(m, 7 H), 1.68 and 1.61 (d, J = 6.9 Hz, 3 H, =CHCH_3).

(*E*,3a*R,5*R**,6a*R**,11b*S**)-5-[1-[[(*tert*-Butyldimethylsilyl)oxy]methyl]propenyl]-7-(methoxycarbonyl)-2,3,3a,4,5,6,6a,7-octahydro-1*H*-pyrrolo[2,3-*d*]carbazole (26b).** Activated zinc[38] (230 mg) was added to a stirred solution of carbamate **22** (141 mg, 0.223 mol), THF (3.5 mL), and KH_2PO_4 (1 M, 0.2 mL) in small portions over 6 h. The resulting suspension was stirred at room temperature overnight. Filtration, followed by basic workup (ether, K_2CO_3), afforded 53.2 mg of crude **26b** as a yellow oil. Chromatography on silica gel (230–400 mesh, 10 g; 1:1:0.2 hexane–ethyl acetate–triethylamine) gave 39.7 mg (39%) of amine **26b** as a clear oil: ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.76 (d, J = 8.0 Hz, 1 H, Ar H), 7.23 (dt, J = 1.4, 8.1 Hz, 1 H, Ar H), 7.13 (dd, J = 1.2, 7.3 Hz, 1 H, Ar H), 7.01 (apparent dt, J = 1.0, 7.4 Hz, 1 H, Ar H), 5.48 (q, J = 7.0 Hz, 1 H, =C*H*CH$_3$), 4.37 (dd, J = 4.7, 6.1 Hz, 1 H, O_2CNCH), 4.16 (AB q, J = 12.8 Hz, $\Delta\nu$ = 12.1 Hz, 2 H, CH_2O), 3.85 (s, 3 H, OCH_3), 3.15 (m, 2 H), 2.76 (m, 1 H), 2.14–1.87 (m, 5 H), 1.70–1.52 (m, 2 H), 1.54 (d, J = 6.9 Hz, 3 H, =CHCH_3), 0.92 (s, 9 H, t-Bu), 0.08 (s, 6 H, $SiMe_2$); IR (CCl_4) 2937 (s), 2861 (m), 1716 (s), 1479 (s), 1466 (m), 1440 (s), 1383 (s), 1249 (m), 1093 (m), 826 (m) cm^{-1}; MS (EI, 18 eV), m/z 456 (M, 33%), 311 (100%), 283 (23%), 254 (42%).

(*E*,3a*R,5*S**,6a*R**,11b*S**)-5-[1-(Hydroxymethyl)propenyl]-7-(methoxycarbonyl)-2,3,3a,4,5,6,6a,7-octahydro-1*H*-pyrrolo[2,3-*d*]carbazole (26).** Tetrabutylammonium fluoride (0.015 mL of a 1.0 M solution in THF, 0.015 mmol) was added to a stirred solution of silyl ether **26b** (6.0 mg, 0.013 mmol) and THF (0.7 mL) at room temperature. The resulting solution was stirred for 15 min. Aqueous workup (ether, K_2CO_3) gave 4.2 mg (94%) of crude amino alcohol **26** as a light yellow oil: ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.78 (d, J = 8.1 Hz, 1 H, Ar H), 7.22 (dd, J = 1.3, 8.0 Hz, 1 H, Ar H), 7.12 (dd, J = 1.2, 7.4 Hz, 1 H, Ar H), 7.03 (m, 1 H, Ar H), 5.53 (q, J = 6.8 Hz, 1 H, =C*H*CH$_3$), 4.41 (t, J = 5.2 Hz, 1 H, O_2CNCH), 4.15 (AB q, J = 12.4 Hz, $\Delta\nu$ = 10.0 Hz, 2 H, CH_2O), 3.86 (s, 3 H, OCH_3), 3.36 (m, 2 H), 3.16 (m, 1 H), 2.88 (m, 1 H), 2.03 (m, 2 H), 1.85–1.59 (m, 2 H), 1.57 (d, J = 6.8 Hz, 3 H, =CHCH_3), 1.44 (m, 2 H); IR (CCl_4) 3450–3150 (br w), 2831 (s), 2769 (s), 1712 (s), 1477 (s), 1440 (s), 1379 (s), 1255 (m) cm^{-1}; MS (EI, 18 eV), m/z 342 (M, 100%), 324 (47%), 311 (25%), 271 (31%).

