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SYNTHESES OF ACYLCYCLOPROPENE DERIVATIVES ‡

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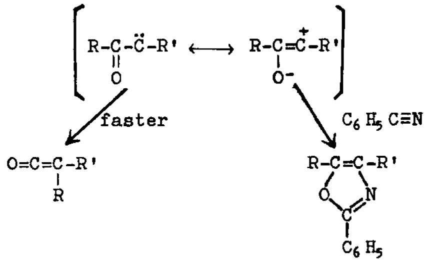
We wish to report 'one step syntheses' of cyclopropene derivatives by utilizing the addition reaction of keto-carbene to triple bond.

Huisgen and his co-workers[1-5] have done a series of investigation on the keto-carbenes. They studied their nature by 1,3-dipolar addition to unsaturated compounds and concluded that the keto-carbene, in general, undergoes 'Wolff rearrangement' much more easily than the competing 1,3-addition. In certain cases, they were able to conduct the reaction to 1,3-addition route with the aid of copper powder as the catalyst.



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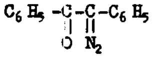
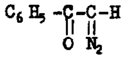
‡ Compounds reported here showed satisfactory results on elemental analysis and molecular weight determination. Melting points are uncorrected.

Several workers studied the carbenic addition of benzoyl-[6-9] and acetylcarbene[10] to various double bonds and isolated cyclopropane derivatives in certain yields.

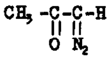
Thus we have taken following three diazoketones and studied their thermal decomposition in the presence of diphenylacetylene.


$C_6H_5-\underset{\underset{O}{\|}}{C}-\underset{\underset{N_2}{\|}}{C}-C_6H_5$

(I)


$C_6H_5-\underset{\underset{O}{\|}}{C}-\underset{\underset{N_2}{\|}}{C}-H$

(II)

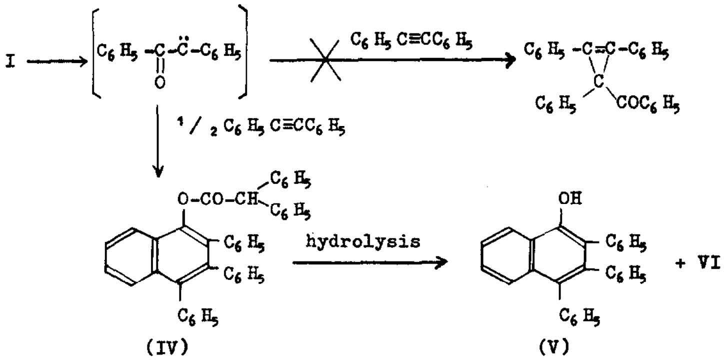

$CH_3-\underset{\underset{O}{\|}}{C}-\underset{\underset{N_2}{\|}}{C}-H$

(III)

In each cases, two equivalents of diphenylacetylene in diglyme was heated at 140° and diazoketone in diglyme was added dropwise into a hot solution. Diazocompounds decomposed almost instantly. In the presence of copper powder as the catalyst, the reaction temperature was kept at 100°. After working up as usual, reaction products were separated by means of alumina column chromatography.

Decomposition of azibenzil(I) resulted a crystalline material IV, $C_{42}H_{30}O_2$, m.p. 169.5-170°, containing ester group, in 46% yield. In the presence of copper powder the yield was 26%. Alkaline hydrolysis of IV resulted phenolic compound V, $C_{28}H_{20}O$, m.p. 162-163°, and diphenylacetic acid(VI). Compound IV and V were found to be identical materials with those obtained by Smith et al.[11] They prepared these compounds by the reaction of diphenylacetylene with diphenylketene. Reported melting points are 168-169° for IV and 163° for V. We have also synthesized 1,2,3-triphenylnaphthalene through known route[12] and compared its nmr and UV spectrum with those of IV and V. Results were strongly suggesting that IV should be 2,3,4-triphenyl-1-naphthyl diphenylacetate.

There were obtained some other unidentified materials, however, these fractions did not contain cyclopropene skeleton on UV study.[‡] Moreover, the recovered amounts of diphenylacetylene indicated that diphenylacetylene did not participate to the compounds in later fractions. Consequently we concluded that there was obtained no cyclopropene derivatives in this case. Benzoylphenylcarbene produced did not undergo carbenic addition, but rearranged preferentially to diphenylketene and latter reacted with diphenylacetylene resulting compound IV.

