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SYNTHESIS OF ADAMANTANE DERIVATIVES—XXX[1]

SYNTHESIS OF SOME ADAMANTANE SPIRO HETEROCYCLES BY UTILIZING IONIC- AND CYCLOADDITIONS

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Abstract—Synthesis and some reactions of adamantane spiro heterocycles such as aziridine, oxaziridine, azetidine and 1,2-diazetidine derivatives have been described.

The 1,3-dipolar cycloadditions of methyleneadamantane (**2**) and adamantylidenecyanoacrylate (**14**) have also been reported as a facile route to some 5-membered adamantane spiro heterocycles.

Adamantane spiro compounds have attracted much attention recently because of their utility as synthetic intermediate,[2] as model compounds for physical organic studies,[3] and as potent antiviral agent,[4] and also for unusual stability of some derivatives involving reactive functional groups or strained ring system.[5] We now describe a facile synthesis of some 3-, 4- and 5-membered adamantane spiro heterocycles by utilizing ionic- and cycloadditions to methyleneadamantane (**2**)[6] readily accessible from adamantanone (**1**).

RESULTS AND DISCUSSION

Although some of adamantane spiro 3-membered ring compounds have been reported,[2,3a,b,5,7] other interesting compounds are not recorded, and we investigated aziridine- (**4**) and oxaziridine derivatives (**5a** and **5b**) as useful synthetic intermediates.

The synthesis of adamantanespiro-2'-aziridine (**4**) been achieved by treatment of **2** with bromine azide generated *in situ*.[8] The azidobromide **3a** formed on reduction with LAH afforded aziridine **4** in 64% yield. The structure of **4** was proved by analytical and spectral data. In the NMR spectrum, **4** had a characteristic singlet (2H) at δ 1·34. Application of the Hassner's method[9] by using iodine azide gave **3b** (78%) which was converted similarly to **4** (Scheme 1).

Above method is superior to others because direct epimination of a C=C double bond is not so easy as epoxidation and also the triazoline route is not satisfactory due to the low reactivity of **2** toward azide as a 1,3-dipole as discussed later.[10]

As one of the routes to spirooxaziridine **5a**,[11] adamantanone (**1**) was treated with O-mesitylenesulfonylhydroxylamine,[12] a useful aminating agent. IR absorptions at 3220, 1660 and 1715 cm^{-1} and TLC and GLPC analyses of the crude product indicated the formation of lactam **6a**[13] which was isolated in 45% yield (unreacted **1** was recovered in 54%). The amination in the presence of excess sodium bicarbonate gave the same results. These facts and the reported oxaziridine formation via amination of carbonyl compounds[11] suggest that **5a** was thermally unstable and rearranged quantitatively to **6a**. This is of interest in view of the fact that the photochemical Beckmann rearrangement of **1**-oxime in acetic acid affords a high yield of **6a**, in which **5a** is postulated as an intermediate.[14,15] The above quantitative rearrangement of **5a** to **6a** is in accord with the postulation, though the photochemical rearrangement of **5a** to **6a** may be the competent path in the photo-Beckmann rearrangement. Very recently Lattes *et al.*[16] isolated N-benzyl- and N-methyl-adamantanespiro-oxaziridne and showed that they rearrange photochemically to the corresponding lactams.

Adamantylideneaniline (**7**) was oxidized with *m*-chloroperbenzoic acid but the product was N-phenyl lactam **6b** (35%), indicating that **5b** was also prone to rearrange nonphotochemically.

As one of the most facile and direct routes to adamantane spiro 4-membered heterocycles, reactions of **2** with chlorosulfonyl isocyanate (CSI) and 4 - phenyl - 1,2,4 - triazoline - 3,5 - dione (PTAD) were examined.

Treatment of **2** with CSI[17] afforded a 1 : 1 adduct **8**, m.p. 90–92° in 51% yield. The structural assignment was supported by the analytical and spectral data. Reductive hydrolysis of **8** with sodium sulfite gave azetidinone **9**, m.p. 153–156°, which revealed characteristic IR absorptions at 3260 and 1725 cm^{-1} and NMR signal at δ 2·70 for 2H supporting the assigned structure.[18] Adamantanespiro-2'-azetidine **10** was obtained by LAH reduction of **9** (Scheme 1).

