To a solution of VI (35 g) in 250 ml of DMF, 6.3 g of NaH was added with stirring. After 30 min at room temperature, 20 ml of methyl iodide was added portionwise to the mixture and stirring was continued for 2 h. Insoluble materials were filtered off and the filtrate was concentrated *in vacuo*. Water was added to the residue and the mixture was extracted with $CHCl_3$. After removal of $CHCl_3$, 6.2 g of crystals was obtained. Recrystallization of the crystals from MeOH gave 4.9 g (13%) of III, mp 126—128°C. *Anal.* Calcd for $C_{20}H_{21}NO_2$: C, 78.14; H, 6.89; N, 4.56. Found: C, 78.32; H, 7.03; N, 4.56. PMR (60 MHz) (δ): 1.23 (3H, t, $OCH_2C\underline{H}_3$), 2.58 (3H, s, 2-$C\underline{H}_3$), 3.32 (3H, s, $NC\underline{H}_3$), 4.12 (2H, q, $OC\underline{H}_2CH_3$), 5.12 (1H, s, 4-H), 6.80—7.42 (9H, m, Ph). UV λ_{max}^{EtOH} nm (log ε): 230 (sh) (4.09), 331 (4.08).

Mannich Reaction——A representative example is described below. A mixture of 1.0 g (4.1 mmol) of I, 1.34 g (12.2 mmol) of dimethylamine hydrochloride, 0.37 g (12.3 mmol) of paraformaldehyde and 30 ml of dioxane was refluxed for 20 h. After removal of the solvent by evaporation *in vacuo*, water was added to the residue and the resulting mixture was extracted with $CHCl_3$. The $CHCl_3$ layer was washed with NaCl solution and concentrated *in vacuo*. The oily residue was converted to the HCl salt with EtOH–HCl and recrystallization of the salt from EtOH gave 1.04 g (70%) of IIb·HCl, mp 186—187°C. See Table I.

References and Notes

1) J. Aritomi, S. Ueda, and H. Nishimura, *Chem. Pharm. Bull.*, **28**, 3163 (1980); J. Aritomi and H. Nishimura, *Chem. Pharm. Bull.*, **29**, 1193 (1981).
2) B.P. Bangdiwala and C.M. Desai, *J. Indian Chem.*, **31**, 555 (1954).
3) A eutectic mixture containing 26.5% of diphenyl and 73.5% of diphenyl ether.
4) R.T. Couts and D.G. Wibberley, *J. Chem. Soc.*, **1962**, 2518.
5) Bayer A.G., German Patent 2310746 (1974) [*C.A.*, **82**, 4226*u* (1975)].

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Studies on Ketene and Its Derivatives. CVI.[1] Photoreaction of Diketene with *N*-Phenylmaleimide and Dimethyl-*N*-phenylmaleimide

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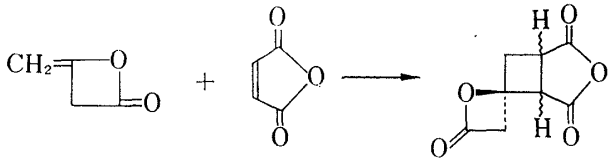
Photoreaction of diketene with *N*-phenylmaleimide (**2**) and its dimethyl derivative **3** gave *rel*-(4*R*,5*S*,6*S*)- and *rel*-(4*R*,5*R*,6*R*)-2-oxo-1-oxaspiro[3.3]heptane-5,6-dicarboximides (**4a** and **4b**) and their dimethyl derivatives **5a** and **5b**, respectively. Alcoholysis of compounds **4a** and **4b** with alcoholic hydrogen chloride gave 5-alkoxycarbonyl-4-oxo-*N*-phenyl-1,2-pentanedicarboximides **7** and **8**, which were transformed to the corresponding 5-alkoxycarbonyl-3-oxoheptanedioates **9** and **10** by further alcoholysis. Compounds **4a** and **4b** were hydrolyzed with 10% hydrochloric acid to give 3-carboxy-5-oxohexanoic acid (**11**). Thermolysis of compounds **4a** and **4b** gave 3-methylenecyclobutane-1,2-dicarboximide (**12**).

