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Syntheses and Thermal Rearrangements of N-Imino-1,2,5,6-tetrahydropyridinium and N-Imino-Δ^3-pyrrolinium Ylides[1]

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The thermolysis of the N-ethoxycarbonylimino-1,2,5,6-tetrahydropyridinium ylides (**8**), which were prepared from the corresponding parent N-ethoxycarbonyliminopyridinium ylides (**10**) by successive sodium borohydride reduction and methylation with methyl iodide, gave the [2,3] rearrangement products, 3-vinyltetrahydropyrazoles (**15**), and the elimination products, pentadienylhydrazines (**16**). In contrast, the thermolysis of the pyrrolinium ylide (**9**), which was prepared from N-methyl-Δ^3-pyrroline by N-amination and ethoxycarbonylation, gave the [1,2] rearrangement product, tetrahydropyridazine derivative (**18**), and did not give the [2,3] rearrangement product (**20**).

Keywords——thermolysis; [1,2]-sigmatropic rearrangement; [2,3]-sigmatropic rearrangement; N-ylides; N-iminotetrahydropyridinium ylides; N-iminopyrrolinium ylides; tetrahydropyrazoles; pentadienylhydrazines; ^{13}C–NMR

Thermal reactions of aminimides have been well documented[3] and the allyl-N-acylammonium ylides (**1**) are known to undergo competing [1,2]- and [2,3]-sigmatropic rearrangements to give the corresponding products (2) and (3) in a ratio that depends upon the ylide structure and the reaction conditions.[4] It has also been reported that the five-membered cyclic C-ylides (4) undergo a Stevens-type [1,2] rearrangement, however, in contrast, the six-membered ylides (5) give only [2,3] rearrangement products.[5] On the other hand, both

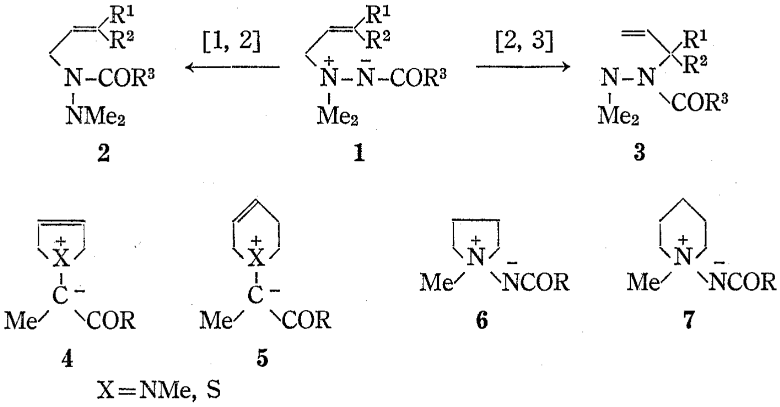

Chart 1

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[2] Location: *Kanagawa-machi, Kanazawa, 920-11, Japan.*

[3] For examples: A.R. Lepley and A.G. Giumanini, "Mechanisms of Molecular Migrations," ed. by B.S. Thyagrajan, Wiley-Intersciences, New York, 1971, Vol. 3, p. 297; W.J. McKillip, E.A. Sedor, B.M. Culbertson, and S. Wawzonek, *Chem. Rev.*, **73**, 255 (1973); and refs. cited therein.

[4] D.G. Morris, *Chem. Commun.*, **1969**, 1345; K. Chantrapromma, W.D. Ollis, and I.O. Sutherland, *J. Chem. Soc. Chem. Commun.*, **1977**, 97.

[5] S. Mageswaran, W.D. Ollis, and I.O. Sutherland, *J. Chem. Soc. Chem. Commun.*, **1973**, 656; W. Ando, S. Kondo, K. Nakayama, K. Ichibori, H. Kohoda, H. Yamato, I. Imai, S. Nakaido, and T. Migita, *J. Am. Chem. Soc.*, **94**, 3870 (1972).

saturated cyclic N-ylides (6)[6] and (7)[7] have been shown to undergo the [1,2] rearrangement by heating to give the corresponding ring expansion products.

