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Deamination of Methylenecyclopropylcarbinylamine. The Formation of a Vinyl Cation by Carbon–Carbon Bond Cleavage[1]

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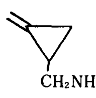
The deamination of methylenecyclopropylcarbinylamine, prepared from ethyl methylenecyclopropanecarboxylate *via* the corresponding amide, gave acetylcyclopropane, methylenecyclopropylcarbinol, and 3-methylenecyclobutanol. On the basis of these results and the deuterium distribution of the deamination products of methylenecyclopropylcarbinylamine-α,α-d_2, the homoallylic (III) and cyclopropylvinyl (VIII) cations are proposed as intermediates.

The deamination reactions of cyclopropylcarbinylamine derivatives have been very scrupulously investigated in connection with the problem of the structure of the intermediate cation.[3] The deamination reaction of methylenecyclopropylcarbinylamine (**1**), which we wish to report on here, merits even further investigation because the introduction of an *exo*-methylene group leads to some stereochemical features which are absent in the heretofore-investigated cyclopropylcarbinyl systems.

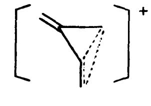
Two bicyclobutonium intermediates, I and II, are possible for this ring system; of them, I may be further stabilized by two allylic resonances with the *exo*-methylene group (I′), though the stabilization by such an interaction would be decreased by an unfavorable configuration of the *exo*-methylene group and the cationic center at the transition state. On the other hand, the formation of II requires the loosening of a relatively strong sp^2–sp^3 carbon bond and it involves a contribution from a vinyl cation, which is generally considered to be formed only with difficulty.

Another possible intermediate, II, which is a homoallylic-type intermediate, may exist. Although stabilization by homoallylic resonance has been calculated to be less than that by bicyclobutonium resonance,[4] in the particular case of III the scale model indicates that the cationic center is ideally situated for an effective (p-π type) interaction with the *exo*-methylene π-electrons.

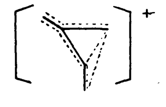
A tricyclobutonium intermediate, IV, may also be considered although the possibility of the intermediacy of such a species has been eliminated in the case of the cyclopropylcarbinyl cation.[5,6]



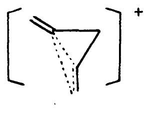
1



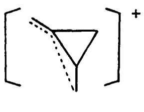
I



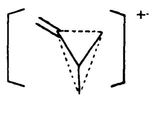
I′



II



III



IV

Results and Discussion

Methylenecyclopropylcarbinylamine (**1**) was prepared as is shown in Scheme 1. Ethyl methylenecyclopropanecarboxylate (**2**)[7] was converted to methylenecyclopropanecarboxamide (**3**) by ammonolysis, or through the steps of the hydrolysis of

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[1] a) Taken from the Master of Science thesis of A. N. b) A part of this work has appeared in a preliminary communication: A. Nishimura, H. Kato and M. Ohta, *J. Amer. Chem. Soc.*, **89**, 5083 (1967).

[2] To whom inquiries should be addressed.

[3] See, for example, a) R. Breslow, " Molecular Rearrangements," Part I, ed. by P. de Mayo, Interscience Publishers, New York (1963), p. 254; b) P. D. Bartlett, " Nonclassical Ions," Benjamin Inc., New York (1965); c) G. D. Sargent, *Quart. Rev.* (London), **20**, 301 (1966).

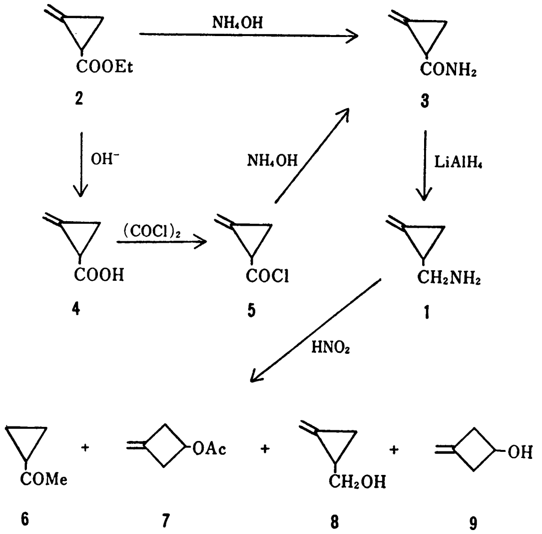
[4] M. E. H. Howden and J. D. Roberts, *Tetrahedron*, **19**, *Suppl.*, **2**, 403 (1963).

