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A NEW SIMPLE SYNTHESIS OF TETRA-CYCLOHEPTANE (TRICYCLO/4.4.1.$1^{3,8}$/ DODECANE) AND ETHYLENE-BRIDGE SUBSTITUTED DERIVATIVES[1]

Danko Škare and Zdenko Majerski*

Rudjer Bošković Institute, 41001 Zagreb, Yugoslavia

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Adamantane can be considered to be a member of an interesting homologous series of tricyclic hydrocarbons beginning with tetrahedrane. The higher members of this series are derived by successive insertion of two methylene groups into two opposite bridges of each lower member (see the Figure). The number of the methylene groups in the bridges may be either a=b=c or a=b, c=a±1. Since each member of this homologous series contains four equivalent faces we suggested the common name tetra-cycloalkanes (4 x cycloalkane) for this series of cage hydrocarbons.[1] The general formula of tetra-cycloalkanes is /$(CH)_4(CH_2)_{2n}$; n=0,1,2.../ with four bridgehead CH groups arranged in tetrahedral or roughly tetrahedral fashion.

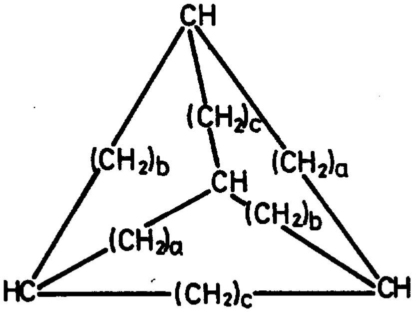
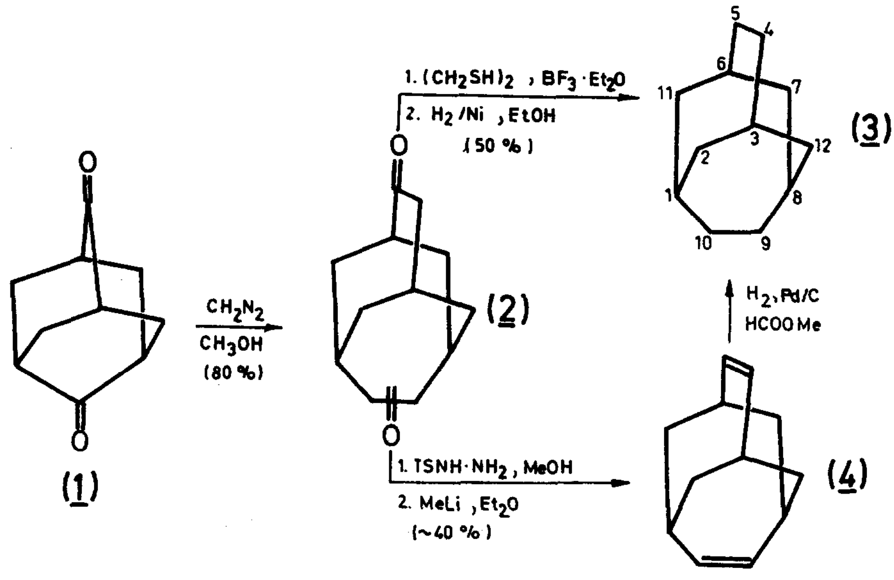


Figure. Tetra-cycloalkanes
(a=b=c or a=b, c=a± 1)

It would be interesting to study the relationship of physical and chemical properties of tetra-cycloalkanes with ring size. Recently Stepanov reported[2] a preparation of tetra-cycloheptane, a=b=1, c=2 (tricyclo/4.4.1.$1^{3,8}$/dodecane) (3), and the corresponding bridgehead alcohol (tricyclo/4.4.1.$1^{3,8}$/dodecane-1-ol) (3a) by deamination of 1-aminomethylhomoadamantane followed by conversion of the alcohol into (3). Two isomeric ring systems could possibly be formed: (3) and tricyclo/4.4.1.1^{3,9}/dodecane. The structure of the product was deducted from the paramagnetic induced chemical shifts in ^{1}H nmr spectrum of (3a). The assigned structure seems to be consistent with the nmr data, but has not been confirmed by other means.