Therefore, it seemed of interest to examine the thermal behaviour of the title unsaturated cyclic N-ylides in connection with the above-mentioned studies. We report here the syntheses and the results of thermolysis of the ylides (**8**) and (**9**).

The ylides (**8a**—**c**) and (**9**) were prepared by the following procedures. The corresponding parent N-ethoxycarbonyliminopyridinium ylides (**10a**—**c**)[8] were reduced with sodium borohydride to give the 1-ethoxycarbonylamino-1,2,5,6-tetrahydropyridines (**11**), which were characterized by spectral comparison with the acyl- and benzoyl-amino analogues already reported.[9] Methylation of **11** with methyl iodide gave the salts (**12**), which were treated with an alkali such as sodium hydroxide to give the desired tetrahydropyridinium N-ylides (**8a**—**c**) in good yields.

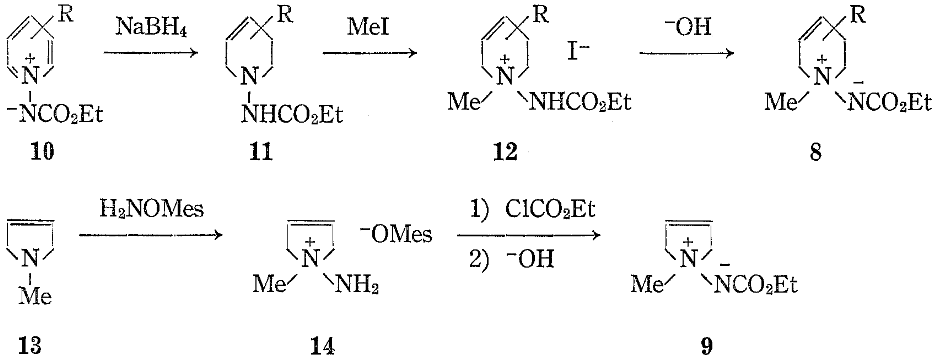

Chart 2

The salt (**14**) was prepared by N-amination of N-methyl-Δ^3-pyrroline (**13**) with O-mesitylenesulfonylhydroxylamine (MesONH$_2$) according to the method of Tamura and co-workers.[10] The pyrrolinium ylide (**9**) was obtained from the salts (**14**) by ethoxycarbonylation with ethyl chloroformate, followed by treatment with an alkali.

All the new ylides obtained were characterized by elemental analysis and infrared (IR), nuclear magnetic resonance (NMR), and mass (MS) spectroscopy.

Thermolysis of the six-membered cyclic ylides (**8a**—**c**) at 150—160° under reduced pressure gave 3-vinyltetrahydropyrazoles (**15**) and pentadienyl hydrazines (**16**) in the yields of 10—12% and 20—25%, respectively. Besides them, the methyl group cleavage products (**11**)[11] and the N–N bond cleavage products, 1-methyl-1,2,5,6-tetrahydropyridines, were also obtained in 10—15% and *ca.* 10% yields. The structures of the products (**15a**—**c**) and (**16a**—**c**) were confirmed by ^{13}C–NMR (Table I), ^{1}H–NMR, and other spectral data (see Experimental Section).

The formation of the pyrazoles (**15**) may involve a [2,3]-sigmatropic rearrangement by analogy with the case of the C-ylides (**5**) and the hydrazines (**16**) may be formed by a cyclic elimination mechanism.[12] However, the Stevens-type rearrangement products, 1,2-diazepine derivatives (**17**), could not be obtained.