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Registry No. (±)-**4a**, 97552-20-0; (±)-**4b**, 97552-21-1; (±)-**5**, 97552-34-6; (±)-**6**, 97570-05-3; **7**, 97552-22-2; **8**, 97552-23-3; (±)-**9**, 97552-42-6; **10**, 97552-44-8; (±)-**11a**, 97552-24-4; (±)-**11a** (mesylate), 97552-43-7; (±)-**11b**, 97552-25-5; **12**, 97552-26-6; **13a**, 97552-27-7; (±)-**14**, 97552-29-9; (±)-**15**, 97552-30-2; **16**, 6141-21-5; (±)-**16a**, 97552-28-8; (±)-**17**, 97552-31-3; (±)-**18**, 97552-32-4; (±)-**19a**, 97552-33-5; (±)-**19b**, 97570-06-4; (±)-**20**, 97552-35-7; (±)-**21**, 97552-36-8; (±)-**22**, 97552-37-9; (±)-**24**, 97552-38-0; (±)-**25**, 97552-39-1; (±)-**26**, 97552-41-5; (±)-**26b**, 97552-40-4; t-BuCOCl, 3282-30-2; o-$BrC_6H_4NH_2$, 615-36-1; o-$BrC_6H_4NHCOBu$-t, 65854-92-4; $ClCO_2CH_2CCl_3$, 17341-93-4.

Studies on Quinolizine Derivatives. 20.[1] Syntheses of Cycl[3.3.3]azine Derivatives

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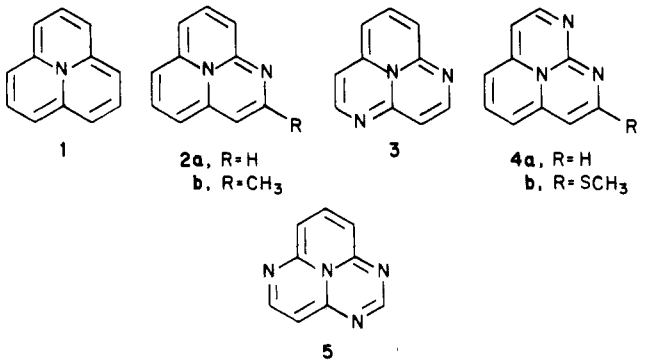
By the Diels-Alder reaction of azacyclazines (**6**, **11**) with dienophiles, methyl acetylenecarboxylate (MAC), dimethyl acetylenedicarboxylate (DMAD), and *N*-phenylmaleimide (PMI), the corresponding cyclazine derivatives (**7–10**, **12**, **13**) were obtained. 1,6-Diazacycl[3.3.3]azine (**15**), which was a very unstable free base, was prepared by the degradation of **13**. The ^{1}H nuclear magnetic resonance spectral data of **15** may be interpreted in terms of a paramagnetic ring current.

Since the first synthesis of cycl[3.3.3]azine[2] by Farquhar and Leaver, this molecule, which exhibits a paratropic ^{1}H NMR shift, has been examined by Dewar and Trinajstic[3], who have advanced a simple and convincing argument to show that **1** is aptly characterized as a nitrogen-bridged, "antiaromatic" [12]annulene. Previously, we reported the synthesis of various azacycl[3.3.3]azines, 1-aza-, 1,4-diaza-, 1,9-diaza–, and 1,3,6-triazacycl[3.3.3]azine derivatives (**2–5**)[4] (Scheme I).

In this paper, we have examined the chemical reactivity of 1-azacyclazine derivatives (**6**) and 4-cyano-1,3,6-triazacycl[3.3.3]azine (**11**) with some dienophiles. The reaction of **6** with methyl acetylenecarboxylate (MAC) readily gave

