Studies of Heteroaromaticity. Part LXV.[1] Reactions of Valence Tautomers of Three Medium-sized Ring Unsaturated Compounds with Iodine Azide

By **Tadashi Sasaki,* Ken Kanematsu,** and **Yusuke Yukimoto,** Institute of Applied Organic Chemistry, Faculty of Engineering, Nagoya University, Chikusa, Nagoya 464, Japan

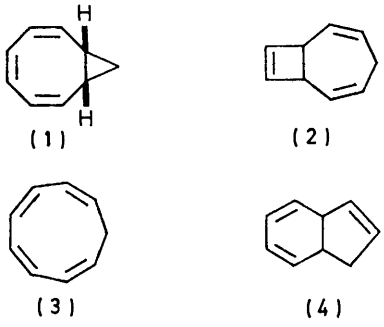
Reactions of valence tautomers of cyclononatetraene, *trans*-7,8-dibromocyclo-octa-1,3,5-triene, and 7-ethoxycycloheptatriene with a mixture of iodine azide and sodium azide have been studied: *cis*-bicyclo[6,1,0]nonatriene gave a diazide, but *trans*-7,8-dibromobicyclo[4,2,0]octa-2,4-diene, and 5-ethoxybicyclo[3,2,0]hepta-2,6-diene gave β-iodo-azides as normal adducts. The structures of these adducts were elucidated from the spectra of the triazolyl derivatives prepared by reactions with dimethyl acetylenedicarboxylate.

We have previously reported that the reactions of the medium-sized ring unsaturated compounds cyclo-octatetraene, 1-ethoxycarbonyl-1*H*-azepine, and tropone ethylene acetal (*i.e.* a cyclic conjugated tetraene and two trienes) with IN_3 solution (a mixture of iodine azide and sodium azide) gave diazides.[2] We have now examined

[1] Part LXIV, T. Sasaki, K. Kanematsu, A. Kakehi, and G. Ito, *Tetrahedron*, 1972, **28**, 4942.

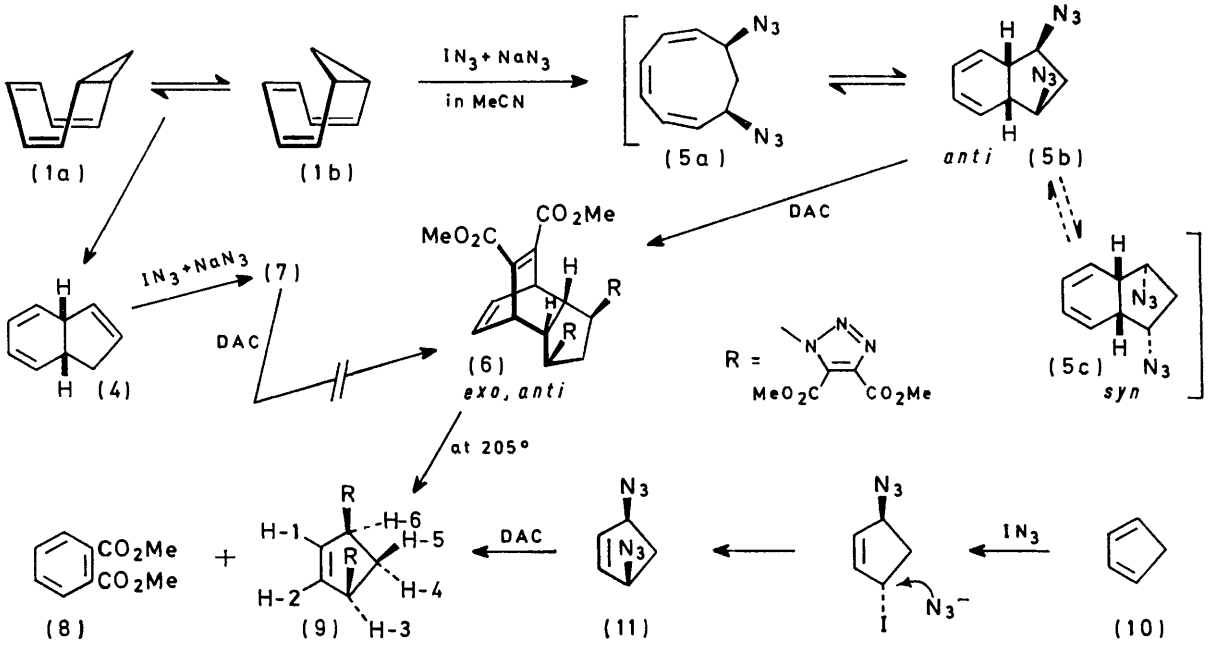
[2] T. Sasaki, K. Kanematsu, and Y. Yukimoto, *J. Org. Chem.*, 1972, **37**, 890.

