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A CONVENIENT METHOD FOR THE PREPARATION OF ALKYLATED FULVENES FROM UNSATURATED ACID CHLORIDES AND ACETYLENIC COMPOUNDS

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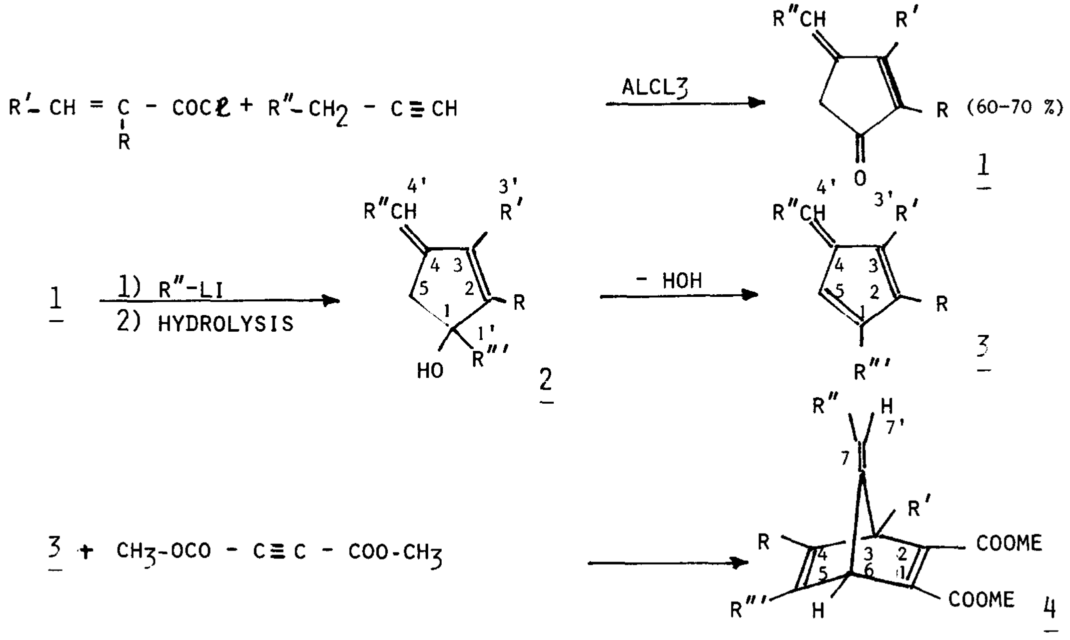
Several methods for synthesing fulvenes are described in the literature[1-2-3-4-5-6]. However, it is often very difficult to synthesize the alkylsubstituted starting materials such as cyclopentadienes or cyclopentadienones. We wish to present here the preparation of alkylated fulvenes from α-unsaturated acid chlorides and monosubstituted alkynes via the readily available 4-alkylidene 2-cyclopentenone 1[7]. Organo lithium compounds add fairly well to the carbonyl group at 213°K and the corresponding unstable alcohols 2 lead directly to fulvenes.



The purification of the alcohols 2 is not easy and their elemental analyses are not significant since these compounds easily lose a molecule of water. They were however unambigously characterized by their NMR spectra. Above 323 - 333°K the clear oil containing 2 becomes yellow orange or red and fülvene 3 is almost quantitatively formed from 2 (overall yield as high as 40 % may obtained from acid chlorides and acetylenic compounds). The following fulvenes have been synthesized : R = CH_3, R' = H, R" = C_2H_5, R"' = CH_3 ; R = R' = CH_3, R" = C_2H_5, R"' = CH_3 ; R = CH_3, R' = H, R" = C_3H_7, R"' = CH_3 ; R = CH_3, R' = H, R" = C_2H_5, R"' = C_6H_5; R=R'=R"=R"'=CH_3; Spectroscopic properties (NMR, IR and UV) of two stable fulvenes are summarized in the experimental part and agree with previous data[8]. An additional proof of the structure 3 has been furnished by a Diels-Alder reaction of 3 with $CH_3OCO-C\equiv C-COO-CH_3$: 7-alkylidene-1,4 norbornadienes 4 are obtained in quantitative yields. The structure of adducts 4 has been etablished by PMR spectroscopy.

PREPARATION, PHYSICAL AND SPECTROSCOPIC PROPERTIES

FULVENES : To a solution of 0,12 M alkyllithium (from 0,25 g atom of lithium and 0,12 M of alkylbromide) in 100 ml anhydrous ether was slowly added (3 h) a solution of 0,1 M cyclopentenone 1 (prepared as described in ref[7]) in 50 ml anhydrous ether at 203°K. The resulting mixture was stirred for an hour at 203°K, then gently heated to room temperature and was hydrolysed with a solution of 1 g acetic acid in 100 ml water.

- R = CH_3, R' = H, R" = C_2H_5, R"' = CH_3 : bp : 53°C/0,2 Torr ; ^1H NMR (δ/TMS ppm in CCl_4) $\delta_{1'} \simeq \delta_{2'} \simeq 1{,}94$; $\delta_3 \simeq 5{,}98$, $\delta_{4'} = 5{,}83$, $\delta_5 = 5{,}67$; IR(KBr) $\nu_{C=C} = 1645\ cm^{-1}$, Skeletal 1325, 1375 cm^{-1} ; UV : heptan λ_{max} : 350,5 and 260 nm ; ε_{max} : 236 and $1{,}51.10^4$; methanol : λ_{max} : 350 and 260 nm : ε_{max} : 189 and 130.10^4.

- R = R'= CH_3, R" = C_2H_5, R"' = CH_3. bp : 57°C/0,1 torr ; ^1H NMR (/TMS in CCl_4) $\delta_{1'} \simeq \delta_{2'} \simeq 1{,}85$, $\delta_{4'} = 5{,}85$, $\delta_5 = 5{,}85$; IR(KBr) : $\nu_{C=C} = 1648\ cm^{-1}$, Skeletal : 1320, 1375 cm^{-1} ; UV : heptan λ_{max} : 360,5 and 254,5 nm, ε_{max} : 211 and $1{,}49.10^4$; methanol λ_{max} : 365 and 255,5 nm, ε_{max} : 190 and $1{,}24.10^4$.

ADDUCTS : To a solution of 10^{-2} M fulvene in 5 ml carbon tetrachloride was added 10^{-2} M $CH_3OCO-C\equiv C-COOCH_3$ at room temperature : the reaction was complete in 2 hrs. The adduct 4 is a visquous product which decomposes on heating. R=CH_3,R'=H,R"=C_2H_5,R"'=CH_3, $^1H_{NMR}$ ($\delta_{ppm/TMS}$ and J(Hz) in CCl_4) : $\delta_{COOCH_3} = 3{,}815$, $\delta_3 = 3{,}815$, $\delta_{4'} = \delta_{5'} = 1{,}82$, $\delta_6 = 4{,}04$, $\delta_7 = 4{,}195$, $J_{63} = 2{,}7$, $^4J_{67'} = 0{,}65$.

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