

THE CHEMISTRY OF CYCLOPROPENONE. REACTIONS AT THE CARBON-CARBON DOUBLE BOND.

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The accompanying communication describes chemistry at the carbonyl group of cyclopropenone, including cleavages between carbons 1 and 2. Cyclopropenone also undergoes a number of additions to the carbon-carbon double bond, and in some cases these additions result in complete cleavage of the double bond. Such additions, or cleavages, are the subject of the present paper.

We have already reported<sup>1</sup> the addition of cyclopropenone to diphenylisobenzofuran to afford the adduct 1, a remarkably stable cyclopropanone which is unaffected by heating at 100° for several hours. Further transformations of 1 are of interest. On photolysis through Pyrex, it is smoothly and rapidly transformed into 2, a colorless liquid with the correct spectroscopic properties; also interestingly, this with BF<sub>3</sub>·etherate affords the known naphthol derivative 3. We<sup>1</sup> have also described the formation of hemiketal 4, m.p. 141°. This is rearranged with triethylamine to 5, identical with one of the adducts of methyl acrylate to diphenylisobenzofuran. Treatment of 4 with BF<sub>3</sub>·etherate affords the naphthoic ester 6, m.p. 162.5-163.5°, a known compound<sup>2</sup>. On treatment with BF<sub>3</sub>·etherate, compound 1 itself affords the tropolone 7, convertible to the methyl ether 8. Both of these compounds have characteristic spectra.

With 1,3-butadiene cyclopropenone gives only polymeric material, but if the reaction is run in the presence of methanol then compound 9, the hemiketal of the expected Diels-Alder adduct, can be obtained in quantitative yield. With base 9 is converted to the well-known 10.

Cyclopropenone reacts with tetracyclone via the postulated adduct 11; if this reaction is run in methylene chloride in the presence of methanol then 12, m.p. 195-197°, can be isolated in 88% yield. On treatment with base 12 is converted to 13, m.p. 187-189°, in 95% yield. The infrared spectrum of 13 is very similar to that of the methyl ester of 14. If instead the Diels-Alder reaction is performed with acetic acid present then the endo acid 14, m.p. 211-212°, is obtained in 27% yield along with acetate 15, m.p. 224-226°, in 72% yield. The methyl ester of 14 is identical with the Diels-Alder product of methyl acrylate and tetracyclone. Acetate 15 could be reduced to diketone 16, m.p. 216-217°, with zinc in boiling acetic acid.

Finally, if the Diels-Alder reaction is performed at room temperature in the inert solvent methylene chloride the products are the tropone 17, m.p. 217-218°, in 58% yield along with diketone 18, m.p. 178-179°, in 11% yield. The latter structure is supported by extensive spectroscopic studies, and results from bond switching in intermediate 11.

Similar bond switching is involved in the Diels-Alder reaction of cyclopropanone with 6,6-dimethylfulvene. In methylene chloride at room temperature ketone 19 was produced in 50-63% yield as a colorless liquid whose 2,4-dinitrophenylhydrazone had m.p. 157-159°. Again, the structure is supported by extensive spectroscopic work, including nmr studies on the adduct derived from dideuterocyclopropanone.

The use of methanol to trap an otherwise reactive cyclopropanone intermediate can also be applied to catalytic hydrogenation. Thus we have reported<sup>1</sup> that in most solvents cyclopropanone is hydrogenated to produce acetone; we find that in methanol a little of the hemiketal 20 can also be detected by nmr.

We have described<sup>1</sup> the reaction of diazo compounds with the carbon-carbon double bond of cyclopropanone, leading to addition followed by cleavage. An additional example is the reaction of cyclopropanone with benzyldiazomethane, to afford the diazo ketone 21, m.p. 119° (dec.), in 27% yield.

Cyclopropanone undergoes a truly remarkable reaction with Grignard reagents. Thus, with methyl magnesium iodide a 30-50% yield of 2-methylresorcinol was obtained as the only characterizable product no matter which order of addition was used. Similar results were obtained with other Grignard reagents, affording the resorcinols shown (24). The most obvious mechanism for this unusual process involves conjugate addition yielding intermediate 22, addition to a second cyclopropanone to afford 23 in what amounts to an ene reaction, and subsequent cyclization and fragmentation of 23. It is striking that the Grignard reagent reacts with 2 equivalents of cyclopropanone no matter which order of mixing is used. On the other hand, only polymeric materials have so far been obtained on treatment of cyclopropanone with organolithium reagents, lithium dimethyl copper, or lithium aluminum hydride. When cyclopropanone is allowed to stand at room temperature in ether solution with 1% sodium amalgam it is converted to a 57% yield of hydroquinone 25 together with brown polymeric solid. Various mechanisms can be suggested for this striking process.

It is apparent from these brief studies that the chemistry of cyclopropanone cannot be extrapolated either from previous results on substituted cyclopropanones or from simple ideas about "carbonyl reagents" and "double bond reagents". We hope that with its remarkable and vigorous activity and ready availability<sup>1</sup> cyclopropanone will become a useful synthetic reagent in a variety of chemical transformations.<sup>3</sup>

#### References

1. R. Breslow and M. Oda, *J. Amer. Chem. Soc.*, 94, 4787 (1972).
2. R. Weiss, A. Abeles and F. Knapp, *Monatsh.*, 61, 162 (1932).
3. Support of this work by the National Institutes of Health is gratefully acknowledged.