the reactivity of some strained unsaturated bicyclic hydrocarbons (valence tautomers of medium-sized ring unsaturated compounds) with IN_3 solution.



Recently, considerable interest has been shown in the mechanism of thermal [3] and photochemical [4] reorganization of *cis*-bicyclo[6,1,0]nona-2,4,6-triene (1) based on orbital symmetry considerations, and intricate interconversions have been observed to occur amongst the structure determination was based on a study of its 1,3-dipolar cycloadduct; treatment of (5) with dimethyl acetylenedicarboxylate (DAC) gave a crystalline compound (6). Analytical data indicated that this was the Diels–Alder cycloadduct of the ditriazolyl derivative. A nearly symmetrical pattern in the n.m.r. spectrum (see Experimental section) suggested the structure (6) as depicted in Scheme 1. To obtain further evidence the adduct (6) was pyrolysed at 205° and gave a mixture of dimethyl phthalate (8) and the ditriazolyl derivative (9) in high yield; compound (9) was identified as the *cis*-3,5-ditriazolylcyclopentene on the basis of its completely symmetrical n.m.r. spectrum: τ 3·62 (s, H-1 and H-2), 3·75 (dd, $J_{3,4} = J_{6,4} = 7{\cdot}5$, $J_{3,5} = J_{6,5} = 6{\cdot}8$ Hz, H-3 and H-6), 6·00 and 6·08 (each s, MeO_2C), 6·50 (dt, $J_{4,5}$ −13·6, $J_{4,3} = J_{4,6} = 7{\cdot}5$ Hz, H-4), and 7·36 (dt, $J_{5,4}$ −13·6, $J_{5,3} = J_{5,6} = 6{\cdot}8$ Hz, H-5). In addition compound (9) was identical with the 1,3-dipolar cycloadduct from the diazide (11) and DAC.*

Although the stereochemistry of compound (6) was not clearly revealed by the n.m.r. data, the *exo,anti*-configuration (6) was tentatively assigned by consideration of steric effects; *i.e.* configuration (5b) is more favoured than (5c) because of the interaction between the two azide functions and the vinyl hydrogen atoms. It should be noted that the reaction of the bicyclic conjugated triene (1) with IN_3 did not afford the normal *vic*-diazide which had been formed in the reactions of



SCHEME 1

structures (2)—(4) *etc.*; some cycloaddition reactions of (1) have also been reported.[5] In contrast, electrophilic additions to (1) have been little scrutinized.[6] The reaction of the triene (1) with IN_3 solution [2] in acetonitrile afforded an oily compound (5), which showed strong azide absorption at 2100 cm^{-1} in the i.r. and no cyclopropane ring protons in the n.m.r. spectrum. Since the azide was expected to be explosive at room temperature,

* The diazide (11) is thought to be formed by initial *trans*-1,4-addition of IN_3 followed by S_N2 attack of azide ion.

[3] (*a*) J. C. Barborak, T. M. Su, and P. von R. Schleyer, *J. Amer. Chem. Soc.*, 1971, **93**, 279; (*b*) J. E. Baldwin and A. H. Andrist, *ibid.*, 1971, **93**, 4055.