[5] R. H. Mazur, W. N. White, D. A. Semenow, C. C. Lee, M. S. Silver and J. D. Roberts, *J. Amer. Chem. Soc.*, **81**, 4390 (1959). See, however, I. Lillien and L. Handloser, *Tetrahedron Lett.*, **1969**, 1035.

[6] J. E. Baldwin and W. D. Foglesong, *J. Amer. Chem. Soc.*, **90**, 4311 (1968).

[7] a) J. A. Carbon, W. B. Martin and L. R. Swett, *ibid.*, **80**, 1002 (1958). b) E. F. Ullman and W. J. Fanshawe, *ibid.*, **83**, 2379 (1961).

2 to the acid **4**, the conversion to acid chloride, **5**, with oxalyl chloride, and the treatment of **5** with ammonia. The amide, **3**, was converted to methylenecyclopropylcarbinylamine (**1**) by treatment with lithium aluminum hydride.



Scheme 1. Preparation and deamination of methylenecyclopropylcarbinylamine.

The deamination of **1** with nitrous acid in aqueous acetic acid gave four major products[8] (**A**—**D**) in a vpc-area ratio of 1.0 : 2.3 : 1.9 : 12.7 ; these products were separated by vpc and were identified as acetylcyclopropane (**6**), 3-methylenecyclobutyl acetate (**7**), methylenecyclopropylcarbinol (**8**), and 3-methylenecyclobutanol (**9**) respectively on the basis of the facts to be presented below.

The presence of an acetyl group in the component **A** could be detected by means of an NMR signal at τ 7.85 together with an infrared band at 1700 cm^{-1}, while a multiplet NMR signal at τ 9.0—9.4 was indicative of the presence of a cyclopropane ring. Its mass spectrum established its molecular weight and the presence of an acetyl group by peaks at *m/e* 84 and 43 (base peak). Its structure was confirmed to be **6** by a comparison of its spectral data and vpc retention times with those of authentic acetylcyclopropane.[9]

The infrared spectra of the component **C** suggested the presence of a hydroxyl group and of a terminal methylene group by bands at 3350, 3070, and 890 cm^{-1}. Its NMR spectrum displayed a broad two-proton singlet at τ 4.70 and a one-proton singlet at τ 7.09, supporting the idea of the presence of a terminal methylene group and of a hydroxyl group ; a two-proton doublet at τ 6.65 suggestive of a methylene group adjacent to the hydroxyl group, and a three-proton multiplet at τ 8.10—9.35 indicative of the presence of a cyclopropyl group. It was proved identical with methylenecyclopropylcarbinol, (**8**), prepared by the lithium aluminum hydride reduction of **2**.[7a]

The infrared spectrum of the component **D** showed absorption bands at 3320 and 1100 and at 3070, 1670, and 880 cm^{-1}, suggesting the presence of a secondary hydroxyl group and a terminal methylene group respectively. Its NMR spectrum indicated a terminal methylene proton by a two-proton quintet (J=2 Hz) at τ 5.23, a methine proton by a one-proton quintet (J=7 Hz) at τ 5.75, and a four-proton multiplet at τ 6.85—7.75. These spectral data are in accord with those of 3-methylenecyclobutanol (**9**).[10]

The NMR spectrum of the component **B** was similar to that of **9** except that the hydroxyl proton signal of **9** was replaced by a new three-proton singlet at τ 8.15,[11] and its infrared spectrum showed the bands of a terminal methylene group (3080, 1680 and 882 cm^{-1}) and bands at 1740 and 1240 cm^{-1} assignable to an ester group. These spectral data are consistent with 3-methylenecyclobutyl acetate (**7**) structure for the component **B**. This assignment was further corroborated by the fact that the acetylation of **9** gave **7**, and by the fact that the lithium aluminum hydride reduction converted **7** to **9**, as judged by their vpc retention times.

One of the components present in a minor proportion had, on a vpc column, a retention time identical with that of the acetylation product of methylenecyclopropylcarbinol, but it could neither be isolated nor further characterized.