Scheme I

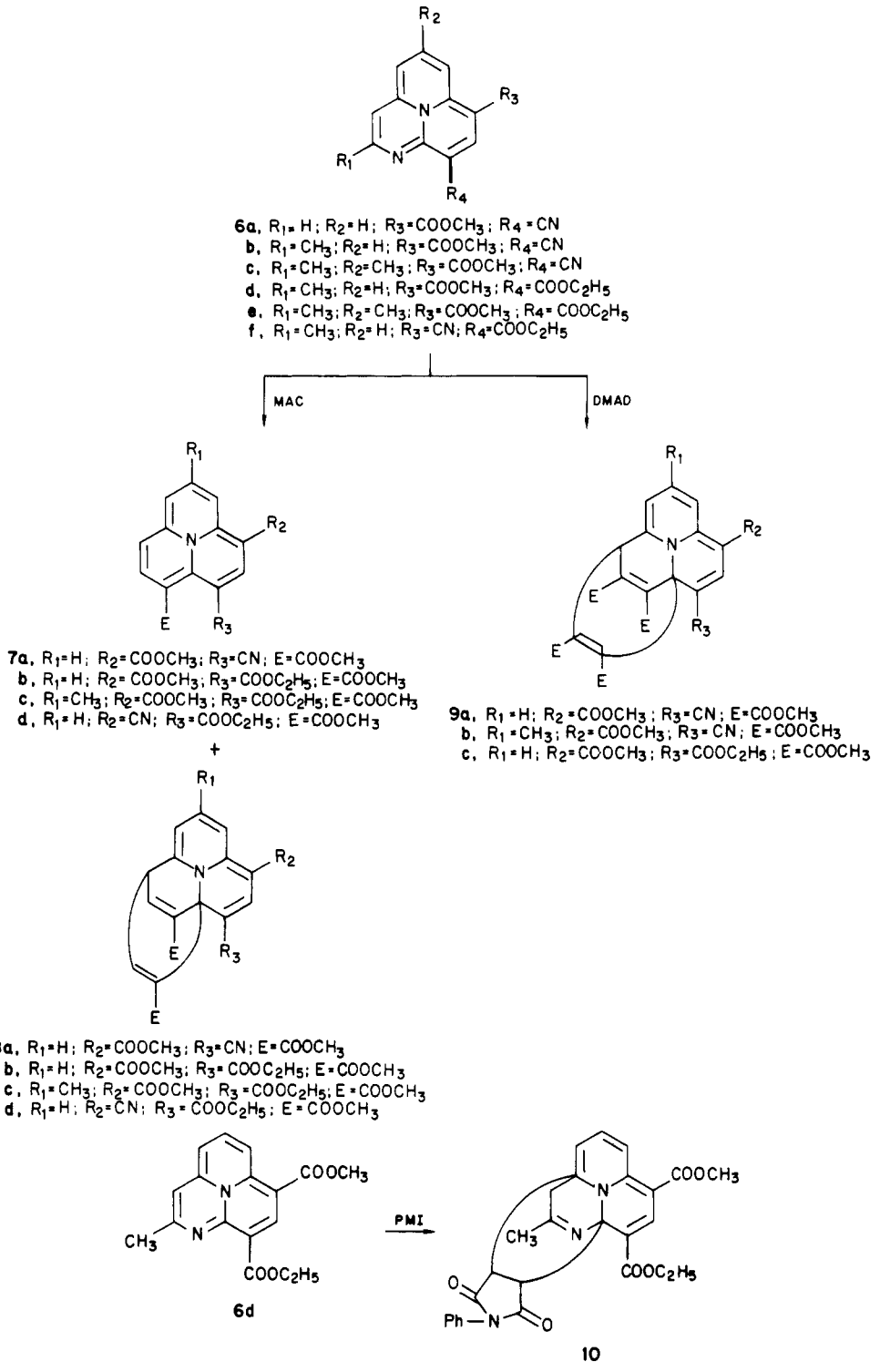


cycl[3.3.3]azine derivatives **7**. Furthermore, our attempts to extend this Diels-Alder reaction to **11** with dimethyl acetylenedicarboxylate (DMAD) led to the formation of a new ring system, as shown by the 1,6-diazacycl[3.3.3]-azine derivatives **12** and **13**. We now report the full details of this work, including a new preparation of 1,6-diazacycl[3.3.3]azine (**15**) as an unstable free base.[5]

(1) Part 19: Kuya, K.; Kurata, K.; Awaya, H.; Tominaga, Y.; Matsuda, Y.; Kobayashi, G. *Chem. Pharm. Bull.* **1978**, *28*, 680.
(2) Farquhar, D.; Leaver, D. *Chem. Commun.* **1964**, 24.
(3) (a) Dewar, M. T. S.; Trinajstic, N. *J. Chem. Soc. A* **1969**, 1754. (b) Leupin, W.; Wirz, J. *J. Am. Chem. Soc.* **1980**, *102*, 6068.
(4) (a) Kobayashi, G.; Matsuda, Y.; Tominaga, Y.; Awaya, H.; Kurata, K. *Chem. Pharm. Bull.* **1975**, *23*, 2759. (b) Kurata, K.; Yamada, M.; Awaya, H.; Tominaga, Y.; Matsuda, Y.; Kobayashi, G. *Yakugaku Zasshi* **1978**, *98*, 623. (c) Awaya, H.; Maseda, C.; Tominaga, Y.; Natsuki, R.; Matsuda, Y.; Kobayashi, G. *Chem. Pharm. Bull.* **1974**, *22*, 1424.

0022-3263/85/1950-4028$01.50/0

Scheme II



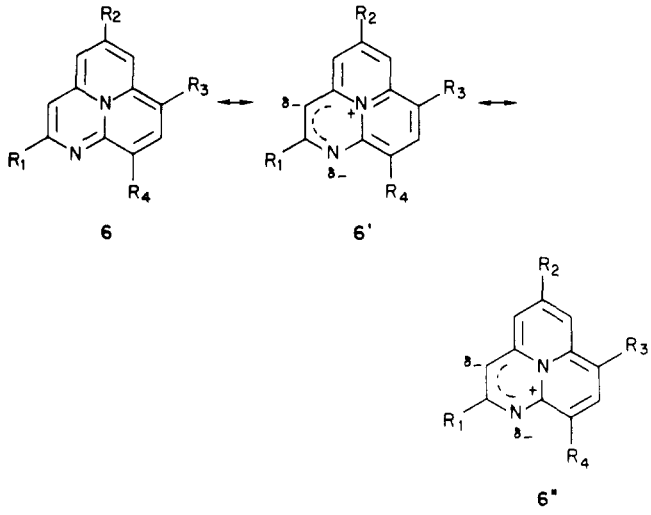
Results and Discussion

Reaction of 6 with Some Dienophiles. The reaction of **6** with MAC in acetonitrile converted **6** to **7** (Scheme II). Presumably **6** first underwent a reverse Diels-Alder reaction with the elimination of acetonitrile, followed by the addition of MAC to give **7**; a second addition of MAC then led to 1,3a-ethenocycl[3.3.3]azine derivatives **8**. The compounds represented by **7** are very stable in the solid state or in solution, in contrast to the parent compound **1**, presumably because of the three electron-attracting groups in **7**. Furthermore, it was shown independently that **7** reacts with MAC to give **8** in good yield.

