, No. 22, 33 (1960); *Idem* : This Bulletin, **9**, 619 (1961); H. Minato : *Ibid.*, **9**, 625 (1961); *Idem* : Tetrahedron, **18**, 365 (1962).
3) E. J. Eisenbraun, T. George, B. Riniker, C. Djerassi : J. Am. Chem. Soc., **82**, 3648 (1960).

On treatment of these two isomeric ketones with semicarbazide hydrochloride, the *levorotatory* ketone (Ⅲa) afforded the crystalline semicarbazone, m.p. 205~206° (Plattner's semicarbazone), whereas the *dextrorotatory* ketone afforded only a small amount of Plattner's semicarbazone (due to the contamination of the starting dihyroguaiol (Ⅱb) with a small amount of Ⅱa). The mother liquid in the latter case was extracted with ether giving a colorless viscous oil, which was soon turned into an amorphous powder. The infrared spectrum of this product showed the absorption bands corresponding to semicarbazone, and showed no band corresponding to the carbonyl group. Therefore, it is assumed that the above-mentioned amorphous powder is the semicarbazone of *dextrorotatory* ketone.

The exchange reaction of this amorphous semicarbazone with other carbonyl compounds or other carbonyl reagents was then examined : the following carbonyl compounds were added to the ethanol solution of the semicarbazone of *dextrorotatory* ketone containing a few drops of acetic acid.

On addition of Ⅲa in the above-mentioned solution, the semicarbazone of Ⅲa, m.p. 205~206°, was obtained in 87% yield leaving *dextrorotatory* ketone in the mother liquid. When acetaldehyde, benzaldehyde or acetophenone were added, these semicarbazones were also obtained in 62.5%, 72.9% or 70% yield respectively, also leaving *dextrorotatory* ketone in the solution.

Moreover, application of 2,4-dinitrophenylhydrazine to the solution of the semicarbazone of *dextrorotatory* ketone afforded a crystalline 2,4-dinitrophenylhydrazone of *dextrorotatory* ketone, m.p. 120~121° (83% yield). On treatment of this 2,4-dinitrophenylhydrazone with pyruvic acid or glyoxal, the pure *dextrorotatory* ketone (Ⅲb), b.p. 100~101°/3 mm., $[\alpha]_D$ $+104.5°$ was obtained. On the other hand, the pure *levorotatory* ketone (Ⅲa), b.p. 107~108°/4 mm., $[\alpha]_D$ $-107.4°$, was similarly obtained by reaction of the semicarbazone of Ⅲa with oxalic acid or glyoxal. As already reported by Djerassi,3) the optical rotatory dispersion studies of these ketones show that Ⅲa exhibits a negative Cotton effect and Ⅲb possesses a Cotton effect curve of an opposite sign.

When 2,4-dinitrophenylhydrazone of Ⅲa recrystallized from ethanol, it gave yellowish orange needles, m.p. 129~140°, while on fractional recrystallization from petr. ether-ether it afforded yellow plates, m.p. 163~163.5° and reddish orange needles, m.p. 164~165° (Mixed melting point of these hydrazones was 128~140°). The ultraviolet spectra of the two hydrazones were completely identical (see Table I).

Table I. UV Spectra of 2,4-Dinitrophenylhydrazones of Ⅲa and Cycloheptanone in Ethanol

	λ_{max}				λ_{min}	
	mμ	log ε	mμ	log ε	mμ	log ε
Yellow crystals	230	4.32	362	4.36	295	3.36
Reddish orange crystals	229	4.34	362	4.38	295	3.46
Cycloheptanone	228.5	3.92	362	3.94	295	3.00

On treatment with pyruvic acid, the isomeric hydrazones were both recovered to the parent ketone (Ⅲa). Moreover, when the two hydrazones were individually heated in the ketone (Ⅲa) as a solvent at 160° for 15 minutes, there was obtained a mixture of these two hydrazones, m.p. 129~140°, which afforded them at a ratio of about 1:1 by fractional recrystallization, respectively.

The infrared spectra of the two hydrazones in chloroform showed them to be almost identical except for the differences of absorption bands at near 1430, 1280~1250 and 1060~1030 cm^{-1}, and showed that the absorption bands corresponding to 2,4-dinitrophenylhydrazone groups are completely identical. Thus, it may be elucidated that the two hydrazones are geometrical isomers.

