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ON THE DECOMPOSITION OF α-DIAZOKETONES AND β-KETOSULFONIUM YLIDES
CYCLOPROPANATION OF α-DIAZOKETONES

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ALTHOUGH there is good evidence that α-diazoketones (Ia) and β-ketosulfonium ylides (Ib) are decomposed by light, heat and various catalysts to give the same intermediate (II), the ultimate products are not identical. Whereas α-diazoketones, in inert solvents, give either trans-1,2-diacylethylenes (IV) or butenolides (XII) as the main products, depending upon the decomposition procedure (1)(2), β-ketosulfonium ylides give always trans-1,2,3-triacylcyclopropanes (VI)(3)(Chart I) -often in nearly quantitative yields.

The statement that "purely thermal decomposition of α-diazoketones leads to cyclopropane derivatives" found in otherwise excellent reviews (4) has no experimental support. Actually, two references can be found in the chemical literature reporting the formation of cyclopropanes from α-diazoketones but the yields reported are not greater than 1.4% (1a) (2b).

In connection with some other work done in our Laboratory, we were interested in finding out which should be the optimal experimental conditions favoring cyclopropanation over the normal dimerization in the decomposition of α-diazoketones.

In agreement with some previously reported results (1), we have found that Cu-bronze induced decomposition of 1-diazo-3,3-dimethyl-2-butanone (diazomethyl ter-butyl ketone; Ia, R = $(CH_3)_3C$), in inert solvents, gives trans-1,2-dipivaloylethylene (IV, m.p. 116º) in 70% yield. In the presence of 2,3-dimethyl-2-butene the catalytic decomposition leads to cyclopropane VIII (5) in 47% yield, together with a 37% yield of the dimer IV. However, when diazomethyl ter-butyl ketone was decomposed, under an atmosphere of nitrogen, with Cu-bronze in thioanisole solution at 70º, trans-1,2,3-tripivaloylcyclopropane (VI, m.p. 164,5º) was formed in high yield (90%), no traces of the dimer (IV) being detected[+]. Cyclopropane VI (R = $(CH_3)_3C$) was identical in all respects with a sample prepared by the reaction of α-bromopinacolone (VII) with potassium *ter*-butylate (6). On the other hand, purely thermal decomposition, even in thioanisole solution, leads to 2,4-di-*ter*-butyl-3-buten-4-olide (XII, m.p. 41º)(2).

These results, together with some data already reported in the chemical literature (1-5), clearly demonstrate that *the nature of the products obtained from the decomposition of α-diazoketones and β-ketosulfonium ylides depends exclusively on the nucleophilicity of the species originally present in the reaction mixture*. From this assertion four corollaries follow:

1) Since α-diazoketones are much less nucleophilic species than β-ketosulfonium ylides[++], the free ketocarbenes generated from the former have greater opportunity of surviving and, therefore, of undergoing Wolff rearrangement (8) to the corresponding ketenes (IX) which will be the starting point of a new series of compounds not present (or rarely found) in the decomposition of β-ketosulfonium ylides, namely: Arndt-Eistert synthesis derivatives (XIII)[+++], butenolides (XII) and monoacylethylenes (XI)[++++]. However, in the absence of other nuclephiles, α-diazoketones are efficient traps for "deactivated" ketocarbenes (in coordination with copper) leading to 1,2-diacylethylenes by loss of nitrogen (II $\xrightarrow{+Ia}$ IIIa $\xrightarrow{-N_2}$ IV).

2) Since β-ketosulfonium ylides are strong nucleophiles they are more efficient traps for ketocarbenes than olefins and low yields of cyclopropanes derived from these (VIII) should be expected in competitive experiments, as shown by Trost (3a) in the decomposition of dimethylsulfonium phenacylide. The same is not true for α-diazoketones (5).

3) Since thioethers generated from β-ketosulfonium ylides are themselves strong nucleo-

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[+] Some phenyl methyl sulfone -an artifact very tedious to removed from cyclopropane VI- is formed if the colloidal copper has not been carefully eliminated before the working up process.

[++] α-Diazoketones are not true ylides and structures such as $R-CO-CH=\overset{+}{N}=\overset{-}{N}$ are also significant. A good measure of the small degree of negative charge on the α-carbon atom of α-diazoketones compared to β-ketosulfonium ylides is the C=O st frequency which is found, respectively, near 1630 (as amides) and below 1540 cm^{-1} (as phosphonium ylides) (See footnote 4 in ref. 2a; also ref. 3c and 7).

[+++] In fact, products similar to Arndt-Eistert synthesis from β-ketosulfonium and sulfoxonium ylides have been reported (3a)(9).

[++++] Since ketenes are decomposed by light to carbenes and CO (10), monoacylethylenes XI presumably arise from coupling of the former with α-diazoketones.

philes they should also be efficient traps for "deactivated" ketocarbenes and cyclopropanation should be expected in the catalytic decomposition of α-diazoketones in thioether solutions $\mathrm{(Ia \longrightarrow II \longrightarrow Ib \xrightarrow{+II} \longrightarrow VI)}$.