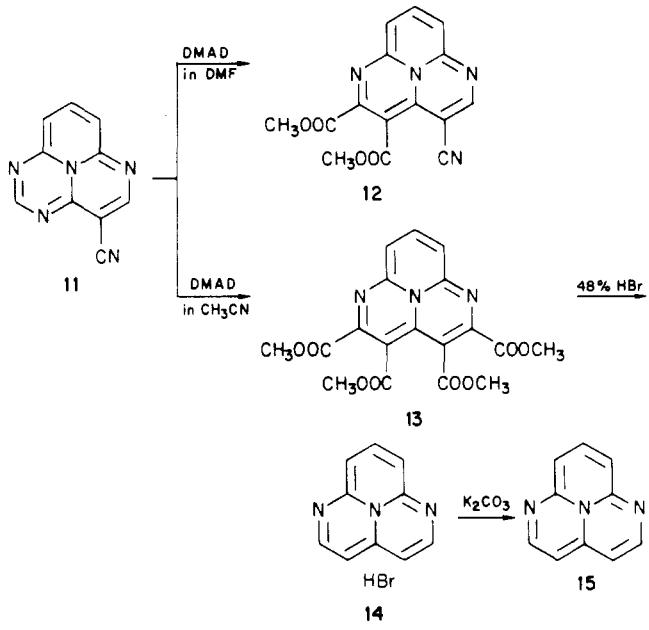
The reaction of **6** with DMAD in *N*,*N*-dimethylformamide (DMF) gave only **9**, corresponding to the addition of two molecules of DMAD with the elimination of acetonitrile. However, the reaction of **6d** with *N*-phenylmaleimide (PMI) gave the expected Diels-Alder adduct **10** (see Table I). In our previous paper,[4a] we observed that the ^{1}H NMR signals of the protons of stable 1-azacyclazines (**6**) appear at a lower magnetic field than that of the unstable free base **2**. Since these protons are affected by

(5) (a) Kurata, K.; Matsuo, M.; Awaya, H.; Tominaga, Y.; Matsuda, Y.; Kobayashi, G. *Chem. Pharm. Bull.* **1975**, *23*, 1629. (b) Kurata, K.; Awaya, H.; Tominaga, Y.; Matsuda, Y.; Kobayashi, G. *Chem. Pharm. Bull.* **1976**, *24*, 2270.

Scheme III



Scheme IV



the electron-attracting groups, the effect can not be due to the diatropicity of **6** but is the result of partial polarization of charge in the azacyclazine nucleus, as represented by formulas **6′** and **6″** in Scheme III. The resonance contribution of such polarized structures must, nevertheless, be relatively small since the proton chemical shifts showed no evidence of the aromaticity which would be associated with the quinolizinium system in the fully polarized structures (**6′**, **6″**). As pointed out by Farquhar and Leaver, the lack of aromatic character in the stable 1-azacycl[3.3.3]azine (**6**) is reflected in the ease with which addition reactions occur. Especially, we think that a partial polarized structure of **6″** may be an important contribution in the addition reactions of **6** with dienophiles.

The Synthesis of 1,6-Diazacycl[3.3.3]azine. As an extension of the above addition reaction, we examined the reaction of **11** with DMAD (Scheme IV). Thus a mixture of **11** and DMAD in DMF was heated at 100 °C for 10 h to give **12**. On the other hand, when the reaction of **11** and DMAD was tried in acetonitrile, the product was **13**.

Previously, we reported the syntheses of **2b** and 2-(methylthio)-1,9-diazacycl[3.3.3]azine (**4b**) and the fact that they exhibit a paramagnetic ring current. The question of whether 1,6-diazacycl[3.3.3]azine (**15**) is aromatic or

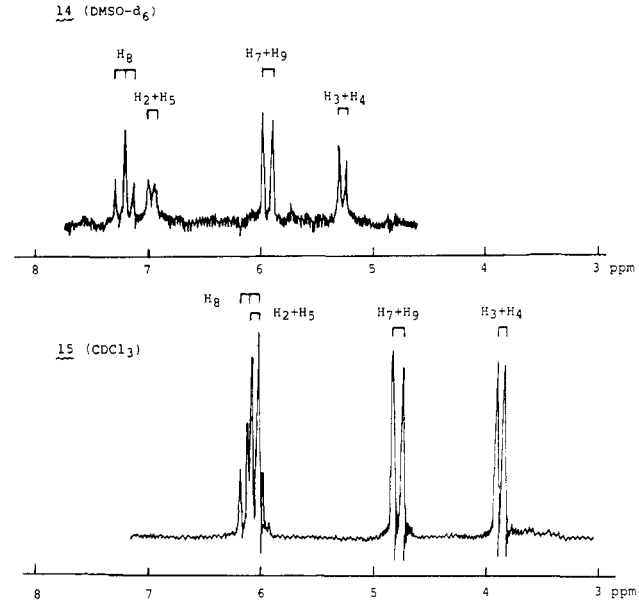


Figure 1. NMR spectra of **14** and **15**.