Keywords——diketene; photoreaction; *N*-phenylmaleimides; 1-oxaspiro[3.3]-heptanedicarboximides; 4-oxo-1,2-pentanedicarboximides; 3-methylenecyclobutane derivatives; decarboxylation

It is reported that radical reaction of diketene with maleic anhydride in the presence of α,α'-azobisisobutyronitrile gave rise to a maleic anhydride-diketene copolymer.[2] In a previous paper of this series,[3] we reinvestigated this reaction under irradiation and obtained different results; that is, photolysis of a solution of diketene and maleic anhydride afforded adducts, *rel*-(4*R*, 5*S*, 6*S*)- and *rel*-(4*R*, 5*R*, 6*R*)-2-oxo-1-oxaspiro[3.3]heptane-5,6-dicarboxylic anhydride (**1a** and **1b**). The present paper reports an extension of our studies to the photoreaction of diketene with *N*-phenylmaleimide (**2**) and dimethyl-*N*-phenylmaleimide (**3**) to give the

corresponding oxaspiro[3.3]heptane derivatives **4** and **5**, respectively. The same reaction in acetonitrile as a solvent instead of acetone resulted in the recovery of the starting imide.



1a, b

Chart 1

Photoreaction of Diketene with *N*-Phenylmaleimide (2)

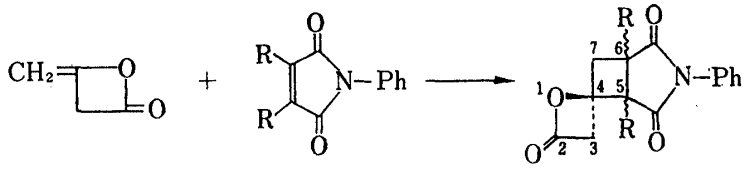
When a solution of diketene and *N*-phenylmalemide (**2**) in acetone was irradiated, a crystalline substance was obtained. Purification by silica gel column chromatography afforded two crystalline products, *rel*-(4*R*, 5*R*, 6*R*)-2-oxo-*N*-phenyl-1-oxaspiro[3.3]heptane-5,6-dicarboximide (**4a**), and its *rel*-(4*R*, 5*S*, 6*S*) isomer **4b**, in 24 and 55% yields, respectively. Structural assignments were made on the basis of the following results. First, elemental analyses and mass spectra showed both to be 1:1 adducts of diketene and the imide **2**. Infrared (IR) spectra indicated the presence of the β-lactone carbonyl (**4a**, 1840 cm^{-1}; **4b**, 1845 cm^{-1}) and the imide carbonyl (**4a**, 1780 and 1705 cm^{-1}; **4b**, 1790 and 1715 cm^{-1}). Nuclear magnetic resonance (NMR) spectra showed signals due to two methylene, two methine, and aromatic protons. These data are consistent with the spirobicyclic structure **4**. Concerning the C_5–C_6 conformation, we assigned the *cis* configuration in view of the report by Robson *et al.*,[4] who investigated the photoreaction of maleic anhydride with cyclohexene to yield bicyclo-[4.2.0]octane-7,8-dicarboxylic anhydride (**6**) as an intermediate, to which they gave the *endo* and *exo cis* configurations **6a** and **6b** because four-membered rings fused to five-membered rings in the *trans* configuration would be very strained. Indeed, as far as we know, there is no example of such a ring system. Next, NMR spectra showed the signals of C_3 methylene protons of compound **4a** at higher field (3.43—3.88 ppm) than those of compound **4b** (3.72—4.12 ppm). This observation suggests that the C_3 methylene of compound **4a** exists on the opposite side to the C_5-imide carbonyl, while that of compound **4b** exists on the same side. Therefore, we concluded that the C_4–C_5 conformation of compound **4a** is *cis*, while that of compound **4b** is *trans*.

Photoreaction of Diketene with Dimethyl-*N*-phenylmaleimide (3)

Similar reaction of diketene with dimethyl-*N*-phenylmaleimide (**3**) afforded 5,6-dimethyl-2-oxo-*N*-phenyl-1-oxaspiro[3.3]heptane-5,6-dicarboximide (**5**) in good yield. Purification by silica gel column chromatography gave the *rel*-(4*R*, 5*R*, 6*R*) **5a** and the *rel*-(4*R*, 5*S*, 6*S*) **5b**, in 28 and 59% yields, respectively. Structural assignments were made as follows. First, elemental analyses and mass spectra indicated the two to be 1:1 adducts of diketene and **3**. IR spectra showed the presence of β-lactone carbonyl (**5a**, 1850 cm^{-1}; **5b**, 1845 cm^{-1}) and imide carbonyl (**5a**, 1785 and 1715 cm^{-1}; **5b**, 1780 and 1715 cm^{-1}). NMR spectra showed the presence of two methyl, two methylene, and aromatic protons. These data are consistent with the spirobicyclic structure **5**. The C_5–C_6 conformation was assigned the *cis*- structure by analogy with compound **4**. Since the C_3 methylene protons of compound **5a** (3.38—3.85 ppm, ABq) appeared at higher field in the NMR spectra than those of compound **5b** (3.54—4.00 ppm, ABq), the conformations of the C_4–C_5 linkage of compounds **5a** and **5b** were assigned as *cis* and *trans*, respectively.