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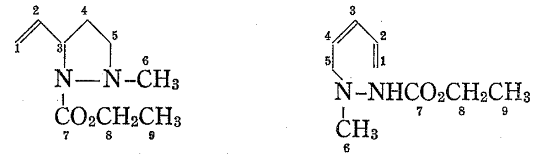
6) S. Wawzonek and R.C. Gueldner, *J. Org. Chem.*, **30**, 3031 (1965).
7) S. Wawzonek and J.G. Stephanie, *J. Org. Chem.*, **36**, 2467 (1971).
8) T. Sasaki, K. Kanematsu, A. Kakehi, I. Ichikawa, and K. Hayakawa, *J. Org. Chem.*, **35**, 426 (1970); A. Balasubramanian, J.M. McIntosh, and V. Snieckus, *ibid.*, **35**, 433 (1970).
9) A. Ohsawa, M. Hirobe, and T. Okamoto, *Yakugaku Zasshi*, **92**, 73 (1972); E.E. Knaus and K. Redda, *J. Heterocyclic Chem.*, **13**, 1237 (1976).
10) Y. Tamura, J. Minamikawa, and M. Ikeda, *Synthesis*, **1977**, 1; and refs. cited therein.
11) cf. G. Wittig and H. Sommer, *Ann. Chem.*, **594**, 1 (1955).
12) R. Paul and S. Tchelitcheff, *Bull. Soc. Chim. France*, **1967**, 1289.

Table I. ^{13}C–NMR Chemical Shifts[a] of **15a** and **16a**



15a **16a**

Position	ppm	ppm
C-1	115.338(t)[b]	119.036(t)
C-2	139.242(d)	126.016(d)
C-3	60.974(d)	131.535(d)
C-4	31.366(t)	132.991(d)
C-5	54.664(t)	55.939(t)
C-6	45.564(q)	45.321(q)
C-7	155.561(s)	155.866(s)
C-8	61.520(t)	61.035(t)
C-9	14.743(q)	14.621(q)

a) δ-values in CDCl$_3$ with reference to internal TMS.
b) (s) indicates singlet, (d) doublet, (t), triplet, and (q), quartet measured at partially decoupled conditions.

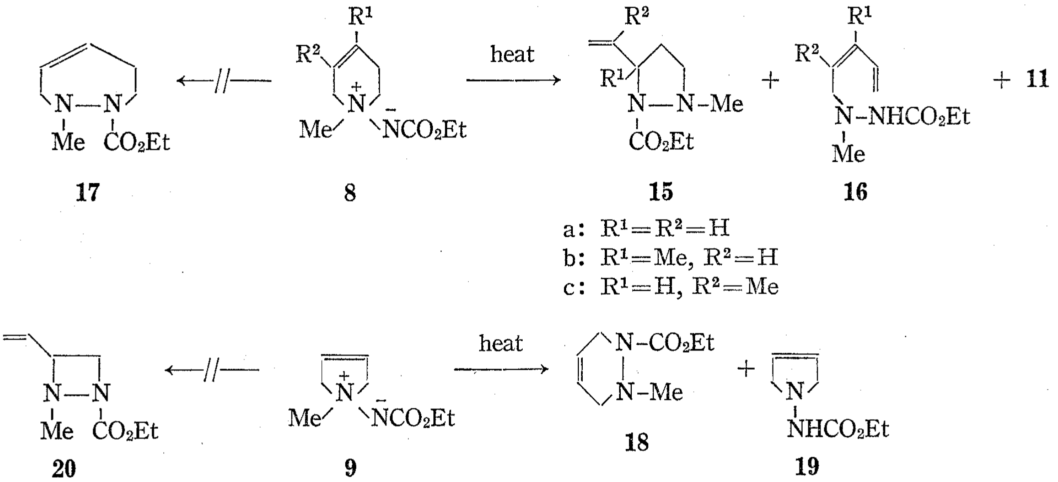


Chart 3

Next, the thermolysis of the five-membered cyclic ylide (**9**) in mesitylene at 160—165° for 50 hr resulted in the formation of the ring expansion product, tetrahydropyridazine derivative (**18**), and the demethylation product, N-amino-Δ^3-pyrroline derivative (**19**), in 35% and *ca.* 5% yields, respectively. The structure of **18** was confirmed by comparison with an authentic sample prepared from the known compound, 1-ethoxycarbonyl-1,2,5,6-tetrahydropyridazine,[13] by successive lithium aluminum hydride reduction and ethoxycarbonylation with ethyl chloroformate. In contrast to the six-membered cyclic ylides, the Stevens-type [1,2] rearrangement predominated in the thermolysis of the five-membered cyclic ylides (**9**) and the [2,3] rearrangement product (**20**) was not obtained.

