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De synthese van sterisch gehinderde alkenen reacties aan 3,3,6,6-tetramethylthiepaan

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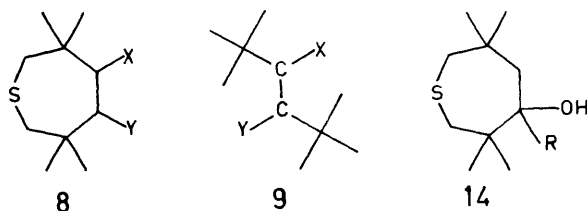
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Summary

The research described in this thesis can be divided into two parts: reactions of derivatives of 3,3,6,6-tetramethylthiepane (Chapter II) and efforts to synthesize tetra-*t*-butylethylene (Chapters III, IV and V).

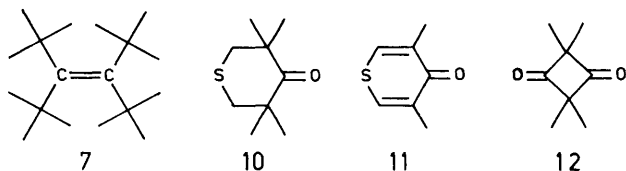
Chapter I deals with some literature concerning strain in organic compounds, especially in ethylenes.

The reactions of some derivatives of 3,3,6,6-tetramethylthiepane (8) are described in Chapter II. These reactions are compared with the reactions of comparable derivatives of 2,2,5,5-tetramethylhexane (9). Influences arising from the cyclic nature of 8 were invoked to explain differences relative to noncyclic

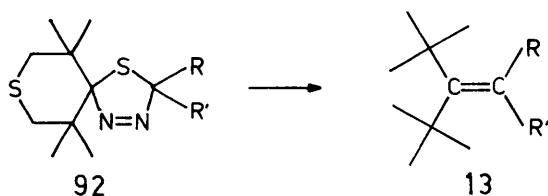


compounds for the benzilic acid rearrangement of 8 ($X=Y=O$) and for the Wolff rearrangement ($X=O$, $Y=N_2$). The chloro-ketone of type 8 did not give a normal Favorskii reaction with base. The hydroxyketone of type 8 was found to give annelation reactions with phosgene and thionylchloride. In the reaction of 8 ($X=Y=OH$) with sulfuric acid the sulfur atom participated transannularly, as was found in the reaction of the hydroxyketone of type 8 with dibromotriphenylphosphine. Some insight into the conformation of the compounds 14 is forthcoming from the observation of transannular hydrogen bridging.

Chapters III and IV deal with efforts to synthesize tetra-*t*-butylethylene (7). The starting compounds for these syntheses were derivatives of 3,3,5,5-tetramethyltetrahydrothiapyran-4-one (10) (Chapter III), 3,5-tetramethylthiapyran-4-one (11) (Chapter IV) and 2,2,4,4-tetramethylcyclobutanedione (12) (Chapter IV). It was hoped that the starting compounds (10, 11 and 12) could be "dimerized" at the carbonylfunctions. The steric hindrance in the dimerized products could then be enlarged by different sequences of reactions. The highly strained compound 7 could not be synthesized by us.



The subject of research described in Chapter V is the synthesis and some physical and chemical properties of some 1,1-di-*t*-butylethylenes (13). These compounds were synthesized by the promising sequence beginning from thia-



diazolines (92). This method was shown to have its limitations in the synthesis of alkenes with bulky substituents.

The UV spectra of 13 ($R=R'$ =aryl) do not differ significantly from the UV spectra of other 1,1-diarylethylenes. The ethylenic double bond in 13 proved to be very unreactive in olefinic addition reactions. It was shown that the phenylrings in 13 ($R=R'$ =phenyl) do not give electrophilic substitutions under normal conditions. This lack of reactivity was explained by assuming a perpendicular position of the phenyl rings and the double bond in 13, by which the ethylenic double bond destabilizes the Wheland intermediate in electrophilic aromatic substitution reactions.