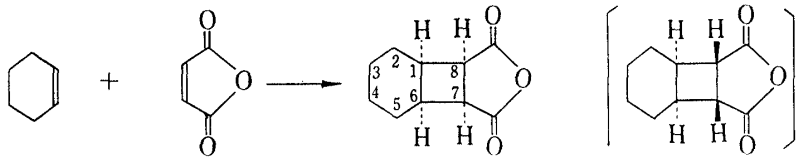
Reaction of 2-Oxo-*N*-phenyl-1-oxaspiro[3.3]heptane-5,6-dicarboximide (4a and 4b)

Methanolysis of the *rel*-(4*R*, 5*R*, 6*R*)-spiro[3.3]heptane **4a** with methanol saturated with hydrogen chloride at room temperature for 1 h gave 4-methoxycarbonyl-4-oxo-*N*-phenyl-



2 : R=H
3 : R=Me

4 : R=H
4a : *rel*-(4*R*,5*R*,6*R*)
4b : *rel*-(4*R*,5*S*,6*S*)
5 : R=Me
5a : *rel*-(4*R*,5*R*,6*R*)
5b : *rel*-(4*R*,5*S*,6*S*)

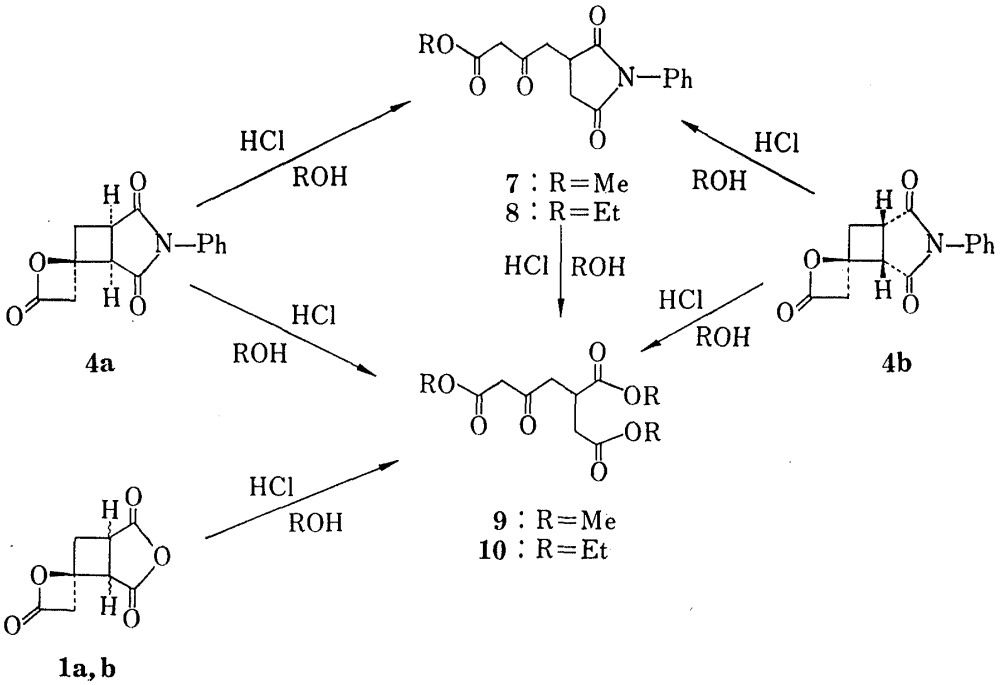


6a **6b**

Chart 2

1,2-pentanedicarboximide (**7**) in 80% yield. Similar reaction of the *rel*-(4*R*, 5*S*, 6*S*) isomer **4b** under the same conditions gave the same product **7** in 77% yield. When the reaction was carried out under reflux or at room temperature for several days, dimethyl 5-methoxycarbonyl-3-oxoheptanedioate **9** or diethyl 5-ethoxycarbonyl-3-oxoheptanedioate **10** was obtained. The dioates **9** and **10** were also obtained by further alcoholyses of the pentanedicarboximides **7** and **8** in 66 and 70% yields, respectively.