Many studies[4,14] on thermal reactions of open chain allylic ylides have shown that the [2,3] rearrangement predominates over the [1,2] rearrangement and the former involves a

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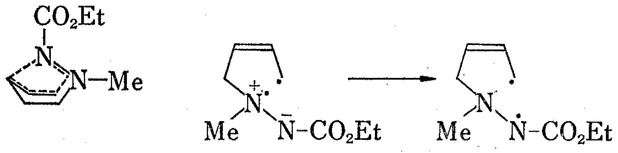
13) R.Y. Levina, Y.S. Shabarov, and M.G. Kuzmin, *Zh. Obshch. Khim.*, 30, 2469 (1960) [*C.A.*, 55, 13436*f* (1961)].

14) For examples: J.E. Baldwin and J.E. Patrick, *J. Am. Chem. Soc.*, 93, 3556 (1971); P.A. Grieco, D. Boxler, and K. Hiroi, *J. Org. Chem.*, 38, 2572 (1973).

concerted process through suprafacial bonded transition states, whereas the latter proceeds by a non-concerted process of higher activation energy involving radical pairs. Therefore, in the present work, the thermolysis of the six-membered ylides (**8**) may also proceed *via* the relatively stable bonded transition state (**21**) to give **15** predominantly. However, the five-membered ylide (**9**) may be unable to form the similar transition state because of the involvement of a highly strained four-membered ring and undergoes homolytic C–N bond fission to the radical pair (**22**), followed by recombination to give the ring expansion product (**18**) by analogy with the cases of the ylides (**4**).[5)]



21 **22**

Chart 4

In contrast to the dihydrothiophene ylide (**4**: X=S), the thermolysis of the ylide (**9**) showed a less complex reaction probably because of involving no tetracovalent intermediates. The N-ylides (**8** and **9**) rearrange only at higher temperature, while the corresponding cyclic C- and S-ylides rearrange in boiling benzene. This low susceptibility of the N-ylides toward rearrangements may decrease the yields of the rearrangement products and, thus, increase those of the elimination and demethylation products.

Experimental

Melting points were measured on a Yamato MP-21 apparatus and are uncorrected. IR spectra were determined with a JASCO IRA-2 spectrometer and MS spectra were obtained on a JEOL JMS-D100 instrument. ^1H–NMR spectra were recorded on a JEOL JNM-MH-100 spectrometer in $CDCl_3$ solution using tetramethylsilane as internal standard unless otherwise stated and spectral assignments were confirmed by spin-decoupling experiments and, in the case of NH protons, by exchange with D_2O. ^{13}C–NMR spectra were recorded on a JEOL FX-100 spectrometer. Microanalyses were performed in the Microanalytical laboratory of this school by Miss R. Hamano.

1-Ethoxycarbonylamino-1,2,5,6-tetrahydropyridines (11a—c)——To a solution of the corresponding N-iminopyridinium ylides (**10a—c**: 15 g), prepared by the method of the literatures,[8)] in MeOH (100 ml) cooled in an ice bath was added solid $NaBH_4$ (*ca.* 4 g) in small portions with stirring. The solution was stirred further for 7—8 hr at room temperature and then evaporated to dryness *in vacuo* below 30°. The residue was extracted with CH_2Cl_2 and the extract was washed with satd. NaCl, dried over K_2CO_3, and evaporated. The resulting residue was recrystallized from benzene–*n*-hexane to give **11a—c**.