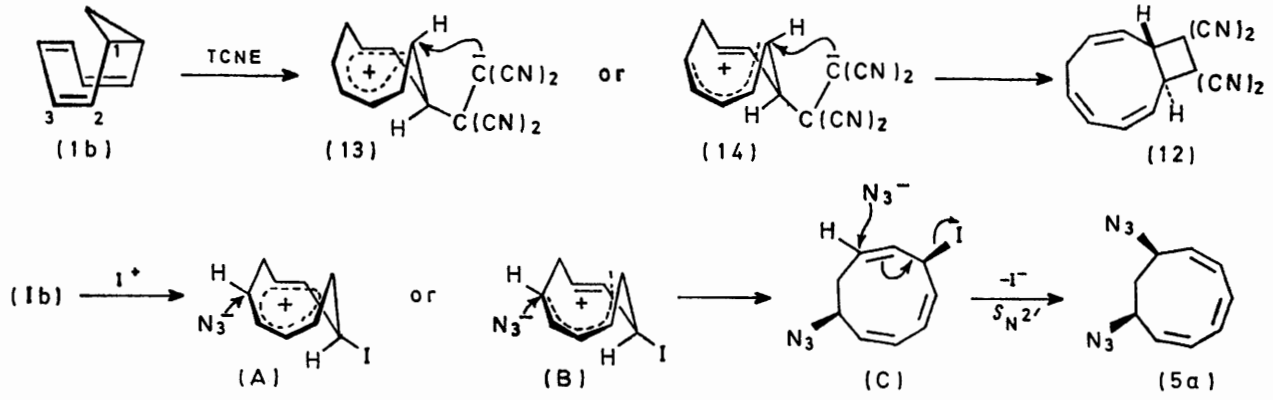
[4] A. G. Anastassiou and E. Yakali, *J. Amer. Chem. Soc.*, 1971, **93**, 3803.

[5] (*a*) W. H. Okamura and T. W. Osborn, *J. Amer. Chem. Soc.*, **92**, 1061; (*b*) A. G. Anastassiou and R. C. Griffith, *ibid.*, 1971, **93**, 3083.

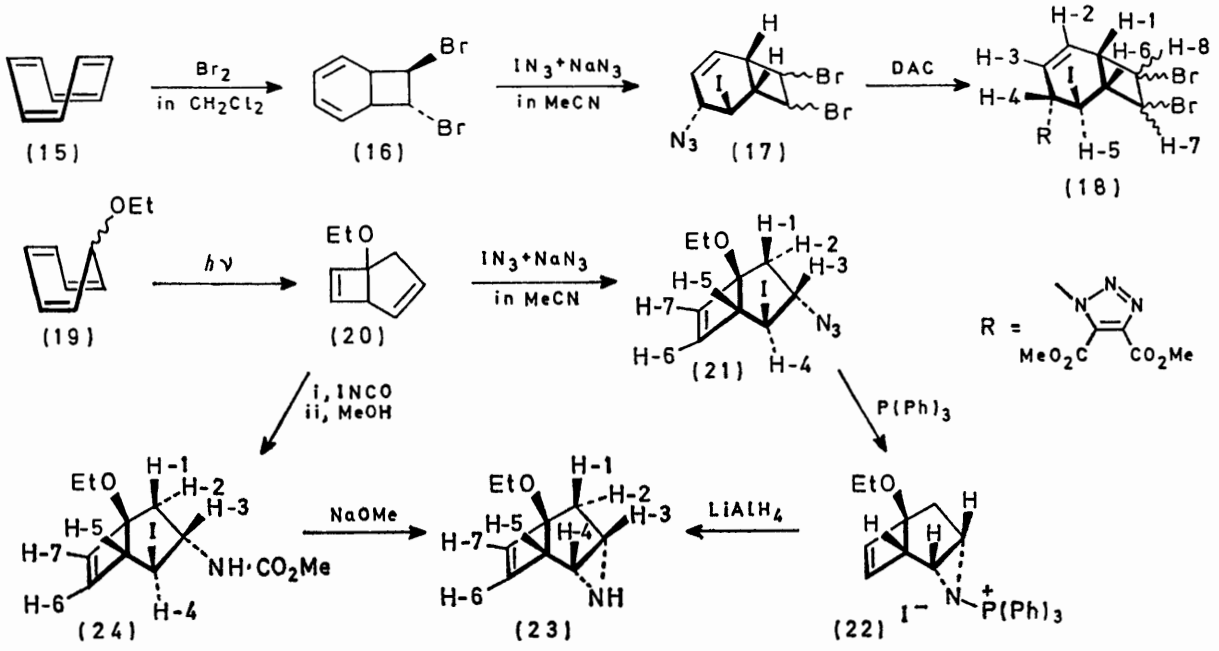
[6] L. A. Paquette, M. J. Broadhurst, C. Lee, and J. Clardy, *J. Amer. Chem. Soc.*, 1972, **94**, (*a*) p. 630; (*b*) p. 632; (*c*) J. Clardy, L. K. Read, M. J. Broadhurst, and L. A. Paquette, *ibid.*, p. 2904.

