Synthesis, Crystal, and Molecular Structure of 3,4-Di-t-butylthiophen

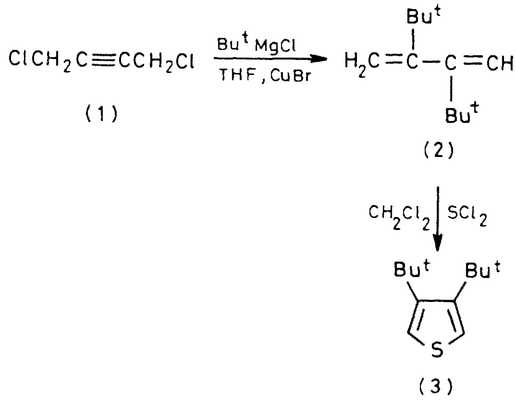
By Lambert Brandsma,* Johnny Meijer, and Herman D. Verkruijsse
(*Department of Organic Chemistry of the State University, Croesestraat 79, Utrecht, The Netherlands*)

and Gysbertus Bokkers, Albert J. M. Duisenberg, and Jan Kroon
(*Laboratory for Structural Chemistry of the State University, Padualaan 8, Utrecht, The Netherlands*)

Summary. A successful synthesis of the hitherto unknown 3,4-di-t-butylthiophen and the results of its crystal structure determination are reported.

The first synthesis of *o*-di-t-butylbenzene[1] provoked an interest in molecules with similar, overcrowded arrangements of bulky groups. Wijnberg and his co-workers have made major contributions to this field by their successful preparation of 2,3,5-tri-t-butylfuran,[2] 2,4-di-t-butylthiophen,[3] 2,5-di-t-butylthiophen,[3] 2,5-di-t-butylfuran,[3] 1,2-di-t-butylimidazole,[4] and 2,3-di-t-butylquinoxaline.[5] However, despite several attempts,[6] 3,4-di-t-butylthiophen had not been obtained.

We report here a surprisingly simple synthesis of the title compound (**3**), which is outlined in the Scheme. Addition, at 0 to −20 °C, of 2 equiv. of a solution of t-butyl magnesium chloride in tetrahydrofuran (THF) to a mixture of 1,4-dichlorobut-2-yne (**1**), THF, and a catalytic (2—5 mol %) amount of copper(I) bromide, gave 2,2,5,5-tetramethyl-3,4-dimethylenehexane (**2**) in a yield > 90%. This synthesis, which gives unsatisfactory results with primary alkylmagnesium halides, is a good alternative to that reported by Backer.[7] Addition of freshly distilled sulphur dichloride to a solution (*ca.* 20% v/v) of (**2**) in dichloromethane gave a mixture of (**2**), (**3**), and largely high-boiling compounds of unknown structure.



Scheme.

Treatment of the residue remaining after evaporation of the solvent with excess of $KOBu^t$ in dimethyl sulphoxide (DMSO) at 40—50 °C, followed by the usual work-up, gave (**2**) (*ca.* 50% recovery) and (**3**) (12—15% yield), m.p. 42 °C. The structure of (**3**) was in accordance with the mass spectrum (expected parent peak), the microanalytical results, and the ^1H n.m.r. spectrum (10% v/v solution in CCl_4, Me_4Si as internal standard, δ 7·15, 2 H, and 1·45, 18 H). The spectrum of the 2,5-isomer, prepared according to ref. 8, showed signals at δ 6·44 and 1·24.