On the other hand, the ketone (Ⅲb) always furnished only one 2,4-dinitrophenylhydrazone although the recrystallization and the exchange of solvent were repeatedly carried out.

2) 6,10-Dimethylbicyclo[5.3.0]decan-4-one

We wished to prepare 6,10-dimethylbicyclo[5.3.0]decan-4-one (Ⅺ) in order to compare the behavior of its carbonyl derivative with those of 6,10-dimethylbicyclo[5.3.0]decan-3-ones (Ⅲa and Ⅲb) and as a starting material for syntheses of azulenes.

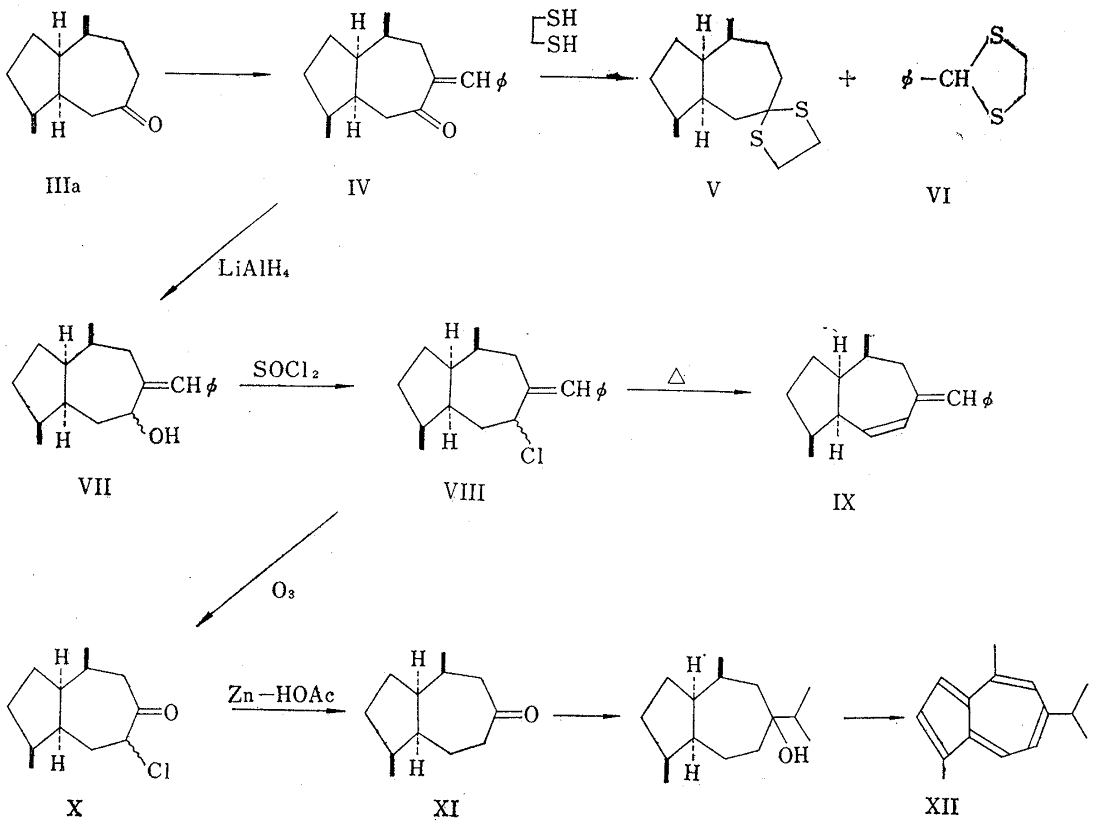

Chart 2.

On treatment of Ⅲa with benzaldehyde, the benzylidene compound (Ⅳ), m.p. 149°, was obtained. The benzylidene compound (Ⅳ) was already reported by Plattner and Magyar,[1d] and the position of condensation with benzaldehyde was established unequivocally by the fact that the ketone (Ⅺ) afforded 1,4-dimethyl-6-isopropylazulene[4] (Ⅻ).

It may be expected that the reduction of the carbonyl group of Ⅳ followed by the oxidizing cleavage of its ethylenic linkage easily afford the objective ketone (Ⅺ).

