

THE CHEMISTRY OF CYCLOPROPENONE. REACTIONS AT THE CARBONYL GROUP, AND 1,2 CLEAVAGES

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Recently we have reported¹ a convenient preparation of pure cyclopropenone, which makes this fundamental substance available for chemical investigations. We now wish to describe a number of the chemical explorations we have carried out with unsubstituted cyclopropenone. For rough classification purposes, we have (somewhat arbitrarily) divided these reactions into chemistry which takes place at the carbonyl group, the subject of this communication, and chemistry which takes place at the carbon-carbon double bond, the subject of the accompanying communication.

On reaction of cyclopropenone with one equivalent of Br₂ in CDCl₃ solution at -30° a solid separates which has an nmr singlet at δ 9.35, 0.2 ppm lower than cyclopropenone, and to which we assign structure 1. This material reacts with cyclohexene to regenerate cyclopropenone and form cyclohexane dibromide quantitatively. On warming to 0°, 1 is converted to trans- β -bromoacryloyl bromide (2) in 69% yield; the cis isomer could not be detected. Thus Br₂, a "double bond reagent", successively reacts with the carbonyl and the single bond of cyclopropenone but does not add to the double bond.

As expected, reaction of cyclopropenone with triethyloxonium fluoroborate at 0° in CDCl₃ leads to the formation of the related ethoxycyclopropenium fluoroborate 3, whose sharp singlet is shifted 0.3 ppm downfield from the signal of cyclopropenone and which shows J_{13C-H} of 252 Hz and J_{H-H} of 1.2 Hz. However, in trifluoroacetic anhydride cyclopropenone reversibly affords the covalent derivative 4; the sharp singlet in the nmr is now 1.08 ppm upfield from the signal of cyclopropenone, and J_{13C-H} is 240 Hz while J_{H-H} is 1.1 Hz. These data are in good agreement with those for other 3,3-disubstituted cyclopropenes.

Cyclopropenone is moderately stable in trifluoroacetic acid, but at 35° \pm 0.1° it reacts with a half-life of 15.8 hr to afford compound 5. Of course, in this case there is some ambiguity about the sequence of reactions, since in the product there has also been an addition across the 2,3 bond. Similarly, thioacetic acid reacts with cyclopropenone to yield a cyclopropane 6 in which two thioacetic acids have added across both the carbon-carbon double bond and the carbonyl group, and in which again the sequence of reaction is ambiguous.

When cyclopropanone is treated with *t*-butyl hypochlorite at room temperature in CH_2Cl_2 the product is *cis*-*t*-butyl β -chloracrylate 7, in 45% yield. Some of the *trans* isomer is also formed, but it seems likely that this is the result of isomerization of 7. If cyclopropanone is instead irradiated with a solution of *t*-butylhypochlorite at low temperature a polymer results which may well reflect free radical polymerization of cyclopropanone, since it does not occur in the absence of *t*-butylhypochlorite.

When a CDCl_3 solution of cyclopropanone (0.7 M) was heated at 100° it afforded brown amorphous polymer together with a small amount of unstable dimer 8, whose nmr was consistent with this structure. This mode of dimerization has been observed previously³ with substituted cyclopropanones. When cyclopropanone was heated with one equivalent of diphenylcyclopropanone under the same conditions a 52% yield of the related stable adduct 9 could be obtained, m.p. $143\text{--}144^\circ$. It seems likely that the formation of 8 and 9 involve nucleophilic attack on the carbonyl carbon of cyclopropanone, followed by 1,2 cleavage and cyclization.

Of course, cleavage of the 1,2 bond could also in principle be initiated by attack on carbon 2. Apparently this happens with a sulphur ylide, with which cyclopropanone at -78° in CH_2Cl_2 affords a 50% yield of the pyrone 10, m.p. $63\text{--}64^\circ$, whose structure was confirmed by an independent synthesis. As shown, we believe that this process involves initial attack on the carbon-carbon bond of cyclopropanone, leading to 1,2 cleavage and a ketene intermediate. Even more striking, the Wittig ylid benzylidene triphenylphosphorane affords α -naphthol (11), presumably again by such a sequence involving a ketene. Here a typical "carbonyl reagent" attacks the double bond instead. A similar attack occurs with Grignard reagents, as the accompanying communication describes.

Finally, photolysis leads to 1,2 cleavage; while cyclopropanone absorbs only at short wavelengths, when it is irradiated through quartz it eliminates carbon monoxide, in common with other cyclopropanones.^{3,4}

References

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