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SYNTHESIS OF 1,3-DI-1-ADAMANTYLIMIDAZOL-2-CARBONYL FROM 1,3-DI-1-ADAMANTYLIMIDAZOL-2-YLIDENE

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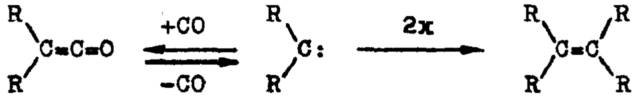
Abstract: Synthesis of a new stable sterically-hindered ketene, 1,3-di-1-adamantylimidazol-2-carbonyl, from 1,3-di-1-adamantylimidazol-2-ylidene was studied through direct reaction with CO in THF.

It is known that in the processes of ketenes photolysis and thermolysis the short-lived carbenes form[1]. The latters can be trapped and observed only at the temperature below 20K.



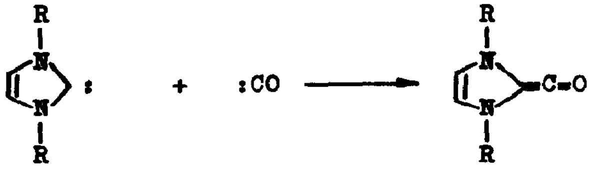
The strong tendency of obtained carbenes to dimerize even at rather low temperatures results in a fast transformation of its to ethylene and, therefore, a shift of equilibrium to the right.

The stable under ordinary conditions nucleophilic carbenes (1,3-di-R-imidazol-2-ylidenes) that were recently isolated by J.Arduengo and co-workers[2] are convenient objects for examination of the possibility of synthesis of the sterically-hindered ketenes from corresponding carbenes.

Calculation of carbene (I) affinity to CO made to a semi-empirical quantum-chemical MNDO[3] approximation by the use of equation

$$A(CO) = \Delta H^{o}_{f,298}(\mathbf{I},g) + \Delta H^{o}_{f,298}(CO,g) - \Delta H^{o}_{f,298}(\mathbf{II},g)$$

where $\Delta H^{o}_{f,298}(\mathbf{I},g)$, $\Delta H^{o}_{f,298}(CO,g)$ and $\Delta H^{o}_{f,298}(\mathbf{II},g)$ are heats formation of carbene (I), CO and ketene (II), respectively, indicates that this process is exothermic (A(CO)= 67.37 kJ mol^{-1}).



Carbenes: R= H(I); R= Ad(III). Ketenes: R= H(II); R= Ad(IV).

In fact, the treatment of 1,3-di-1-adamantylimidazol-2-ylidene (III) by CO in THF under 10-15°C leads to formation of corresponding 1,3-di-1-adamantylimidazol-2-carbonyl (IV)[4-6] in 20-30% yield.

Stability of ketene (IV), apparently, is connected with simultaneous acting of two main factors: presence of bulky adamantyl substituents at the nitrogen atom that strong restrict the dimerization of ketene; and delocalization of electron density on the terminal carbon atom of cumulene fragment. Comparison of distribution of the effective atomic charges in ketene itself (V) and (II) indicate the strong decrease of positive charge on the central carbon atom of cumulene chain (about 5 times) in the second case and very strong decrease of electron density on the terminal carbon (the sign of charge is change).

Peculiarities of ketene (IV) structure, apparently, must be manifested by it low reactivity in the reaction both electrophiles and nucleophiles. In this case, the electrophilic attack must occur from above the plane of the ketene skeleton (on O for (II) and (V), and on terminal carbon for (V) (Fig.1)), while nucleophilic attack must occur on the plane (on central carbon). However, for (IV) the central carbon atom is completely hide by bulky adamantyl substituents (Fig.2). Therefore, for (IV) may be expected an extremely low reactivity in the reaction with nucleophiles. Thus, when (IV) was refluxed in ethanol about 1 hour a very small yields (7-10%) of esters observed.

Further experiments and studies are currently in progress in our laboratory to investigate the reactivity of (IV) with compact reagents.