11a: 14.3 g (93% yield), mp 64—65°, colorless needles. IR ν_{max}^{KBr} cm^{-1}: 3200 (NH), 1700 (C=O). MS *m/e*: 170 (M^+). NMR δ: 1.28 and 4.18 (3H, t, and 2H, q, CO_2Et), 2.30(2H, m, 5-H_2), 3.00 (2H, t, 6-H_2), 3.40 (2H, m, 2-H_2), 5.70 (2H, m, 3- and 4-H), 6.10 (1H, br, NH). *Anal.* Calcd. for $C_8H_{14}N_2O_2$: C, 56.45; H, 8.29; N, 16.46. Found: C, 56.44; H, 8.35; N, 16.41.

11b: 13.4 g (87% yield), mp 78.5—79.5°, yellow prisms. IR ν_{max}^{KBr} cm^{-1}: 3200 (NH), 1700 (C=O). MS *m/e*: 184 (M^+). NMR δ: 1.26 and 4.19 (3H, t, and 2H, q, CO_2Et), 1.70 (3H, s, 4-Me), 2.18 (2H, m, 5-H_2), 2.97 (2H, t, 6-H_2), 3.34 (2H, m, 2-H_2), 5.32 (1H, m, 3-H), 5.88 (1H, br, NH). *Anal.* Calcd. for $C_9H_{16}N_2O_2$: C, 58.67; H, 8.75; N, 15.21. Found: C, 58.47; H, 8.79; N, 15.07.

11c: 13.3 g (87% yield), mp 97—98.5°, colorless prisms. IR ν_{max}^{KBr} cm^{-1}: 3200 (NH), 1700 (C=O). MS *m/e*: 184 (M^+). NMR δ: 1.27 and 4.20 (3H, t, and 2H, q, CO_2Et), 1.64 (3H, s, 3-Me), 2.24 (2H, m, 5-H_2), 2.94 (2H, t, 6-H_2), 3.28 (2H, br, 2-H_2), 5.46 (1H, m, 4-H), 6.0 (1H, br, NH). *Anal.* Calcd. for $C_9H_{16}N_2O_2$:, C, 58.67; H, 8.75; N, 15.21. Found: C, 58.44; H, 8.94; N, 15.17.

1-Methyl-1-ethoxycarbonylamino-1,2,5,6-tetrahydropyridinium Iodides (12a—c)——A mixture of **11** (13 g) and methyl iodide (50 ml) was refluxed for 8 hr and then evaporated to dryness *in vacuo*. The resulting crystalline residue was washed with ether and recrystallized from MeOH–ether to give **12** almost quantitatively.

12a: mp 140—141° (dec.), colorless prisms. NMR δ: 1.34 and 4.29 (3H, t, and 2H, q, CO_2Et), 2.6 (2H, m, 5-H_2), 3.92 (3H, s, NMe), 4.5—5.3 (4H, m, 2- and 6-H_2), 5.80 and 6.05 (1H, m, and 1H, m, 3- and 4-H), 5.6—6.7 (1H, br, NH). *Anal.* Calcd. for $C_9H_{17}IN_2O_2$: C, 34.64; H, 5.49; N, 8.98. Found: C, 34.68; H, 5.56; N, 8.91.

12b: mp 131—132° (dec.), pale yellow prisms. *Anal.* Calcd. for $C_{10}H_{19}IN_2O_2$: C, 36.84; H, 5.87; N, 8.59. Found: C, 36.77; H, 5.95; N, 8.48.

12c: mp 106—107° (dec.), pale yellow prisms. *Anal.* Calcd. for $C_{10}H_{19}IN_2O_2$: C, 36.84; H, 5.87; N, 8.59. Found: C, 36.76; H, 5.90; N, 8.43.

1-Methyl-1-ethoxycarbonylimino-1,2,5,6-tetrahydropyridinium Ylides (8a—c)——A solution of the salts (**12**: 15 g) in water (50 ml) was titrated with 5% NaOH using phenolphthalene as an indicator and then evaporated to dryness *in vacuo* below 60°. The resulting yellow residue was extracted with CH_2Cl_2. The extract was passed through a short alumina column and the eluent was evaporated to give **8** as yellow oil in quantitative yield.

