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CARBOCATIONIC CYCLIZATIONS INITIATED BY DEHALOGENATION OF UNSATURATED α-BROMOIMINE

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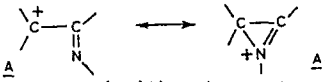
Summary: Electrophilic dehalogenation ($AlCl_3$-CH_2Cl_2) of the ω-olefinic α-bromo α'-phenyl imine 1 leads by two successive carbocationic cyclizations to the 5-9 methanobenzocyclooctene system

Only few data concerning α-imidoyl carbenium ions A are available. Nevertheless, to this date, some conclusions can be drawn:

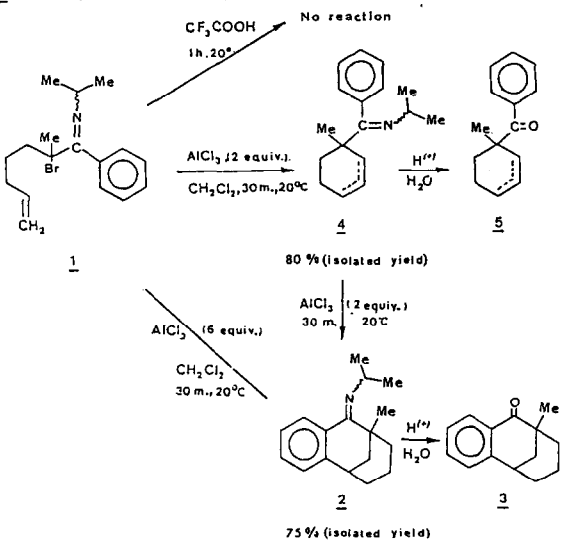
- Ab initio calculations have shown that the energy of the favored bridged form A_1 of these carbocations is close to that of the ethyl cation (1).



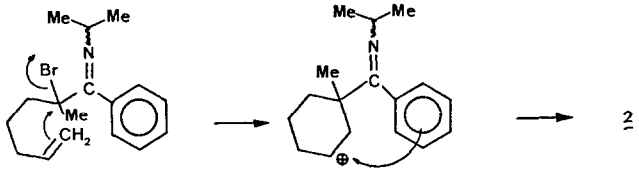
- These carbocations have been generated either by protonation of azirines (2) or by electrophilic dehalogenation of α-haloimines (3).

- α-imidoyl carbenium ions can lead to classical reactions of non-substituted carbenium ions, for example: nucleophilic addition (2) and arylation (3).

After Johnson's extensive pioneer work (4a), carbocationic cyclisations initiated by protonation of an olefinic double bond have now become major reactions in Synthetic Organic Chemistry (4b). This note reports preliminary results in this field, using the terminally unsaturated α-bromoimine 1 as a precursor (5).



The structure of 2 could be assigned by spectrosopic data (7). Furthermore, 2 and 4 have been hydrolysed to 3 and 5. The spectroscopic data for these compounds (^{1}H and ^{13}C NMR) are in complete agreement with the litterature (8)(in this last work, 3 and 5 have been obtained in a very poor yield (< 10%) and no selectivity.



1 7

Presumably 2 arises from two sucessive cyclizations. The remote participation of the olefinic bound of 1 to the departure of bromine leads to carbenium ion 7 which in turn gives rise a cyclialkylation reaction leading to 2. To our knowledge, such a participation to the departure of a leaving group α to an imino groupe had never been described.

From a synthetic point of view, it is interesting to note that this type of reaction is a new route to 5-9 methanobenzocyclooctene which is a basic structure for potentially biologic active compounds (9).

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(5) 1 has been prepared, according to an imine alkylation method recently proposed by de KIMPE (6) : alkylation of Me-CHBr-C(C_6H_5)=N-CH(Me)$_2$ was performed using LDA and Bromo-5pent-1ene

(6) N. de KIMPE, personal Communication.

(7) Spectroscopic data for 2 : IR (film):$\upsilon_{C=N}$= 1655 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 1.18 and 1.29(d,6H, (CH_3)$_2$-CH); 1.44 (s,3H,CH_3); 2.05 (m,1H,C_6H_4-CH-); 4.40 (s, 1H,CH-(CH_3)$_2$); 7.25 (m,1H) and 8.20 (m,1H) (C_6H_4). ^{13}CMR ($CDCl_3$)δ : 19.5, 23.6, 24.5, 28.0, 31.4, 36.4, 38.2, 45.1, 50.3, 126.2, 126.6, 127.3, 128.7, 133.3, 138.9, 143.6, 146.6, 146.9, 163.9. MS (70eV) m/e: 241 (M^+), 57%; 226, $(M-15)^+$, 100%; 198, $(M-43)^+$, 22%; 184, $(M-57)^+$, 18%.

(8) A.G. ISMAILOV, M.A. RUSTAMOV and A.A. AKHMEDOV, Zh. Org. Khim.,(1975), 11, 2278; A.G. ISMAILOV, M.A. RUSTAMOV, F.A. AKOUROV and A.A. AKHMEDOV, Zh. Org. Khim., (1978), 14, 811.

(9) See for example M.E. FRED, J.R. POTOSKI, E.H. FREED, G.L. CONKLIN and J.L. MALIS, J. Med. Chem., (1973), 16, 595.

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