The deamination, in aqueous acetic acid, of methylenecyclopropylcarbinylamine - α,α - d_2 (**1** - **d₂**), itself prepared by the lithium aluminum deuteride reduction of **3**, gave α,α-dideuteriomethylenecyclopropylcarbinol and 2,2-dideuterio-3-methylenecyclobutanol (and its acetate). The quantity of deuterated acetylcyclopropane isolated in this experiment was too small to permit the determination of the position(s) of deuteration.

Among the reaction products, 3-methylenecyclobutanol (**9**) and acetylcyclopropane (**6**) deserve special consideration.

The bicyclobutonium intermediate I appears to be favored because of a possible stabilization of the cation I by allylic resonance (I′). Such an allylic resonance, however, should not be considered an efficacious one because the *exo*-methylene group cannot interact effectively with the cationic center at the transition state because of their unfavorable

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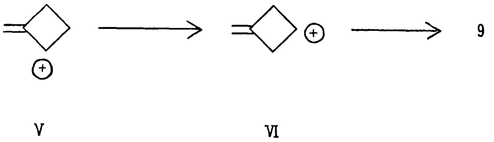
[8] These four components constituted 87% of the total products in the peak area, and most of other minor products had shorter retention times than those of **A**—**D**.

[9] G. W. Cannon, R. C. Ellis and J. R. Leal, " Organic Syntheses," Coll. Vol. IV, p. 597 (1963).

[10] D. E. Applequist and G. F. Fanta, *J. Amer. Chem. Soc.*, **82**, 6393 (1960).

[11] Other NMR signals (τ): 5.12—5.50 (3 H, m; $=CH_2+H\text{-}C\text{-}O$), 6.8—7.5 (4 H, m; ring protons).

configurations. Moreover, neither 2-methylenecyclobutanol nor 2-methylene-3-buten-1-ol was found to be formed in a detectable quantity, as would be the case with a reaction product arising from the intermediate I. Appelquist,[10,12] on the basis of the results of the deamination of spiropentylamine, suggested the rearrangement of the 2-methylenecyclobutyl cation (V) to the 3-methylenecyclobutyl cation (VI) by a hydride migration. The possibility of the formation of **9** in the present experiment by this mechanism can, however, be eliminated since, if **1** first formed the cation V and it was then rearranged to VI, then the alcohol, **9**, formed should be deuterated equally on the 1- and 2-positions. The 3-methylenecyclobutanol isolated from the present experiment, however, had all the deuterium atoms solely on the 2-position.

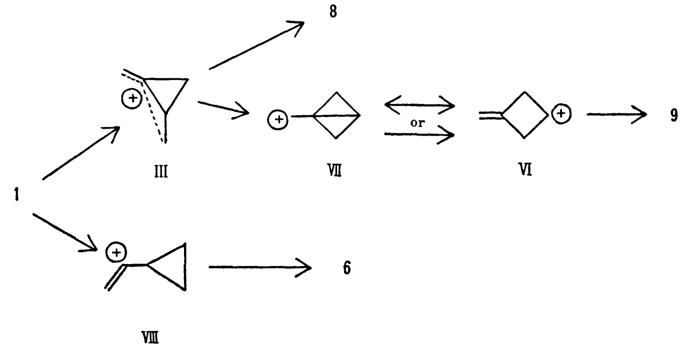


An alternative bicyclobutonium ion II[6] can structurally account for the formation of both methylenecyclopropylcarbinol (**8**) and 3-methylenecyclobutanol (**9**). However, methylenecyclopropylcarbinol was deuterated only on the α-methylene group. This means that the bicyclobutonium ion II is not in equilibrium with another bicyclobutonium ion of an identical structure. The presence of such an equilibirum has been established with the bicyclobutonium ion;[5] thus, the intermediacy of II in this case is open to question.

Finally, the homoallylic intermediate, III, can be considered to be the precursor of the formation of both **8** and **9** if the isomerization of the intermediate III to VI is taken into account.

