

(2+4) CYCLOADDITIONS OF TETRAMETHYLBUTADIENYLIMMONIUM ION TO  
*CIS*-FIXED DIENES

Jacqueline Marchand-Brynaert and Léon Ghosez\*

Laboratoire de Chimie Organique de Synthèse

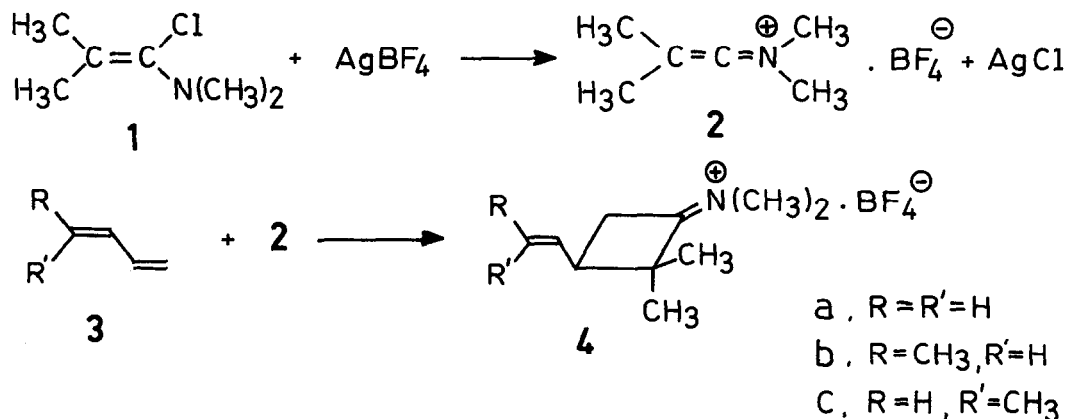
Université Catholique de Louvain, Place Louis Pasteur 1

B - 1348 Louvain-la-Neuve, Belgium

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The exceptional reactivity of tetramethylketeneimmonium ion in (2+2) cycloadditions has been demonstrated<sup>1</sup> by several examples of direction- and stereospecific formation of cyclobutaneimmonium salts from 1-chloro-N,N-dimethylpropenylamine **1** and olefins in the presence of AgBF<sub>4</sub>.

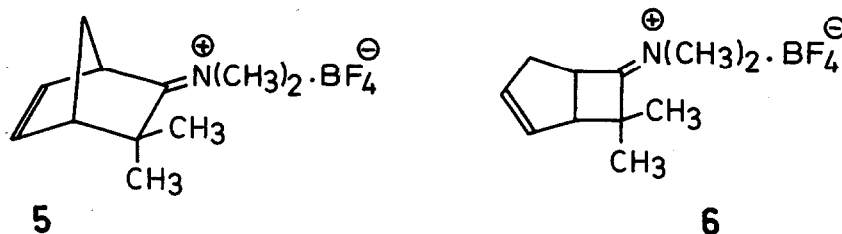
Reactions with conjugated dienes **3a-c** gave only (2+2) cycloadducts and, with **3b** and **3c**, the addition occurred at the less substituted double bond, the configuration of the side chain remaining unchanged.



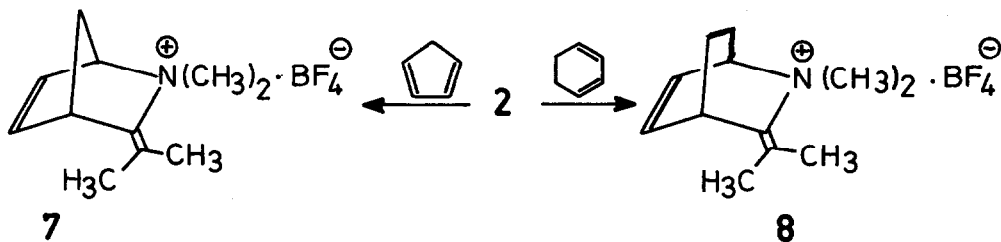
With *cis*-fixed dienes, however, we found that tetramethylketeneimmonium ion reacted as a dienophile. The reactions were conducted as described previously<sup>1</sup>. Cyclopentadiene reacted with **2** to give a 1:1 adduct in 85% yield<sup>2</sup>. The sole other identified product was N,N dimethylisobutyramide resulting

probably from unreacted 2 after work-up.

The adduct did not exhibit the strong band in the 1715-1730  $\text{cm}^{-1}$  region which was found in all cyclobutaneimmonium salts <sup>1</sup> but showed a strong absorption at 1055  $\text{cm}^{-1}$ . It was quite soluble in water but totally resistant to hydrolytic conditions (refluxing NaOH 1N) which converted 4a-c into the corresponding ketones. These data showed that immonium structures such as 5 or 6 must be rejected.