8a: IR $\nu_{\max}^{\text{liq.}}$ cm^{-1}: 1625 (C=O). NMR δ: 1.23 and 4.00 (3H, t, and 2H, q, CO_2Et), 2.5 (2H, m, 5-H_2), 3.39 (3H, s, NMe), 3.5—4.5 (4H, m, 2- and 6-H_2), 5.74 and 5.92 (1H, m, and 1H, m, 3- and 4-H). *Anal.* Calcd. for $C_9H_{16}N_2O_2$: C, 58.67; H, 8.75; N, 15.21. Found: C, 58.61; H, 8.88; N, 15.10.

8b: IR $\nu_{\max}^{\text{liq.}}$ cm^{-1}: 1620 (C=O). NMR δ: 1.24 and 4.00 (3H, t, and 2H, q, CO_2Et), 1.83 (3H, s, 4-Me), 2.4 (2H, m, 5-H_2), 3.40 (3H, s, NMe), 3.5—4.3 (4H, m, 2- and 6-H_2), 5.4 (1H, m, 3-H). *Anal.* Calcd. for $C_{10}H_{18}N_2O_2$: C, 60.58; H, 9.15; N, 14.13. Found: C, 60.31; H, 8.98; N, 14.01.

8c: IR $\nu_{\max}^{\text{liq.}}$ cm^{-1}: 1620 (C=O). NMR δ: 1.24 and 4.00 (3H, t, and 2H, q, CO_2Et), 1.73 (3H, s, 3-Me), 2.4 (2H, m, 5-H_2), 3.36 (3H, s, NMe), 3.4—4.3 (4H, m, 2- and 6-H_2), 5.6 (1H, m, 4-H). *Anal.* Calcd. for $C_{10}H_{18}N_2O_2$: C, 60.58; H, 9.15; N, 14.13. Found: C, 60.42; H, 9.38; N, 13.89.

1-Methyl-1-amino-Δ^3-pyrrolinium mesitylenesulfonates (14)——A solution of O-mesitylenesulfonylhydroxylamine (14 g) in CH_2Cl_2 (50 ml) was added dropwise to a solution of N-methyl-Δ^3-pyrroline (**13**: 5 g) in CH_2Cl_2 (20 ml) with stirring in an ice bath. The reaction mixture was stirred further for 1 hr. After addition of ether (100 ml) to the mixture, the resulting crystalline precipitates were collected and recrystallized from MeOH–AcOEt to give **14** quantitatively. mp 167—168°. IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 3400 and 3200 (NH_2), 1600 (C=C). NMR (CD_3OD) δ: 3.4 (3H, s, NMe), 4.45 (4H, br, 2- and 5-H_2), 4.7 (2H, br, NH_2), 5.92 (2H, br s, 3- and 4-H), 2.22 and 2.61 (3H, s, and 6H, s, Ar–Me), 6.84 (2H, s, Ar–H). *Anal.* Calcd. for $C_{14}H_{22}N_2O_3S$: C, 56.35; H, 7.43; N, 9.39. Found: C, 56.04; H, 7.78; N, 9.29.

1-Methyl-1-ethoxycarbonylimino-Δ^3-pyrrolinium Ylide (9)——A mixture of the salt (**14**: 15 g) and ethyl chloroformate (100 ml) was refluxed for 7 hr and then evaporated to dryness *in vacuo*. The resulting residue was dissolved in water (20 ml) and the solution was made alkaline with 5% NaOH in an ice bath. The alkaline solution was evaporated to dryness *in vacuo* below 60° and the residue was extracted with CH_2Cl_2. The extract was passed through an alumina column and the eluent was evaporated to give **9** as dark oil in 93% yield, which was used in the following thermolysis without further purification. Further rechromatography over alumina furnished an analytical sample. MS *m/e*: 170 (M$^+$). NMR δ: 1.22 and 3.95 (3H, t, and 2H, q, CO_2Et), 3.40 (3H, s, NMe), 4.1—4.8 (4H, m, 2- and 5-H_2), 5.92 (2H, br s, 3- and 4-H). *Anal.* Calcd. for $C_8H_{14}N_2O_2$: C, 56.45; H, 8.29; N, 16.46. Found: C, 56.59; H, 8.06; N, 16.41.