Reaction of **2** with PTAD[19] afforded a 2 + 2 adduct **11** in 15% yield. In the NMR spectrum, appearance of a singlet at δ 4·28 (2H) was compatible with the assigned structure.

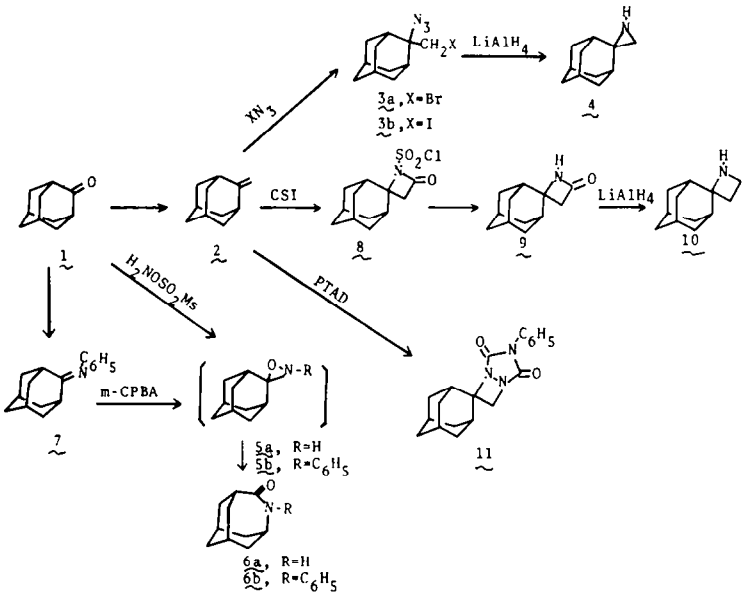
Thus, 2 + 2 cycloaddition of **2** afforded the spiro-4-membered heterocycles, though the reactivity of **2** was only modest.

The 1,3-dipolar cycloadditions of **2** were examined using benzonitrile oxide, C,N-diphenylnitrone, phenylazide and diazomethane as a facile route to some adamantane spiro 5-membered heterocycles (Scheme 2).

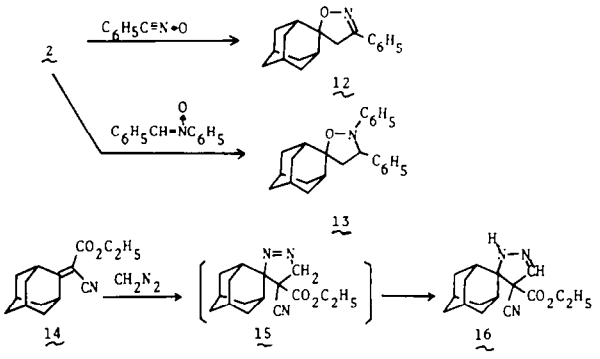
The reaction of **2** with benzonitrile oxide afforded regioselectively Δ^2-isooxazoline **12** in 56% yield. The assigned regiochemistry was supported by the appearance of a characteristic NMR singlet at δ 3·14 for 2H. Such a high regioselectivity is expected from both steric and electronic effects.[20,21]

The reaction of C,N-diphenylnitrone with **2** afforded a 1 : 1 adduct in 43% yield, which was characterized as diphenylisooxazolidine **16** based on analysis and spectral data. The orientation of this addition is also sterically favored.[20,22]

The very lower reactivity of **2** toward azide or



Scheme 1.



Scheme 2.

diazoalkane could be predicted from recent theoretical[23] and earlier experimental studies.[20,24] In fact, treatment of **2** with excess phenylazide (25° for 2 weeks, and 85° for 10 hr) and diazomethane (25° for 2 weeks) did not afford any adducts.

