AUTOXIDATION OF ARYLCYCLOALKENES : A METHOD FOR THE PREPARATION OF EPOXIDES

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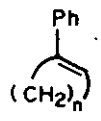
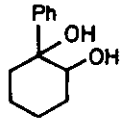
Abstract - A method for the preparation of arylcycloalkene epoxides has been developed via the autoxidation of the corresponding arylcycloalkenes.

The autoxidation of 1-phenylcycloalkenes has not been carefully investigated. Most of the literature reports[1-6] deal with the autoxidation of 1-phenylcyclohexene 1. To the best of our knowledge no work on the autoxidation of compounds 2 - 4 has been reported.

Razuvaev and Zateev[1] have studied the products obtained by heating 1 with benzoyl peroxide for 12 hours. The main product obtained was the monobenzoate of the diol 5. Since this reaction involved benzoyl peroxide as an initiator, it can be considered as a free radical reaction and not a true autoxidation.



1, n = 4
2, n = 3
3, n = 5
4, n = 6



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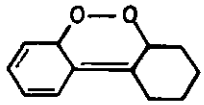

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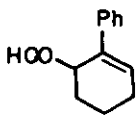

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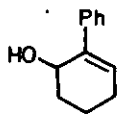

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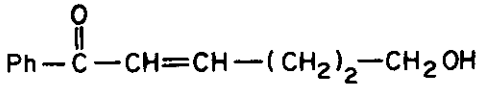

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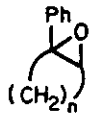


10, n = 4, 11, n = 3
12, n = 5, 13, n = 6

Hock and Siebert[2] carried out the autoxidation of 1 at 35-40° by passing a stream of oxygen through it for 96 hours and obtained mainly the peroxide 6 and the hydroperoxide 7 in a 3:2 ratio.

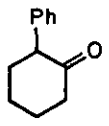
In their studies on the autoxidation of 1 (50°, 30 hours), in the presence of various initiators, Erofeev et al[3] have reported the formation of 6 (40%), 8 (16%) and 9 (33%). The most effective catalysts were manganese butyrate, cobalt butyrate or cobalt stearate. However,

the conversions obtained were only about 33%.

Rubailo and coworkers[4-6] have studied in depth the kinetics of autoxidation of 1 and determined the rate constants for chain propagation and termination during the liquid phase oxidation.

In the present study we report the autoxidation of compounds 1 to 4 at 50° using cobalt naphthenate (1%) as catalyst. In each case the major reaction product isolated is the corresponding epoxide 10 - 13. To the best of our knowledge, this represents the first example of epoxide formation in the autoxidation of 1-phenylcycloalkenes. Furthermore, in case of compounds 3 and 4 this represents a useful method for the formation of the corresponding epoxides, 12 and 13, as these are obtained in 60 and 71% yields respectively.

Initially, we carried out the autoxidation of 1 in chloroform at 50° using cobalt naphthenate as catalyst. The solution was stirred in a sealed system having an atmosphere of oxygen, till sufficient oxygen was absorbed. The reaction product was treated with potassium iodide and acetic acid in order to reduce any hydroperoxides that may be present. The treated material was then separated by column chromatography using silica gel.



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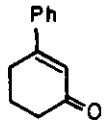

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The major product isolated was shown, by its spectral properties (IR, NMR), to be 2-phenylcyclohexanone 14. The identity was confirmed by direct comparison (TLC, IR, NMR) with an authentic sample[7]. From the formation of this product, it was suspected that initially 1-phenylcylohexene epoxide 10 might have been formed, and under the conditions of work up it was converted to 14. It is quite well known[8] that epoxides in the presence of trace amounts of acids rearrange to carbonyl compounds.

In fact, epoxide 10 prepared by using perbenzoic acid[8] showed a weak carbonyl band at 1710 cm^{-1}. Distillation increased the intensity of this band due to the formation of 14. However, pure epoxide could be obtained by distillation over powdered KOH.