At present, it cannot be concluded whether or not the relief of strain in passing from the methylenecyclopropylcarbinyl to the 3-methylenecyclobutyl cation and the stabilization by conversion to a secondary cation is enough to compensate for the delocalization energy usually attainable by having a bicyclobutonium ion. Although it is generally accepted that a bicyclobutonium ion is, in general, capable of much more stabilization than a homoallyl cation, in the special case of III the conformation of III may favor the homoallylic cation by permitting an effective interaction of the cationic center with the *exo*-methylene π-electrons with a small entropy change, and/or the degree of stabilization of a bicyclobutonium ion may be lessened because of the extra strain imposed by the introduction of an *exo*-methylene group. In fact, the participation of the nitrogen atom to form an aza-bicyclobutonium ion, structurally analogous to III, in the solvolysis of both 1-*t*-butyl-3-azetidinyl- and 1-*t*-butyl-2-aziridinylcarbinyl derivatives has already been discussed.[13]

Considered in a classical way, the predominant formation of **9** rather than **8** may be considered to be a result of a vinyl group being a much better migrating group than a methyl group. Here, also, an intermediate similar to the homoallylic cation is considered to play an important role in creating this good migrating aptitude of a vinyl group.[14,15]



Scheme 2. Deamination pathway of methylenecyclopropylcarbinylamine.

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[12] This mechanism has been questioned: E. F. Kiefer and J. D. Roberts, *J. Amer. Chem. Soc.*, **84**, 784 (1962). See also: L. M. Konzelman and R. T. Conley, *J. Org. Chem.*, **33**, 3828 (1968).

[13] V. R. Gaertner, *Tetrahedron Lett.*, **1968**, 5919; J. A. Deyrup and C. L. Moyer, *ibid.*, **1968**, 6179. An unpublished work of Martin and Anderson on the participation of sulfur atom in the solvolysis of 3-thietane derivative has been cited in these reports and in Ref. 10. These authors, however, also state that the ability of such a participation is poorer in the three-membered than in the four-membered ring, and absence of π-election participation in 3-methylene-cyclobutyl cation has been reported.[12]

[14] W. Herz and G. Caple, *J. Org. Chem.*, **29**, 1691 (1964); R. S. Bly and R. T. Swindell, *ibid.*, **30**, 10 (1965), and references cited therein.

[15] A completely different mode of ring cleavage has recently been reported with acid-catalyzed dehydration of phenyl-substituted methylenecyclopropylcarbinols. A. W. Herriott, E. P. Olavarria and W. M. Jones, *ibid.*, **33**, 3804 (1968).

The most unexpected result of the present work is the formation of acetylcyclopropane, albeit in a low yield. A tricyclobutonium intermediate, IV, may be considered to be an attractive candidate for the formation of **6**. The possibility of such a type of intermediate has, however, been denied with the cyclopropylcarbinyl system ; also, the results of the labeling experiment with **1** is not in accord with this intermediate. The intermediate IV should give methylenecyclopropylcarbinol (**8**) with an equal deuterium distribution on the α-methylene and the cyclopropane ring.

Thus, the only remaining possible precursor for the formation of **6** is the cyclopropylvinyl cation (VIII). It is rather unexpected that a vinyl cation, which is generally believed to be obtainable only with difficulty, is formed even by the cleavage of a carbon-carbon bond, although there have recently been several examples of the formation of a vinyl cation intermediate by protonation and by π-electron migration.[16] The relief of strain in going from 1 to the cyclopropylvinyl cation, and the stabilization of the cationic center by the cyclopropane ring, probably accounts for this anomalous result.

To conclude, no adequate discussion is possible on the exact nature of the intermediate(s) or transition state(s) on the basis solely of the findings of a rather indiscriminate " hot cation " generated by deamination reaction. A solvolysis study of this and related systems would afford more fruitful information on this problem. Our preliminary attempt along this line, however, was unsuccessful because the reaction of methylenecyclopropylcarbinol with naphthalene-2-sulfonyl chloride gave a rearrangement product, 3-methylenecyclobutyl naphthalene-2-sulfonate.

Experimental[17]

Methylenecyclopropanecarboxylic Acid (4).[18] A solution of 5 g of ethyl methylenecyclopropanecarboxylate (**2**)[7] in 140 m*l* of methanol containing 4 g of potassium hydroxide was refluxed for one hour. The mixture was then diluted with 50 m*l* of water, acidified with hydrochloric acid, and extracted with ether. The extract was dried over magnesium sulfate and subsequently distilled to give 3.0 g (89% yield) of an acid, **4**, boiling at 101—103°C/17 mmHg; n_D^{25} 1.4660.

