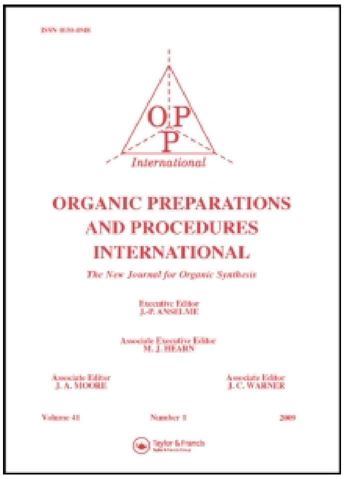

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# 4-SUBSTITUTED-BICYCLO[5.2.1]DECAN-10-ONES

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# 4-SUBSTITUTED-BICYCLO[5.2.1]DECAN-10-ONES

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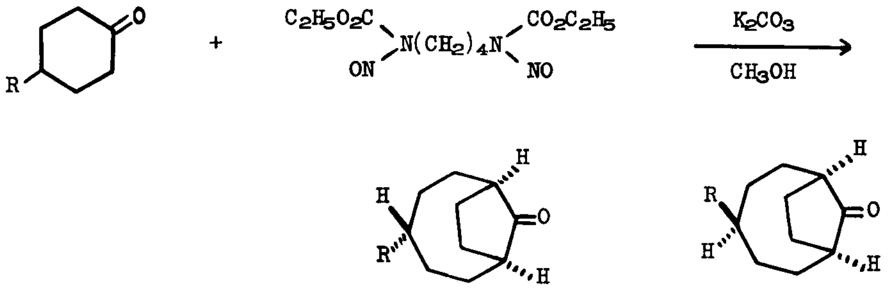

The present procedure extends the scope of the previously-described bis-homologation of cyclohexanone via bis-1,4-diazobutane, generated *in situ* by the action of methanolic potassium carbonate on N,N'-dinitroso-N,N'-dicarbethoxy-1,4-butanediamine.[1] The presence of a substituent at the 4-position makes possible the existence of a pair of epimers, and approximately equal amounts of each is formed in the ring expansion process.

## Experimental

Ring Expansion of 4-Methylcyclohexanone: - Following previously-published procedures,[1] a solution of 11.22 g. (0.100 mole) of 4-methylcyclohexanone[2] in 40 ml. of anhydrous methanol contained in a 500 ml 3-necked flask equipped with a magnetic stirrer, an alcohol thermometer, a reflux condenser, an addition funnel, and a nitrogen wet-test meter, was cooled in an ice bath and treated with 1.00 g. of powdered, anhydrous potassium carbonate. A solution of 29.0 g. (0.100 mole) of N,N'-dinitroso-N,N'-dicarbethoxy-1,4-butanediamine in 40 ml. of methylene chloride was added, dropwise, to the stirred mixture over a period of 5 hrs. at such a rate that the reaction mixture was maintained at 0-10°. After 6 hrs. the theoretical amount of nitrogen had been evolved, but the mixture was allowed to stand at room temperature for 40 hrs. To the thoroughly-stirred mixture 100 ml. of water was then added, and the mixture was transferred to a separatory funnel. The methylene chloride layer was removed, the aqueous phase was extracted with three 30 ml. portions of methylene chloride, and the combined organic extract was dried over anhydrous potassium carbonate and concentrated under vacuum. The residual oil was distilled, and 11.47 g. (69%) of a mixture was obtained which contained approximately equal portions of the _exo_ and _endo_ epimers of 4-methylbicyclo[5.2.1]decan-10-one along with small amounts of starting material and 2-allyl-5-methylcycloheptanone. A pure sample of the α-epimer was obtained via vpc separation[3]: $\nu^{liquid}$ in $cm^{-1}$, 1740 (cyclopentanone carbonyl); n.m.r. ($CCl_4$) in p.p.m., 3-proton doublet at 0.88 with J = 4.5 Hz ($CH_3$ at C-4), 15-proton multiplet at 1.00 - 2.50. A 2,4-dinitrophenylhydrazone of this epimer was obtained as pale orange needles after purification on alumina and recrystallization from ethanol, m.p. 151-153.5°.

_Anal_. Calcd. for $C_{17}H_{22}N_4O_4$: C, 58.94; H, 6.40. Found: C, 58.92; H, 6.40.

A pure sample of the β-epimer was also obtained _via_ vpc separation[3]: $\nu^{liquid}$ in $cm^{-1}$ 1740 (cyclopentanone carbonyl); n.m.r. ($CCl_4$) in p.p.m., 3-proton doublet with J = 6.0 Hz at 0.80 ($CH_3$ at C-4), 15-proton multiplet at 1.00 - 2.50. A 2,4-dinitrophenylhydrazone of this epimer was obtained as pale orange needles after purification on alumina and recrystallization from ethanol, m.p. 107.5 - 109°.

Anal. Calcd. for $C_{17}H_{22}N_4O_4$: C, 58.94; H, 6.40. Found: C, 59.00; H, 6.24.

Ring Expansion of 4-methoxycyclohexanone: - In a fashion similar to that described above, 4-methoxycyclohexanone[4] was converted in good yield to a mixture from which the α-epimer of 4-methoxybicyclo[5.2.1]-decan-10-one was isolated by vpc[3] and obtained as a colorless oil: $\nu^{\text{liquid}}$ in $cm^{-1}$, 1738 (cyclopentanone carbonyl); n.m.r. ($CCl_4$) in p.p.m., 14-proton multiplet at 1.50 - 2.35, 1-proton multiplet at 2.55 - 2.98 (CH at C-4), 3-proton singlet at 3.11 ($CH_3O$). A 2,4-dinitrophenylhydrazone of the α-epimer was obtained as yellow needles after chromatography on alumina and recrystallization from ethanol, m.p. 140-141°.

Anal. Calcd. for $C_{17}H_{22}N_4O_5$: C, 56.34; H, 6.12. Found C, 56.94; H, 6.21.

Similarly, the β-epimer of 4-methoxybicyclo[5.2.1]decan-10-one was isolated by vpc[3] and obtained as a colorless oil: $\nu^{\text{liquid}}$ in $cm^{-1}$, 1738 cyclopentanone carbonyl); n.m.r. ($CCl_4$) in p.p.m., 14-proton multiplet at 1.0 - 2.45, 1-proton multiplet at 3.00 - 3.50 (CH at C-4), 3-proton singlet at 3.19 ($CH_3O$). A 2,4-dinitrophenylhydrazone of the β-epimer was obtained as orange needles after chromatography on alumina and recrystallization from ethanol, m.p. 134-136°.

Anal. Calcd. for $C_{17}H_{22}N_4O_5$: C, 56.34; H, 6.12. Found: C, 56.00; H, 5.98.

## References

1. C. D. Gutsche and T. D. Smith, J. Am. Chem. Soc., 82, 4067 (1960).
2. Commercial material (Aldrich Co.) was used without purification.
3. The vpc separations were effected on a 1/4 in. x 16 ft. column packed with 15% w/w neopentylglycol sebacate polymer on 40-50 mesh type ABS Anakrom.

4. Prepared by reduction of p-methoxyphenol followed by oxidation of 4-methoxycyclohexanol according to the procedure of D.S.Noyce and B.N. Bastian, J. Am. Chem. Soc., 82, 1246 (1960).

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