4) Since ketocarbenes are much more electrophilic species than 1,2-diacylethylenes (IV) cyclopropanation cannot occur by the reaction of the latter with β-ketosulfonium ylides as has been suggested (3) -even if they do react when put together (3a)(3c). In other words, if the reaction of the ketocarbene with β-ketosulfonium ylide leads to 1,2-diacylethylene as an intermediate this compound, rather than cyclopropane exclusively, should be the predominant product in the reaction mixture.

$$\mathrm{Ib \longrightarrow II \xrightarrow[fast]{+Ib} IV \xrightarrow[slow]{+Ib} V \longrightarrow VI}$$

In fact, the primary addition intermediate IIIb resulting from the coupling of the ketocarbene with unreacted β-ketosulfonium ylide[+] is a strong nucleophile and stable enough to capture a second molecule of ketocarbene to give the new intermediate V which cyclizes to cyclopropane VI by irreversible lost of thioether (11).

$$\mathrm{Ib \longrightarrow II \xrightarrow[fast]{+Ib} IIIb \xrightarrow[\substack{very\\fast}]{+II} V \longrightarrow VI}$$

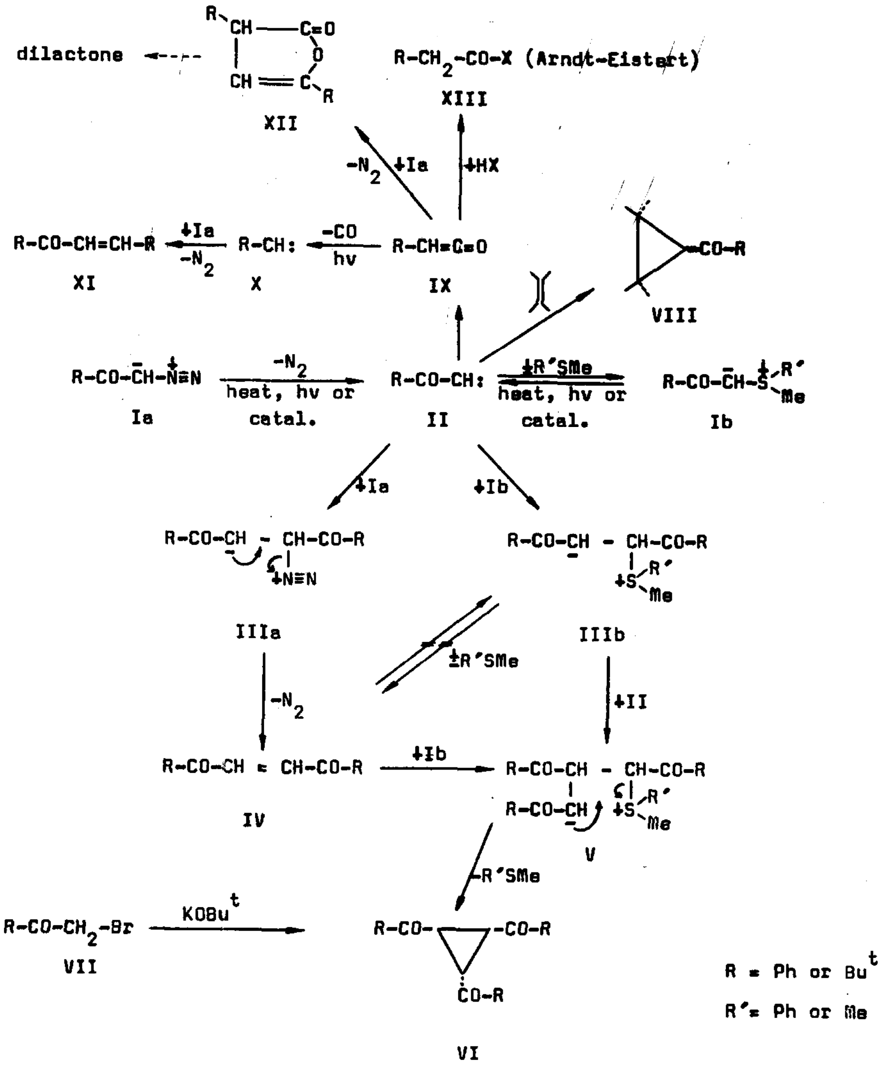
However, in the α-diazoketone series the primary addition intermediate IIIa easily looses nitrogen to give 1,2-diacylethylenes which are unreactive towards α-diazoketones[++].

Since α-diazoketones are more accesible and familiar than β-ketosulfonium ylides, the reported Cu-bronze induced decomposition in thioether solution appears as a promising synthetic method leading to cyclopropane derivatives.

[+] Since thioethers are much less nucleophilic species than β-ketosulfonium ylides an equilibrium between ethylene IV and the intermediate IIIb in thioanisole solution seems very unlikely ($\mathrm{IV + R'SMe \rightleftharpoons IIIb}$) and n.m.r. studies have actually failed to detect it.

[++] Whether the small amount of cyclopropane found in "purely thermal decompositions of α-diazoketones" (1a)(2b) arise from the intermediate IIIa or ethylene IV is not clear.

CHART I



R = Ph or Bu^t

R' = Ph or Me

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