

pendant la nuit, puis extraire à l'éther. Laver la solution étherée d'abord par l'acide sulfurique dilué, ensuite par la soude diluée et finalement de nouveau par l'acide sulfurique dilué. Sécher la solution étherée sur sulfate de sodium et évaporer l'éther. Distiller l'huile obtenue sous vide. Rendement 4,6 g (72 %). p.éb. 64–66°C/0,1 mm. Le produit se solidifie assez vite; p.f. 39°C (recristallisé dans l'éthanol dilué). Analyse C_8H_8IO Calculé C 38,71; H 3,63; I 51,17. Trouvé C 38,78; H 3,90; I 51,12. RMN ($CDCl_3$) multiplet à 2,4–3,3 τ (3H), singulets à 6,23 τ (3H) et 7,75 τ (3H).

Diméthoxy-3,3' diméthyl-2,2' biphenyle (I). Mélanger 7,6 g d'iodo-2 méthoxy-6 toluène (XII) et 15 g de bronze de cuivre. Chauffer au bain d'huile vers 220°C où la réaction commence. Faire monter la température à 270°C pendant 20 min. Laisser refroidir et extraire au chloroforme. Evaporer le chloroforme sous vide et chromatographier le produit sur une courte colonne de Al_2O_3 (neutre) en éluant par le benzène. Evaporer le benzène sous vide et recristalliser le produit obtenu (rendement 3,4 g; 92 %) dans l'éther de pétrole (60–80°C). p.f. 112–113°C. Pour obtenir un produit plus pur sublimer à 105°C/0,01 mm. p.f. 117–118°C. Analyse $C_{16}H_{18}O_2$ Calculé C 79,31; H 7,49. Trouvé C 79,35; H 7,45. RMN (CCl_4) multiplet à 2,8–3,5 τ (6H), singulets à 6,21 τ (6H) et 8,13 τ (6H).

1. Forrest, J. J. *Chem. Soc.* **1960** 594; et les publications antérieures dans cette série.
2. Riedl, W. *Ann.* **597** (1955) 148, 153.
3. Bacon, R. G. R. et Lindsay, W. S. *J. Chem. Soc.* **1958** 1376, 1382.
4. Erdtman, H. et Stjernström, N. E. *Acta Chem. Scand.* **13** (1959) 654; **14** (1960) 1275; **15** (1961) 1761; **16** (1962) 555.
5. Lounasmaa, M. *Acta Chem. Scand.* **19** (1965) 540.
6. Fanta, P. E. *Chem. Rev.* **38** (1946) 139; **64** (1964) 613; Pour les autres mécanismes possibles, voir p.ex. Bell, F. et Morgan, W.H.D. *J. Chem. Soc.* **1954** 1716; Nursten, H. E. *J. Chem. Soc.* **1955** 3081; Nilsson, M. *Svensk Kem. Tidskr.* **80** (1968) 196, et références citées; Voir aussi Bacon, R.G.R. et Hill, H.A.O. *Quart. Rev. (London)* **19** (1965) 95.
7. Dizabo, P. et Mouneyrac, M.-F. *Bull. Soc. Chim. France* **1968** 2958.
8. Noelting, E. *Ber.* **37** (1904) 1019.
9. Ullmann, F. et Panchaud, L. *Ann.* **350** (1906) 112.
10. Brady, O. L. et Taylor, A. *J. Chem. Soc.* **117** (1920) 876.

11. Kupchan, S. M. et Wormser, H. C. *J. Org. Chem.* **39** (1965) 3798.
12. Noelting, E. *Ber.* **37** (1904) 2562.
13. Jones, E. T. et Robertson, A. *J. Chem. Soc.* **1930** 1699.
14. Simonsen, J. L. et Nayak, M. *J. Chem. Soc.* **107** (1915) 828.
15. Ruggli, P. et Leonhardt, W. *Helv. Chim. Acta* **7** (1924) 701.
16. Beckett, A. H., Daisley, R. W. et Walker, J. *Tetrahedron* **24** (1968) 6093.

Manuscrit reçu le 20 août 1968.