Methylenecyclopropanecarbonyl Chloride (5).[18] Oxalyl chloride (43 g) was added to 6.8 g of the acid, **4**, with external cooling, and then the resulting mixture was refluxed for two hours. Distillation gave 5.0 g (70% yield) of a liquid boiling at 42—43°C/19 mmHg; n_D^{25} 1.4695.

This substance, on treatment with methanol, was converted to methyl methylenecyclopropanecarboxylate.[19]

Methylenecyclopropanecarboxamide (3).

a). Into 10 m*l* of concentrated aqueous ammonia, 5 g of acid chloride **5** was added with stirring while the temperature was kept below 10°C. The mixture was concentrated under reduced pressure, and the residue was extracted with hot ethyl acetate. The extract, on cooling, afforded 2.4 g (62% yield) of **3** melting at 102.5—104°C. Its infrared spectrum was identical with, and its melting point was undepressed on admixture with, the specimen of **3** prepared by the procedure *b*.

b) A mixture of 14.2 g of the ester **2** and 50 m*l* of supersaturated aqueous ammonia was sealed in a pressure bottle and then allowed to stand for ten days. The residue which remained after the removal of the ammonia was recrystallized from benzene to give 7.8 g (71% yield) of **3** melting at 102—104°C.

Found: C, 62.16; H, 7.27; N, 14.16%. Calcd for C_5H_7NO: C, 61.84; H, 7.27; N, 14.42%.

Methylenecyclopropylcarbinylamine (1). To a stirred suspension of 4.5 g of lithium aluminum hydride in 120 m*l* of ether, 7.7 g of the amide **3** was added in portions, after which the resulting mixture was refluxed for eight hours. Aqueous sodium hydroxide (30%) was added to decompose the excess hydride, and the organic layer was decanted from the precipitate. The precipitate was washed with ether, and the combined extract was dried over magnesium sulfate and then distilled to give 2.8 g (42.5% yield) of a colorless liquid boiling at 105—115°C. Its purity was estimated to be *ca*. 90% by vpc (Carbo wax 20 M on Diasolid A). This crude product was used for the deamination study; the product composition was calibrated by the deamination of the vpc-purified sample of **1**. n_D^{25} 1.4725 (pure sample).

IR (cm^{-1}): 3360, 3295 (NH_2), 3065, 1745, 886 ($=CH_2$), 3040, 1019 (cyclopropane ring). NMR (τ): 4.90 (2H, m, $=CH_2$), 7.52 (2H, d, $J=6$ Hz; CH_2–N), 8.30—9.40 (3 H, m, ring protons), 9.02 (2 H, s, NH_2).

Phenyl isothiocyanate adduct: mp 70—71°C.

Found: C, 66.29; H, 6.68; N, 12.91%. Calcd for $C_{12}H_{14}N_2S$: C, 66.03; H, 6.47; N, 12.84%.

Methylenecyclopropylcarbinylamine-α, α-d_2 (1-d_2). This was prepared, by the method described above, from 3.0 g of the amide **3** and 2 g of lithium aluminum deuteride. A fraction distilling at 100—102°C was col-

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[16] M. Bertrand and M. Santelli, *Chem. Commun.*, **1968**, 718; D. S. Noyce and K. E. DeBruin, *J. Amer. Chem. Soc.*, **90**, 372 (1968); D. S. Noyce and M. D. Schiavelli, *ibid.*, **90**, 1020 (1968); M. Hanack, S. Bocher, K. Hummel and V. Vött, *Tetrahedron Lett.*, **1968**, 4613; M. Hanack and V. Vött, *ibid.*, **1968**, 4617; H. Fischer, K. Hummel, and M. Hanack, *ibid.*, **1969**, 2169; and references cited therein and in Ref. 1b.

[17] All melting and boiling points are uncorrected, and the melting points were determined on a micro hot stage. The infrared spectra were recorded as neat liquid on a Hitachi model EPI-SII Spectrophotometer. The NMR spectra were determined using a JEOLCO C-60 (60 MHz) Spectrometer on solutions of carbon tetrachloride containing tetramethylsilane as internal standard, and the chemical shifts are reported by τ values. Mass spectra were taken on a Hitachi RMU-5 Spectrometer, and the vpc analyses were performed with a Shimadzu model GC-1B chromatograph.