medium-sized ring unsaturated compounds. Furthermore, it is noteworthy that the cyclopropane ring is affected in the reaction of (1) with IN_3 solution.

Similar treatment of bicyclo[4,3,0]nona-2,4,7-triene (4) with IN_3 solution under the same conditions gave a labile 1 : 1 adduct (7). Compound (7) exhibited a strong azide i.r. absorption at 2100 cm^{-1} and gave a positive Beilstein halogen test, but did not afford the 1,3-dipolar cycloadduct (6) on treatment with DAC (only intractable materials were obtained). Thus, the possibility of formation of the diazide (5) from compound (1) by way of bicyclo[4,3,0]nona-2,4,7-triene (4) is excluded.



SCHEME 2



SCHEME 3

However, the mechanism for the stereospecific formation of the diazide (5) is not clear at present. Recently, Paquette *et al.*[6c] reported that the reaction pathway in the cycloaddition of (1) with TCNE (tetracyanoethylene) involved electrophilic attack of TCNE at C-3 of the bicyclononatriene tub conformation (1b) and that the generation of the *trans*-1,3-bishomotropylium ion (13) or the pentadienyl cation (14) is followed by C–C bond formation affording uniquely a *trans*-fused cyclobutane ring (12). Similarly, the mechanism for formation of the diazide (5) could involve a bishomotropylium or cyclopentadienyl cation; initial IN_3 addition to compound (1) might be expected to lead to the intermediate (C) *via* a cationic intermediate [(A) or (B)]; S_N2' reaction with the azide ion would then give (5a) as illustrated in Scheme 2.

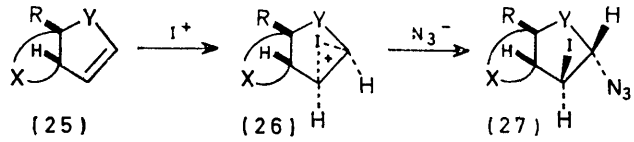
Treatment of *trans*-7,8-dibromobicyclo[4,2,0]octa-2,4-diene (16) with IN_3 solution gave an oily compound (17), which was converted into the cycloadduct (18) with DAC. The analytical data indicated that the adduct (18) was an iodo-triazolyl derivative. The n.m.r. spectrum showed characteristic signals at τ 4·20 (dd, $J_{4,5}$ 6·7, $J_{4,3}$ 3·0 Hz, H-4) and 5·20 (t, $J_{5,4} = J_{5,6} = 6{\cdot}7$ Hz, H-5).