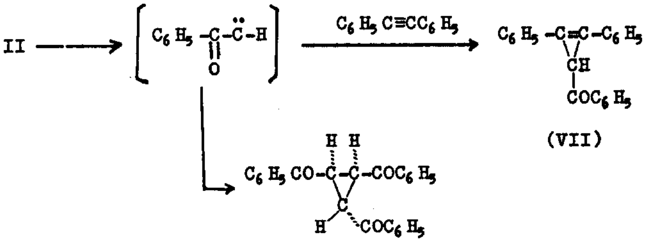


The reaction of diazoacetophenone(II) with diphenylacetylene resulted 3-benzoyl-1,2-diphenylcycloprop-1-ene(VII), m. p. 152-153°, in 1.2% yield, and trans-1,2,3-tribenzoylcyclopropane(VIII), m.p. 216-217°(reported 215-217°[15,16]), in 7.8% yield. The presence of copper powder markedly increased yields up to 8.1% and 30.8%, respectively.

Compound VII showed characteristic IR peaks at 1840cm^{-1}(cyclopropene) and 1660cm^{-1}(ketone), and UV maxima in ethanol at 228mμ (logϵ 4.39), 235mμ(4.41), 244mμ(4.28), 294mμ(4.31), 308mμ(4.40)

[‡] It was reported very characeteristic UV and IR spectra for cyclopropene derivatives.[13]

and 321mμ(4.24).[13] Its nmr exhibited multiplet at 1.75-2.80 τ (total of 15 H) and sharp singlet at 6.15τ(1 H). These results

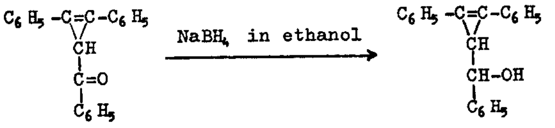

(VII)

(VIII)

all indicate that VII has the cyclopropene skeleton and structure of VII should be as shown in figure.

Same ketone VII was prepared by the reaction of known 1,2-diphenylcyclopropenylcarboxylic acid chloride with phenyl magnesium bromide in ether at 0°.‡ Yield of VII based on 1,2-diphenylcyclopropenylcarboxylic acid was 42%. Mixed melting point of VII with new sample showed no depression and IR and UV spectra of both sample were superimposable. Thus the structure of VII is firmly established.

Ketone VII gave 2,4-dinitrophenylhydrazone, m.p. 193-194°, and reduction with $NaBH_4$ produced alcohol IX, m.p. 84-85°, both holding the cyclopropene structure (IR and UV). Nmr of IX


(VII) (IX)

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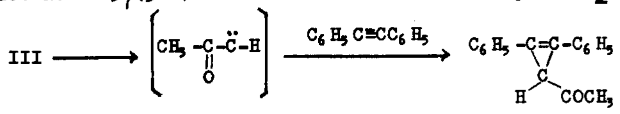
‡ Breslow[14] reported the synthesis of VII by the reaction of acid chloride with diphenyl cadmium, however, they gave no details for this compound, even the melting point of VII.

showed multiplet at 2.27-2.95τ(15 H), doublet at 5.54τ(1 H, J=7cps), doublet at 7.57τ(1 H, J=7cps), and a broad peak at 7.94τ(1 H).

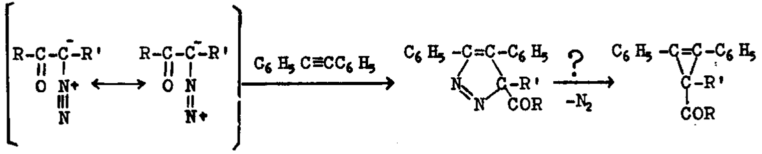
Compound VIII was identified as trans-1,2,3-tribenzoylcyclopropane, because several workers[6-10] obtained same material, also in the absence of olefin.[15,16] Moreover, its nmr spectrum was superimposable with that reported in a literature.[17]

Diazoacetone(III) was decomposed in the presence of copper powder and resulted 3-acetyl-1,2-diphenylcycloprop-1-ene(X), m.p. 101-102°, in 3.3% yield. Compound X showed IR maxima at 1830cm^{-1} and 1680cm^{-1}, and UV maxima at 226.5mμ(logϵ 4.37), 234mμ(4.32), 283mμ(4.24), 294mμ(4.35), 318mμ(4.38) and 330mμ(4.34). Its nmr showed multiplet at 2.28-2.75τ(10 H), singlet at 7.17τ(1 H) and singlet at 8.25τ(3 H). Ketone X reacted smoothly with p-tosylhydrazine and gave hydrazone, m.p. 180-181°. Hydrazone obtained showed all characteristic IR and UV peaks for cyclopropene derivative.



(X)

There shall be a question whether the formation of cyclopropene is taking a route of carbenic addition to a triple bond or thermal decomposition of pyrazolenine, which is formed by the 1,3-addition of diazocompound to triple bond. However, the formation of trans-1,2,3-tribenzoylcyclopropane in a relatively large



amounts strongly suggest that the carbenic decomposition of diazo-compound is predominating in the present case. It is known besides that the intermediate pyrazolenine derivatives usually undergo facile rearrangement to aromatized pyrazol.[18,19]

We are attempting to study the chemistry of intramolecular carbenic reaction of these cyclopropene derivatives. The results will be reported in near future.

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