

CYCLOADDITIONS OF THIOPHENE 1,1-DIOXIDES TO CYCLOPROPENES

A NOVEL ROUTE TO ALKYL-SUBSTITUTED CYCLOHEPTATRIENES

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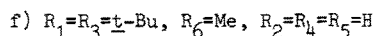
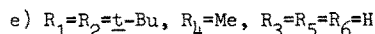
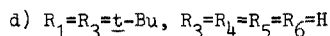
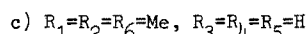
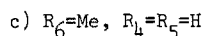
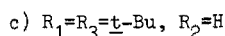
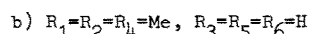
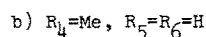
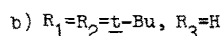
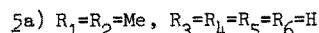
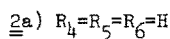
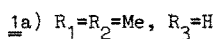
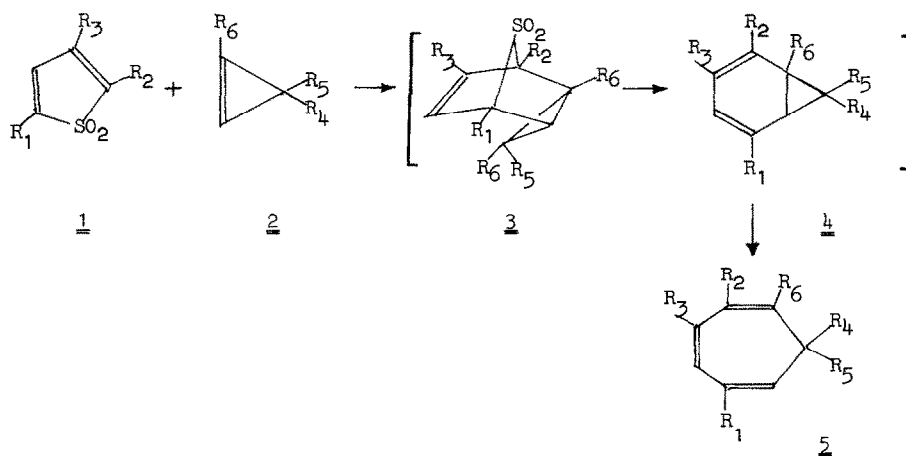
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Derivatives of cycloheptatriene have been the subject of much study over the past few decades. The three methods of their synthesis, viz isomerization of bicyclo[2.2.1]-2,5-heptadienes¹, pyrolysis of 7,7-dibromobicyclo[4.1.0]heptanes², and addition of methylene carbene to aromatic compounds^{3,4} all suffer from the disadvantage that they invariably afford mixtures of isomeric cycloheptatrienes, from which the pure compounds can only be isolated with great difficulty. We here wish to report a new facile synthesis which gives high yields of substituted cycloheptatrienes not contaminated by isomeric products.

Treatment of the thiophene 1,1-dioxides⁵ 1a-c - dienes with inverse electron demand⁶ - with an excess⁷ of a suitably substituted cyclopropene (2a-c) at temperatures between -50 and +50 °C in methylene chloride produces the substituted cyclohepta-1,3,5-trienes 5a-f in virtually quantitative yield⁸. The reaction is thought to proceed via a rate-determining [$\pi^4_s + \pi^2_s$] cycloaddition⁹, giving the Diels-Alder adduct 3, subsequent cheletropic cleavage¹⁰ of 3 results in the expulsion of SO₂ to afford the cycloheptatriene 5, which is probably formed via the corresponding norcaradiene 4¹. The reaction is analogous to that of 1,2,3-triphenylcyclopropene with tetraphenylcyclopentadienone¹² yielding 1,2,3,4,5,6,7-heptaphenyltricyclo[3.2.1.0^{2,4}]oct-6-en-8-one, which upon being heated splits off CO to give heptaphenylcycloheptatriene¹³. In our reaction, the proposed intermediate 3 was not detectable by NMR, even at temperatures as low as -60 °C. We attribute this to the excellent leaving ability of the SO₂ fragment¹⁴.



As expected¹⁵, the cycloaddition step is greatly influenced by steric effects. For example, whereas 3-methylcyclopropene ($\underline{2b}$) reacts with 2,5-dimethylthiophene 1,1-dioxide ($\underline{1a}$) to give the corresponding cycloheptatriene $\underline{5b}$ in high yield, no reaction occurs between $\underline{1a}$ and 1,3,3-trimethylcyclopropene or 3,3-dimethylcyclopropene. Similarly, 2,4-di-*t*-butylthiophene 1,1-dioxide ($\underline{1c}$) affords the cycloheptatriene $\underline{5f}$ on treatment with 1-methylcyclopropene at 49 °C, but the latter does not react with 2,5-di-*t*-butylthiophene 1,1-dioxide ($\underline{1b}$), even on prolonged heating to 60 °C.

The synthetic route described above¹⁶ allows a wide range of isomerically pure substituted cycloheptatrienes to be isolated in high yield (> 95 %), the only limiting factor being any excessive steric crowding in the transition state of the cycloaddition.

R E F E R E N C E S

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- 3 W Doering and C H Knox, J Amer Chem Soc 72, 2305 (1950), 73, 828 (1951), 75, 297 (1953)
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- 5 J L Melles and H J Backer, Rec Trav Chim 72, 491 (1953)
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- 7 In order to obtain a high yield of cycloheptatrienes from the reaction of 1a with 2a-b, hardly any excess of the cyclopropene is necessary. Less reactive thiophene 1,1-dioxides (1b-c), however, require a 50 to 100 % molar excess of cyclopropene, because of the loss of the latter by concurrent polymerization.
- 8 Satisfactory IR, ¹H-NMR, MS and elemental analysis data were obtained for all compounds.
- 9 The reaction of 1a with 2a was found to follow second order kinetics (NMR), i.e. first order in each of the reactants.
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- 11 G Maier, Angew. Chemie 79, 446 (1967) See also R Hoffmann, Tetrahedron Letters 1970, 2907
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- 13 A similar reaction - with N₂ as the leaving group - leading to benzo-annulated cycloheptatrienes was reported very recently (R E Moerck and M A Battiste, J Chem Soc Chem Comm 1972, 1171)

14. W L. Mock, J Amer. Chem Soc. 92, 6918 (1971) See also A.I. Meyers and T Takaya, Tetrahedron Letters 1971, 2609, and E W Duck, Research Correspondence, Suppl to Research (London) 8, S 47 (1955)
- 5 M.L. Deem, Synthesis 1972, 675 See also G L Closs, "Advances in Alicyclic Chemistry", Vol. 1, Acad Press, New York, 1966, p 78.
16. During the preparation of this manuscript two new cycloheptatriene syntheses appeared in the literature. One of them (S. Miyano and H Hoshimoto, J Chem. Soc. Comm., 1973, 216) suffers from the disadvantage of being aselective with respect to the location of substituents, the other (J. Steigel and J Sauer, Tetrahedron Letters 1972, 1213) is far more limited in scope