antiaromatic led us to synthesize the parent compound. Thus a solution of **13** in 48% hydrobromic acid was refluxed for 3 h to give stable green salt **14**. By the treatment of **14** with potassium carbonate, 1,6-diazacycl[3.3.3]azine (**15**) was obtained. Compound **15** was a very unstable green crystalline solid, which decomposed on exposure to air within ca. 20 min. Thus, the evidence for the structure of **15** is limited to the ^1H NMR spectrum of the crude product (see Figure 1).

The signals for all of the protons of **15** appear at lower magnetic fields than those of **1** and **2b**. However, they appear between δ 3.90–6.10, a region in accord with the presence of a paramagnetic ring current. The results clearly establish that **15** is an example of a new nitrogen-bridged hereto[12]annulene which, on the basis of Dewar's and Breslow's concepts, is properly termed an antiaromatic compound. The C-7 and C-9 protons, for example, become more shielded by 1.17 ppm in going from **13** to **15**. This large shielding effect can be interpreted as being the result of either one or a combination of the following two factors: an increase in the electron density at the carbon atom and/or the presence of a paramagnetic ring current. An increase in the electron densities caused by the central nitrogen atom would not be expected to be very significant in view of the properties of diazacyclopent[*fg*]-acenaphthylene[6] and especially in view of the quantum chemical calculations (SCF–MO method) done by Dewar[3] and Trost,[7] who have shown that there is a very small, if any, contribution to the periphery by the central nitrogen atom in cycl[3.3.3]azine (**1**) and by the central carbon atoms in pyracyclene. The major factor of the shielding effects in **15** is, in all probability, due to its ability to maintain a paramagnetic ring current. We are in the process of preparing other azacyclazine with the hope of expanding our understanding of these interesting compounds.

Experimental Section

Melting points were determined by using a Mitamura Mel-Temp and are uncorrected. Infrared (IR) and ultraviolet (UV)

(6) Atwood, J. L.; Hrncir, D. C.; Wong, C.; Paudler, W. *J. Am. Chem. Soc.* **1974**, *96*, 6132.
(7) Trost, B. M.; Bright, G. M.; Frihart, C.; Brittell, D. *J. Am. Chem. Soc.* **1971**, *93*, 737.