Electron-withdrawing substituents or conjugation of the dipolarophile are known to increase the 1,3-dipolar cycloaddition reactivity toward azide or diazoalkane.[20,23] Ethyl adamantylidenecyanoacrylate (**14**)[4b] was treated with phenylazide but no adduct was obtained. However, treatment of **14** with diazomethane afforded a Δ^2-pyrazoline derivative **16** in 34% yield, which should be produced via a tautomeric isomerization of the initial adduct **15**.

Although the 1,3-dipolar cycloadditions are not many, the above results indicate the usefulness of the cycloadditions for synthesis of some adamantane spiro 5-membered heterocycles if appropriate 1,3-dipoles and methyleneadamantane derivatives are employed.

EXPERIMENTAL

Microanalyses were performed with a Perkin-Elmer 240 elemental analyzer. M.ps were determined with a Yanagimoto micro-m.p. apparatus (hot-stage type) and are uncorrected. IR spectra were obtained with a JASCO IRA-1 spectrometer. NMR spectra were taken with a JEOL-C-60HL spectrometer using TMS as internal standard, and mass spectra with a JEOL-01SG spectrometer at 75 eV.

Adamantane-2-spiro-2'-aziridine (**4**)

(a) To a stirred and ice-cooled soln of **2** (148 mg, 1·00 mmol) in dimethylformamide (6 ml) was added slowly sodium azide (326 mg, 5·00 mmol) in water (2 ml) and then N-bromosuccinimide (250 mg, 1·40 mmol) in small portions successively. After the stirring for 8 hr under ice-cooling, n-pentane (50 ml) was added and the organic layer separated, washed and dried (Na_2SO_4). Removal of the solvent under reduced pressure afforded 2-*bromomethyl-2-adamantylazide* (**3a**) as an oil (270 mg, 100%), IR (film) 2120 cm^{-1}, which was directly reduced with LAH (114 mg, 3·00 mmol) in ether (20 ml) for 12 hr at room temp. Work-up as usual afforded crude **4** as a colorless solid (140 mg) which was purified on preparative TLC (silica gel, $CHCl_3$) followed by sublimation (100–120°, 25 mm) to give pure **4** (112 mg, 64%): m.p. 141–143°; IR (KBr) 3240, 3055, 1215 and 875 cm^{-1}; NMR ($CDCl_3$) δ 1·34 (s, 2H), 1·3–2·2 (m, 14H) and 2·31 (s, 1H, disappeared on shaking with D_2O); mass spectrum *m/e* 163 (M^+). (Found: C, 80·91; H, 10·49; N, 8·60. $C_{11}H_{17}N$ requires: C, 80·92; H, 10·50; N, 8·58%).

(b) To a stirred slurry of sodium azide (272 mg, 4·20 mmol) in acetonitrile (3·5 ml) was added slowly iodine monochloride (250 mg, 1·55 mmol) at *ca.* −15°.[9] After the stirring for 5 hr, **2** (74 mg, 0·50 mmol) was added to the mixture and the stirring was

continued for 12 hr while the temp. was allowed to rise room temp. The mixture diluted with water was extracted with ether (10 ml × 5). The combined extracts were washed with 5% $NaHSO_4$ (10 ml × 2) and water (5 ml) and dried (Na_2SO_4). Removal of the solvent gave **3b** as an yellowish oil (247 mg, 78·0%), IR (film) 2100 cm^{-1}, which was reduced with LAH without further purification to afford **4** (24 mg, 38%).

Reaction of adamantanone (**1**) *with o-mesitylenesulfonylhydroxylamine* (*MSHA*). To a stirred and ice-cooled slurry of O-(mesitylenesulfonyl)acetohydroxamate[12] (375 mg, 1·30 mmol) in dioxane (0·25 ml) was added slowly 70% perchloric acid (0·15 ml). After stirring for 10 min, the mixture was diluted with ice-water (10 ml) and the resulting ppt filtered off, dissolved in methylene chloride (10 ml) and dried (Na_2SO_4). To this soln of MSHA was added **1** (120 mg, 0·800 mmol) and the mixture was stirred for 15 hr at *ca.* 20°. Dilution with n-hexane (10 ml) afforded a ppt of mesitylene-sulfonic acid which was removed by filtration. Removal of the solvent afforded a solid residue which was purified on a silica gel column (CH_2Cl_2–$CHCl_3$) to give *4-azahomoadamantan-5-one* (**6a**)[13] (60 mg, 45%, 100% based on the consumed **1**) and unreacted **1** (65 mg, 54%). **6a** was identical with an authentic sample by IR, NMR and GLPC analyses. The reaction in the presence of $NaHCO_3$ (20 mole excess) resulted in the formation of the same product.