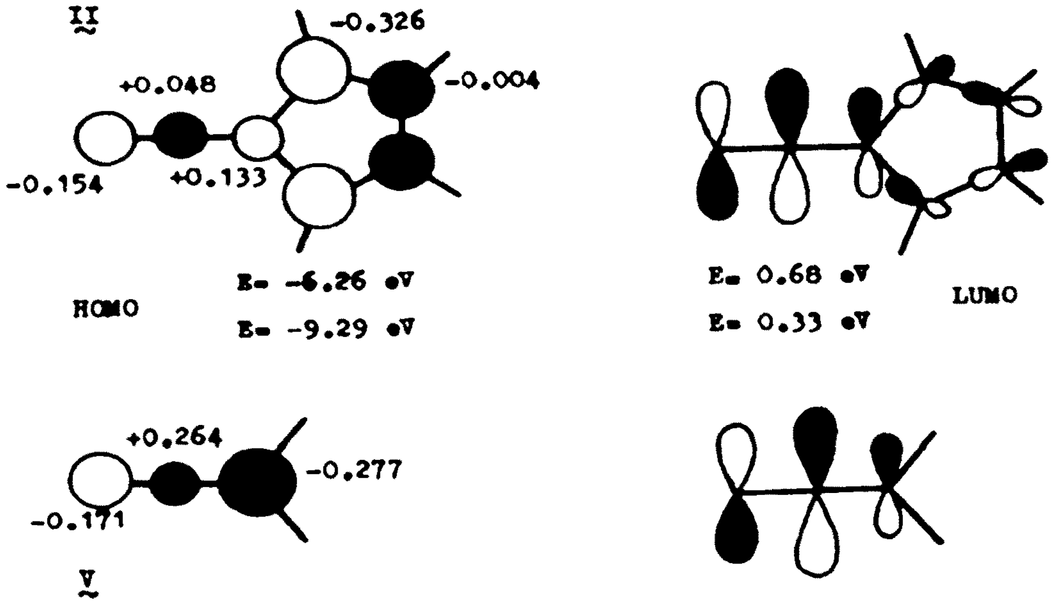


Fig.1 HOMO, LUMO of ketenes (II) and (V) and charges on the atoms. as determined by MNDO calculations.

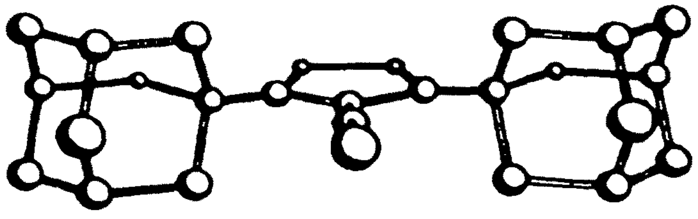


Fig.2 Perspective view of ketene (IV) as determined from it crystal structure. For clarity hydrogen atoms are omitted.

References and Notes

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(4) The typical procedure for preparation of (IV). In a 250-ml three-neck flask, fitted with a stirring bar, a thermometer, a carbon monoxyde inlet and placed in dry box, were placed carbene (III)(3.36g, 0.01 mol) and dry THF (100 ml). This mixture was stirred over 10 min till dissolve of (III). Then the dry CO was bubbled through the solution (500 ml min^{-1}) during 1 hour. Then the solvent was evaporated under reduced pressure till 30 ml; the mixture was diluted with toluene (70 ml). Cooling to -10°C for 1 hour afforded slightly yellow crystals which were isolated by filtration, washed with petroleum ether, and vacuum dried (1.24 g, yield 34%), mp 250-255°C (dec). Anal. Calcd for $C_{24}H_{32}N_2O$,% : C 79.08, H 8.85, N 7.68, O 4.39. Found,% : C 78.81, H 8.96, N 7.95, O 4.28.

(5) Spectroscopic data for ketene (IV): ^1H NMR (300.13 MHz,$CDCl_3$) δ=1.63 ppm (s,$Ad_{4,6,10}$,12H), 2.06 (s,$Ad_{3,5,7}$,6H), 2.34 (s,$Ad_{2,8,9}$,12H), 6.94 (s,NCH,2H); ^{13}C NMR (75.47 MHz,$CDCl_3$) δ= 171.42 ppm (s,CO), 116.32 (dd, $^1J_{CH}$=181.2 Hz,$^2J_{CH}$=13.5 Hz,$C_{4,5}$), 56.1 (s,Ad_1), 43.4 (tm,$^1J_{CH}$=134.6 Hz,$Ad_{2,8,9}$), 36.9 (tm,$^1J_{CH}$=127.2 Hz,$Ad_{4,6,10}$); 31.4 (dm,$^1J_{CH}$=127.8 Hz,$Ad_{3,5,7}$), -8.7 (s,C_2). IR(KBr) ν= 2925 cm^{-1},2163, 1511, 1448, 1372, 1355, 1307, 1220, 1283, 1128, 835,698. UV(CH_2Cl_2) λ_{max} (lgε)= 232 nm (3.2), 248 (2.4). MS (m/z): 364.5 (M+).

(6) X-ray analysis data for ketene (IV): $C_{24}H_{32}N_2O$, M= 364.53, monoclinic, space group $P2_{1/n}$, a=1486.3(2), b=1127.2(2), c=1074.4(2), β= 102.12(1)°, Z=4, Dx=1.18 g/cm^3,radiation Mo Kα, μ(Mo)=6.83 1/cm, T=-90°C, 6496 reflections, R(Rw)=0.042(0.053) for 2248 reflections with $I > 3\sigma$.

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