Similar treatment of 5-ethoxybicyclo[3,2,0]hepta-2,6-

diene (20) with IN_3 solution gave a 1 : 1 adduct. Characteristic n.m.r. signals at τ 5·50 (dd, $J_{3,1}$ 7·0, $J_{3,2}$ 1·0 Hz, H-3), 5·87br (s, H-4), 6·25br (s, H-5), 7·44 (dd, $J_{1,2}$ −15·0, $J_{1,3}$ 7·0 Hz, H-1), and 7·94 (dd, $J_{2,1}$ −15·0, $J_{2,3}$ 1·0 Hz, H-2) indicate structure (21) as shown in Scheme 3. Since the β-iodo-azide (21) is very labile even at room temperature and furthermore does not give a 1,3-dipolar cycloadduct with DAC, it was converted with triphenylphosphine into the triphenylphosphonioaziridine iodide (22). Lithium aluminium hydride reduction of (22) afforded the aziridine (23), τ 6·53 (d, H-5), 7·27 (dd, H-3), and 7·55 (t, H-4). Since the H-5 signal appeared as a singlet for structure (21) and a doublet for structure (23), compound (23) could be assigned the *syn*-configuration.

Analogously, treatment of compound (20) with iodine isocyanate and then with methanol at room temperature gave a crystalline *trans*-iodo-carbamate (24) in 60% yield. The n.m.r. spectrum of compound (24) was similar to that of the *trans*-β-iodo-azide (21). Further reaction of (24) with sodium methoxide afforded an aziridine (23) in 80% yield, identical with the reduction product of the triphenylphosphonium iodide salt (22).

We have thus shown that the reactions of the conjugated and non-conjugated bicyclo-dienes with IN_3 give only the 1 : 1 adducts, as illustrated in Scheme 4.



SCHEME 4

From the structure of compounds (18) and (21), it might be suggested that the cyclic iodonium cation is formed by attack from the less hindered side; attack of azide ion from the opposite side would then give compound (27).

Attempts to effect the reactions of some bicyclo-diene valence tautomers of 2-acylaminotropone and *N*-alkoxycarbonyl-1*H*-azepines with IN_3 solution were unsuccessful; only labile and intractable tarry compounds were obtained.

EXPERIMENTAL

M.p.s were measured with a Yanagimoto micro-apparatus. Microanalyses were performed with a Perkin-Elmer 240 Elemental Analyser. N.m.r. spectra were taken with a Varian A-60 recording spectrometer, with tetramethylsilane as internal standard. I.r. spectra were taken with a JASCO IR-S spectrophotometer.

General Procedure for Iodine Azide Addition Reactions.—To sodium azide (3·9 g, 0·06 mol) in acetonitrile (25 ml) at −20° iodine monochloride (3·6 g, 0·022 mol) was added during 5—10 min. The mixture was stirred for an additional 5 min. The unsaturated compound (0·02 mol) was then added, and the mixture was left at room temperature overnight. The resulting slurry was poured into water (50 ml) and the mixture was extracted with ether. The extract was washed with aqueous 5% sodium thiosulphate (40 ml), and then with water, dried ($MgSO_4$), and evaporated at room temperature to afford the yellow oily product in 80—90% yield. The products were used in the following reactions without further purification, owing to their explosive nature. Compounds (5), (11), (17), and (21) were prepared by this procedure.

