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TEN-ELECTRON CROSS-CONJUGATED DIANIONS

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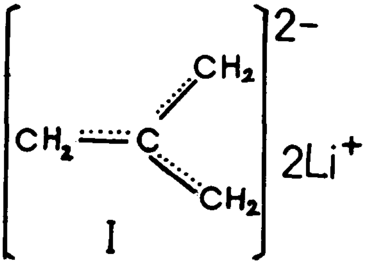
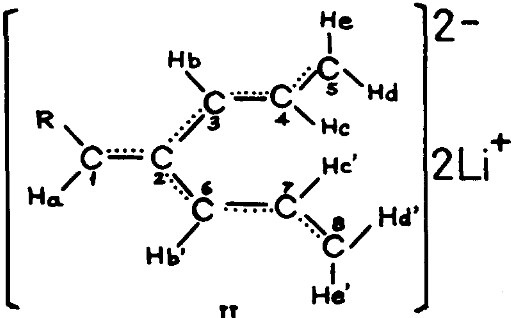
The dilithium derivative of trimethylenemethane a six-π-electron cross-conjugated dianion[1] (I), parent dianion of a class of compounds[2,3] was obtained by dimetalation of isobutene with butyllithium in the presence of tetramethylethylenediamine (TMEDA).

We are reporting now that the formation of the interesting ten-π-electron cross-conjugated dianions (II), bis-vinylogs of I is even more facile than that of I and proceeds in THF or ether unusually fast even in the absence of TMEDA.

The starting materials 1-phenyl-2-allyl-1,4-pentadiene (IIIa) and 2-allyl-1,4-pentadiene (IIIb) were obtained by the action of allylmagnesium bromide and cuprous bromide on β,β-dibromostyrene and 1,1-dibromoethylene respectively.



I

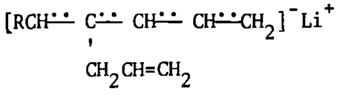


II

Treatment of IIIa with butyllithium in THF at room temperature did not permit to characterize the monolithium compound (IVa), since the second step was fast and IIa was the only product.

$RCH{=}C(CH_2\text{-}CH{=}CH_2)_2$

III



$[RCH\cdots C\cdots CH\cdots CH\cdots CH_2]^-Li^+$, C bearing $CH_2CH{=}CH_2$

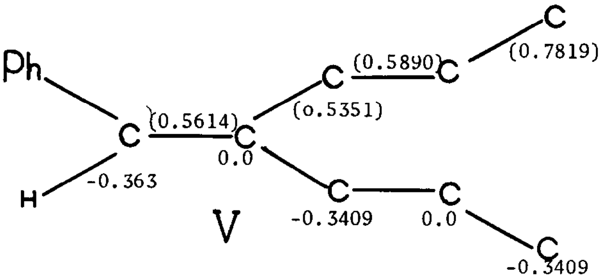
IV

a: R = Ph
b: R = H

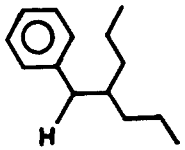
Although metalation in ether slowed down the reaction in general, the second step of metalation was still faster than the first one and the product consisted mainly of starting material and IIa. The determinations of the pmr spectrum of IVa has proved possible only by carrying out the metalation in THF at 0°. The acceleration of the second step of metalation relative to the first one despite the additional charge introduced in the π-system points to a special stabilization[1,2,5] of this type of dianions.

The pmr spectrum of IIa in THF at 31°C consisted of the aromatic protons, ortho δ6.53 ppm (2H, m); meta 6.66 ppm (2H, m) and para 5.68 ppm (1H, t) and the protons of the chain: Ha 4.14 ppm (1H, s); $H_bH_{b'}$ 4.60 ppm (2H,d,12.5 Hz); H_d $H_{d'}$ H_e $H_{e'}$ 3.30 ppm (4H,d,12.5Hz). The H_c signal is hidden under the aromatic protons. Lowering of the temperature of the probe slowed down the rotation around the terminal C_4-C_5 bond and separated the signal of $H_dH_{d'}$ from $H_eH_{e'}$. The cis protons H_d $H_{d'}$ appeared at 3.0 ppm (d, 8Hz) and the trans H_e $H_{e'}$ at 3.41 ppm (d, 16Hz). Further lowering of the temperature slowed down the rotation around the C_1-C_2 bond and separated the signals of the two allylic branches. The doublet at 4.60 ppm separates at -50°C into two broad doublets, one at 4.84 ppm assigned to H_b and another at 4.38 ppm to $H_{b'}$. The signals of the terminal protons at -50°C were assigned in the following way: H_d-2.83 ppm (br); $H_{d'}$-3.15 ppm (br); H_e-3.23 ppm (d, 16Hz); $H_{e'}$ - 3.47 ppm (d, 16Hz). The mean chemical shift of the pairs of protons $H_bH_{b'}$; $H_dH_{d'}$ and $H_eH_{e'}$ is at higher field than their average shift at higher temperatures. This is due probably to the formation of solvent separated ion pairs at lower temperature, as assumed before by Glaze[6] for neopentylallyllithium and by Young[7] for diphenylallyllithium. The signals at lower field of each pair were assigned to the protons located in the allyl branch trans to the phenyl group, since delocalization of the negative charge from side chains into the phenyl ring is more pronounced in a transoid arrangement[8].

