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THE SYNTHESIS OF A METHYLENECYCLOPROPENE (TRIAFULVENE) BY PROTON ABSTRACTION FROM A CYCLOPROPENYL CATION

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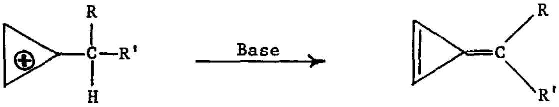
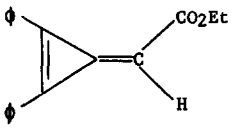
In light of the recent flurry of activity in the area of methylenecyclopropene syntheses,[2-6] we are prompted to report our work on a potentially simple approach to this general problem. This method is one that has been applied successfully to the analogous heptafulvene[7] system and involves simply proton abstraction from the appropriate carbonium ion.



In theory, there are three basic requisites for this scheme to work. First, the carbonium ion must be available. Second, the proton must be acidic enough to be removed by a base faster than the base attacks the cyclopropenyl cation. Third, the resulting methylenecyclopropene must be stable to the conditions of the proton removal.

As a prototype system for application of this method, the known methylenecyclopropene I was selected.[*][+]



I

As a potential source of the necessary precursor cation III, 1,2-diphenyl-3-carboethoxymethylcyclopropene II was synthesized (Scheme 1) in 17% yield from 1,2-diphenylcyclopropene-3-carboxylic acid by the

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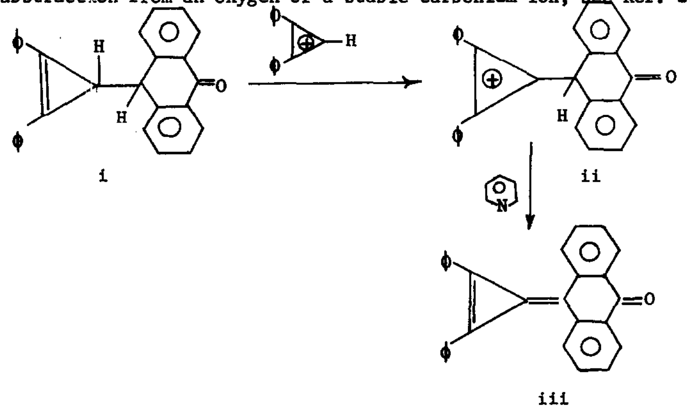
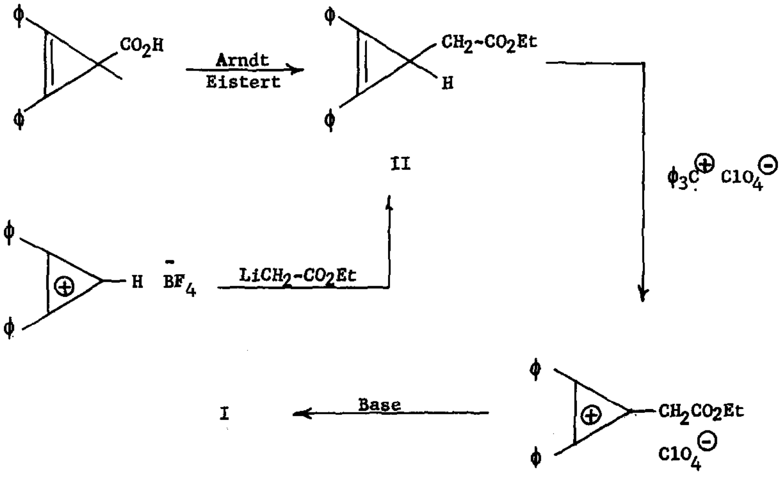
[*] We have also successfully applied this method to the synthesis of some substituted calicenes[8] (5,5-cyclopropenylidenecyclopentadienes). These results will be reported elsewhere.

[+] The essence of this method was quite recently reported by Föhlisch and Bürgle[6] for the synthesis of iii from reaction of diphenylcyclopropenyl perchlorate with anthrone in a mixture of pyridine and acetic acid. In their case, it is believed that, following initial formation of i, a second molecule of the cyclopropenyl cation abstracts a hydride to give cation ii which then loses a porton (presumably to the pyridine). For an example of a straightforward synthesis of a quinocyclopropene by proton abstraction from an oxygen of a stable carbonium ion, *see* Ref. 2.



Arndt Eistert synthesis according to the method of Newman.[9,10] It was obtained more simply in 27% yield by simply treating a cold solution of the alpha-lithioethyl acetate (from reaction of butyl lithium with ethyl bromoacetate) with diphenylcyclopropenyl fluoborate.