Therefore, it became necessary to modify the reaction conditions. Autoxidation of 1 was carried out at 50°, on the neat liquid using cobalt naphthenate as catalyst (1% by wt.), in a special reactor originally designed by Vodnar[9].

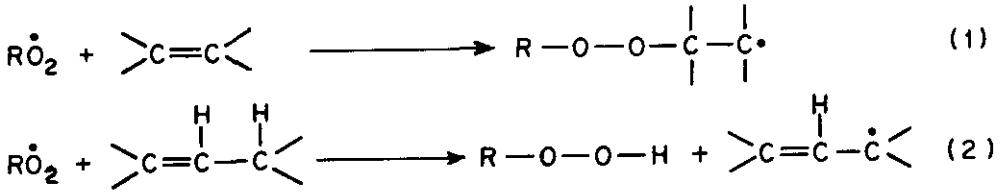
It consists of a tank with a sintered glass plate near its bottom. Towards the upper part of the tank is a spiral tube having a recirculatory tube fitted with a capillary tip on the lower end. A reflux condenser and a sampling device complete the assembly. The substrate is taken in the tank which is maintained at the desired temperature (oil bath), and dry oxygen is passed in it through the sintered plate. The gas bubbles through the liquid into the spiral tube. The entrained liquid is carried upwards with the gas and thrown against the sides of the tube to form a liquid-gas interface where the reaction actually takes place. The large contact area provided by the liquid-gas interface in the spiral tube results in increased autoxidation rates than those obtained in the usual systems.

The progress of autoxidation was monitored by TLC at regular intervals. It was stopped when almost all of the olefin has been consumed. The reaction mixture was dissolved in ether, filtered and treated with a saturated solution of sodium sulphite. Column chromatography of the treated mass on basic alumina (grade III)[10] gave a compound in 35-40% yield. The compound was identified by direct comparison (TLC, IR, NMR) with an authentic sample[8] as the epoxide 10. During the chromatography a second pure product was also isolated in 5-6% yield. This was identified as 15 by comparison of its spectral properties (IR, NMR) with that of a reported sample[11]. However, our attempts to isolate the cyclic peroxide 6 were not successful.

Similar autoxidation of compounds 2, 3 and 4 furnished products identified as the corresponding epoxides 11, 12 and 13. The identity was established by direct comparison with authentic samples prepared from the olefins by reaction with perbenzoic acid. Table I shows the percentage of epoxides and the conditions under which they were obtained starting with different phenylcycloalkenes. For compounds 1-3 autoxidation is completed within 12-13 hours at a flow rate of 4-5 liters of oxygen per hour. In case of 4 the reaction was more sluggish and even after a much longer period some starting olefin could be recovered from the autoxidation product.

It can be concluded that as the ring size increases the percentage of the epoxide formed is increased. This observation can be explained on the following lines.

The two competitive reactions taking place during the oxidation of these olefins involve addition (reaction 1) and abstraction (reaction 2) mechanisms.



(1)

(2)

TABLE I

Autoxidation of 1-phenylcycloalkenes at 50°
(using cobalt naphthenate)

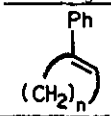
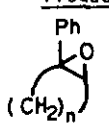
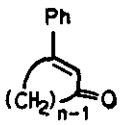
Starting olefin 	Period of oxidation	Conversion, %	Products isolated, % 	
Comp. 2 1-phenylcyclopentene (n=3)	12 hrs.	100	37 (n=3)	-
Comp. 1 1-phenylcyclohexene (n=4)	17 hrs.	100	40 (n=4)	5-6 (n=4)
Comp. 3 1-phenylcycloheptene (n=5)	12 hrs.	100	60 (n=5)	-
Comp. 4 1-phenylcyclooctene (n=6)	37 hrs.	80	71 (n=6)	-

TABLE II

PMR Spectral Data for Epoxides of 1-Phenylcycloalkenes, in CCl_4 :