Adamantylideneaniline (**7**). A mixture of **1** (450 mg, 3·00 mmol), aniline (931 mg, 10·0 mmol), *p*-toluenesulfonic acid (10 mg) in benzene (80 ml) was refluxed for 15 hr using a Dean-Stark trap. Removal of the solvent and excess aniline under reduced pressure, the oily residue (0·69 g) was purified by a Kugelrohr distillation at 90–120° (0·25 mm) to afford unstable **7** as an oil (495 mg, 73·3%). On standing the oil crystallized: m.p. 60–64°; IR (KBr) 1655, 1600, 788 and 690 cm $^{-1}$; NMR ($CDCl_3$) δ 1·7–2·2 (m, 12H), 2·70 (broad s, 2H) and 6·55–7·45 (m, 10H). (Found: C, 85·40; H, 8·66; N, 5·93. $C_{16}H_{19}N$ requires: C, 85·28; H, 8·50; N, 6·22%).

Oxidation of **7** *with m-chloroperbenzoic acid* (*MCPBA*). A mixture of **7** (241 mg, 1·00 mmol) and 85% MCPBA (203 mg, 1·00 mmol) in methylene chloride (10 ml) was stirred under ice-cooling for 5 hr. The mixture was washed with 5% $NaHCO_3$ aq (10 ml × 2) and water (10 ml) and dried (Na_2SO_4). Removal of the solvent gave crude products which were purified on a silica gel column ($CHCl_3$) to afford *N-phenyl-4-azahomodamantan-5-one* (**6b**) as colorless crystals (91 mg, 35%): m.p. 70–72°; IR (KBr) 1640, 1600, 1500, 760 and 695 cm $^{-1}$; NMR ($CDCl_3$) δ 1·6–2·3 (m, 12H), 2·93 (m, 1H), 3·65 (m, 1H), and 6·86–7·43 (m, 5H); mass spectrum *m/e* 257 (M^+). (Found: C, 79·49; H, 7·85; N, 5·94. $C_{16}H_{19}NO$ requires: C, 79·63; H, 7·94; N, 5·80%).

Cycloaddition of **2** *with chlorosulfonyl isocyanate* (*CSI*). To a stirred and cooled (−78°) soln of **2** (148 mg, 1·00 mmol) in dry ether (5 ml) was added slowly CSI (250 mg, 1·70 mmol) in dry ether (2 ml) under argon over 0·5 hr. After the stirring was continued for 20 hr, the mixture was allowed to come to room temp. and then, diluted with n-hexane to precipitate colorless crystals (148 mg, 51%) of *1'-chlorosulfonyladamantane-2-spiro-2'-azetidin-4'-one* (**8**): m.p. 90–92°; IR (KBr) 1820, 1410 and 1190 cm^{-1}; NMR ($CDCl_3$) δ 1·6–2·5 (m, 14H) and 3·08 (s, 2H). (Found: C, 49·73; H, 5·56; N, 4·84. $C_{12}H_{16}NO_3SCl$ requires: C, 49·91; H, 5·58; N, 4·85%).

Adamantane-2-spiro-2'-azetidin-4'-one (**9**). A mixture of **8** (135 mg, 0·468 mmol), ether (10 ml) and 20% Na_2SO_3 aq (8 ml) was stirred at room temp. for 2 days, during which the aqueous phase was kept between pH 8 and 9 by addition of 10% KOH aq. The organic layer was separated and the aqueous layer was extracted with ether (10 ml × 2). The combined organic layer and extracts were dried (Na_2SO_4). Removal of the solvent afforded **9** as colorless crystals after recrystallization from aqueous MeOH (85 mg, 95%): m.p. 153–156°; IR (KBr) 3260 and 1725 cm^{-1}; NMR ($CDCl_3$) δ 1·60–2·2 (m, 14H), 2·70 (d, J = 2·0 Hz, 2H) and 7·25 (broad s, 1H); On shaking with D_2O the signal at δ 7·25 disappeared and the doublet at δ 2·70 became a singlet. (Found: C, 75·33; H, 8·86; N, 7·19. $C_{12}H_{17}NO$ requires: C, 75·35; H, 8·96; N, 7·32%).