Thermolysis of the Ylides (8a—c)——The ylide (**8**: 6—10 g) was distilled at 150—160° under reduced pressure (10—15 mmHg) and then the resulting distillate was chromatographed over silica gel. From the eluate with CH_2Cl_2–MeOH (50:1), the compounds (**16**), (**11**), and (**15**) were obtained successively. The products (**15**) are all pale yellow oils.

1-Methyl-2-ethoxycarbonyl-3-vinyltetrahydropyrazole (**15a**): 12% yield. IR $\nu_{\max}^{\text{liq.}}$ cm^{-1}: 1690 (C=O). MS *m/e*: 184 (M$^+$). NMR δ: 1.28 and 4.20 (3H, t, and 2H, q, CO_2Et), 1.9—2.5 (2H, m, 4-H_2), 2.62 (3H, s, NMe), 2.9—3.2 (2H, m, 5-H_2), 4.3—4.6 (1H, m, 3-H), 5.05—5.35 (2H, m, =CH_2), 5.7—6.1 (1H, m, –CH=). *Anal.* Calcd. for $C_9H_{16}N_2O_2$: C, 58.67; H, 8.75; N, 15.21. Found: C, 58.63; H, 8.93; N, 15.58.

1-Methyl-2-ethoxycarbonyl-3-methyl-3-vinyltetrahydropyrazole (**15b**): 10% yield. IR $\nu_{\max}^{\text{liq.}}$ cm^{-1}: 1690 (C=O). MS *m/e*: 198 (M$^+$). NMR δ: 1.30 and 4.19 (3H, t, and 2H, q, CO_2Et), 1.62 (3H, s, 3-Me), 2.0—2.5 (2H, m, 4-H_2), 2.62 (3H, s, NMe), 2.9—3.3 (2H, m, 5-H_2), 5.09 and 5.13 (1H, d J=10 Hz, and 1H, d J=18 Hz, =CH_2), 6.10 (1H, dd J=10 and 18 Hz, –CH=). *Anal.* Calcd. for $C_{10}H_{18}N_2O_2$: C, 60.58; H, 9.15; N, 14.13. Found: C, 60.67; H, 9.12; N, 14.32.

1-Methyl-2-ethoxycarbonyl-3-isopropenyltetrahydropyrazole (**15c**): 12% yield. IR $\nu_{\max}^{\text{liq.}}$ cm^{-1}: 1690 (C=O). MS *m/e*: 198 (M$^+$). NMR δ: 1.28 and 4.17 (3H, t, and 2H, q, CO_2Et), 1.78 (3H, s, =C–CH_3), 1.9—2.5 (2H, m, 4-H_2), 2.26 (3H, s, NMe), 2.7—3.2 (2H, m, 5-H_2), 4.37 (1H, t, 3-H), 4.82 and 4.92 (1H, br, and 1H, br, =CH_2). *Anal.* Calcd. for $C_{10}H_{18}N_2O_2$: C, 60.58; H, 9.15; N, 14.13. Found: C, 60.71; H, 9.25; N, 14.01.

1-Ethoxycarbonyl-2-methyl-2-[1′-(2′,4′-pentadienyl)]hydrazine (**16a**): 25% yield, mp 53—54°, colorless needles (from *n*-hexane). IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 3200 (NH), 1700 (C=O). MS *m/e*: 184 (M$^+$). NMR δ: 1.25 and 4.19 (3H, t, and 2H, q, CO_2Et), 2.64 (3H, s, NMe), 3.56 (2H, d J=7 Hz, 1′-H_2), 5.8 (1H, br, NH), 5.1—6.9 (4H, m, olefinic H). *Anal.* Calcd. for $C_9H_{16}N_2O_2$: C, 58.67; H, 8.75; N, 15.21. Found: C, 58.59; H, 8.72; N, 15.30.

