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RETRODIENIC REACTIONS XVI $^{+}$ - FLASH THERMOLYTIC GENERATION OF REACTIVE FUNCTIONAL ALLENES^{++}

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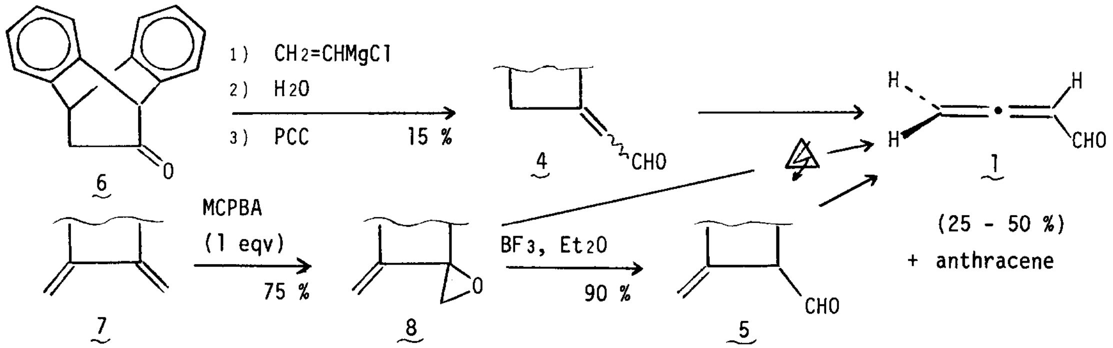
Abstract : Butadienal 1, propadienol 2 and propadienamine 3 are synthesized by flash vacuum thermolysis of their anthracenic Diels-Alder adducts and characterized at low temperature.

It the chemistry of many allenes, functionalized by carbonyl, alkoxy or dialkylamino groups, is now well documented [1], the simplest allenic aldehyde butadienal 1, generated from a cyclic acetal [2], remained non-isolated by the usual techniques and the more reactive propanediol 2 and propadienamine 3 have not been experimentally evidenced (MNDO [3] or EHM [4] calculations concerning compounds 2 or 3 have been published).

After the obtention of reactive cumulenes, enols and primary enamines by retro-Diels-Alder cleavage of anthracenic adducts [5], we present herein the synthesis of compounds 1 - 3, using the same, thermal and out of chemical media, method (a retro-Diels-Alder reaction has already led to stable α-functionalized allenes [6]).

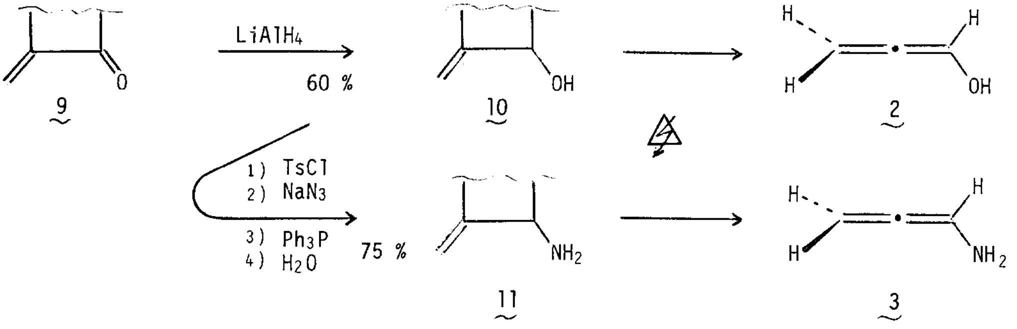
Aldehydes 4 (2 isomers : m p = 192-195°C ; ir : 1675, 1590, 1580 cm^{-1}) and 5 (crystallized with 1 mol. benzene : m p = 72°C ; ir : 1715, 1640 cm^{-1}), precursors of butadienal 1, have been prepared from ketone 6 [7] or diene 7 [8], respectively.



Flash thermolysis (see [5] for description of the technique) of aldehyde 4 (700°C, 10^{-5} torr) leads in a 50 % yield to butadienal 1, trapped at -196°C in a practically pure state, m/e (70 eV) : 68 ($M^{+\cdot}$) ; δ ^{1}H ($CFCl_3$, -90°C) : 5.39 (d, 6 Hz, 2H) - 5.90 (dt, 6 and 7 Hz, 1H) - 9.80 (d, 7 Hz, 1H) ; ir (solid, -196°C) : 1960, 1930 (C=C=C), 1690 cm^{-1} (C=O), (spectra in good agreement with [2]) ; the formation of propyne and furan [9] was also evidenced when the thermolysis was performed at higher temperatures (750 - 800°C). Aldehyde 5 and epoxide 8 (mp= 188°C ; ir : 1650, 1250 cm^{-1}) give also upon thermolysis, in lower yield (∿ 25 %), butadienal 1, involving in the case of 8 thermal rearrangement of the epoxide ring.

Substance 1 is stable up to room temperature in dilute solution (half life ∿ 24 h in $CDCl_3$).

Reduction of methyleneketone 9[10] affords allylic alcohol 10 (mp= 147°C ; ir : 3280, 1650 cm^{-1}) which can be conveniently converted, by a recent method [11], into amine 11 (mp= 112°C ; ir : 3380, 3310, 1650 cm^{-1}).



Thermolysis of alcohol 10 (760°C, 10^{-5} torr) leads, besides a small amount of acrolein , to propadienol 2 (45 %) ; m/e (70 eV) : 56 (M$^{+\cdot}$, base peak) ; δ ^{1}H (CFCl$_3$, -90°C) : 5.30 (d, 6 Hz, 2H) - 6.56 (dt, 6 and 10 Hz, 1H) - 7.00 (d, 10 Hz, OH) ; ir (solid, -196°C) : 1980 — 1960 (C=C=C, broad). By warming up to -50°C, 2 tautomerizes quantitatively into acrolein.

Thermolysis of allylamine 11 under similar conditions gives propadienamine 3, m/e (70 eV) : 55 (M$^{+\cdot}$, base peak) ; ir (solid, -196°C) : 1960 cm^{-1} (C=C=C). The nmr spectrum of the thermolysis products (CFCl$_3$ + CD$_2$Cl$_2$, -85°C) showed the presence of 3 [2.62 (d, 7 Hz, NH$_2$) - 5.14 (d, 6 Hz, 2H) - 5.67 (1H)] (yield ∿ 20 %, peaks no more observable at -65°C) already accompanied by the tautomeric imine 1-aza-1,3-butadiene [12] (∿ 20 %) and polymeric materials (∿ 25 %).

Full description of precursors, experimental details and further work concerning these and other functional allenes will be published later.

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