Adamantane-2-spiro-2'-azetidine (**10**). A mixture of **9** (35 mg, 0·18 mmol) and LAH (76 mg, 2·0 mmol) in dry THF (5 ml) was refluxed for 27 hr. After decomposition of the excess reagent by addition of water under ice-cooling, work-up as usual with ether, followed by sublimation (140°, 25 mm) afforded **10** as colorless crystals (18 mg, 55%): m.p. 53–56°; IR (KBr) 3240, 1250, 1015 and 800 cm $^{-1}$; NMR ($CDCl_3$) δ 1·5–2·3 (m, 14H), 2·16 (t, J = 7 Hz, 2H), 2·47 (s, 1H, disappeared on shaking with D_2O) and 3·44 (t, J = 7·0 Hz, 2H). (Found: C, 81·50; H, 10·70; N, 7·79. $C_{12}H_{19}N$ requires: C, 81·30; H, 10·80; N, 7·90%).

Cycloaddition of **2** *with* 4 *- phenyl - 1,2,4 - triazoline - 3,5 - dione* (*PTAD*). To a stirred soln of 4-phenylurazole (130 mg, 0·860 mmol) in acetone (2 ml) was added t-butyl hypochlorite (96 mg, 0·88 mmol) at −78°. After stirring for 10 min, the solvent was removed under reduced pressure to give PTAD which was dissolved in benzene (6 ml) containing **2** (90 mg, 0·61 mmol). The mixture was refluxed for 9 hr and the resulting ppt was removed by filtration. The filtrate was evaporated to dryness to afford a crude product which was purified on a silica gel column (CH_2Cl_2) to give *adamantane - 2 - spiro - 6' - (3' - phenyl - 1',3',5' - trazabicyclo[3.2.0]hepta - 2',4' - dione* (**11**) as colorless crystals (n-hexane-CH_2Cl_2) (30 mg, 15%): m.p. 153–155°; IR (KBr) 1705, 1600 and 1500 cm^{-1}; NMR ($CDCl_3$) δ 1·5–2·3 (m, 14H), 4·28 (s, 2H) and 7·2–7·8 (m, 5H). (Found: C, 70·51; H, 6·84; N, 12·75. $C_{19}H_{21}N_3O_2$ requires: C, 70·57; H, 6·55; N, 12·99%).

Cycloaddition of **2** *with benzonitrile oxide.* To a stirred and ice-cooled soln of benzhydroxamoyl chloride (200 mg, 1·30 mmol) in dry ether (10 ml) was added triethylamine (142 mg, 1·40 mmol) in dry ether (2 ml). After 3 min, the mixture was washed with cold water and dried (Na_2SO_4) for 10 min. To this soln was added **2** (148 mg, 1·00 mmol) and the mixture was stirred for 20 hr at 25° and refluxed for 1 hr. Removal of the solvent and chromatography of the residue on a silica gel column (n-hexane-benzene) afforded unreacted **2** (50 mg, 34%) and *3'-phenyladamantane - 2 - spiro - 5' - $\Delta^{2'}$ - isooxazoline* (**12**) as crystals (n-hexane-CH_2Cl_2) (54 mg, 20%, 56% based on the reacted **2**): m.p. 84–86°; IR (KBr) 1600, 1570, 1500, 770 and 690 cm^{-1}; NMR ($CDCl_3$) δ 1·5–2·5 (m, 14H), 3·14 (s, 2H),[25] and 7·3–7·5 (m, 5H); mass spectrum *m/e* 266 (M^+). (Found: C, 80·84; H, 7·95; N, 5·19. $C_{18}H_{21}NO$ requires: C, 80·86; H, 7·92; N, 5·24%).