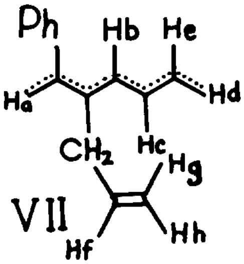
The barriers to the rotation in IIa around the C_4-C_5 bond have been calculated at the coalescence temperature (20°C) to be 14.5 kcal mole^{-1} and for rotation around C_1-C_2-11.5 kcal mole^{-1}. This is consistent with the larger negative charge at C_1 than at C_5, as evidenced by the chemical shifts of the protons attached to them (see pmr of IIb). HMO calculations support the presence of a larger charge at C_1 than at C_5 (V) and a larger bond order for C_4-C_5 than for C_1-C_2 (V) (numbers in parentheses).



V



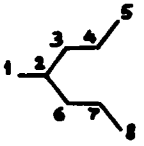
VI



VII

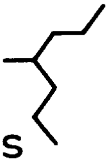
Metalation of IIIb (R=H) with butyllithium in THF led to similar results. The spectrum of the monolithium derivative could not be observed, since the second step of metalation leading to IIb (R=H) was much faster than the first one. All the protons of IIa have been characterized by pmr and their chemical shifts at 31°C were as follows: H_a - 2.2 ppm (br, s); H_b - 3.92 ppm (d, 11.5Hz); H_c - 6.57 ppm (q); H_dH_e - 3.33 ppm (d, 12 Hz). Lowering the temperature to -3°C separated the methylenic protons at C_5. H_d showed up at 2.97 ppm (d, 7Hz) and H_e at 3.41 ppm (d, 14Hz). Rotation around C_1-C_2 cannot be observed due to the symmetry of the molecule.

The dilithium derivatives IIa and IIb are ionic species. This view is supported[9] by the upfield chemical shifts of all protons on the odd-numbered carbons and by the nonequivalence of the methylenic protons at low temperatures. The coupling between protons H_b and H_c indicates their trans arrangement[10,11]. The U conformation is therefore eliminated for each of the two pentadienyl systems ($C_1C_2C_3C_4C_5$) and ($C_1C_2C_6C_7C_8$) composing the dianions, and each of the pentadienyl systems can assume either an extended (W) or sickle (S) conformation[12]. The four possible arrangements for IIb are therefore WW, SS, SW and WS. Since the C_2-C_3 bond order is much lower than that of C_4-C_5 or C_1-C_2 (as obtained by HMO, extended Huckel and CNDO calculations) the barrier for rotation around this bond should be low. All these conformations are therefore interconvertible at the temperatures studied and the presence of each of them depends on their relative energies. Pentadienyllithium compounds prefer to assume the W conformation[10, 11, 13]. However a small amount of S conformers was also found particularly in substituted derivatives[13]. It was found recently that in 1,3,5-triphenylpentadienyllithium the S and W conformers are of comparable energies[14], although 1,5-diphenylpentadienyllithium assumes the W conformation[15]. The barrier for the S_1 to S_2 interconversion in 1,3,5-triphenylpentadienyllithium seems to be very low.[14] Moreover heptatrienyllithium prefers also the extended conformation[16, 17], similar to that in our SS arrangement for the seven carbon chain.

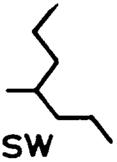


WW

SS



WS



SW

We assume nevertheless that the preferred conformation for IIa and IIb is WW for the only reason that these two compounds have similar pmr spectra, if the influence of the phenyl is taken in account. Since IIa cannot assume the SS nor the SW conformation (as in VI) due to the severe steric interaction between the phenyl and C_4-H, the most probable conformation for IIa and IIb would be WW. However, this question cannot be decided definitively and more data are needed. It is of interest that the p orbitals on C_4 and C_7 are in phase in the HOMO and the repulsion in WW due to the charges on C_5 and C_8 is diminished relative to that present in the U conformation of the pentadienyl anion.

The analysis of the pmr spectrum of IVa led to the following assignments (VII): aromatic protons; para 5.89 ppm (t); ortho and meta 6.66 ppm (m); H_a - 3.98 ppm (s); H_b- 5.38 ppm (d, 12Hz); H_d - 3.36 ppm (d, 8Hz); H_h - 4.7 ppm (d, 8Hz); Hg - 4.84 (d, 16Hz); allylic protons - 2.82 ppm (d, 5Hz). Other protons are obscured by the solvent or the phenyl signals. The conformation assumed for IVa is VII, with phenyl in a cisoid arrangement and the allyl group trans to it. The consideration for this assignment are similar to those in the case of 1-phenyl-2-methylallyllithium[18], including the large chemical shift of H_b in VII relative to that of C_3-H in 1,5-diphenylpentadienyllithium[15].

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