Huang-Minlon reduction of Ⅳ furnished an amorphous powder, λ_{max} 245 mμ (ε 6700), and Hauptmann's method which aimed at the preparation of the ethylene dithioketal of Ⅳ gave the ethylene dithioketal (Ⅴ) of 6,10-dimethylbicyclo[5.3.0]decan-3-one (Ⅲa), m.p. 111~112°, and an oil, which seemed to be ethylene dithioacetal (Ⅵ) of benzaldehyde in contrast to our expectation.

---

[4] H. Minato, M. Ishikawa, T. Nagasaki: This Bulletin, **13**, 717 (1965).

Then, we intended to eliminate the carbonyl group of Ⅳ *via* hydroxyl group. Reduction of Ⅳ with lithium aluminium hydride afforded the hydroxybenzylidene compound (Ⅶ), m.p. 77~78°, λ_{max} 250 mμ (ε 15080), in good yield.

On treatment of Ⅶ with thionyl chloride, there was obtained an oily chloride (Ⅷ), λ_{max} 250 mμ (ε 10300). In order to purify it, this crude chlorobenzylidene compound was distilled under high reduced pressure to give a colorless oil (Ⅸ), b.p. 137~138°/0.01 mm., which possessed only 1.29% chlorine (the theoretical amount is 12.3%) and showed an absorption band at 279 mμ (ε 16500) in the ultraviolet spectrum. From this result, it may be suggested that Ⅷ is mostly converted into Ⅸ by the elimination of hydrogen chloride during its distillation.

Following, the crude chlorobenzylidene compound (Ⅷ) was ozonized and its ozonide was mildly reduced with zinc in acetic acid to give the α-chloroketone (Ⅹ), m.p. 71~72°. When the ozonide or this α-chloroketone (Ⅹ) was refluxed with zinc in acetic acid, 6,10-dimethylbicyclo[5.3.0]decan-4-one (Ⅺ), m.p. 24~25°, was obtained in ca. 70% yield (calculated from Ⅶ). Although the C-3 ketone (Ⅲa) afford two geometrical isomeric 2,4-dinitrophenylhydrazones as mentioned above, the C-4 ketone (Ⅺ) gave only a yellowish orange hydrazone, m.p. 142~143.5°; and the optical rotatory dispersion curve of Ⅺ shows a positive Cotton effect.

The conformational situation in a seven-membered ring is complicated by the fact that the seven-membered ring is flexible and therefore three ketones (Ⅲa, Ⅲb, and Ⅺ) can possess many forms[5] from the examination of molecular models. Therefore, one may not exclude the possibility that the two isomers of 2,4-dinitrophenylhydrazones of Ⅲa, which were elucidated to be geometrical isomers, still could be the conformational isomers.

Experimental[*5]

***levorotatory* and *dextrorotatory* Dihydroguaiol (IIa and IIb)**——The product which was obtained by catalytic hydrogenation of guaiol (I) according to Plattner's method,[1b] was recrystallized from acetone to give Ⅱa, m.p. 78~79°, $[\alpha]_D$ −54.6°. The mother liquid was cooled in dryice-acetone bath or left longer at −10~−20° to remove the contaminated Ⅱa as the crystalline substance. The filtrate was three times fractionally distilled to give almost pure Ⅱb, b.p. 133~136°/6 mm., n_D^{27} 1.4885, $[\alpha]_D$ +46.2°. *Anal.* Calcd. for $C_{15}H_{28}O$: C, 80.29; H, 12.58. Found: C, 80.31; H, 12.49.

***dextrorotatory* 6,10-Dimethylbicyclo[5.3.0]decan-3-one (IIIb)**——Oily dihydroguaiol (Ⅱb, $[\alpha]_D$ +46.2°) (38.5 g.) was oxidized[1d] with chromium trioxide in HOAc to give a pale yellow oil (28.5 g.), which was distilled as shown below.

TABLE Ⅱ.

	b.p./11 mm. (°C)	Product	$[\alpha]_D$	Yield (g.)
Fraction 1	123~129	a colorless oil	+50.5	8.8
〃 2	130~135	〃	+46.1	8.6
〃 3	135~137	〃	+51.9	2.0
〃 4	138~145	a pale yellow oil	+17.0	2.4
Residue	—	a brown viscous oil	—	6.3

As fraction 4 did not give its 2,4-dinitrophenylhydrazone, it was abandoned.

a) The crude ketone (Fractions 1, 2, 3) gave a crystalline 2,4-dinitrophenylhydrazone (24.7 g.), m.p. 110~119°, which was dissolved in HOAc (200 ml.) and pyruvic acid (30 g.) and heated at 80~85° for 3.5 hr.