Cycloaddition of the Diazide (5) *with DAC.*—A solution of the diazide (5) (1·9 g, 0·01 mol) and DAC (4·3 g, 0·03 mol) in acetonitrile (50 ml) was refluxed for 1·5 h. The solvent was removed under reduced pressure and the residue was purified by silica gel chromatography with chloroform as eluant to give *dimethyl* 3,5-*di*(*bismethoxycarbonyltriazol*-1-*yl*)-*tricyclo*[5,2,2,$0^{2,6}$]*undeca*-8,10-*diene*-8,9-*dicarboxylate* (6) (40%), m.p. 215—217° (from methanol), $\nu_{max.}$ (KBr) 1720 (C=O) cm^{-1}, τ ($CDCl_3$) 3·20 (2H, t, *J* 3·8 Hz), 5·15 (2H, m), 6·00 (6H, s, 2 × CO_2Me), 6·05 (6H, s, 2 × CO_2Me), 6·30 (6H, s, 2 × CO_2Me), 6·0—6·8 (5H, complex multiplets), and 7·32 (1H, dt, *J* −14·6 and 7·3 Hz) (Found: C, 51·85; H, 4·55; N, 13·15. $C_{27}H_{28}N_6O_{12}$ requires C, 51·6; H, 4·5; N, 13·35%).

Pyrolysis of the Adduct (6).—A solution of compound (6) (0·2 g) in xylene (10 ml) was heated at 205° for 2 h in a sealed tube. The mixture was cooled to room temperature and the crystalline product was filtered off to give 3,5-*di*(*bismethoxycarbonyltriazol*-1-*yl*)*cyclopentene* (9) (0·12 g, 90%) as needles, m.p. 148—150° (from methanol), $\nu_{max.}$ (KBr) 1720 (C=O) cm^{-1}, τ ($CDCl_3$) 3·62 (2H, s), 3·75 (2H, dd, *J* 7·5 and 6·8 Hz), 6·00 (3H, s), 6·08 (3H, s), 6·50 (1H, dt, *J* −13·6 and 7·5 Hz), and 7·36 (1H, dt, *J* −13·6 and 6·8 Hz) (Found: C, 47·0; H, 4·25; N, 19·3. $C_{17}H_{18}N_6O_8$ requires C, 47·0; H, 4·2; N, 19·35%).

The filtrate was removed under reduced pressure to give an oil (8), identical (spectroscopic properties and g.l.c. retention time) with an authentic sample of dimethyl phthalate.

Cycloaddition of the Diazide (11) *with DAC.*—A solution of the diazide (11) (1·5 g, 0·01 mol) and DAC (2·8 g, 0·02 mol) in acetonitrile (40 ml) was refluxed for 15 h. The solvent was removed under reduced pressure to give compound (9) in 70% yield.

Cycloaddition of the β-*Iodo-azide* (17) *with DAC.*—From compound (17) (1·73 g, 4 mmol) and DAC (0·57 g, 4 mmol) in acetonitrile (20 ml) (reflux, 15 h) was isolated 4-(*bismethoxycarbonyltriazol*-1-*yl*)-7,8-*dibromo*-5-*iodobicyclo*[4,2,0]-*oct*-2-*ene* (18) (1·0 g, 50%), m.p. 122—123° (from methanol); $\nu_{max.}$ (KBr) 1750 and 1725 (C=O) cm^{-1}; τ ($CDCl_3$) 3·90 (2H, m), 4·20 (1H, dd, *J* 6·7 and 3·0 Hz), 5·20 (1H, t, *J* 6·7 Hz), 5·42 (1H, t, *J* 4·5 Hz), 5·45 (1H, t, *J* 4·5 Hz), 5·98 (3H, s), 6·03 (3H, s), and 6·0—6·8 (2H, m) (Found: C, 35·2; H, 3·05; N, 4·5. $C_{14}H_{14}Br_2IN_3O_4$ requires C, 35·2; H, 3·0; N, 4·55%).

3,4-*Epimino*-1-*ethoxybicyclo*[3,2,0]*hept*-6-*ene* (23) [*from* (21)].—To triphenylphosphine (2·15 g) in dry ether (50 ml) was added the β-iodo-azide (21) (2·5 g). After nitrogen evolution had ceased (2·5 h) filtration gave the crude product (22) (1·4 g, 30%).