Compounds **7** and **8** were characterized on the basis of elemental analyses and spectroscopic data detailed in the experimental section. Compounds **9** and **10** were identified by comparison



7 : R=Me
8 : R=Et

4a **4b**

9 : R=Me
10 : R=Et

1a, b

Chart 3

of spectral data with those of authentic samples obtained from compound **1** according to the literature.[3)]

Hydrolysis of compound **4a** with 10% hydrochloric acid gave 3-carboxy-5-oxohexanoic acid (**11**) in 68% yield. Similarly, compound **4b** was hydrolyzed to give the acid **11** in 71% yield. Compound **11** was also obtained by hydrolysis of compound **1**. Heating of compound **4a** at 195°C resulted in the elimination of carbon dioxide to give the known compound 3-methylene-*N*-phenylcyclobutane-1,2-dicarboximide (**12**) in almost quantiative yield, and this compound was also obtained from compound **4b** under the same reaction conditions. Structural assignment was made on the basis of elemental analyses and spectroscopic data as described in the experimental section.

Similarly, thermolysis of compound **1** gave the known compound 3-methylenecyclobutane-1,2-dicarboxylic anhydride **13**.

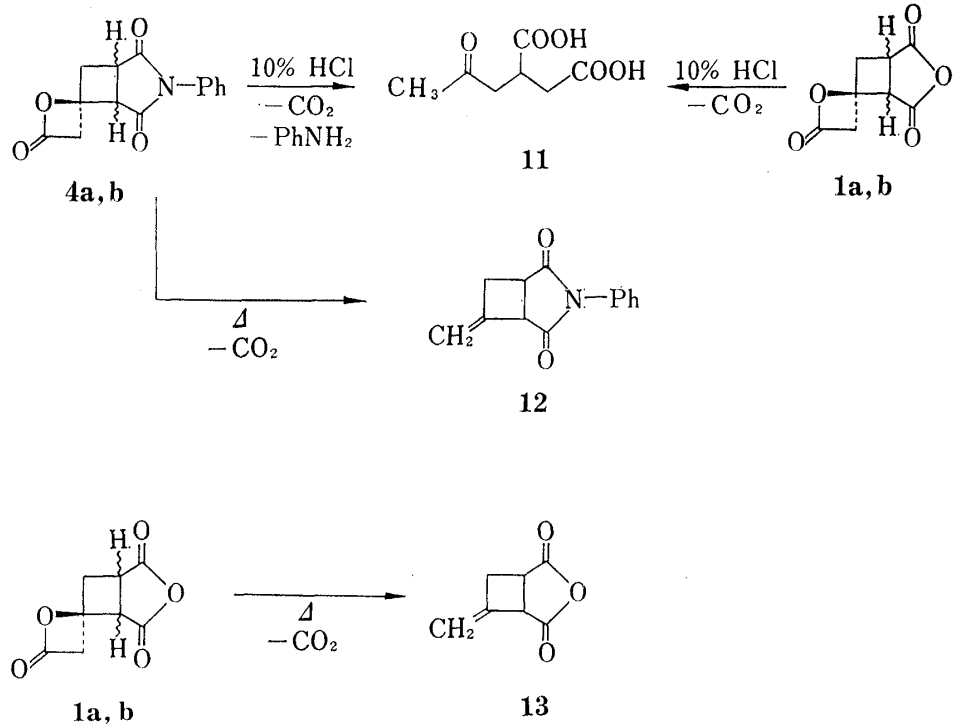


Chart 4

Experimental

A chamber reactor (The Southern New England Ultraviolet Company, trade mark Rayonet) was used for photoreactions. IR spectra were taken with a JASCO model IR-S spectrometer. NMR spectra were recorded (with tetramethylsilane as an internal standard) on Hitachi model R-20A and JEOL model PS-100 spectrometers at 60 and 100 MHz, respectively.

