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PHOTOCHEMISTRY OF EPOXIDES. THE ACETONE SENSITIZED REARRANGEMENT OF 3,4-EPOXYOLEFINS[1a]

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We have recently initiated a general research program to study the photochemistry of epoxyolefins. The present paper describes our initial results on the photochemical rearrangement of the monoepoxides of conjugated dienes.

Irradiation[2] of acetone solutions of 3,4-epoxyolefins (.08M) at 3000Å results in the formation of β, γ-unsaturated ketones. Several examples are shown in the Table. An interesting feature of these reactions is the preference for hydrogen over alkyl migration. In the cyclic examples (1, 3, and 5) the keto-aldehyde which would have formed from alkyl migration was not present in the photolysis product. The quantum yields were measured in the case of 2 and 8

TABLE

Epoxyolefin	Photoproduct	% Yield
3,4-epoxycyclooctene(1)	3-cyclooctenone(2)	30
3,4-epoxycyclohexene(3)	3-cyclohexenone(4)	60
3,4-epoxycyclopentene(5)	3-cyclopentenone(6)	20
2,5-dimethyl-4,5-epoxy-2-hexene(7)	3,5-dimethyl-4-hexen-2-one(8)	60
2,3-dimethyl-3,4-epoxybutene(9)	no reaction	-
3,4-epoxybutene(10)	no reaction	-

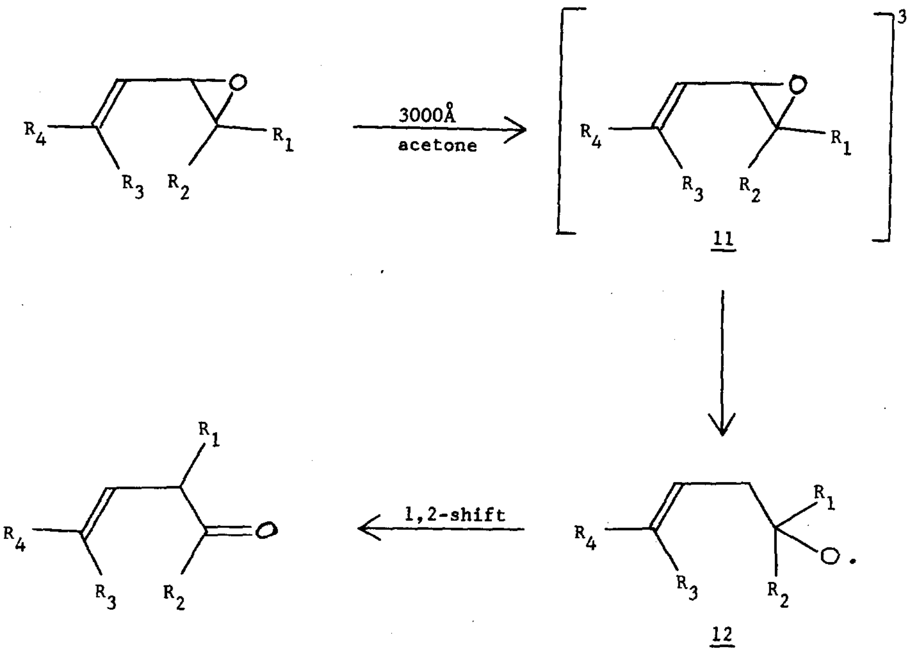
using the benzophenone-benzhydrol actinometer system [3] and found to be 0.15. The products were identified by direct comparison with authentic samples in the case of 2, 4, and 6[4] while 8 was identified from its spectroscopic properties as well as by hydrogenation to the known saturated ketone.[5] In each case the photorearrangement could be readily quenched by 0.05 M piperylene suggesting the intermediacy of the $n-\pi^*$ triplet state of acetone. The maximum chemical yield of each product was considerably diminished by its slow disappearance to nonvolatile material.

Although we have not extensively studied the synthetic aspect of these reactions it does appear that in several cases this method of synthesis may be the best available one. For example 3-cyclohexenone has been isolated in over 50% yield by this procedure. Synthetic generalities cannot be made at this time due to the possibility of either hydrogen or alkyl migration.

Since it has recently been shown that the $n-\pi^*$ triplet state of acetone readily abstracts hydrogen atoms from cyclic ethers,[6] one could consider free radical chain mechanisms initiated by abstraction of a hydrogen atom from the epoxyolefin. The abstraction step would be followed by rearrangement of the radical species and a final hydrogen abstraction would produce the observed product. This final abstraction could occur from the epoxyolefin, the 2-hydroxypropyl-radical (formed in the initial abstraction step), or acetone. The epoxyolefin is an unlikely source since the reaction is zero order in epoxide from .008 M to 0.5 M. The latter two sources were ruled out by the photolysis of 2 in D_6-acetone. Analysis of the product by nmr revealed no deuterium incorporation into the molecule. These considerations make a free radical chain mechanism unlikely.

Mechanistic possibilities are shown below. Energy transfer from the acetone (T1) photosensitizer would yield an excited 3,4-epoxyolefin species which then undergoes C-O bond homolysis to give the allylic biradical 12. Intermediate 12 then produces the observed product *via* a 1,2-shift of alkyl or hydrogen. Analogy for this type of 1,2-shift mechanism is found in the photorearrangement of styrene oxide[7] and indene oxide[8] which proceed to give phenylacetaldehyde and 2-indanone, respectively.

The photochemical reactions of 3,4-epoxyolefins are quite similar to the well studied photochemistry of α,β-epoxyketones.[9] Photolysis of these systems usually produces 1,3-diketones *via* a mechanism quite similar to that presented above. However, in the α,β-epoxyketone systems, alkyl migration is usually preferred over hydrogen migration in contrast to the present results.



Acetone sensitized photolysis of 2,3-dimethyl-3,4-epoxybut-1-ene and 3,4-epoxybut-1-ene failed to produce any photo products. Only a slow disappearance of the epoxide to form a polymer was noted. This lack of reactivity in terminal 3,4-epoxyolefins is probably due to the high triplet energy of these olefins which lie above the triplet energy of acetone. The triplet energy of acetone has recently been found to be 78 Kcal[10] while the triplet energy of ethylene has been estimated to be 82 Kcal.[11]

We are currently investigating the reason for the marked preference of hydrogen over alkyl migration in the cyclic epoxyolefins as well as extending our studies to unsymmetrically substituted epoxyolefins.

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