Functionalization of Polythiaadamantanes via their Bridgehead Alkali Metal Derivatives

KJELL OLSSON

*Department of Chemistry, Div. II,
Agricultural College, S-750 07 Uppsala 7,
Sweden*

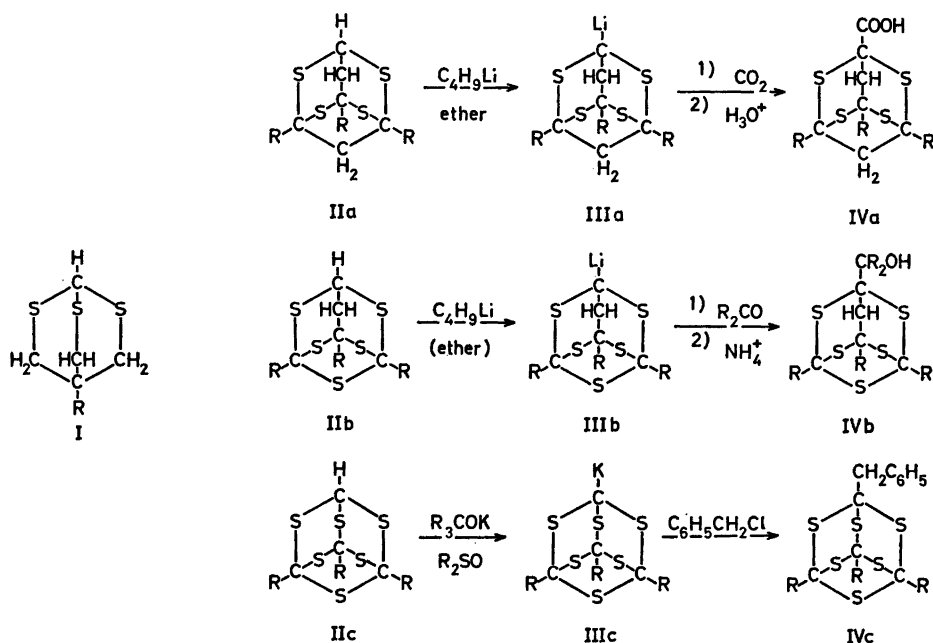
The present paper reports the first general method of preparing polythiaadamantanes other than the well-known simple alkyl derivatives.¹ It is based on the discovery made during the last decade that dithioacetals and trithioorthoformic esters—including *m*-dithianes and one cage compound (I)—are acidic enough to be converted by strong bases into synthetically useful lithium or sodium derivatives.²

Accordingly, polythiaadamantanes (II) with at least one free bridgehead position served as starting materials.* Such substances are now readily available.¹ After metalation (II→III) for a few minutes at ca. 30°, addition of an appropriate reagent afforded a derivative (IV or its salt) of II, which was substituted at the originally free position(s). The method is illustrated here by the three representative examples shown in the scheme.**

* The reduction of a polythiaadamantane with no such position to its dianion was reported recently.³

** Throughout the present paper, R=CH₃.

Acta Chem. Scand. **22** (1968) No. 7



Unlike IIa and IIb, IIc was metalated rapidly by potassium *t*-butoxide or [(methylsulphinyl)methyl] sodium⁴ in dimethyl sulphoxide. In benzene-hexane, butyllithium metalated IIb fairly quickly, IIc almost instantly, but IIa slowly or not at all. In the presence of ether, however, IIa reacted rapidly and IIb almost instantly. Nevertheless, quantitative metalation was often prevented by limited solubility of II and its alkali metal derivative (III), despite a considerable excess of the metalating agent. Low temperatures were therefore avoided, and metalations in ether-hexane assisted by high-speed stirring or by the addition of benzene.

The extremely simple procedures described below were suitable for rapid synthesis of small samples in fair yields. For work on a larger scale, a more careful design of experimental conditions may be warranted and could conceivably lead to higher yields even without excess of the metalating agent.

As indicated above, IIa seems to be metalated less readily than IIb. This unexpected result suggests that the acidity

of polythiaadamantanes is not entirely due to the sulphur atoms adjacent to the free bridgehead position but to some extent to the more remote ones as well. If two or more bridgehead positions are free, poly-substitution is possible, sometimes in one operation and perhaps *via* polymetalated species. A more detailed discussion of these and other aspects of the metalation and its synthetic applications is planned in *Arkiv Kemi*.

Experimental. The syntheses were performed at room temperature under argon in 50 ml conical flasks, with magnetic stirring. All non-aqueous reagents and solvents were anhydrous. Butyllithium was injected through a hypodermic syringe in one 5.0 ml portion of a 2.3 M solution in hexane (50% excess), which caused the temperature to rise *ca.* 10°. Physical data for the products (IV) are presented as previously,¹ but only a few characteristic bands have been selected from the IR spectra. The calculated molecular weights were confirmed by mass spectrometry.