1-Ethoxycarbonyl-2-methyl-2-[1′-(3′-methyl-2′,4′-pentadienyl)]hydrazine (**16b**): 20% yield, colorless oil. IR $\nu_{\max}^{\text{liq.}}$ cm^{-1}: 3200 (NH), 1700 (C=O). MS *m/e*: 198 (M$^+$). NMR δ: 1.28 and 4.24 (3H, t, and 2H, q, CO_2Et), 1.90 (3H, s, 3′-Me), 2.64 (3H, s, NMe), 3.56 (2H, d J=7 Hz, 1′-H_2), 5.24 and 5.32 (1H, d J=12 Hz, and 1H, d J=18 Hz, 5′-H_2), 5.58 (1H, br t, 2′-H), 6.1 (1H, br, NH), 6.85 (1H, dd J=12 and 18 Hz, 4′-H). *Anal.* Calcd. for $C_{10}H_{18}N_2O_2$: C, 60.58; H, 9.15; N, 14.13. Found: C, 60.83; H, 9.08; N, 14.33.

1-Ethoxycarbonyl-2-methyl-2-[1′-(2′-methyl-2′,4′-pentadienyl)]hydrazine (**16c**): 18% yield, mp 56—57°, colorless needles (from *n*-hexane). IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 3200 (NH), 1700 (C=O). MS *m/e*: 198 (M$^+$). NMR δ: 1.24 and 4.12 (3H, t, and 2H, q, CO_2Et), 1.88 (3H, s, 2′-Me), 2.62 (3H, s, NMe), 3.41 (2H, br, 1′-H_2), 4.9—5.2

(2H, m, 5′-H_2), 5.78 (1H, br, NH), 5.98 (1H, br d $J=11$ Hz, 3′-H), 6.45—6.85 (1H, m, 4′-H). *Anal.* Calcd. for $C_{10}H_{18}N_2O_2$: C, 60.58; H, 9.15; N, 14.13. Found: C, 60.56; H, 9.24; N, 14.17.

11a: 11% yield. **11b**: 14% yield. **11c**: 14% yield.

Thermolysis of the Ylide (9)——A solution of the ylide (**9**: 1 g) in mesitylene (10 ml) was heated at 160—165° for 50 hr. After cooling, the reaction mixture was submitted to column chromatography over silica gel. Elution with *n*-hexane–ether (2: 1) gave compounds (**19**) and (**18**) suceessively.

1-Ethoxycarbonyl-2-methyl-1,2,3,6-tetrahydropyridazine (**18**): 35% yield, colorless oil. IR $\nu_{\max}^{\text{liq.}}$ cm^{-1}: 1695 (C=O). MS *m/e*: 170 (M^+). NMR δ: 1.28 and 4.20 (3H, t, and 2H, q, CO_2Et), 2.62 (3H, s, NMe), 3.4 (2H, m, 3-H_2), 4.0 (2H, m, 6-H_2), 5.76 (2H, br, 4- and 5-H). *Anal.* Calcd. for $C_8H_{14}N_2O_2$: C, 56.45; H, 8.29; N, 16.46. Found: C, 56.22; H, 8.30; N, 16.72.

1-Ethoxycarbonylamino-Δ^3-pyrroline (**19**): *ca.* 5% yield, oil. IR $\nu_{\max}^{\text{liq.}}$ cm^{-1}: 3250 (NH), 1710 (C=O). MS *m/e*: 156 (M^+). NMR δ: 1.27 and 4.17 (3H, t, and 2H, q, CO_2Et), 3.84 (4H, s, 2- and 5-H_2), 5.75 (2H, br s, 3- and 4-H). *Anal.* Calcd. for $C_7H_{12}N_2O_2$: C, 53.83; H, 7.74; N, 17.94. Found: C, 53.61; H, 7.78; N, 18.14.