[*5] Optical rotations are for EtOH solution with a Rudolph Photoelectric Polarimeter model 200. Unless otherwise specified, UV spectra were taken in 95% EtOH.

[5] J. B. Hendrickson: J. Am. Chem. Soc., 83, 4537 (1961).

The separated 2,4-dinitrophenylhydrazone of pyruvic acid (m.p. 217°, 17.0 g.) was filtered, and the filtrate was extracted with ether. The ether extract was washed with 2*N* Na_2CO_3 and H_2O, dried (Na_2SO_4) and evaporated, leaving a yellow oily ketone (IIIb, 12.5 g.) b.p. 94~96°/4 mm. This ketone (12.0 g.) was converted into semicarbazone in EtOH. As the separated semicarbazone, m.p. 202~204° (360 mg.) was the one of the contaminated ketone (IIIa), it was filtered. The filtrate was extracted with ether, and the ether extract was washed with 2*N* Na_2CO_3 and H_2O, dried (Na_2SO_4) and evaporated, leaving a colorless viscous oily semicarbazone (16.7 g.). A mixture of the oily semicarbazone (3.0 g.) and small excess of benzaldehyde (or acetaldehyde, acetophenone, IIIa) in 90% EtOH containing a few drops of HOAc was refluxed in a steam bath for 5~10 min. After the separated semicarbazone of benzaldehyde, m.p. 214~215°, was filtered, the filtrate was extracted with ether. The ether extract was washed with 2*N* Na_2CO_3 and H_2O, dried (Na_2SO_4) and evaporated, leaving a colorless oil, which was distilled at 100~101°/3 mm. to give *dextrorotatory* ketone (IIIb, 2.0 g., 87% yield), n_D^{25} 1.4799, $[\alpha]_D^{22}$ +104.5° (c=1.952), $\nu_{max}^{CHCl_3}$ 1706 cm^{-1}, λ_{max} 287 mμ (ε 29.2). *Anal.* Calcd. for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.84; H, 11.26. 2,4-Dinitrophenylhydrazone, yellowish orange needles, m.p. 120~121° (from EtOH). *Anal.* Calcd. for $C_{18}H_{24}O_4N_4$: C, 59.98; H, 6.71; N, 15.55. Found: C, 60.25; H, 6.98; N, 15.65.

b) The crude ketone (corresponding to Fractions 1, 2, and 3) (9 g.) was converted into the semicarbazone of IIIa, m.p. 200~203° (190 mg.) and the oily semicarbazone of IIIb (7.1 g.) as described in the method a). The oily semicarbazone was dissolved in Brady's reagent6) and heated in a steam bath for 5 min., and left for 2~3 hr. at room temperature. The separated 2,4-dinitrophenylhydrazone was recrystallized from EtOH to give yellowish orange needles (2,4-dinitrophenylhydrazone of IIIb), m.p. 119~121° (8.9 g., 83% yield). This hydrazone was quantitatively recovered to IIIb on treatment with pyruvic acid.

2,4-Dinitrophenylhydrazones of *levorotatory* Ketone (IIIa)——2,4-Dinitrophenylhydrazone of IIIa, m.p. 129~140°, was fractionally recrystallized from petr. ether-ether to give yellow plates, m.p. 163~163.5° (*Anal.* Calcd. for $C_{18}H_{24}O_4N_4$: C, 59.98; H, 6.71; N, 15.55. Found: C, 59.74; H, 6.57; N, 15.64) and reddish orange needles, m.p. 164~165° (*Anal.* Found: C, 59.74; H, 6.42; N, 15.58). Both hydrazones were recovered to ketones on treatment with pyruvic acid, respectively. The ketone from hydrazone of yellow plates was a colorless oil, b.p. 87~88°/1.5 mm., $[\alpha]_D$ −102.8°, and it from reddish orange needles was a colorless oil, b.p. 86~87°/1.5 mm., $[\alpha]_D$ −100.0°. Both ketones were identical with IIIa by comparison of elemental analyses and IR spectra.