To a stirred solution of lithium aluminium hydride (0·25 g) in anhydrous tetrahydrofuran (20 ml) (THF) was added the triphenylphosphonium iodide salt (22) (1·4 g). The solution was stirred at room temperature for 5 h and the excess of hydride was destroyed by cautious addition of 20% sodium hydroxide solution. The solution was filtered, the aluminum salts were washed with THF, and the THF was removed under reduced pressure giving the aziridine (23) (40%), $\nu_{max.}$ 3300 cm^{-1} (NH); τ ($CDCl_3$) 3·56 (1H, d, *J* 3·0 Hz), 3·85 (1H, d, *J* 3·0 Hz), 6·53 (1H, d, *J* 4·5 Hz), 6·60 (2H, q, *J* 6·8 Hz), 7·27 (1H, dd, *J* 4·5 and 3·0 Hz), 7·55 (1H,

t, J 4·5 Hz), 7·90 (1H, d, J −14·3 Hz), 8·20 (1H, dd, J −14·3 and 3·0 Hz), 8·75 (1H, m, NH), and 8·80 (3H, t, J 6·8 Hz); *picrate*, m.p. 175° (decomp.) (from methanol) (Found: C, 51·7; H, 5·4; N, 15·7. $C_{15}H_{18}N_4O_6$ requires C, 51·4; H, 5·2; N, 16·0%).

Reaction of the Bicyclo-diene (20) *with Iodine Isocyanate.*—To a cooled (−20°) stirred slurry of compound (20) (4·3 g, 0·031 mol), freshly prepared silver cyanate (6·0 g, 0·04 mol), and anhydrous THF (60 ml) was added iodine (7·6 g, 0·03 mol). The mixture became dark brown, but developed a canary-yellow hue after being stirred for 3 h at this temperature. It was allowed to warm to room temperature; inorganic salts were filtered off and the filtrate was concentrated to about 10 ml under reduced pressure. Anhydrous methanol (60 ml) was added and the solution was stirred at room temperature for 15 h. The methanol was evaporated off and the residue was dissolved in ether (70 ml) and washed with aqueous sodium sulphite (0·5 g in 20 ml). The aqueous layer was extracted with more ether (2 × 20 ml). The combined organic layers were dried and evaporated and the resulting yellow solid was purified by silica gel chromatography (chloroform as an eluant), affording *methyl 1-ethoxy-4-iodobicyclo*[3,2,0]*hept-6-en-3-ylcarbamate* (24) (6·0 g, 60%), m.p. 110—112°, $\nu_{max.}$ (KBr) 3320 (NH) and 1705 (C=O) cm^{-1}, τ ($CDCl_3$) 3·62 (1H, d, J 3·0 Hz), 3·76 (1H, d, J 3·0 Hz), 5·00br (1H, d, J 8·0 Hz, NH), 5·45 (1H, t, J 8·0 Hz), 5·90 (1H, s), 6·25 (1H, s), 6·38 (3H, s, CO_2Me), 6·45 (2H, q, J 6·8 Hz, $O{\cdot}CH_2$), 7·25 (1H, dd, J −14·0 and 8·0 Hz), 8·10 (1H, d, J −14·0 Hz), and 8·77 (3H, t, J 6·8 Hz, $CH_2{\cdot}CH_3$) (Found: C, 39·4; H, 4·75; N, 4·05. $C_{11}H_{16}INO_3$ requires C, 39·2; H, 4·8; N, 4·15%).

3,4-*Epimino-1-ethoxybicyclo*[3,2,0]*hept-6-ene* (23) [*from* (24)].—A mixture of compound (24) (1·7 g, 5 mmol) and freshly prepared sodium methoxide (0·27 g, 5 mmol) in anhydrous THF (20 ml) was refluxed for 1·5 h. The solvent was removed *in vacuo*, and the residue was dissolved in ether (50 ml). The ether solution was washed with water, dried, and evaporated *in vacuo* to leave the imine (23) (0·6 g, 80%) as an oil; *picrate*, m.p. 175° (decomp.).

[2/2027 *Received*, 30*th August*, 1972]