[18] For the preparation of **4** and **5**, *cf.* Ref. 7 b.

[19] A. Nishimura, M. Ohta and H. Kato, This Bulletin, Manuscript under preparation. This compound was prepared by a base-catalyzed ester exchange of the corresponding ethyl ester **2**.

lected to give 1.0 g of **1-d$_2$**. The NMR peak at τ 7.52 of **1** completely vanished in this compound.

Deamination of the Amine 1. To a cooled and stirred solution of 2 g of **1** in 10 m*l* of 20% aqueous acetic acid, a solution of 3.6 g of sodium nitrite in 7 m*l* of water was added over a period of twenty minutes, after which the stirring was continued for seven hours. The mixture was then saturated with sodium chloride and extracted with ether. The extract was dried over sodium sulfate, and the ether was removed by fractional distillation. The residual oil was separated into four main components by vpc (Carbowax 20 M on Diasolid A). The product composition and pertinent spectral data, and the method used in identifying the products, have been described above.

Methylenecyclopropylcarbinol (8). To a stirred suspension of 3 g of lithium aluminum hydride in 100 m*l* of ether, 8.5 g of **2** was added slowly, and then the resulting mixture was stirred for three hours at room temperature. The mixture was decomposed by the addition of concentrated aqueous sodium hydroxide, the organic layer was separated, and the precipitate was washed with ether. The combined ether extract was dried over magnesium sulfate and subsequently distilled to give 3 g (45% yield) of a colorless liquid boiling at 142—146°C, n_D^{25} 1.4585.

Found: C, 71.06; H, 9.87%. Calcd for C_5H_8O: C, 71.39; H, 9.59%.

IR (cm^{-1}): 3340 (OH), 3070, 890 (=CH$_2$), 1015 (C-O). NMR (τ): 4.73 (2 H, m, =CH$_2$), 6.65 (2 H, d, J=7 Hz; -CH$_2$-O), 8.00 (1 H, s, -OH), 8.10—9.40 (3 H, m, ring protons).

p-Nitrobenzoate of **8:** mp 43.5—45°C.

Found: C, 61.57; H, 4.99; N, 6.29%. Calcd for $C_{12}H_{11}NO_4$: C, 61.80; H, 4.75; N, 6.01%.

Deamination of 1-d$_2$. The deuterated amine **1-d$_2$** (0.8 g) was treated with sodium nitrite by the method described above, and the products were separated by vpc.

The deuteriomethylenecyclopropylcarbinol obtained by this experiment showed no NMR peak at τ 6.6, and the NMR spectrum of deuteriomethylenecyclobutanol showed, among other signals, a two-proton triplet (J=2 Hz) at τ 5.28 and a two-proton multiplet centered at τ 7.3.

3-Methylenecyclobutyl Naphthalene-2-sulfonate. To a stirred solution of 1.0 g of **8** in 10 m*l* of 2,4,6-collidine, 3.0 g of 2-naphthalenesulfonyl chloride was added under cooling with an ice-salt bath; the mixture was kept at this temperature for two hours and then poured into 20 m*l* of 20% sulfuric acid containing ice. The resulting mixture was washed with aqueous sodium bicarbonate, dried over sodium sulfate, and concentrated under reduced pressure, and the residue was recrystallized from ether to give 1.0 g of crystals melting at 85—87°C.

Found: C, 65.86; H, 5.34%. Calcd for $C_{15}H_{14}O_3S$: C, 65.69; H, 5.15%.

NMR (τ; CDCl$_3$): 2.05 (1 H, m), 2.45—3.05 (6 H, m), 5.54 (1 H, t, J=6 Hz), 5.61 (2 H, pentuplet, J=2 Hz), 7.44 (4 H, d×t, J=6 and 2 Hz).

We are indebted to Miss Mizuko Yoshida for her measurement of the NMR spectra, to the microanalysis staff of this laboratory for the elemental analyses, and to Mr. Haruyoshi Sakurai for his measurement of the mass spectra.