Reaction of Benzylidene Compound (IV) with 1,2-Ethanedithiol——A mixture of IV (1.34 g.) in 1,2-ethanedithiol (4 ml.) and BF_3·ether (2 ml.) was left over night at room temperature, poured into ice-water and steam-distilled to remove excess of 1,2-ethanedithiol. The residue was extracted with ether and the ether extract was washed with 10% NaOH and H_2O, dried (Na_2SO_4) and evaporated leaving a yellow oil. The residue was crystallized from ether to give colorless prisms (V, 600 mg.) m.p. 110~112°, λ_{max} 242 mμ (ε 422), ν_{max}^{Nujol} 1005 and, 855 cm^{-1}. *Anal.* Calcd. for $C_{14}H_{24}S_2$: C, 65.59; H, 9.44; S, 24.97. Found: C, 65.46; H, 9.40; S, 24.95. The mother liquid gave a yellow oil (1.1 g.), which was chromatographed on alumina to give a colorless oil (VI) (740 mg.), ν_{max}^{film} cm^{-1}: 3067, 3030, 1603, 1495, 1276, 1005, 854, 744, 698.

Reduction of Benzylidene Compound (IV) with Lithium Aluminium Hydride——A solution of IV (5 g.) in dry ether (100 ml.) and dry tetrahydrofuran (50 ml.) was added dropwise, with stirring, to a suspension of lithium aluminium hydride (500 mg.) in dry ether (100 ml.) and stirred for 2 hr. at room temperature. The mixture was decomposed by addition of ice-water and then 2*N* H_2SO_4, in an ice-bath, and extracted with ether; the extract was washed with 2*N* Na_2CO_3, dried (Na_2SO_4) and evaporated, leaving pale yellow needles (5.0 g.), which was recrystallized from petr. ether to give colorless needles (VII), m.p. 77~78°, λ_{max} 250 mμ (ε 15080), $[\alpha]_D^{23}$ +102.4° (c=1.178). *Anal.* Calcd. for $C_{19}H_{26}O$: C, 84.39; H, 9.69. Found: C, 84.32; H, 9.80.

Treatment of VII with Thionyl Chloride——A solution of VII (2.7 g.) in chloroform (20 ml.) was added dropwise, with stirring, to a solution of thionyl chloride (1.2 g.) in chloroform (20 ml.) in an ice-bath, and then stirred for 30 min. at room temperature. The solution was evaporated *in vacuo* to leave a brown oil, which was dissolved in ether (20 ml.), washed with ice-water, cooled 5% $NaHCO_3$ and ice-water, dried (Na_2SO_4) and evaporated, leaving a brown oil, crude VIII (3.1 g.), λ_{max} 250 mμ (ε 10030). The crude VIII was distilled at 137~138°/0.01 mm. to give a colorless oil, λ_{max} 279 mμ (ε 16500). *Anal.* Calcd. for $C_{19}H_{25}Cl$: Cl, 12.31. Found: Cl, 1.29.

3-Chloro-6,10-dimethylbicyclo[5.3.0]decan-4-one (X) and 6,10-Dimethylbicyclo[5.3.0]decan-4-one (XI)——a) A solution of crude VIII (2.94 g.) in AcOEt (30 ml.) was treated with O_3 stream (3.2% O_3) at −75°. After 2 equiv. of O_3 was passed, the solution was left at −75° for 30 min. and the solvent was removed *in vacuo* at room temperature, leaving a yellow oil, which was dissolved in HOAc (25 ml.) and reduced with addition of zinc dust (10 g.). The mixture was heated for 1.5 hr. in a steam bath and filtered. The filtrate was evaporated and the residue was extracted with ether. The extract was washed with 5% $NaHCO_3$ and H_2O, dried (Na_2SO_4) and evaporated, leaving a yellowish orange oil (2.6 g.). The residue

---

6) O.L. Brady: J. Chem. Soc., **1931**, 756.

was distilled to give a light yellow oil, b.p. 80～100°/0.1 mm. (X+XI, 1.0 g.) and a colorless oil, b.p. 100～102°/0.1 mm. (X, 310 mg.), colorless needles (from petr. ether), m.p. 71～72°, $[\alpha]_D^{25}$ +71.0° (c=0.944), λ_{max} 286 mμ (ε 24.9), $\nu_{max}^{CHCl_3}$ 1720 cm^{-1}, ORD: $[\alpha]_{700}$ +34°, $[\alpha]_{316}$ +1626°, $[\alpha]_{262.5}$ −2448°, $[\alpha]_{250}$ −2187°; c=0.326 in MeOH; temperature 26°. *Anal.* Calcd. for $C_{12}H_{19}OCl$: C, 67.13; H, 8.86; Cl, 16.51. Found: C, 67.20; H, 8.95; Cl, 16.24. A mixture of the oil, b.p. 80～100°/0.1 mm., and zinc dust in HOAc was refluxed in an oil bath for 1～2 hr. to give ketone (Ⅺ).