3,5,7-Trimethyl-2,4,6,8-tetrathiaadamantane-1-carboxylic acid (IVa). Butyllithium was added

to 1.92 g (7.7 mmoles) of powdered 1,3,5-trimethyl-2,4,6,8-tetrathiaadamantane (IIa),¹ suspended in 10 ml of benzene and 10 ml of ether. After 30 sec, most IIa had dissolved, and IIIa began to separate (perhaps as an etherate). After a total of 3 min, the flask was emptied into a stirred slurry of Dry Ice and ether. When above 0°, the mixture was dissolved in 10 ml of 2 M hydrochloric acid and 10–20 ml of ether. The organic layer was extracted with 2 × 10 ml of 1 M sodium hydroxide and evaporated to dryness, leaving 0.83 g of almost pure IIa. Acidification of the alkaline extract precipitated 1.24 g of almost pure IVa (97 or 55 % yield according to whether IIa is recovered or not). After recrystallization from toluene, IVa melted at ca. 235° (decomp.). IR spectrum in RCN: ca. 3050s (very broad), 1740s, 1213s, 693s. PMR spectrum in CHCl₃: 3,5,7-R₃ 1.66s, 10c,10t-H₂ 2.18s (broad), 9,9-H₂ 2.52s, OH 9.6s. (Found: C 40.5; H 4.8; S 43.5. Calc. for C₁₀H₁₄O₂S₄: C 40.8; H 4.8; S 43.6).

α,α,1,5,7-Pentamethylpentathiaadamantane-3-methanol (IVb). Butyllithium was added to 2.06 g (7.7 mmoles) of powdered 1,3,5-trimethylpentathiaadamantane (IIb),¹ suspended in 25 ml of benzene and 4 ml of ether. All IIb dissolved within 5 sec, and IIIb began to separate 10 sec later. After a total of 60 sec, 1.3 ml (18 mmoles) of acetone was added. The temperature rose to ca. 45°, and a clear solution formed immediately. After another 60 sec, this was washed with 15 ml of 2 M ammonium chloride and analyzed by GLC. Only the peaks of IIb and IVb with the relative areas 4:96 were observed. The solvents were evaporated and the residue recrystallized from ligroin, yielding 1.31 g (52 %) of GLC-pure IVb. After repeated recrystallization to remove coloured impurities, IVb melted at 166–169°. IR spectrum in CS₂: 3560m, 3490m (broad), 1322s, 1095s, 958s, 724s. PMR spectrum in CCl₄: CR₂ 1.36s, 7-R 1.66s, 1,5-R₂ 2.02s, 10,10-H₂ 2.24s, OH 5.4s (only after addition of pyridine; broad). (Found: C 40.6; H 5.7; S 49.0. Calc. for C₁₁H₁₈OS₅: C 40.5; H 5.6; S 49.1).

Benzyltrimethylhexathiaadamantane (IVc). 1.43 g (5.0 mmoles) of powdered trimethylhexathiaadamantane (IIc)¹ was added in one

portion to 0.72 g (6.1 mmoles) of 95 % potassium *t*-butoxide, newly dissolved in 10 ml of dimethyl sulphoxide. After 5 min, when most or all of the IIc had dissolved, 1.0 ml (8.7 mmoles) of *α*-chlorotoluene was added. The temperature rose to ca. 55°, and a light brown colour developed immediately. After cooling, the solution was diluted with 10 ml of water and extracted with 2 × 10 ml of carbon tetrachloride. The extract was filtered from any remaining IIc and evaporated to dryness. The residue was recrystallized from acetone–methanol, yielding 1.33 g (70 %) of GLC-pure IVc. After repeated recrystallization to remove coloured impurities, IVc melted at 170.5–172.5°. IR spectrum in CS₂: 3030m, 1092s, 741s, 719s, 695s, 586m. PMR spectrum in CCl₄: R₃ 1.99s, CH₂ 3.58s, C₆H₅ 7.23s. (Found: C 44.7; H 4.4; S 50.2. Calc. for C₁₄H₁₈S₆: C 44.6; H 4.3; S 51.1).

Acknowledgements. I wish to thank Professors Arne Fredga and Nils Hellström for their interest in this work and for all facilities placed at my disposal. I am also indebted to Drs. Ragnar Hoffman and Ragnar Ryhage for making certain equipment available. This work was supported by grants from the *Swedish Natural Science Research Council* and from *Jordbrukets forskningsråd*.

1. Olsson, K. *Acta Univ. Upsaliensis, Abstr. Uppsala Diss. rtiations Sci.* **102** (1967), and its parts I–VI cited therein.
2. Tagaki, W., Ueyama, K., Minamida, I., Kim, Y. H., Ikeda, Y. and Oae, S. *Bull. Chem. Soc. Japan* **39** (1966) 917; Brandsma, L. and Arens, J. F. *The chemistry of the ether linkage*, S. Patai, Ed., p. 554; Interscience, London 1967; Seebach, D. *Angew. Chem.* **79** (1967) 468, 469, and references cited in these papers.
3. Coffen, D. L., Garrett, P. E. and Williams, D. R. *Chem. Commun.* **1968** 652.
4. Sjöberg, K. *Tetrahedron Letters* **1966** 6383.

Received August 31, 1968.