Table I. Properties of Cyclazine Derivatives 7, 8, and 9

compd	mp, °C	yield, %	IR (KBr), cm^{-1}	UV λ_{max}^{EOH}, nm (log ϵ)	^1H NMR, δ
7a	155~156	40	2200 (CN), 1705 (C=O), 1680 (C=O)	289 (4.53), 405 (4.28), 447 (4.14), 488 (4.24)	3.68 (3 H, s, OCH_3), 3.84 (3 H, s, OCH_3), 5.36 (1 H, d, J = 9 Hz, C_6H), 5.64 (1 H, d, J = 9 Hz, C_2H), 6.60 (1 H, d, J = 9 Hz), 6.60 (1 H, t, J = 9 Hz), 1.00 (1 H, s, C_2H), 7.26 (1 H, d, J = 9 Hz, C_9H)
7b	134~135	40	1700 (C=O), 1670 (C=O)	290 (4.49), 330 (3.89, sh), 408 (4.38), 500 (4.33)	1.24 (3 H, t, J = 7 Hz, OCH_2CH_3), 3.60 (3 H, s, OCH_3), 3.64 (3 H, s, OCH_3), 4.04 (2 H, q, J = 7 Hz, OCH_2CH_3), 5.36 (1 H, d, J = 8 Hz, C_7H), 5.56 (1 H, d, J = 8 Hz, C_6H), 6.46 (1 H, t, J = 8 Hz, C_8H), 6.64 (1 H, d, J =8 Hz, C_9H), 7.14 (1 H, d, J = 8 Hz, C_5H), 7.38 (1 H, s, C_2H)
7c	172~173	40	1700 (C=O), 1690 (C=O), 1675 (C=O)	288 (4.52), 330 (3.89, sh), 406 (4.42), 494 (4.37)	1.22 (3 H, t, J = 7 Hz, OCH_2CH_3), 1.84 (3 H, s, CH_3), 3.60 (3 H, s, OCH_3), 3.64 (3 H, s, OCH_3), 4.06 (2 H, q, J = 7 Hz, OCH_2CH_3), 5.44 (1 H, d, J = 10 Hz, C_6H), 5.58 (1 H, s, C_7H), 6.78 (1 H, d, J = 10 Hz, C_5H), 7.24 (1 H, s, C_9H), 7.32 (1 H, s, C_2H)
7d	216~217	60	2180 (CN), 1710 (C=O), 1695 (C=O)	298 (4.47), 412 (4.30), 490 (4.21)	1.20 (3H, t, J = 7 Hz, OCH_2CH_3), 3.56 (3 H, s, OCH_3), 4.00 (2 H, q, J = 7 Hz, OCH_2CH_3), 5.20 (1 H, d, J = 8 Hz, C_6H), 5.34 (1 H, d, J = 8 Hz, C_7H or C_9H), 5.58 (1 H, d, J = 8 Hz, C_7H or C_9H), 6.32 (1 H, t, J = 8 Hz, C_8H), 6.56 (1 H, d, J = 8 Hz, C_5H), 6.68 (1 H, s, C_2H)
8a	251~252	20	2190 (CN), 1730 (C=O), 1712 (C=O), 1675 (C=O)	269 (4.18sh), 279 (4.28), 300 (4.20), 308 (4.18, sh), 372 (3.94), 520 (3.74)	3.76 (3 H, s, OCH_3), 3.88 (6 H, s, 2 OCH_3), 4.60 (1 H, t, J = 7 Hz, C_1H), 6.40 (1 H, d, J = 8 Hz, C_9H), 7.04 (1 H, t, J = 8 Hz C_8H), 7.74 (2 H, d, J = 7 Hz, C_2H and $C_{11}H$), 7.75 (1 H, s, C_5H), 8.46 (1 H, d, J = 8 Hz, C_7H)
8b	220~221	30	1720 (C=O), 1654 (C=O)	272. (4.04, sh), 282 (4.11), 304 (4.25, sh), 313 (4.32), 384 (3.99), 522 (3.77)	1.20 (3 H, t, J = 7 Hz, OCH_2CH_3), 3.60 (9 H, s, 3 OCH_3), 4.06 (2 H, q, J = 7 Hz, OCH_2CH_3), 4.44 (1 H, t, J = 6 Hz, C_1H), 6.6–7.2 (6 H, m, $C_{2,5,7,8,9,11}H$)
8c	220~221	24	1730 (C=O), 1710 (C=O), 1645 (C=O)	279 (4.02), 314 (4.39), 384 (4.03), 506 (3.87)	1.26 (3 H, t, J = 7 Hz, OCH_2CH_3), 2.14 (3 H, s, CH_3), 3.68 (6 H, s, 2 OCH_3), 3.72 (3 H, s, OCH_3), 4.14 (2 H, q, J = 7 Hz, OCH_2CH_3), 4.52 (1 H, t, J = 6 Hz, C_1H), 6.28 (1 H, s, C_9H), 7.54 (2 H, d, J = 6 Hz, C_2H and $C_{11}H$), 8.22 (1 H, s, C_5H), 8.38 (1 H, s, C_7H)
8d	201~202	30	2170 (CN), 1730 (C=O), 1720 (C=O), 1695 (C=O), 1670 (C=O)	264 (4.18, sh), 273 (4.23), 286 (4.06), 388 (3.94), 500 (3.67, sh), 532 (3.72)	1.24 (3 H, t, J = 7 Hz, OCH_2CH_3), 3.64 (6 H, s, 2 OCH_3), 4.08 (2 H, q, J = 7 Hz, OCH_2CH_3), 4.45 (1 H, t, J = 7 Hz, C_1H), 6.21 (1 H, d, J = 8 Hz, C_7H or C_9H), 6.68 (1 H, d, J = 8 Hz, C_7H or C_9H), 6.90 (1 H, t, J = 8 Hz, C_8H), 7.40 (1 H, s, C_5H), 7.47 (2 H, d, J = 7 Hz, C_2H and $C_{11}H$)
9a	269~270	80	2190 (CN), 1744 (C=O), 1732 (C=O), 1722 (C=O), 1660 (C=O)	270 (4.26, sh), 280 (4.35), 300 (4.19, sh), 370 (4.00), 524 (3.80)	3.64 (3 H, s, OCH_3), 3.80 (6 H, s, 2 OCH_3), 3.88 (6 H, s, 2 OCH_3), 5.52 (1 H, s, C_1H), 6.52 (1 H, d, J = 8 Hz, C_9H), 7.10 (1 H, t, J = 8 Hz, C_8H), 7.76 (1 H, s, C_5H), 8.46 (1 H, d, J = 8 Hz, C_7H)
9b	294~296	80	2190 (CN), 1734 (C=O), 1685 (C=O), 1666 (C=O), 1637 (C=O)	278 (4.23), 291 (4.22 sh), 300 (4.27), 373 (4.00), 506 (38.3)	2.20 (3 H, s, CH_3), 3.70 (3 H, s, OCH_3), 3.85 (6 H, s, 2 OCH_3), 3.94 (6 H, s, 2 OCH_3), 5.58 (1 H, s, C_1H), 6.50 (1 H, s, C_9H), 7.88 (1 H, s, C_5H), 8.40 (1 H, s, C_7H)
9c	254~255	80	1725 (C=O), 1700 (C=O), 1670 (C=O), 1652 (C=O)	280 (4.26), 304 (4.34), 384 (4.08), 525 (3.90)	1.29 (3 H, t, J = 7 Hz, OCH_2CH_3), 3.72 (3 H, s, OCH_3), 3.73 (6 H, s, 2 OCH_3), 3.85 (6 H, s, 2 OCH_3), 4.15 (2 H, q, J = 7 Hz, OCH_2CH_3), 5.43 (1 H, s, C_1H), 6.35 (1 H, d, J = 8 Hz, C_9H), 7.14 (1 H, t, J = 8 Hz, C_8H), 8.33 (1 H, s, C_5H), 8.58 (1 H, d, J = 8 Hz, C_7H)