b) A solution of crude Ⅷ (4.56 g.) in AcOEt (45 ml.) was ozonized under the same conditions. A mixture of the ozonide and zinc dust (15 g.) in HOAc (30 ml.) was refluxed for 3 hr. in an oil bath and treated under the same conditions as described above to give a yellowish orange oil (3.7 g.), which was distilled at b.p. 84～85°/1 mm. as a colorless oil (XI, 1.85 g., in 67.5% yield calculated from Ⅶ), n_D^{20} 1.4880, d_4^{20} 1.0034, colorless needles, m.p. 24～25° (from petr. ether), λ_{max} 283 mμ (ε 29.3), $\nu_{max}^{CHCl_3}$ 1703 cm^{-1}, $[\alpha]_D^{20}$ +104° (c=1.154). ORD: $[\alpha]_{700}$ +74°, $[\alpha]_{308.5}$ +2740°, $[\alpha]_{266}$ −2551°, $[\alpha]_{250}$ −1958°; c=0.1078 in MeOH; temperature 25°. *Anal.* Calcd. for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.70; H, 11.12. 2,4-Dinitrophenylhyrazone, yellowish orange prisms, m.p. 142～143.5° (from EtOH). *Anal.* Calcd. for $C_{18}H_{24}O_4N_4$: C, 59.98; H, 6.71; N, 15.55. Found: C, 59.53; H, 6.89; N, 15.70.

Summary

levorotatory and *dextrorotatory* 6,10-Dimethylbicyclo[5.3.0]decan-3-ones (Ⅲa and Ⅲb) were derived from guaiol (I), and the former was converted into *dextrorotatory* 6,10-dimethylbicyclo[5.3.0]decan-4-one (Ⅺ).

(Received March 18, 1965)

[Chem. Pharm. Bull. 13(8) 947～950 (1965)]

UDC 547.963.32.07 : 612.398.145

124. Morio Ikehara and Hitoshi Uno: Polynucleotides. I. Formation of Internucleotidic Linkage by Means of Dimethylformamide-Thionyl Chloride Complex.[*1]

(*Faculty of Pharmaceutical Sciences, School of Medicine, Hokkaido University*[*2])

The synthesis of polynucleotides, either by chemical or biochemical means draw the attention of many investigators because of the important role of nucleic acid in the living cells. Activation of mononucleotides by dicyclohexylcarbodiimide (DCC) so as to polymerize them to polynucleotides was extensively studied by Khorana and colaborators.1) The use of DCC as the condensing reagent of 5′-O-tritylthymidine and 3′-O-acetylthymidine 5′-monophosphate was studied and it proved to be the best among other reagents investigated so far.2,3) But there seems to be a need for further search for new condensing agents to obtain much higher polymerizing potency.

During the course of our study of chlorination of inosine derivatives,4,5) we found that, when inosine 5′-monophosphate was treated with DMF[*3]-thionyl chloride

---

[*1] A preliminary account of this study has appeared in Chem. Pharm. Bull., **12**, 742 (1964).

[*2] Nishi 5-chome, Kita 12-jo, Sapporo, Japan (池原森男, 宇野 準).

[*3] N,N-Dimethylformamide.

1) H. G. Khorana: "Some Recent Developments in the Chemistry of Phosphate Esters of Biological Interest.," John Wiley and Sons, Inc., New York, N. Y. (1961), Chapter 5 and following Series of papers of Studies on Polynucleotides.
2) H. G. Khorana, J. P. Viszolyi, R. K. Ralph: J. Am. Chem. Soc., 84, 414 (1962).
3) T. M. Jacob, H. G. Khorana: *Ibid.*, 86, 1630 (1964).
4) M. Ikehara, H. Uno: This Bulletin, **12**, 267 (1964).
5) *Idem*: *Ibid.*, **13**, 221 (1965).