

THE PROBLEM OF REDUCTIVE COUPLING OF CYCLOPROPENIUM CATIONS.
 BICYCLOPROPENYLSULFONES - SYNTHESIS AND PROPERTIES ¹⁾

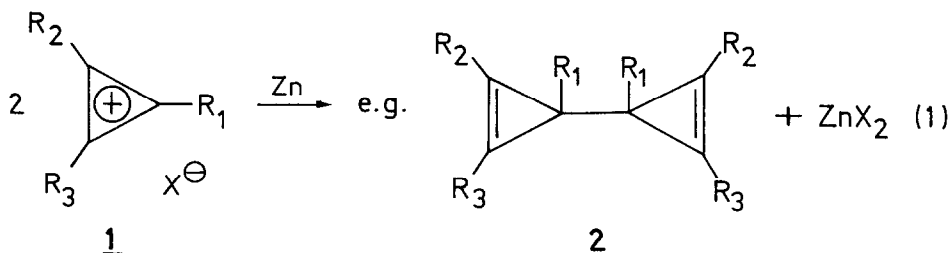
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(Received in Germany 29 August 1973; received in UK for publication 18 October 1973)

Because of the remarkable rearrangement properties of the bicycloprenyl system²⁻⁵⁾ we became interested in a simple and efficient synthesis of this system. We here report on some unexpected observations we made in the course of this study.

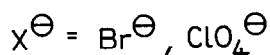
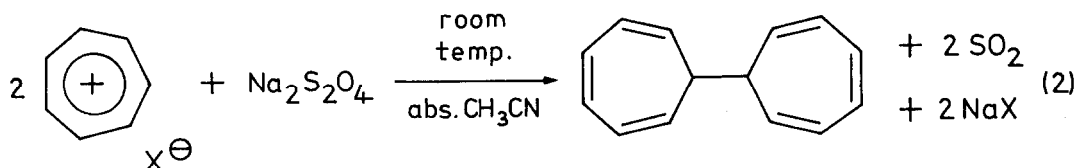
In view of the many readily accessible cyclopropenium salts the most obvious general strategy to synthesize the bicycloprenyl system is by reductive coupling according to eq. (1):



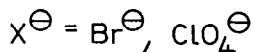
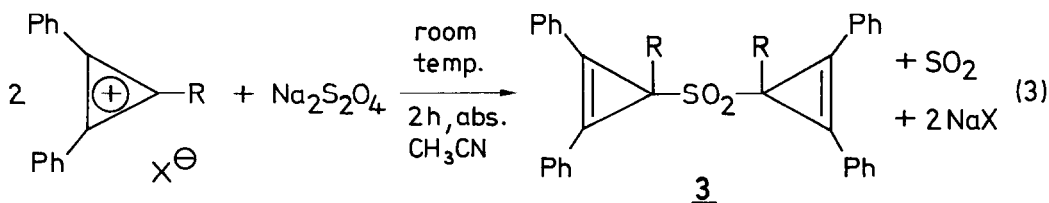
Unfortunately this reaction so far is limited to the single case where R₁=R₂=R₃=Ph²⁾. According to our observations there are a number of reasons why the reactions fail in other cases (cf. loc. cit. 2)): 1) for strongly stabilized species 1 (e.g. R₁=R₂=R₃=NR₂) the reduction potential of metals like Zn and Mg is too low: in order to bring about reduction of 1 strongly reducing agents like alkali metals or amalgams are required; these however tend to irreversibly destroy the amount of 2 formed⁶⁾. 2) For cyclopropenium cations that are equally or less stable than the triphenylcyclopropenium ion the reduction potentials of Zn and Mg are sufficient-but now the difficulties encountered are of a different kind. This was studied in some detail for 1a (1: R₁=H, R₂=R₃=Ph) where 6b rather than 2a (2: R₁=H, R₂=R₃=Ph) is the only identifiable product²⁾. The bicycloprenyl system is known to be particularly

prone to rearrangement by electrophilic agents³⁻⁵) and - not surprisingly - independently synthesized 2a could be shown to rearrange both under the influence of starting 1a and Lewis-acids ZnX_2 - with 6b being one of the reaction products. Although these results do not allow one to conclude whether reductive coupling of 1a yields 2a or an isomeric bicyclopropenyl system²) they are clearly a warning that any bicyclopropenyl synthesis on the basis of reductive coupling must be able to cope with the sources of self-destruction inherent in the system.

