# Metallation Reactions: the Trimethylenemethane Dianion

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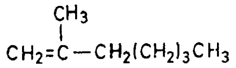
*Summary* Metallation of isobutene in the presence of tetramethylethylenediamine gave consecutively the methylallyl anion and the trimethylenemethane dianion.

TRIMETHYLENEMETHANE with its four $\pi$-electrons is somewhat stabilized in its planar form[1] but exists as a diradical in the ground state. Stabilization by aromatization could occur by its transformation into a Möbius system[2] with end-to-end overlap of the $p$-orbitals when the H–C–H planes of the methylene groups are perpendicular to the plane containing the carbon atoms. Introduction of two electrons should make the 6-$\pi$-electron system stable in its planar form and even impart to it aromatic stability related to that of cyclic 6-$\pi$-aromatic compounds.

We report on the formation of a dilithio-derivative of the trimethylene methane dianion by lithiation of isobutene and on the allylic lithiation of an additional olefin.

Metallation of isobutene with butyl-lithium in hexane in the presence of tetramethylethylenediamine[3] (TMEDA) for 40 h at room temp. with a ratio of olefin: butyl-lithium: TMEDA of 1 : 1 : 1 gave, after subsequent overnight reaction with butyl bromide, two compounds (I)[4] and (II)† in a 1 : 1 ratio.

A similar reaction with a ratio of the reagents of 1 : 2 : 2 in cyclohexane gave after 24 h (I) and (II) in a 1 : 11 ratio. The products (I) and (II) were formed from the methylallyl anion[5] (III) and the trimethylenemethane dianion (IV), respectively.

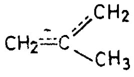


$CH_2{=}C(CH_3){-}CH_2(CH_2)_3CH_3$

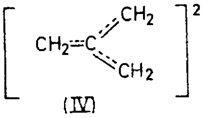
(I)

$CH_2{=}C[CH_2(CH_2)_3CH_3]_2$

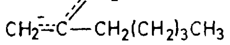
(II)



(III)



(IV)



(V)

Lithiation of (I) occurred in conditions similar to those of isobutene, as indicated by the formation of (II) on treatment of the metallation product with butyl bromide. However, (II) was not formed from isobutene in a two-step reaction, each step involving a monolithiated compound, *i.e.* (III) to give (I) and subsequently (V) to give (II), during the treatment with butyl bromide. Addition of butyl bromide to (I) treated with the metallating mixture for a short time did not yield (II). The dianion (IV) was therefore an intermediate. We have characterised (III) in the reaction mixture by the signals of the $CH_2$ at $\delta$ 1·95 (s) and $CH_3$ at 1·73 (s) and (IV) by the $CH_2$ singlet at 1·48. The

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† Analysed correctly for $C_{12}H_{24}$.

chemical shifts were taken relative to the lowest-field signal of TMEDA (2·15).

Compound (I) exhibited $=CH_2$ as a broad singlet at $\delta$ 4·63, $=CMe$ at 1·70 (s), $=C{-}CH_2^-$ at 2·0 (t), CMe at 0·91 (t), and the other $CH_2$ (6H) at 1·31 (m). Product (II) also showed a broad singlet at $\delta$ 4·67, allylic methylenes at 2·0 (t), CMe at 0·90 (t), and a multiplet (12H) at 1·30 for the other methylenes.

It appears that dimetallation proceeds faster than monometallation in spite of the introduction of the second charge in the same conjugated system and on the same carbons of this system. This ready dimetallation is related to the stability of (IV). A recent paper[6] analysed cross-conjugated Y systems containing six electrons in four parallel *p*-orbitals in terms of aromatic stabilization. Our calculations[7] support this interpretation of a closed electronic shell of aromatic character for the dianion (IV) and also for the corresponding dication.

The calculations[7] show that there is no direct overlap of the peripheral *p*-orbitals, due to the distance between the involved carbons. We have, therefore, an example of aromaticity by delocalization through the centre and not along a cyclic perimeter.

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