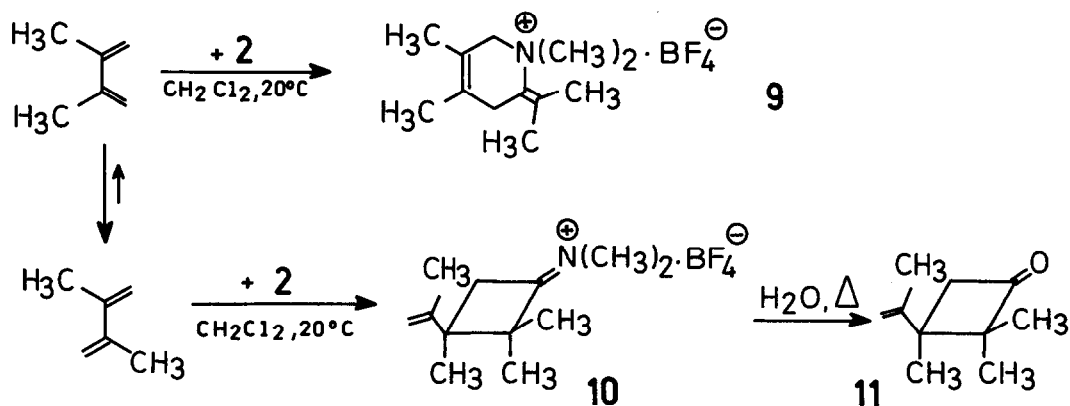
However they were in full agreement with structure 7. Further support came from the following spectral data: the weak ir absorptions at 1628 and 1573  $\text{cm}^{-1}$  confirm the presence of the exo- and endocyclic double bonds <sup>3</sup> respectively ; the two olefinic protons gave rise to two multiplets at 6.9 and 6.6  $\delta$ . The two pairs of singlets at 3.58 and 3.25  $\delta$  and 2.00 and 1.90  $\delta$  can be assigned to pairs of methyl protons corresponding respectively to the  $\text{N}(\text{CH}_3)_2^+$  grouping and to the allylic  $\text{CH}_3$ .



1,3 Cyclohexadiene behaved in the same way and yielded a 1:1 adduct 8 (75%)<sup>2</sup> showing spectral and chemical properties similar with 7.

The behaviour of 2 is rather striking in view of the usually complete dichotomy among molecules cycloadding to conjugated dienes: e.g. ketenes <sup>4</sup>

which are structurally related to 2 react entirely in a (2+2) process with cyclopentadiene whereas electrophilic olefins such as acrylic, maleic or fumaric acid derivatives and even allene give Diels-Alder adducts <sup>5</sup>. It shows that 2 should not only be regarded as a "superketene", being highly reactive in (2+2) cycloadditions <sup>1,6</sup> but also as an activated allene and, as such, capable of reacting as a dienophile. The fact that the addition takes place across the  $\text{>C} = \overset{+}{\text{N}} <$  double bond is not surprising in view of the well-known dienophilic properties of the immonium salts <sup>7</sup>. An important factor governing the mode of cycloaddition seems to be the population of transoid and skew conformations of the dienes: *cis*-fixed dienes such as cyclopentadiene or cyclohexadiene yield (2+4) cycloadducts whereas transoid acyclic dienes 3 a-c give (2+2) adducts. An increase in skew conformation in the diene might be expected to favour the (2+4)- over the (2+2)- cycloaddition. Therefore, 2,3-dimethylbutadiene <sup>8</sup> was reacted with 2 at room temperature; the oily mixture which showed only a weak absorption at  $1720 \text{ cm}^{-1}$  ( $\text{>C} = \overset{+}{\text{N}} <$ ) was treated with water at  $100^\circ\text{C}$  for eight hours to give products 9 and 11.



The quaternary ammonium tetrafluoroborate 9 resulting from the (2+4) cycloaddition was obtained in 46% yield: ir: no absorption for  $\text{>C} = \overset{+}{\text{N}} <$ ; nmr ( $\text{CDCl}_3$ ): 1.83  $\delta$  (t, 3H,  $J \simeq 1\text{Hz}$ ), 1.87  $\delta$  (s, 6H), 2.10 (t, 3H,  $J \simeq 1\text{Hz}$ ), 3.13 (m, 2H), 3.44 (s, 6H), 4.02 (m, 2H). The cyclobutanone 11 which resulted from the hydrolysis of a primary (2+2) cycloadduct 10 was obtained in 20% yield as determined by glpc: ir ( $\text{CCl}_4$ ):  $1780$  ( $\nu_{\text{C=O}}$ ) and  $1645$  ( $\nu_{\text{C=C}}$ )  $\text{cm}^{-1}$ ; nmr ( $\text{CCl}_4$ ): 1.11  $\delta$  (s, 6H), 1.27  $\delta$  (s, 3H), 1.78 (broad s,

3H), 2.39 (d, 1H, J = 16 Hz), 3.43  $\delta$  (d, 1H, J = 16 Hz), 4.8  $\delta$  (m, 2H).

These observations are consistent with a mechanistic scheme involving competitive concerted cycloadditions of the cisoid (skew) conformation of the diene for the (2+4) process and the transoid conformation for the (2+2) process.

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