We felt that at least part of the difficulties could be overcome by using a different type of reducing agent which would not in the course of the reaction be transformed into an effective catalyst for bicyclopropenyl rearrangement. Earlier we found that the tropylium cation is quantitatively reduced to ditropyli according to eq. (2):



By analogy one would expect then that dithionite ion ought to be the reagent of choice for reductive coupling of cyclopropenium salts. When this was tested for triphenyl- and diphenylcyclopropenium salts we found that the reaction proceeded according to eq. (3) instead:



a) R = Ph, b) R = H

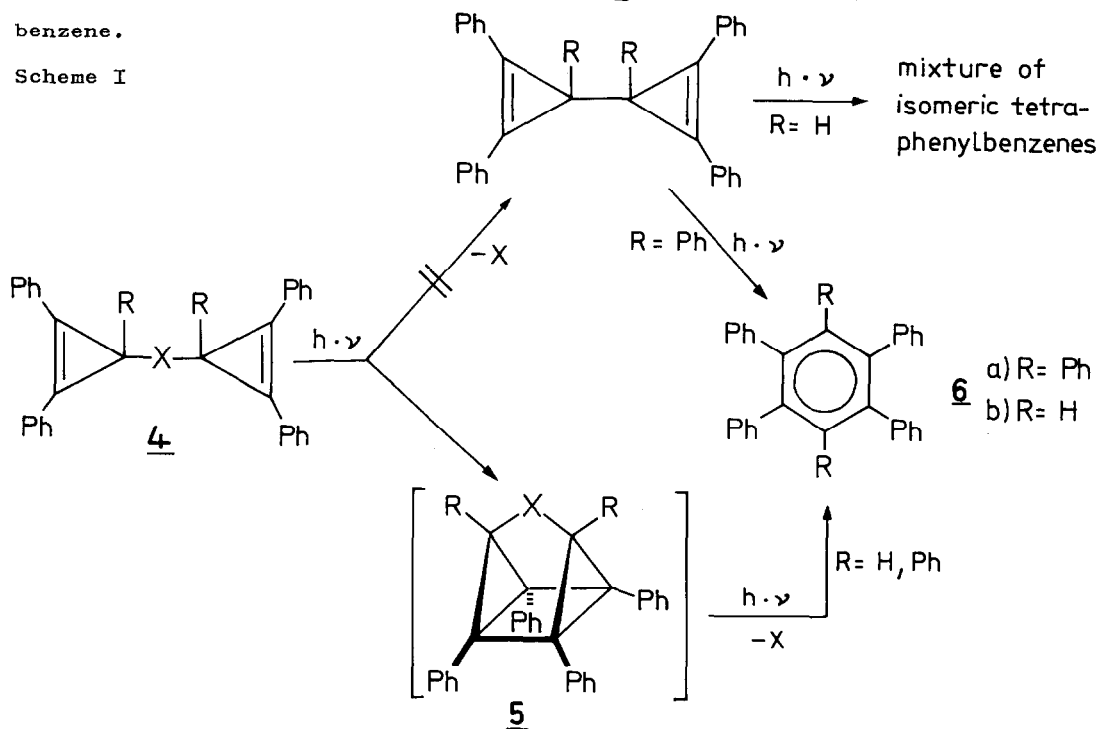
After appropriate work-up the first representatives of the hitherto un-

known bicycloprenylsulfones 3 are isolated in 60-80% yield as crystalline moderately stable solids. Structures can be unequivocally assigned on the basis of analytical and spectroscopic data (3a: mp. 204°C (dec.); ir(KBr): $\nu_{C=C}$ 1820 cm^{-1} , ν_{SO_2} 1100, 1380 cm^{-1} ; 3b: mp. 190°C (dec.); ir(KBr): $\nu_{C=C}$ 1810 cm^{-1} , ν_{SO_2} 1120, 1300 cm^{-1} ; nmr(CDCl₃, TMS): $\tau = 6.33$ (2H,S); uv(CHCl₃): $\lambda_{\text{max}} = 314 \text{ nm}$ ($\log \epsilon = 4.62$)).

The mass spectra of 3a and 3b indicate facile loss of SO₂ and formation of the corresponding cyclopropenium ions (base peak).

Attempts to use cpds. 3 as precursors for the corresponding bicycloprenyl systems failed so far: upon thermolysis in various solvents cpds. 3 rearranged completely beyond $\sim 100^\circ\text{C}$ to give an unidentified mixture of products. Photolysis of 3a and 3b (320nm, C₆H₆) however, cleanly yielded 6a (quantitatively) and 6b (70%, besides polymeric material) respectively. These results are easily understood on the basis of scheme I (pathway 4→5→6) recently proposed by Trost⁷) for the photochemical rearrangement of bis(1,2,3-triphenylcyclopropenyl)-thioether (4: X = >C=S, R=Ph) to hexaphenylbenzene.

Scheme I



There is a reasonable alternative to this mechanism not discussed by

Trost: photochemical extrusion of X with subsequent rearrangement of immediately formed bicyclopropenyl systems. As hexaphenylbicyclopropenyl quantitatively rearranges to hexaphenylbenzene under the reaction conditions of ref. 7) no decision is possible as to which route is taken. For the same reason our results concerning the photochemical rearrangement of 3a (4: X = SO₂, R=Ph) are inconclusive. However, with the rearrangement of 3b (4: X = SO₂, R=H) sufficient labeling is introduced to decide between the two alternatives: under reaction conditions where 3b exclusively yields 6b upon photolysis 2a gives a mixture of (non-interconverting) isomeric tetraphenylbenzenes⁸⁾. This result is uniquely in favour of a mechanism with a thiaquadracyclane-S.S-dioxide 5 (X=SO₂) as intermediate.

The mode of formation of bicyclopropenylsulfones as well as their chemical properties are being investigated further.

Support of this work by the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

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