Reaction of Diketene with *N*-Phenylmaleimide (2)——A solution of compound **2** (1.73 g, 0.01 mol) and diketene (8.4 g, 0.1 mol) in acetone (100 ml) was irradiated with light at 3000 Å for 24 h. The reaction mixture was concentrated under reduced pressure. The residue (2.6 g) was subjected to silica gel (50 g) column chromatography using benzene and ethyl acetate as eluents. The benzene elution gave the starting imide **2**. Elution with the mixture of benzene and ethyl acetate (95 : 5) gave *rel*-(4*R*,5*R*,6*R*)-2-oxo-*N*-phenyl-1-oxaspiro[3.3]heptane-5,6-dicarboximide (**4a**) as leaves (from benzene) (0.62 g, 24%), mp 189°C (dec.). *Anal.* Calcd for $C_{14}H_{11}NO_4$: C, 65.36; H, 4.31; N, 5.45. Found: C, 65.35; H, 4.20; N, 5.18. IR ν_{max}^{KBr} cm^{-1}: 1840, 1780, 1705. NMR (DMSO-d_6) δ: 2.84—3.32 (2H, m, CH_2), 3.43—3.88 (2H, ABq, J=17.5 Hz, CH_2), 3.47—3.70 (1H, m, CH), 3.96—4.06 (1H, m, CH), 7.26—7.64 (5H, m, C_6H_5). Elution was continued with ethyl acetate to give the *rel*-(4*R*,5*S*,6*S*)-1-oxaspiro[3.3]heptanedicarboximide **4b** as needles (from ethyl acetate) (1.41 g, 55%), mp 179—181°C (dec.). *Anal.* Calcd for $C_{14}H_{11}NO_4$: C, 65.36; H, 4.31; N, 5.45. Found: C, 65.39; H, 4.34; N, 5.41. IR ν_{max}^{KBr} cm^{-1}: 1845, 1790, 1715. NMR (DMSO-d_6) δ: 2.65—3.42 (3H, m, CH_2

and CH), 3.72—4.12 (2H, ABq, $J=17.5$ Hz, CH_2), 4.06—4.11 (1H, m, CH), 7.22—7.63 (5H, m, C_6H_5).

Reaction of Diketene with Dimethyl-*N*-phenylmaleimide (3)——A solution of the imide 3 (0.6 g, 0.003 mol) and diketene (2.52 g, 0.03 mol) in acetone (30 ml) was irradiated for 22 h. After removal of the solvent and excess diketene by distillation under reduced pressure, the resulting residue (1.2 g) was subjected to silica gel (18 g) column chromatography. Elution with *n*-hexane–ether (10: 1) gave the recovered imide 3. Elution was continued with *n*-hexane–ether (10: 4) to give *rel*-(4*R*,5*R*,6*R*)-5,6-dimethyl-2-oxo-*N*-phenyl-1-oxaspiro[3.3]heptane-5,6-dicarboximide (**5a**) as prisms (from benzene) (0.24 g, 28%), mp 154—155°C. *Anal.* Calcd for $C_{16}H_{15}NO_4$: C, 67.36; H, 5.30; N, 4.91. Found: C, 67.26; H, 5.56; N, 4.78. IR ν_{max}^{KBr} cm^{-1}: 1850, 1785, 1715. NMR (DMSO-d_6) δ: 1.38 (3H, s, CH_3), 1.41 (3H, s, CH_3), 2.64—3.16 (2H, ABq, $J=16$ Hz, CH_2), 3.38—3.85 (2H, ABq, $J=17$ Hz, CH_2), 7.30—7.60 (5H, m, C_6H_5). Elution with ether gave the *rel*-(4*R*,5*S*,6*S*)-1-oxaspiro[3.3]heptanedicarboximide **5b** as scales (from ether) (0.5 g, 59%), mp 184—185°C. *Anal.* Calcd for $C_{16}H_{15}NO_4$: C, 67.36; H, 5.30; N, 4.91. Found: C, 67.62; H, 5.11; N, 4.83. IR ν_{max}^{KBr} cm^{-1}: 1845, 1780, 1715. NMR (DMSO-d_6) δ: 1.36 (3H, s, CH_3), 1.44 (3H, s, CH_3), 2.88 (2H, s, CH_2), 3.54—4.00 (2H, ABq, $J=$ 17 Hz, CH_2), 7.26—7.56 (5H, m, C_6H_5).