spectra were recorded on a Nippon-Bunko IRA-2 spectrometer and a Hitachi EP-S-2 spectrometer. ^1H NMR spectra were run on a JNM-PS-100 (100 MHz) spectrometer with $CDCl_3$ as solvent, except otherwise mentioned, and $(CH_3)_4Si$ as the internal standard. The mass spectra were run on a JEOL JMS-01SG spectrometer. Elementary analyses (C, H, N) of all compounds described here were performed on a Yanagimoto MT-2 CHN recorder. All analytical results were within ±0.3% of the theoretical values.

General Procedures for Reaction of 6 with MAC. A mixture of **6** (0.0015 mol), MAC (0.006 mol), and CH_3CN (30 mL) in a sealed tube was heated at 250 °C for 20 h. The reaction mixture was evaporated under reduced pressure. The residue was submitted to column chromatography on silica gel. From the benzene–acetone (20:1) fraction, cycl[3.3.3]azine derivatives **7** were obtained; from the benzene–acetone (10:1) fraction, 1,3a-dihydro-1,3a-ethanocycl[3.3.3]azine derivatives **8** were obtained,

respectively. The physical and spectroscopic properties of the products are given in Table I.

General Procedure for Reaction of 7 with MAC. A mixture of 7 (0.001 mol), MAC (0.002 mol), and CH_3CN (30 mL) in a sealed tube was heated at 200 °C for 20 h. The resulting mixture was treated by the same method described in 8. From the benzene–acetone (10:1) fraction, the compounds shown by 8 were obtained (40%).

General Procedure for Reaction of 6 with DMAD. A mixture of 6 (0.0015 mol) and DMAD (0.006 mol) in DMF (30 mL) was heated at 100 °C for 10 h. The reaction mixture was evaporated under a reduced pressure. The residue was recrystallized from $CHCl_3$–MeOH to give 9. The physical and spectroscopic properties of the products are given in Table I.

***N*-Phenyl-3,9a-dihydro-3,9a-ethano-9-(ethoxycarbonyl)-7-(methoxycarbonyl)-2-methyl-1-azacycl[3.3.3]azine-10,11-dicarboximide (10).** A mixture of 6d (0.002 mol) and PMI (0.004 mol) in DMF (30 mL) was heated at 100 °C for 10 h. The reaction mixture was evaporated under a reduced pressure. The residue was submitted to column chromatography on alumina. From the benzene–acetone (2:1) fraction, 10 was obtained in 80% yield (recrystallization solvent, $CHCl_3$–MeOH): mp 193–194 °C; mass spectrum, m/e 312 (M^+ – PMI); IR (KBr) 1720, 1660 cm^{-1}; UV λ_{max} (EtOH) 265 (log ϵ 4.15, sh), 272 (4.20), 306 (4.28), 375 (3.90), 505 (3.89), nm; ^1H NMR δ 1.37 (3 H, t, OCH_2CH_3), 2.40 (3 H, s, CH_3), 3.37 (1 H, dd, J = 3, 10 Hz, $C_{11}H$), 3.68 (3 H, s, OCH_3), 4.19 (1 H, d, J = 3 Hz, $C_{10}H$), 4.20 (2 H, q, OCH_2CH_3), 4.47 (1 H, d, J = 10 Hz, C_3H), 6.25 (1 H, d, J = 7 Hz, C_4H), 6.76–6.88 and 7.20–7.40 (5 H, m, Ph) 7.10 (1 H, dd, J = 7, 10 Hz, C_5H), 8.24 (1 H, s, C_8H), 8.60 (1 H, d, J = 10 Hz, C_6H).

Dimethyl 4-Cyano-1,6-diazacycl[3.3.3]azine-2,3-dicarboxylate (12). A mixture of 11 (0.01 mol) and DMAD (0.02 mol) in DMF (30 mL) was heated at 100 °C for 10 h. The resulting mixture was treated by the same method described in 10. From the benzene–acetone (20:1) fraction, 12 was obtained in 20% yield (recrystallization solvent, $CHCl_3$–MeOH): mp 197–198 °C; mass spectrum, m/e 310 (M^+); IR (KBr) 2200, 1735 cm^{-1}; UV λ_{max} (EtOH) 236, 284, 363, 415, 428 nm; ^1H NMR δ 3.23 (3 H, s, OCH_3), 3.76 (3 H, s, OCH_3), 5.68 (1 H, d, J = 8 Hz, C_7H or C_9H), 5.82 (1 H, d, J = 8 Hz, C_7H or C_9H), 6.76 (1 H, s, C_5H), 6.84 (1 H, t, J = 8 Hz, C_8H).

