

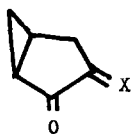
THERMAL WOLFF REARRANGEMENT OF 3-DIAZO-BICYCLO(3,1,0)HEXAN-2-ONE: A NEW ROUTE TO 2-SUBSTITUTED BICYCLO(2,1,0) PENTANES.

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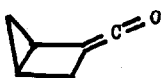
Bicyclo(3,1,0) hexan-2-one, with ethyl formate and sodium hydride, gave the hydroxymethylene derivative (I, 74%; m.p. 62-64^o); this, treated with diethylamine followed by tosyl azide (1), gave the 3-diazoketone (II, 80%; b.p. 69-72^o/0.02 mm.†). Boiling *N*-methylaniline smoothly converted the diazoketone to an oily epimeric mixture of ring-contracted *N*-methylcarboxanilides (III and IV, ratio ~ 80:20) which analysed correctly and had the expected spectral properties (cyclopropyl methylene: ν_{\max} , 3060 cm.⁻¹ δ 0.4-0.9 mult. 2H; amide: ν_{\max} , 1660 cm.⁻¹; no olefinic signals in p.m.r.). Catalytic reduction of the epimeric anilides led to *N*-methylcyclopentanecarboxanilide (m.p. 31-34^o; 1 mole H₂ uptake). Assigned stereochemistry in the series is based on the chemical shift of the C-(2)H, which occurs at higher field when *cis* to the cyclopropane ring (2).

The epimeric anilides (III and IV) were equilibrated after 30 min. at 225^o *via* the planar, 1,4-diradical (3), and the mixture contained 53% *endo*-isomer (III). The high proportion of (III) in the original mixture is therefore the result of kinetically controlled addition to the intermediate ketene (VII).

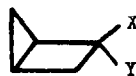


I X = CHOH

II X = N₂



VII



III X = CONMePh, Y = H

IV X = H, Y = CONMePh

V X = CO₂H, Y = H

VI X = H, Y = CO₂H

† The oil-bath temperature was kept below 115^o.

Photochemical conversion of the diazoketone (4) to the ketene in presence of methanol gave a disappointing 13% of methyl esters. However, the diazoketone (1 g. scale) gave good yields of the glycol half esters in boiling ethylene glycol containing 15% v/v collidine (180-185°, 2 min.). Separation of the bicyclopentanes from some 3-2'-hydroxy-ethoxybicyclo(3,1,0) hexan-2-one (2,4-DNPH, m.p. 148°) was best effected by basic hydrolysis and isolation of the epimeric mixture of acids (V and VI: 68% from diazoketone; ratio 55:45). The corresponding methyl esters were separated by preparative g.l.c.

M.ps. of further derivatives which have been prepared are found in the Table.

Table

2-substituent	exo	endo
-CONHPh	188.5°	120-121°
-CONHC ₆ H ₄ Br(p)	173°	132°
-NH.CO ₂ Me	55-57°	34-36°
-COCH ₃	170 ^{oa}	141 ^{oa}

^am.p. of 2,4-Dinitrophenylhydrazones

Boiling ethylene glycol for Wolff rearrangement of diazoketones, may be of use in the synthesis of other strained ring systems when photochemical yields are low.

References

- 1 M. Rosenberger, P. Yates, J. B. Hendrickson and W. Wolf, Tet. Lett., 1964, 2285.
- 2 P. K. Freeman, M. F. Grostic, and F. A. Raymond, J. Org. Chem., 1965, 30, 771.
- 3 J. P. Chesick, J. Amer. Chem. Soc., 1962, 84, 3250.
- 4 W. Kirase, Carbene Chem., Academic Press, N.Y., 1964, p. 120.