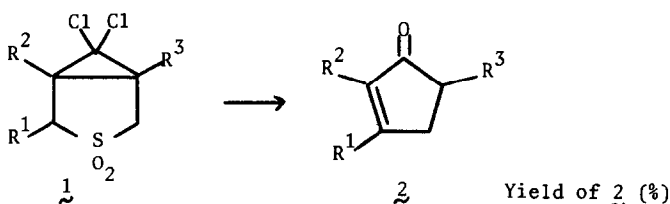


CYCLOPENTENONES FROM DICHLOROCARBENE ADDUCTS OF SULFOLENES

Yehiel Gaoni

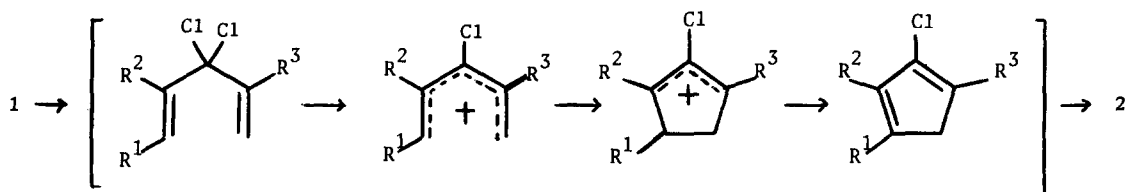
Department of Organic Chemistry, The Weizmann Institute of Science, Rehovot, Israel

In an earlier attempt to produce a cyclopentenone from the bicyclic dichlorocarbene adduct of 3,4-dimethyl-sulfolene (1a) by fragmentation in acids, only thiopyran derivatives were obtained.<sup>1</sup> A later attempt to use the product of thermal decomposition of 1a, namely, 1,3-dichloro-2,4-dimethyl-2,4-pentadiene, likewise did not yield the expected cyclopentenone.<sup>2</sup> This particular case of 1a or its fragmentation product seems, however, to be rather the exception. It has now been found that in the more general case adducts 1 are converted into cyclopentenones (2) by simple reflux in 80% acetic acid for a period of one to three hours, usually in good yields.<sup>3</sup>



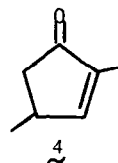
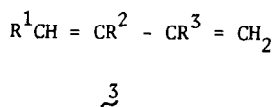
- |   |    |
|---|----|
| a. $R^1 = \text{H}, R^2 = R^3 = \text{CH}_3$                          | -  |
| b. $R^1 = R^3 = \text{CH}_3, R^2 = \text{H}$                          | 67 |
| c. $R^1 = \text{CH}_3, R^2 = \text{C}_5\text{H}_{11}, R^3 = \text{H}$ | 70 |
| d. $R^1, R^2 = (\text{CH}_2)_4, R^3 = \text{H}$                       | 26 |
| e. $R^1, R^2 = (\text{CH}_2)_5, R^3 = \text{H}$                       | 80 |
| f. $R^1, R^2 = (\text{CH}_2)_{10}, R^3 = \text{H}$                    | 60 |

The reaction seems to involve a thermal cheletropic elimination of  $\text{SO}_2$  followed by solvolysis of the intermediate dienylic dichloride according to Scheme 1.<sup>2</sup> This also agrees with the mechanism suggested by Hiyama *et al* for the conversion of dichlorocarbene adducts of allylic alcohols into cyclopentenones.<sup>4</sup> When  $R^2$  and  $R^3$  are methyls (or alkyls?) the intermediate terminally alkylated cyclic allylic cation is greatly stabilized<sup>5</sup> and the reaction may take then a different course.<sup>2</sup>



Scheme 1

The merit of the present reaction is in producing the cyclopentenones in two or three simple steps from available sulfolenes or from 1,3-dienes (3), respectively. The addition of



dichlorocarbene to the sulfolenone in a catalytic two-phase system proceeds, usually, in good to high yields.

Adduct 1b produced ketones 2b and 4 in a ratio of 6 to 1. Ketone 4 can be separated from 2b by chromatography. It is known, however, to be converted into 2b thermally or by acid treatment.<sup>4</sup> In the case of 1d, aromatization lowers the yield of 2d and propiophenone is produced (25%) besides other, unidentified aromatic products.

The diene which leads to dihydrojasmonone (2c) was prepared from 3-octanone by reaction with vinyl magnesium chloride and dehydration with potassium hydrogen sulfate. A mixture of diene isomers was obtained, of which 3 ( $\text{R}^1 = \text{CH}_3$ ,  $\text{R}^2 = \text{C}_5\text{H}_{11}$ ,  $\text{R}^3 = \text{H}$ ) was the major constituent. The sulfolenone was prepared from this mixture by reaction with sulfur dioxide and purified by chromatography.

#### References

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