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# ASYMMETRICAL NON-BRIDGEHEAD NITROGEN

## I. DIASTEREOMERIC N-HALO-2-ALKYLAZIRIDINES

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An asymmetrical C(2) center in 2-alkylaziridines determines the formation of a stable asymmetrical nitrogen center in the stereoselective N-halogenation reaction (Table I) yielding N-haloaziridines with known hindered

TABLE I

| | NaOCL | $(CH_2CO)_2NCl$ | NaOBr | $(CH_2CO)_2NBr$ |
|---|---|---|---|---|
| Me-⟨ NH | trans/cis | trans/cis | trans | trans |
| | I.38/I.0 | 2/I Ib | | |
| Pr-⟨ NH | — | trans | trans | trans |

inversion of the nitrogen atom[I]:

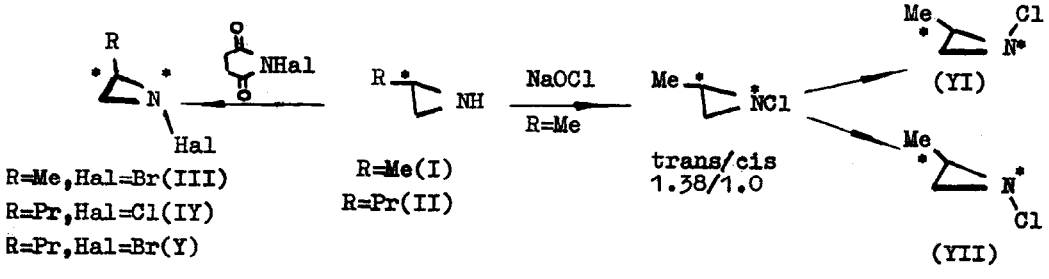
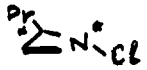
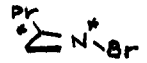
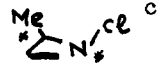
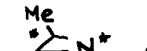


TABLE 2

| Compounds | | Yield % | B.p. °C(mm) | $n_D^{20}$ | $[\alpha]_D^{20}$ |
|---|---|---|---|---|---|
| I |  a) | 37 | 66-67(760) | 1.4120 | -8.I (C 3,n-$C_9H_{20}$) |
| II |  b) | 76.7 | 115(760) | 1.4245 | -19.2 (C 0.5,n-$C_7H_{16}$) |
| III |  c) | 56 | 31-32 (35) | 1.4858 | +497 (C 0.08,n-$C_9H_{20}$) |
| IV |  | 55.5 | 41-42 (18) | 1.4430 | +16.6(C 1.1,n-$C_7H_{16}$) |
| V |  | 59 | 27-28 (I) | 1.4763 | +87.8 (C 6,n-$C_7H_{16}$) |
| VI |  c) | 42 trans/cis 1.38/1.0 | 38-42(110) | - | -81 (C 0.8,n-$C_9H_{20}$) |
| VII |  c) | | | - | +94 (C 0.8, n-$C_9H_{20}$) |

a) Had been described in ref. 2b.

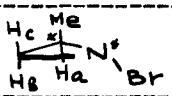
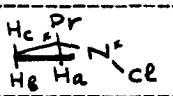
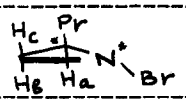
b) Optically inactive compound had been described in ref. 3.

c) $\lambda_{max}$(n-$C_9H_{20}$) : III 293, VI 257 and VII 253 mμ . For 7-chloro-7-azabicyclo(4.1.0)heptane: cis 260 and trans 257 mμ [Id].

VI and VII were resolved by GC (Varian Model 705,20 ft column SE-30,30°)

The structure of analytically pure products was confirmed by PMR*) (Table 3, Fig.1) and mass-spectra.

TABLE 3

| |  | |  | |  | |
|---|---|---|---|---|---|---|
| | δ ppm | J Hz | δ ppm | J Hz | δ ppm | J Hz |
| Me | I.I(doubl.) | $J_{MeHa}$ 5.7 | 0.93(tripl.) | $J_{MeCH_2}$ 6.5 | 0.93(tripl.) | $J_{MeCH_2}$ 6.0 |
| $CH_2CH_2$ | - | - | I.38(mult.) | - | I.34(mult.) | - |
| $H_a$ | 2.21(mult.) | $J_{ab}$ 7.35 | 2.21(mult.) | $J_{ab}$ 7.83 | 2.17(mult.) | $J_{ab}$ 7.1 |
| $H_b$ | 1.98 " | $J_{bc}$ -3.35 | 2.08 " | $J_{bc}$ -3.09 | 1.99 " | $J_{bc}$ -3.2 |
| $H_c$ | 1.70 " | $J_{ac}$ 5.5 | 1.89 " | $J_{ac}$ 5.7 | 1.75 " | $J_{ac}$ 5.4 |

*) See ref.4.

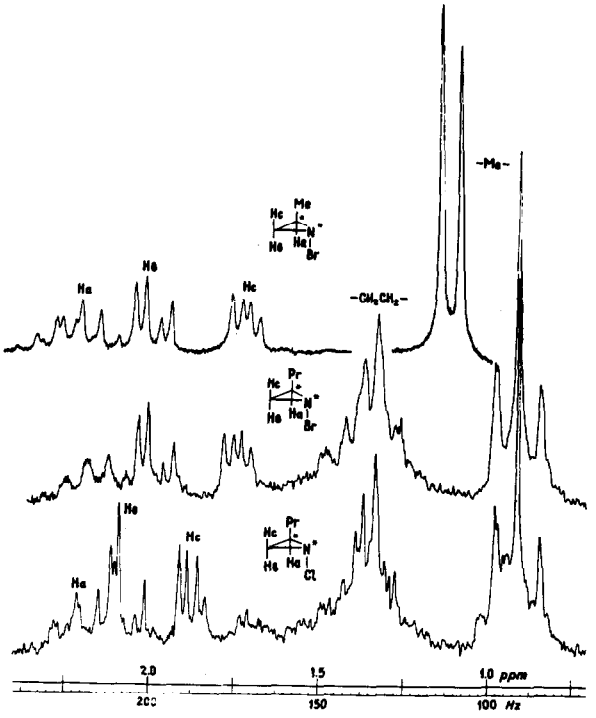



FIG. I

ORD curves were measured on JASCO ORD/UV-5 spectropolarimeter (fig.2,3).

