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METABRIDGED TROPONE AND PHENOLS

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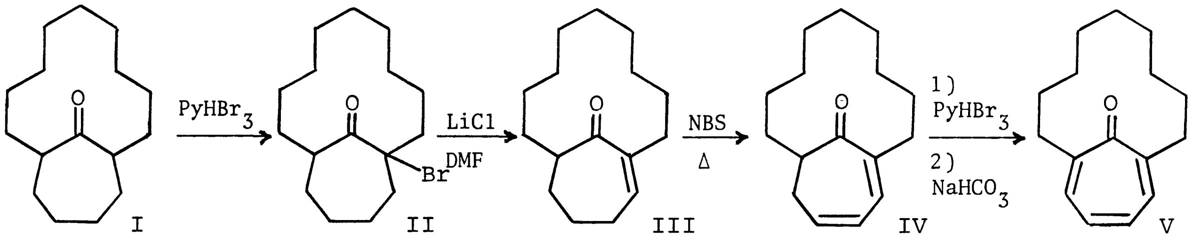
Bromination, dehydrobromination and subsequent dehydrogenation of bicyclo[9.4.1]hexadecan-16-one afford [9](2,7)troponophane, whereas the same treatment of bicyclo[9.3.1]pentadecan-15-one gives 15-hydroxy[9]-metacyclophane. 15-Hydroxy-12-methyl[9]metacyclophane is prepared by dehydrogenation of 13-methylenebicyclo[9.3.1]pentadecan-15-one. PMR study of these compounds suggests that the nonamethylene chain is restricted to reside in the one side of the aromatic rings.

We wish to report the synthesis of title compounds[1] and to refer to their structures as evidenced by spectroscopic methods.[3]

Bicyclo[9.4.1]hexadecan-16-one (I)[4] was brominated with pyridinium hydrobromide perbromide (PyHBr$_3$) to give monobromoketone (II)[5] (78%, mp 156-157°C). Subsequent dehydrobromination (LiCl-DMF, 140°C, 8 hr) gave enone III[5] (82%, bp 120-130°C/0.07 mmHg, IR: 1683 cm^{-1}, m/e 234). Allylic bromination of III by means of N-bromosuccinimide (NBS) in boiling carbon tetrachloride gave an unstable dienone IV (69%, bp 120-140°C/ 0.09 mmHg, IR: 1660 cm^{-1}, m/e 232). Bromination of IV with PyHBr$_3$ afforded [9](2,7)-troponophane (V)[5,6] (33%, mp 60-64.5°C, IR: 1624, 1588 cm^{-1}, λ_{max}(EtOH) (log ε): 239 nm (4.31), 314 nm (3.78), m/e 230). PMR spectrum of V shown in Fig. 1 indicates the non-equivalence of the two benzylic protons, which implies that the polymethylene chain is fixed to the one side of the tropone ring. Addition of a little more than equivalent trifluoroacetic acid caused down field shift of the olefinic (0.73 ppm) and benzylic



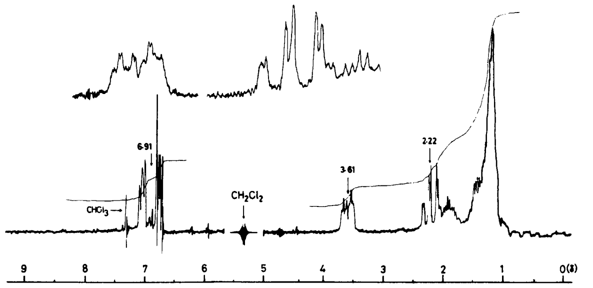


Fig. 1 PMR of V (100 MHz, CDCl$_3$, 31.5°)

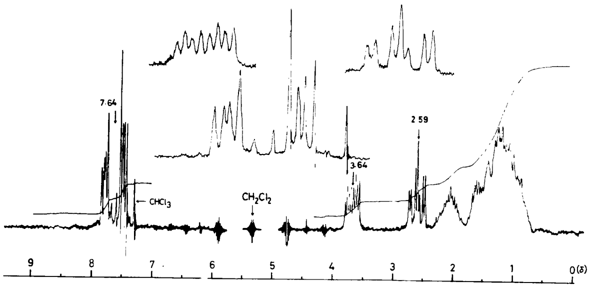
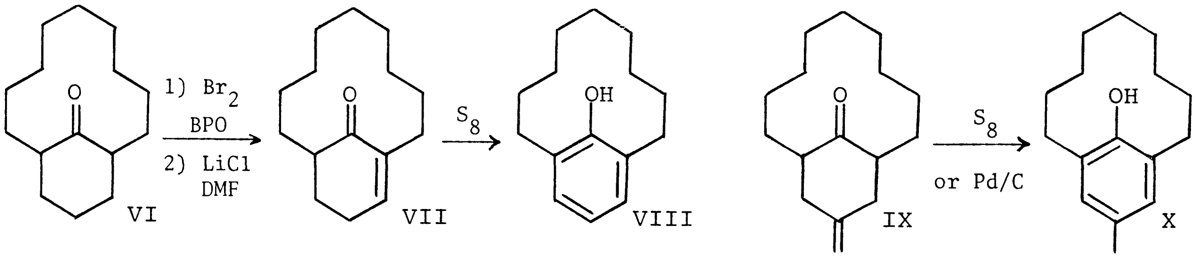