The cyclopropenylacetate II was quite readily converted to the cation III (78% yield) by hydride abstraction with triphenylmethyl perchlorate in acetonitrile.[7,11] The structure of the cation was confirmed by its ultraviolet spectrum in acetonitrile containing fluoboric acid[12] [λ_{max} (log e); 246 (4.24), 293 (4.50) and 308 (4.52)] and by comparison with an authentic sample prepared by treating the methylenecyclopropene prepared by the method of Battiste[4] with perchloric acid in acetic anhydride.



Scheme 1

III

The most satisfactory method of proton abstraction was found to be with dilute aqueous base. In a typical experiment, 37 mg. (0.098 mmoles) of the perchlorate III was suspended in 3 ml. of dry ether. To this suspension was added 9 ml. of water containing ca. 0.06 mmoles of sodium bicarbonate. The mixture was vigorously shaken until all solid had disappeared to give a deep yellow ether layer and a colorless aqueous layer. The ether layer was removed and was found by ultraviolet analysis to contain 74% of the calculated amount of the methylenecyclopropene. Isolation of the pure methylenecyclopropene is a bit difficult due to its tendency to polymerize.[4] However, it was found that it could be isolated in crystalline form in the following manner. The ether solution was dried and most of the ether (to ca. 0.25 ml.) was removed by bubbling argon through the ice-cooled solution. The cold, concentrated solution was diluted to ca. 1.5 ml. with pentane. A small amount of insoluble material was removed by centrifuging. The resulting solution was concentrated in the same manner as before and, again, diluted to ca. 1.5 ml. with pentane. Again, a small amount of solid was removed and the resulting clear solution was concentrated with argon to about 0.5 ml. This solution was then cooled in ice-salt at -10° until crystallization was complete. The product is a light yellow crystalline material, m.p. 71-73° (reported m.p. 72-75°) which shows all of the reported ultraviolet and infrared absorptions.[4]

Finally, it should be pointed out that we found the solid perchloric acid salt III of the methylenecyclopropene to be quite stable at room temperature over long periods of time. This presents a convenient way to store the methylenecyclopropene which has a notable propensity for polymerization.[4]

A typical synthesis of the ethyl cyclopropenylacetate (II) from the cation-anion combination follows. Ethyl bromoacetate (0.286 ml., 2.5 mmoles) was added during 2 min. to a cold (-75°) stirred solution of 1.61 ml. (2.5 mmoles) of a 1.55 molar solution of n-butyllithium in hexane (Foote Mineral Co.) in 8.0 ml. of dry ether. The mixture was stirred for 8 min. at this temperature and was then rapidly transferred with a cold syringe to a stirred slurry of 278 mg. (1.0 mmole) of diphenylcyclopropenium fluoborate in 8.0 ml. of methylene chloride at -75°. After stirring at this temperature for 50 min. under an atmosphere of argon, the mixture was poured into very dilute acid and extracted with ether. The ether layer was washed with brine, dried over magnesium sulfate and filtered through Drierite. Removal of the ether left an oil which was chromatographed on 18 g. of acid Woelm alumina (Activity I). Elution with 9:1 pentane:ether gave 8 mg. of yellow oil followed by 75 mg. (27%) of the cyclopropenyl acetate II as a pale yellow oil. Its infrared spectrum (CCl_4) showed significant peaks at 5.52 (cyclopropene double bond)[12] and 5.75μ (carbonyl). The ultraviolet spectrum was that of a typical diphenylcyclopropene.[12] $\lambda_{max}^{cyclohexane}$ (log e); 228 (4.22), 237 (4.13), 302 sh. (4.26), 307 (4.31), 316 (4.39). 323 sh. (4.30) and 355 mμ (4.28). The positions of n.m.r. resonances (CCl_4, external acetaldehyde standard, reported as shifts from tetramethyl silane) appeared at tau = 2.40 and 2.73 (unresolved aromatic proton multiplets), 5.96 (methylene of ethyl group, quadruplet), 7.51 and 7.69 (methylene and methine protons in a characteristic A_2B heptuplet) and 8.83 (methyl triplet). An analytical sample was obtained by short path distillation at 0.6 mm. and 135° (bath temp.). Calcd. for $C_{19}H_{18}O_2$: C, 82.0; H, 6.5. Found: C, 81.7; H, 6.6.

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