Tetramethyl 1,6-Diazacycl[3.3.3]azine-2,3,4,5-tetracarboxylate (13). A mixture of 11 (0.01 mol) and DMAD (0.02 mol) in CH_3CN (100 mL) was refluxed for 10 h. The resulting mixture was treated by the same method described in 10. From the benzene–acetone (20:1) fraction, 13 was obtained in 15% yield (recrystallization solvent, CH_3Cl–MeOH): mp 248–249 °C; mass spectrum, m/e 401 (M^+); IR (KBr) 1760, 1730, 1710 cm^{-1}; UV λ_{max} (EtOH) 262 (log ϵ 4.28), 286 (4.28), 364 (4.31), 437 (4.13) nm; ^1H NMR δ 3.59 (6 H, s, 2 OCH_3), 3.80 (6 H, s, 2 OCH_3), 5.95 (2 H, d, J = 8 Hz, C_7H and C_9H), 6.98 (1 H, t, J = 8 Hz, C_8H).

1,6-Diazacycl[3.3.3]azine Hydrobromide (14). A solution of 13 (0.5 g) in 48% HBr (20 mL) was refluxed for 3 h. The green solution was evaporated under a reduced pressure. The residue was recrystallized from MeOH to give 14 in quantitative yield: mp >300 °C; mass spectrum, m/e 169 (M^+ – HBr); UV λ_{max} (EtOH) 220 (log ϵ 4.00, sh), 268 (4.21), 273 (4.20, sh), 336 (3.49), 356 (3.56), 392 (3.72), 414 (3.66) nm; ^1H NMR (Me_2SO-d_6) δ 5.25 (2 H, d, J = 6 Hz, C_3H and C_4H), 5.92 (2 H, d, J = 8 Hz, C_7H and C_9H), 6.95 (2 H, d, J = 6 Hz, C_2H and C_5H), 7.20 (1 H, t, J = 8 Hz, C_8H).

1,6-Diazacycl[3.3.3]azine (15). A solution of 14 (0.5 g) in water (50 mL) was made basic to litmus with K_2CO_3 and instantly extracted with $CHCl_3$ (30 mL). The extract was dried (Na_2SO_4) and evaporated under a reduced pressure. The residue was dried in vacuum desiccator (2 mmHg) for 5 min. The NMR spectrum of crude free base 15 was recorded: ^1H NMR δ 3.90 (2 H, d, J = 5 Hz, C_3H and C_4H), 4.78 (2 H, d, J = 8 Hz, C_7H and C_9H), 6.05 (2 H, d, J = 5 Hz, C_2H and C_5H), 6.10 (1 H, t, J = 8 Hz, C_8H) (see Figure 1).

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Organoboranes. 41. Reaction of Organoboranes with (Dichloromethyl)lithium. Scope and Limitations. Synthesis of Homologated Primary and Secondary Alcohols

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Homologated primary alcohols were prepared from alkylboronic esters by the reaction with (dichloromethyl)lithium, $LiCHCl_2$, followed by KIPBH treatment and oxidation. Homologated secondary alcohols were prepared from representative dialkylborinic esters and trialkylboranes by the reaction with $LiCHCl_2$, followed by treatment with base and oxidation. The yields are generally good with both boronic and borinic esters. On the other hand, the reactions with trialkylboranes exhibited a sensitivity to large steric requirements in the trialkylborane reactant.

In the last decade, many new reactions and reagents have been developed for converting organoboranes into organic molecules, particularly by C–C bond formation.[2] Now, a variety of synthetically interesting organoboranes are readily available,[2,3] including chiral alkyl derivatives.[4] For further transformations of these valuable intermediates, it is desirable not only to find new reactions or reagents but also to define the scope and limitation of their applicability.

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(2) (a) Brown, H. C. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, G. A., Abel, E. W., Eds.; Pergamon Press: New York, 1983; Vol. 7, Chapter 45.1. (b) Negishi, E., ref 2a, Chapters 45.6–45.11.

(3) (a) Zaidlewicz, M. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, G. A., Abel, E. W., Eds.; Pergamon Press: New York, 1983; Vol. 7, Chapters 45.2–45.5. (b) Pelter, A.; Smith, K. In "Comprehensive Organic Chemistry"; Barton, D. H. R., Ollis, W. D., Jones, D. N., Eds.; Pergamon Press: Oxford, 1979; Vol. 3, Part 14.

(4) (a) Brown, H. C.; Jadhav, P. K.; Mandal, A. K. *Tetrahedron* **1981**, *37*, 3547–3587. (b) Brown, H. C.; Jadhav, P. K. In "Asymmetric Synthesis"; Morrison, J. D., Ed.; Academic Press: New York, 1983; Vol. 2, pp 1–43.

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