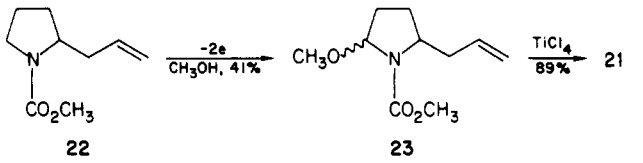
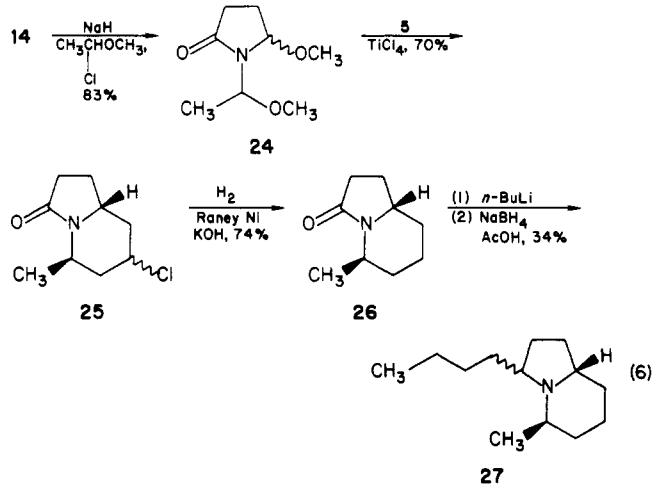


22 23 (5)

The stereochemistry of this [3 + 3]-type annelation was investigated in the preparation of **25**. Although **25** can have four stereoisomers, the product actually obtained showed the stereostructure depicted in eq 6,[14] though the stereochemistry of the chloro substituent was not clear.[15]



24 25 26 27 (6)

The pharaoh ant trail pheromone stereoisomers **27**[16] could be prepared from **25**. Thus, the hydrogenation of **25** under basic conditions followed by butylation of the dechlorinated product **26** with *n*-BuLi and reduction with $NaBH_4$ gave a mixture of stereoisomers **27** in the ratio of about 2:1 (eq 6).

Nucleophilic olefinic reagents other than **5** can lead to other new [3 + *n*]-type annelations, which will be reported elsewhere.

Acknowledgment. One of the authors (T.S.) wishes to thank the Asahi Glass Foundation for Industrial Technology for supporting this work.

Registry No. **5**, 762-72-1; **6b**, 97316-65-9; **7**, 6642-30-4; **8**, 28482-71-5; **9**, 6781-03-9; **10**, 97316-66-0; **11**, 81790-10-5; **12**, 97316-67-1; **13**, 616-45-5; **14**, 63853-74-7; **15**, 97316-68-2; **16**, 97316-69-3; **17**, 71779-55-0; **18**, 62279-67-8; **19**, 56475-80-0; **20**, 66893-74-1; **21**, 97316-70-6; **22**, 97316-71-7; **23**, 97316-72-8; **24**, 97316-73-9; **25** (isomer I), 97316-74-0; **25** (isomer II), 97371-87-4; **26**, 97316-75-1; **26** (butylated, isomer I), 97316-77-3; **26** (butylated, isomer II), 97371-90-9; **27** (isomer I), 97371-88-5; **27** (isomer II), 97371-89-6; **28**, 97316-56-8; *cis*-**29**, 97316-60-4; *trans*-**29**, 97316-76-2; **30**, 63853-82-7; **31**, 97316-64-8; methyl butylcarbamate, 2594-21-0; 2-piperidinone, 675-20-7; hexahydro-2-azepinone, 105-60-2; 2-oxazolidinone, 497-25-6; methyl 1-piperidinecarboxylate, 1796-27-6; methyl (1-methoxybutyl)carbamate, 76469-96-0; hexahydro-7-methoxy-2-azepinone, 63853-81-6; 4-methoxy-2-oxazolidinone, 14441-94-2; methyl 2,6-dimethoxy-1-piperidinecarboxylate, 66893-72-9; 1-(methoxymethyl)-6-methoxy-2-piperidinone, 97316-57-9; 1-(1-methoxyethyl)-6-methoxy-2-piperidinone, 97316-58-0; 1-(methoxymethyl)-7-methoxy-2-oxohexamethyleneimine, 80953-74-8; 3-(methoxymethyl)-4-methoxy-2-oxazolidinone, 97316-59-1; 8-chlorooctahydro-2*H*-quinolizin-4-one, 97316-61-5; 6-methyl-8-chlorooctahydro-2*H*-quinolizin-4-one, 97316-62-6; 2-oxo-9-chloro-1-azabicyclo[5.4.0]undecane, 97316-63-7; 4-chloro-9-oxo-1-aza-8-oxabicyclo[4.3.0]nonane, 97336-12-4; 1-chloroethyl methyl ether, 1538-87-0; (±)-δ-coniine, 3238-60-6; 1-(methoxycarbonyl)-2-propylpiperidine, 92599-71-8.