Thus, III - VII are the first diastereomers with a stable optically active non-bridgehead nitrogen atom.

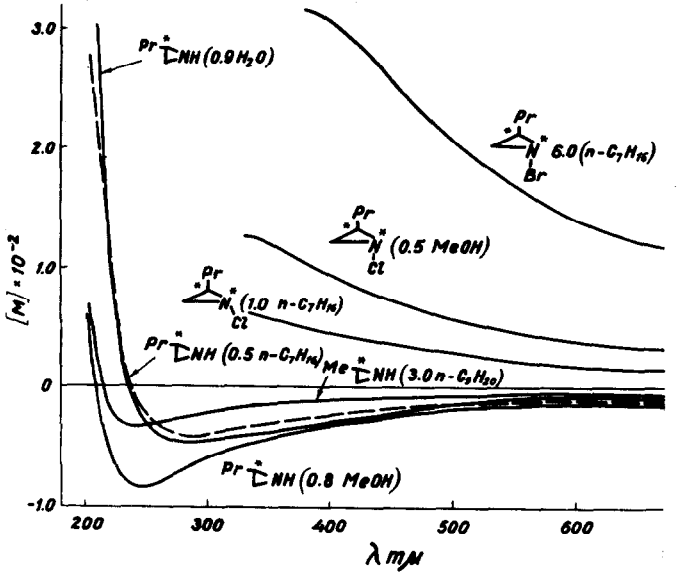



FIG. 2

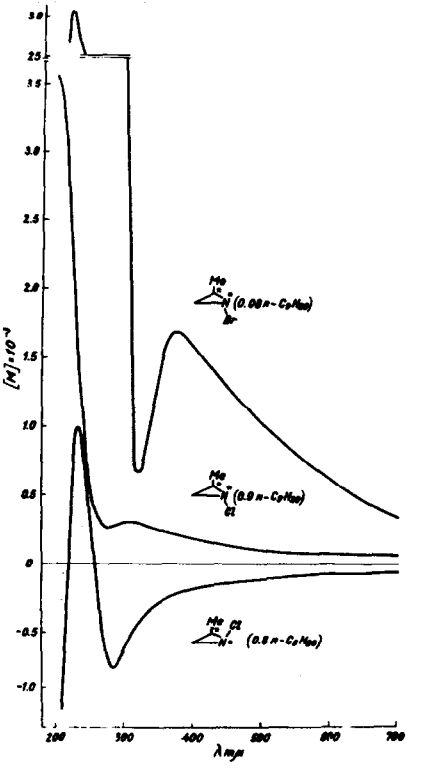



FIG. 3

## NOTES AND REFERENCES

I. Heating of the N-haloaziridines up to 125°([a])R.G.Kostyanovsky,I.I. Tchervin,O.A.Panshin,Izvest.Akad.Nauk USSR,ser.chim.,1423(1968) ), up to 140° ([b])S.Brois,J.Am.Chem.Soc.,90,506 (1968) ) and even up to 180° ([c])J.M.Lehn, J.Wagner,Chem.Commun.,148 (1968) ) did not cause the inversion of the nitrogen atom in the NMR time scale.We have estimated the nitrogen inversion barrier in cis-N-chloro-2-methylaziridine to be 20 ± 2 kcal/mole on the basis of epimerization rate measurements of VI⇌VII in $CCl_4$ : $k_{80°}$ $2.08 \cdot 10^{-4}$; $k_{110°}$ $2 \cdot 5 \cdot 10^{-3} sec^{-1}$. D.Felix and A.Eschenmoser give only one value $k_{29.5°}$ $4.3 \cdot 10^{-5} sec^{-1}$ for the cis-trans epimerization of 7-chloro-7-azabicyclo (4.I.0)heptane ([d])Angew.Chem., 80,197 (1968) ).

2. I and II are prepared by $LiAlH_4$/THF reduction ([a])P.G.Gassman,A.Fentiman,J.Org.Chem., 32, 2388 (1967) ) of ℓ-alanine, $[\alpha]_D^{20}$ +14.5°(C 2,6n HCl) and ℓ-norvaline, $[\alpha]_D^{20}$ +5.5° (C 0.7,$H_2O$),respectively (yields of the intermediate aminoalcohols are 31.5 - 55.5%) followed by Wenker cyclization ([b])Y.Minoura, M.Takebayashi, Ch.C.Price, J.Am.Chem.Soc., 81, 4689 (1959) ).

3. K.Ichimura,M.Ohta, Bull.Chem.Soc.Japan., 40, 432 (1967).

4. PMR parameters of VI-VII (Varian HA-100 spectrometer,HMDS as an internal standard) coincide with those of the corresponding optically inactive aziridines (Ib) with the exception of the $J_{bc}$ sign: VI -2.80,VII -3.02 Hz A.A.Fomichov, I.I.Tchervin, V.A.Afanasjev, R.G.Kostyanovsky, Izvest.Akad.Nauk USSR,ser.chim., in press.