Cycloaddition of **2** *with* C,N-*diphenylnitrone.* A mixture of **2** (148 mg, 1·00 mmol) and C,N-diphenylnitrone (220 mg, 1·12 mmol) in toluene (6 ml) was refluxed for 28 hr. Removal of the solvent and chromatography on a silica gel column (n-hexane-benzene) afforded unreacted **2** (52 mg, 35%) and *2',3'-diphenyladamantane-2-spiro-5'-isooxazolidine* (**13**) as crystals (n-hexane-CH_2Cl_2) 95 mg, 27·5%, 43% based on the reacted **2**): m.p. 93–95°; IR (KBr) 1600, 1500, 765, 755, 700 and 690 cm $^{-1}$; NMR ($CDCl_3$) δ 1·4–2·5 (m, 14H), 2·23 (d, d, J = 8·0 and 12·0 Hz, 1H), 2·86 (d,d, J = 8·0 and 12·0 Hz, 1H), 4·57 (t, J = 8·0 Hz, 1H) and 6·7–7·6 (m, 10H). (Found: C, 83·61; H, 7·99; N, 3·99. $C_{24}H_{27}NO$ requires: C, 83·44; H, 7·88; N, 4·05%).

Cycloaddition of ethyl adamantylidenecyanoacrylate (**14**) *with diazomethane.* **14**[4b] (245 mg, 1·00 mmol) was added to an ether soln (60 ml) of diazomethane (*ca.* 45 mmol) and the mixture was allowed to stand at room temp. (*ca.* 25°) for 3 weeks. Removal of the solvent and excess diazomethane afforded an oily residue which was purified on a silica gel column ($CHCl_3$-ether) to afford *4' - cyano - 4' - ethoxycarbonyl - adamantane - 2 - spiro - 5' - $\Delta^{2'}$ - pyrazoline* (**16**) as an oil (87 mg, 34%): n_D^{19} 1·5384; IR (film) 3320, 3100, 1740, 1680 and 1580 cm $^{-1}$; NMR ($CDCl_3$) δ 1·47 (t, J = 7·0 Hz, 3H), 1·5–2·5 (m, 14H), 4·28 (q, J = 7·0 Hz, 2H), 6·24 (s, 1H, disappeared on shaking with D_2O) and 7·00 (s, 1H);[26] mass spectrum *m/e* 287 (M^+). (Found: C, 66·66; H, 7·28; H, N, 14·72. $C_{16}H_{21}N_3O_2$ requires: C, 66·87; H, 7·37; N, 14·62%).

REFERENCES

[1]Part XXIX: T. Sasaki, S. Eguchi and M. Mizutani, *Tetrahedron Letters* 2685 (1975).

[2a]D. Farcasiu, *Synthesis*, 615 (1972); [b]J. Scharp, H. Wynberg and J. Strating, *Rec. Trav. Chim. Pays-Bas* **89**, 18 (1970); [c]S. D. Isaev, A. G. Yurchenko, F. N. Stepanov, G. G. Kolyada, S. S. Novikov and N. F. Karpenko, *Zh. Org. Khim.* **9**, 724 (1973); *Chem. Abstr.* **79**, 18613t(1973); [d]S. D. Saev, A. G. Yurchenko, Z. N. Marzinova, F. N. Stepanov, G. G. Kolyada and S. S. Novikov, *Ibid.* **10**, 1338 (1974); *Chem. Abstr.* **81**, 120075x (1974).