Supplementary Material Available: Experimental details and spectral and physical data for new compounds (11 pages). Ordering information is given on any current masthead page.

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(13) For a review of *N*-acyliminium ions cyclization, see: Speckamp, W. N. *Recl. Trav. Chim. Pays-Bas* **1981**, *100*, 345.
(14) The high stereoselectivity of the intramolecular cyclization of *N*-acyliminium ion with a C–C double bond has been reasonably explained in terms of $A^{(1,3)}$ strain: Hart, D. J. *J. Am. Chem. Soc.* **1980**, *102*, 397. The high stereoselectivity observed in the formation of **25** may be elucidated by the same factor.
(15) The stereochemistry between 8a-H and 5-CH_3 in **25** was determined at the step of **26**. The ratio of stereoisomers of **25** was 26 to 74, which was determined by GLC.
(16) Macdonald, T. L. *J. Org. Chem.* **1980**, *45*, 193 and references cited therein.
(17) The yields of **29** and **31** were improved by modification of the typical procedures. Thus, a solution of **4** and **5** in CH_2Cl_2 was added dropwise into a solution of $TiCl_4$ in CH_2Cl_2 at room temperature.

Additions and Corrections

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L. F. R. Cafferata,* G. N. Eyler, and M. V. Mirífico. Kinetics and Mechanism of Acetone Cyclic Diperoxide (3,3,6,6-Tetramethyl-1,2,4,5-tetraoxane) Thermal Decomposition in Benzene Solution.

Page 2107. At 165.0 °C, the ACDP thermolysis in benzene solution (0.05 mol kg^{-1}) yields the following gaseous products (ρ, mol of products per mol ACDP decomposed): O_2, 0.6 ± 0.1; CO_2, 0.6 ± 0.1; MeH, 0.21 ± 0.02; EtH, 0.005 ± 0.001. Considering the CO_2 and $MeCO_2Me$ yields, the ACDP decomposed through the intermediate biradical C–C bond rupture step (32%) is practically coincident with the value obtained from the acetone (35%) and oxygen (40%) yields. Then, the rate constant ratio (k_{C-O}/k_{C-C}) = $\rho_{MeCOMe}/(\rho_{MeCO_2Me} + \rho_{CO_2})$ is 2, which is a temperature-independent value.

Andrew A. Chiu, R. Russel Gorby, John E. H. Hancock,* and Eric J. Hustedt. Malonic Ester Derivatives. 2.

Page 4314, column 1, line 1–14. Prof. T. J. Curphey (Department of Pathology, Dartmouth Medical School, Hanover, NH 03756) has supplied a further mechanism which can explain the published results: Michael addition of dimethyl malonate anion to **3**, furnishing **4**, the anion of an unstable heptaester, which then undergoes retrograde Michael reaction forming **1a** and the anion of the triester **5**; this latter exchanges a proton with **1a** (the tetramethyl 1,1,3,3-propenetetracarboxylic ester), forming **2b** and **5**. There appear to be analogies, e.g.: Ingold, C. K.; Perren, E. A. *J. Chem. Soc.* **1921**, *119*, 1582; **1922**, *121*, 1414. We had considered this mechanism but thought it unlikely because of the severe steric hindrance in the initial approach. The two mechanisms lend themselves to distinction via use of an isotopic label, and such aspects will be examined.