Crystal data: $C_{12}H_{20}S$, M 196, rhombohedral, space group $R\bar{3}c$, $a = 15{\cdot}88(6)$ Å, $\alpha = 116{\cdot}7(3)°$, $D_c = 1{\cdot}059$ g cm^{-3}, $Z = 6$. 237 observed independent Mo-K_α ($\lambda = 0{\cdot}7107$ Å) diffractometer data were used. The crystals were of very poor quality (virtually no reflections could be observed at $\theta > 16{\cdot}5°$). The non-hydrogen atoms could be located using MULTAN[9] and the final R index, after anisotropic full-matrix least-squares refinement, is 0·089.† The molecule has approximate C_{2v} symmetry with its two-fold rotation axis forced to coincide with that of the space group. A perspective view of the molecule, together with its atomic numbering, and a summary of the geometrical data, is given in the Figure. The conformational arrangements of the t-butyl groups is such that the bond C(3)–C(31) is nearly coplanar with the thiophen ring and in a synclinical position with the bond C(2)–C(1).

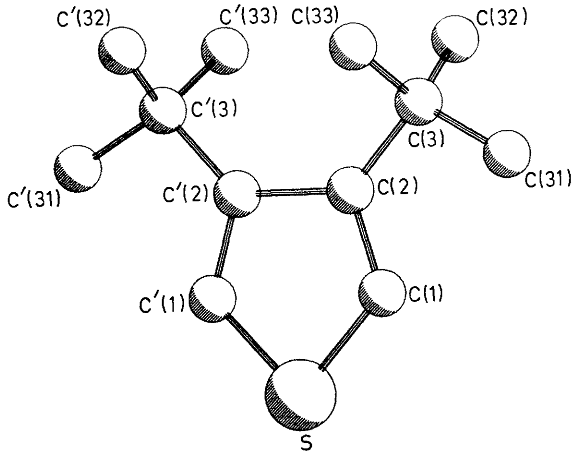


Figure. A perspective view of 3,4-di-t-butylthiophen. Bond lengths: S–C(1) 1·78(5), C(1)–C(2) 1·39(8), C(2)–C(3) 1·49(8), C(2)–C′(2) 1·66(7), C(3)–C(31) 1·49(7), C(3)–C(32) 1·49(8), and C(3)–C(33) 1·54(9); C(32)- -C′(33) 3·37(6) Å. Bond angles: C(1)–S–C′(1) 90(2), S–C(1)–C(2) 117(3), C(1)–C(2)–C(3) 119(4), C(1)–C(2)–C′(2) 108(4), C(3)–C(2)–C′(2) 133(5), C(2)–C(3)–C(31) 104(6), C(2)–C(3)–C(32) 110(5), C(2)–C(3)–C(33) 105(3), C(31)–C(3)–C(32) 113(3), C(31)–C(3)–C(33) 105(5), and C(32)–C(3)–C(33) 119(6)°.

Owing to the lack of a good data set the crystal structure determination is not very accurate. However, it is evident from the results obtained that the internal strain in the molecule is appreciable.

(*Received*, 10*th June* 1980; *Com.* 637.)

---

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

[1] C. Hoogzand and W. Hübel, *Tetrahedron Lett.*, 1961, 637; E. M. Arnett, M. E. Strem, and R. A. Friedel, *ibid.*, 1961, 658.
[2] H. Wijnberg and U. E. Wiersum, *J. Chem. Soc., Chem. Commun.*, 1965, 1.
[3] H. Wijnberg and U. E. Wiersum, *J. Org. Chem.*, 1965, **30**, 1058.
[4] H. Wijnberg and Ae. de Groot, *J. Chem. Soc., Chem. Commun.*, 1965, 171.
[5] Ae. de Groot and H. Wijnberg, *J. Org. Chem.*, 1966, **31**, 3954.
[6] H. Wijnberg, *Acc. Chem. Res.*, 1971, **4**, 65.
[7] H. J. Backer, *Recl. Trav. Chim. Pays-Bas*, 1939, **58**, 643.
[8] U. E. Wiersum, Dissertation, Groningen, 1968.
[9] P. Main, L. Lessinger, M. M. Woolfson, G. Germain, and J.-P. Declercq, MULTAN 77, A System of Computer Programs for the Automatic Solution of Crystal Structures from *X*-ray Diffraction Data, 1977. University of York, England, and Louvain-la-Neuve, Belgium.