We were seeking a simple synthesis of (3) which would unequivocally confirm its structure and provide the opportunity of producing non-bridgehead substituted derivatives as well. The synthetic route is shown in the Scheme.[3] The overall yields from (1) to (3) and (1) to



Scheme

(4) were 40% and ∼ 30%, respectively. Double homologation of (1)[4] with diazomethane readily gave (2) (86% pure by glc, Carbowax 20M, 200°; mp 307-309°; ms: m/e 192 (100%), 95 (77%); ir (KBr): 2900, 1690, 1445, 1355 cm^{-1}; ^{1}H nmr (CCl$_4$): δ 1.8-2.2 (8H, m), δ 2.2-2.45 (2H, m), δ 2.5-2.7 (4H, m), δ 2.7-2.9 (2H, m). Tetra-cycloheptane (3) was obtained by Raney nickel (W-2) desulfurization of the bis(ethylenethioketal) of (2) in boiling abs. ethanol for 20 hrs (92% pure by glc, SE-30, 140°).[5] Ir and nmr spectral data were identical with those reported by Stepanov.[2] The structure of (3) was confirmed by ms (m/e 164 (100%), 149 (94%)) and ^{13}C nmr. The FT^{13}C nmr spectrum in CDCl$_3$ showed three signals (1 : 0.7 : 1) at 38.78, 35.11 and 34.03 ppm downfield from TMS corresponding to the methylene, bridgehead, and ethylene carbon atoms, respectively.[6]

Quite strained tetra-cycloheptadiene (4) was readily prepared in ∼ 40% yield by the addition of ditosylhydrazone of (2) (4 mmole) to a solution of methyl lithium (20 mmoles) in dry ether followed by stirring for 24 hrs at room temperature[7] (50-60% pure by glc, SE-30, 90° ; ms : m/e 160 (92%), 91 (100%), 79 (88%) ; ir (KBr) : 3015, 2900, 2840, 1425, 930, 861, 752, 700 cm^{-1} ; ^1H nmr ($CDCl_3$) : δ 1.76 (8H, t, J=4Hz), δ 2.4-2.75 (4H, m), δ 6.02 (2H, d, J=6Hz), δ 6.07 (2H, d, J=6Hz). Catalytic reduction of (4) gave a hydrocarbon which was proved to be identical with (3) obtained by the first route.

Compound (3) should be rather strained.[1] This was confirmed by $AlBr_3$ catalysed rearrangement and the reaction with bromine. In the former reaction (CS_2, 25°), after about five minutes almost no (3) remained.[9] Reaction with bromine (35 ⟶ 85°, 3 hrs) followed by Raney nickel catalysed reduction afforded exclusively 1,3-dimethyladamantane.[10]

Acknowledgement

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References

1. Tetra-cycloalkanes . II. Part I: Z. Majerski and N. Trinajstić, Croat. Chem. Acta, 1971, 53, 199.
2. F. N. Stepanov, M. I. Novikova, and A. G. Yurchenko, Synthesis, 1971, 653.
3. Satisfactory elemental analyses were obtained for all compounds; (2) - (4) were purified by preparative glc before the analyses and recording of the spectra.
4. H. W. Geluk and J. L. M. A. Schlatmann, Rec. Trav. Chim., 1971, 90, 516; J. Janku and S. Landa, Coll. Czech. Chem. Comm., 1970, 35, 375; H. Stetter, H. G. Thomas, and K. Meyer, Chem. Ber., 1970, 103, 863; O. W. Webster and L. H. Sommer, J. Org. Chem., 1964, 29, 3103.
5. Hydrocarbon (3) could probably be obtained as well by the Wolff-Kishner and the Clemmensen reduction of (2) since both reactions readily gave homoadamantane from homoadamantanone.
6. Application of the proton half decoupling technique gave a doublet flanked by two triplets. The triplets were assigned by comparison with the ^{13}C nmr spectrum of homoadamantane where the methylene carbon signals were found to be farther

downfield than the ethylene signal.

7. Attempts to prepare (4) from tetra-cycloheptane 4,9(10)-ditosylate by pyrolysis or elimination using basic Al_2O_3 in benzene[8] or t-BuOK in DMSO gave mixtures of products rather than the expected diene. The pyrolysis of 4-homoadamantyl tosylate (80°, 12 mm) afforded homoadamantene in 24% yield.
8. Cf. T. Nakano, M. Hasegawa, and C. Djerassi, Chem. Pharm. Bull., 1963, 11, 465 (CA, 1963, 59, 8827c).
9. Two major reaction products were observed. Details will be published in the full paper.
10. The product obtained upon glc analysis had the same retention time on 3 different columns as did an authentic sample of 1,3-dimethyladamantane.