Fig. 2 PMR of V (100 MHz, CDCl$_3$ + CF$_3$COOH, 31.5°)



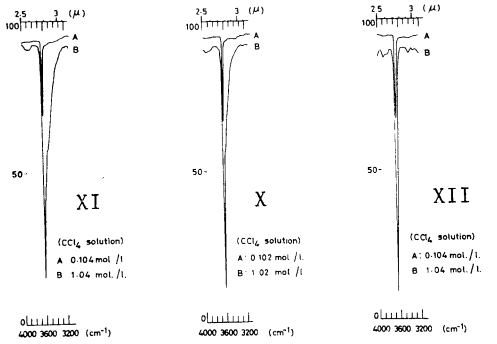


Fig. 3 IR of X, XI, and XII (CCl_4 solution)

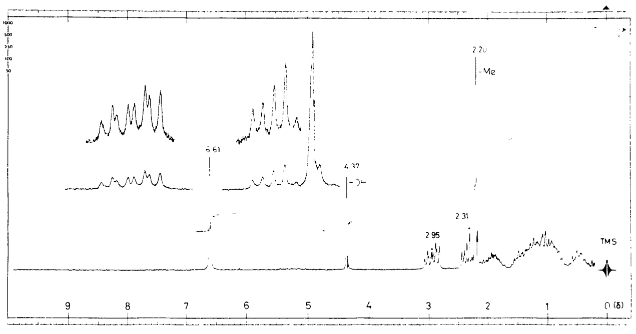


Fig. 4 PMR of X (100 MHz, CCl_4, 31.5°)

protons, owing to the formation of the tropylium cation (Fig. 2). The diamagnetic ring current of the tropylium cation was evidenced by the broadening of the polymethylene signals.[7]

15-Hydroxy[9]metacyclophane (VIII) was prepared according to the scheme shown above. Bromination (70-80°C, 15 hr, a trace of BPO) of VI[5], followed by dehydrobromination, gave enone VII[5] (88%, bp 120-125°C/0.1 mmHg, IR: 1680 cm^{-1}, m/e 220). Subsequent dehydrogenation with sulfur (190-210°C, 2 hr) afforded VIII[5] (56%, bp 130-140°C/0.07 mmHg, m/e 218). 12-Methyl-substituted derivative X[5] (mp 82-83°C) was obtained from IX (57%). Both VIII and X gave no coloration with ferric chloride. IR spectrum of X shown in Fig. 3 suggests that the hydroxyl group is hindered intermediately between 2,6-xylenol (XI) and 2,6-di-tert-butylphenol (XII). The bathochromic absorption of X (λ_{max} (EtOH) 286 nm, (log ε 3.28)) compared with those of 2,4,6-trialkylphenol (λ_{max} 275-278 nm)[8] should be ascribed to the constraint by polymethylene chain. The PMR spectrum of X (Fig. 4) also indicates that the nonamethylenene chain resides only in the one side of the aromatic ring: the non-equivalence of the benzylic protons remained unchanged up tp 196°C.

Footnotes and References

1) This is the first synthesis of 2,7-polymethylenetropones and 2,6-polymethylenephenols. The derivatives have been obtained by condensation reaction, see ref. 2.
2) R. W. Griffin, Jr., Chem. Rev., **63**, 45 (1963).
3) For PMR spectroscopic study of 2,6-polymethylenebromobenzene and its derivatives, see S. Fujita, S. Hirano, and H. Nozaki, Tetrahedron Lett., 403 (1972); S. Hirano, T. Hiyama, S. Fujita, and H. Nozaki, Chemistry Lett., 707 (1972).
4) H. Nozaki, H. Yamamoto, and T. Mori, Can. J. Chem., **47**, 1107 (1969).
5) All the new compounds gave the satisfactory analyses.
6) As to the nomenclature, see F. Vögtle and P. Neumann, Tetrahedron, **26**, 5847 (1970).
7) Recently [9](1,3)cyclopentadienidophane has been reported. S. Bradamante, A. Marchesini, and G. Pagani, Tetrahedron Lett., 4621 (1971).
8) N. D. Coggeshall and A. S. Glessner, Jr., J. Amer. Chem. Soc., **71**, 3150 (1949).

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