5-Methoxycarbonyl-4-oxo-*N*-phenyl-1,2-pentanedicarboximide (7)——a) Compound **4a** (0.26 g) was dissolved in methanol (6 ml) saturated with dry hydrogen chloride. After being stirred for 1 h at room temperature, the reaction mixture was condensed under reduced pressure. Water was added to the residue, and the mixture was extracted with chloroform. The chloroform solution was washed with water, dried over sodium sulfate, and concentrated *in vacuo*. The residue was purified by silica gel (10 g) column chromatography using ether as an eluant to give the product **7** as an oil (0.23 g, 80%). *Anal.* Calcd for $C_{15}H_{15}NO_5$: C, 62.28; H, 5.23; N, 4.84. Found: C, 62.42; H, 5.24; N, 4.91. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1785 (sh), 1740 (sh), 1715. NMR ($CDCl_3$) δ: 2.38—3.05 (2H, m, CH_2), 3.05—3.40 (2H, m, CH_2), 3.45 (2H, s, CH_2), 3.55—3.67 (1H, m, CH), 3.69 (3H, s, OCH_3), 7.15—7.60 (5H, m, C_6H_5).

b) Similarly, compound **4b** (0.26 g) was treated with methanol saturated with dry hydrogen chloride to give the product **7** (0.2 g, 77%).

5-Ethoxycarbonyl-4-oxo-*N*-phenyl-1,2-pentanedicarboximide (8)——Following a procedure similar to that given for the methyl ester **7**, compound **4b** (0.26 g) was treated with ethanol saturated with dry hydrogen chloride to give the product **8** as an oil (0.26 g, 81%). *Anal.* Calcd for $C_{16}H_{17}NO_5$: C, 63.36; H, 5.65; N, 4.62. Found: C, 63.12; H, 5.58; N, 4.54. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1780 (sh), 1740 (sh), 1715. NMR ($CDCl_3$) δ: 1.28 (3H, t, $J=7$ Hz, $OCH_2\underline{CH_3}$), 2.41—3.40 (5H, m, $2\times CH_2$ and CH), 3.47 (2H, s, CH_2), 4.22 (2H, q, $J=7$ Hz, $OC\underline{H_2}CH_3$), and 7.20—7.65 (5H, m, C_6H_5).

Dimethyl 5-Methoxycarbonyl-3-oxoheptanedioate (9)——a) Compound **4b** (0.26 g) was dissolved in methanol (5 ml) saturated with dry hydrogen chloride. After being stirred for 6 d at room temperature, the mixture was concentrated *in vacuo*. The residue was diluted with water, and the mixture was extracted with dichloromethane. The dichloromethane extract afforded the product **9** (0.17 g, 65%), bp 109—110°C (0.02 mmHg), whose IR spectrum was identical with that of an authentic sample (lit.[3] bp 109—110°C (0.02 mmHg)).

b) A solution of compound **4b** (0.02 g) in methanol (5 ml) saturated with dry hydrogen chloride was refluxed for 5 h. Treatment as described above gave the product **9** (0.16 g, 61%).

c) A solution of compound **7** (0.29 g) in methanol (5 ml) saturated with dry hydrogen chloride was stirred for 5 d at room temperature. Treatment as described above gave the product **9** (0.17 g, 66%).

Diethyl 5-Ethoxycarbonyl-3-oxoheptanedioate (10)——a) Following the procedure described for the methyl ester **9**, compound **4a** (0.26 g) was treated with ethanol (5 ml) saturated with dry hydrogen chloride to give the product **10** (0.2 g, 66%), bp 116—120°C (0.05 mmHg) (lit.[3] bp 116—120°C (0.05 mmHg)).

b) Similar reaction of compound **4b** (0.26 g) with dry hydrogen chloride in ethanol (5 ml) gave the product **10** (0.21 g, 70%).

c) Similarly, compound **8** (0.3 g) was treated with ethanol (5 ml) saturated with dry hydrogen chloride to give the product **10** (0.21 g, 70%).

3-Carboxy-5-oxohexanoic Acid (11)——a) A mixture of compound **4a** (0.26 g) in 10% hydrochloric acid (2 ml) was heated on a water bath at 85—90°C for 3 h. The mixture was extracted with ether, and the ether solution was concentrated. The residue was rubbed with a glass rod in light petroleum. Crystals that separated were collected and recrystallized from a mixture of ether and light petroleum to give the product **11** (0.12 g, 68%), mp 105—106°C (lit.[5] mp 107°C).

b) Similar treatment of compound **4b** (0.26 g) gave the product **11** (0.12 g, 71%).