[3a]B. R. Ree and J. C. Martin, *J. Am. Chem. Soc.* **92**, 1660 (1970);

[b]P. v. R. Schleyer, V. Buss and R. Gleiter, *Ibid.* **93**, 3927 (1971); [c]D. A. Lightner and T. C. Chang, *Ibid.* **96**, 3015 (1974).
[4a]K. Lundahl, J. Schut, J. L. M. A. Schlatmann, G. B. Paerels and A. Peters, *J. Med. Chem.* **15**, 129 (1972); [b]R. van Hes, A. Smit, T. Kralt and A. Peters, *Ibid.* **15**, 132 (1972).
[5a]E. R. Talaty and A. E. Dupuy, Jr., *Chem. Commun.* 790 (1968); [b]H. Wynberg, S. Reiffers and J. Strating, *Rec. Trav. Chim. Pays-Bas*, **89**, 982 (1970); [c]J. H. Wieringa, J. Strating, H. Wynberg and W. Adam, *Tetrahedron Letters* 169 (1972); [d]A. P. Scharp and G. R. Faler, *J. Am. Chem. Soc.* **95**, 3381 (1973).
[6]P. v. R. Schleyer and R. D. Nicholas, *Ibid.* **83**, 182 (1961).
[7]C. Woodworth, V. Bus and P. v. R. Schleyer, *Chem. Commun.* 569 (1968).
[8]D. Van Ende and A. Krief, *Angew. Chem.*, Int. Ed. Engl. **13**, 279 (1974).
[9]F. W. Fowler, A. Hassner and A. Levy, *J. Am. Chem. Soc.*, **89**, 2077 (1967); A. Hassner, G. J. Mattews and F. W. Fowler, *Ibid.* **91**, 5046 (1969).
[10]O. C. Dermer and G. E. Ham, *Ethyleneimine and Other Aziridines*, pp. 1–83. Academic Press, New York (1969).
[11a]E. Schmitz, R. Ohme and D. Murawski, *Angew. Chem.* **73**, 708 (1961); [b]E. Schmitz, R. Ohme and D. Murawski, *Chem. Ber.* **98**, 2516 (1965).
[12]Y. Tamura, J. Minamikawa, K. Sumoto, S. Fujii and M. Ikeda, *J. Org. Chem.* **38**, 1239 (1973); and refs cited.
[13a]T. Sasaki, S. Eguchi and T. Toru, *Chem. Commun.* 1285 (1969); [b]T. Sasaki, S. Eguchi and T. Toru, *J. Org. Chem.* **35**, 4109 (1970).
[14]T. Sasaki, S. Eguchi and T. Toru, *Chem. Commun.* 1239 (1970).
[15]G. Just and M. Cunningham, *Tetrahedron Letters* 1151 (1972).
[16]E. Oliveros-Desherces, M. Riviere, J. Parello and A. Lattes, *Synthesis* 812 (1974).
[17a]R. Graf, *Angew. Chem.*, Int. Ed. Engl., **7**, 172 (1968); [b]H. Bestian, *Cycloaddition Reactions*, p. 611. Butterworth, London (1971).
[18]T. Sasaki, S. Eguchi and H. Yamada, *J. Org. Chem.* **38**, 679 (1973).
[19]R. C. Cookson, S. S. H. Gilani and I. D. R. Stevens, *J. Chem. Soc.* 1905 (1967).
[20]R. Huisgen, R. Grashey and J. Sauer, *The Chemistry of Alkenes* (Edited by S. Patai), p. 806. Interscience, New York (1964).
[21a]C. Grundmann, *Synthesis* 344 (1970); [b]C. Grundmann and P. Grünanger, *The Nitrile Oxides*. Springer-Verlag, Heidelberg-New York (1971).
[22]R. Huisgen, R. Grashey, H. Houk and H. Seidl, *Chem. Ber.* **101**, 2043 (1968).
[23a]R. Sustmann, *Tetrahedron Letters* 2717 (1971); [b]R. Sustmann and H. Trill, *Angew. Chem.*, Int. Ed. Engl., **11**, 838 (1972); [c]K. N. Houk, *J. Am. Chem. Soc.* **94**, 8973 (1972).
[24]For phenylazide, see R. Huisgen, G. Szeimies and L. Moebius, *Chem. Ber.* **100**, 2494 (1967).
[25]R. Sustmann, R. Huisgen and H. Huber, *Chem. Ber.* **100**, 1802 (1967).
[26]N. Rabjohn, H. R. Havens and J. L. Rutter, *J. Heterocyclic Chem.* **3**, 413 (1966).