3-Methylene-N-phenylcyclobutane-1,2-dicarboximide (12)——a) Compound **4a** (0.51 g) was heated at 195°C for 15 min. The residual oil was distilled under reduced pressure to give the product **12** (0.38 g, 95%), bp 114°C (0.006 mmHg), mp 90°C (lit.[6] mp 86—86.5°C).

b) Similarly, heating of compound **4b** (0.51 g) gave the product **12** (0.38 g, 90%).

3-Methylenecyclobutane-1,2-dicarboxylic Anhydride (13)——Compound **1** (0.91 g) was heated at 175°C for 20 min. Vacuum distillation gave the product **13** (0.56 g, 82%), bp 79—80°C (0.45 mmHg) (lit.[6] bp 155°C (25 mmHg)).

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tion, Science and Culture, Japan. The authors are indebted to the staff of the Central Analysis Room of this Institute for elemental analyses and spectral measurements.

References and Notes

1) Part 105: T. Kato, M. Sato, Y. Kitagawa, and R. Sato, *Chem. Pharm. Bull.*, **29**, 1624 (1981).
2) K. Hayashi, R. Toepfl, and A. Maeder (Ciba-Geigy A.-G.) Ger. Patent, 2342300/1974 [*Chem. Abstr.*, **81**, p121399*t* (1974)].
3) T. Kato, T. Chiba, and S. Tsuchiya, *Chem. Pharm. Bull.*, **28**, 327 (1980).
4) R. Robson, P.W. Grubb, and J.A. Berltrop, *J. Chem. Soc.*, **1964**, 2153.
5) K. Alder and H. Soll, *Ann.*, **565**, 57 (1949).
6) H.N. Cripps, J.K. Williams, V. Tullio, and W.H. Sharkey, *J. Am. Chem. Soc.*, **81**, 4904 (1959).

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Cannabis. XIV.[1] Two New Propyl Cannabinoids, Cannabicyclovarin and Δ^7-*cis*-Iso-tetrahydrocannabivarin, from Thai Cannabis

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Two new neutral propyl cannabinoids, cannabicyclovarin and Δ^7-*cis*-iso-tetrahydrocannabivarin have been isolated from Thai cannabis, "Meao strain." This is the first report of isolation of the latter, which has a novel skeleton, from natural sources.

Keywords——Moraceae; Cannabis; propyl cannabinoid; cannabicyclovarin; Δ^7-*cis*-iso-tetrahydrocannabivarin; structure

As a continuation of our studies on cannabis, we have isolated new neutral propyl cannabinoids[2] and propyl cannabinoid acids[3] from Thai cannabis, 'Meao strain'. We now wish to describe the isolation and the structure elucidation of two new propyl cannabinoids from this Thai cannabis.

Cannabinoid acid fraction, which was obtained as described previously,[3] was decarboxylated and repeatedly purified by column chromatography on Silica gel and finally by preparative thin-layer chromatography (TLC) to give two new compounds, **1** and **2**, together with tetrahydrocannabivarin (THCV),[4] cannabichromevarin (CBCV),[2] tetrahydrocannabinol (THC), cannabichromene (CBC) and cannabivarin (CBV).[5]

The first compound, **1**, $C_{19}H_{26}O_2$, $[\alpha]_D$ 0°, colorless needles, mp 134—135.5°C, showed positive coloration with diazotized benzidine (red). The ultraviolet (UV) spectrum suggested the presence of a non-conjugated benzene ring (276, 284 nm). The proton nuclear magnetic resonance (^{1}H-NMR) spectrum showed signals for one methyl group at δ 0.79 which was at abnormally high field compared with other cannabinoids, two methyl groups at δ 1.37, one benzyl methylene group at δ 2.44 as a triplet, one methine proton at δ 2.56 (dd, J=8 and 9 Hz), one benzyl methine proton at δ 3.04 (d, J=9 Hz), a hydroxyl proton at δ 4.40, and two aromatic protons at δ 6.17 and δ 6.32 (each d, J=2 Hz). This ^{1}H-NMR spectrum was similar to that of cannabicyclol (CBL)[6] except for the methylene region. The mass spectrum (MS) exhibited fragments, m/z 286 (M^+), 271, 204, 203 (100%) and 174. This fragmentation pattern is also the same as that of CBL,[7] except that all the masses are 28 units smaller. These data suggest that the new neutral propyl cannabinoid may be cannabicyclovarin (CBLV) and the structure