Compound	Methine proton, δ	Methylene protons, δ	H-Ar, δ
1-phenylcyclopentene epoxide	3.33 (s, 1H) *	1.46 - 2.33 (bm, 6H)	7.15 (s,5H)
1-phenylcyclohexene epoxide	2.9 (t, 1H, J=2Hz)*	1.3 - 2.4 (bm, 8H)	7.25 (s,5H)
1-phenylcycloheptene epoxide	2.86 (t, 1H, J=5Hz)	1.33 - 2.43 (bm, 10H)	7.23 (s,5H)
1-phenylcyclooctene epoxide	2.77 - 3.13 (m, 1H)	2.23 (bm, 2H) 1.57 (bs, 10H)	7.1 (m, 5H)

* These values agree with those given in ref.10.

Energy of activation for reaction (1) does not vary in the series of olefins; while the energy of activation of reaction (2) depends greatly on the size of the given olefin. Thus, the composite rate constants for abstraction vary with a regular decrease from cyclopentene to cis-cyclooctene.

This difference in behaviour of various olefins may stem from transition state requirements. Thus, for maximum overlap of the developing radical with π-orbitals of the double bond, the carbon-hydrogen bond to be broken must be directed axially to the plane of the double bond. The following two factors can then contribute to the difference in the reactivity of these olefins.

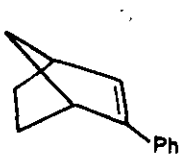
(1) The number of hydrogen atoms which may participate effectively in the radical substitution reaction decreases from 4 in cyclopentene to about 2 in cis-cyclooctene.

(2) Since among C_5-C_8 olefins, the cyclopentene ring is the most nearly planar, the removal of an α-hydrogen atom from cyclopentene by a peroxy radical leads to the formation of an allyl radical, which already has the correct geometry for maximum π-overlap; therefore the least realignment of nuclei is necessary. Cyclohexene, however, has a skew ring with four carbon atoms in a plane, and one below and one above this plane. To gain maximum overlap for the allyl radical, which presumably resembles the transition state for abstraction, one of the non-coplanar carbon atoms must be brought into the plane of others. This can be readily achieved by overcoming a very small potential energy barrier of only 5.2 kcal/mole. With cycloheptene and cyclooctene, the skewing is more pronounced and interference between the ring hydrogen atoms, in models, makes the rings increasingly rigid. This could account for an increase in the energy of activation by increase in strain or from loss of allylic resonance.

Thus, from 1-phenylcyclopentene to 1-phenylcyclooctene as the ring size increases the percentage of products from allylic hydrogen abstraction decreases and consequently the percentage of products from addition across the double bond increases or in other words epoxide formation becomes the more prominent reaction.

It is worth noting that autoxidation of cyclohexene (chloroform as solvent, 50°, cobalt naphthenate catalyst) has been reported[12] to give mainly (about 85% yield) the allylic alcohol and the α,β-unsaturated ketone. When a substituent like methyl, ethyl, isopropyl or tert-butyl is present on the carbon carrying the double bond, as in 1-alkylcyclohexenes, the products of allylic oxidation are between 60-90% whereas epoxide formation occurs to the extent of 10-16% only, depending on the bulk of the substituent[13]. It is interesting to observe that in the present studies epoxide formation is the major reaction. Furthermore, epoxide formation becomes more important as the ring size increases from 5 to 8 membered. It may be emphasised that the literature on autoxidation of 1-phenylcyclohexene contains no mention of epoxide formation.

Autoxidation of 2-phenylnorbornene, 16, in aprotic solvent is reported to give the corresponding epoxide 17 in about 25% yield[14].



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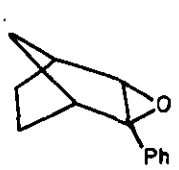

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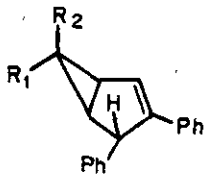
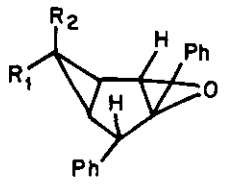


18 , $R_1 = Ph, R_2 = H$

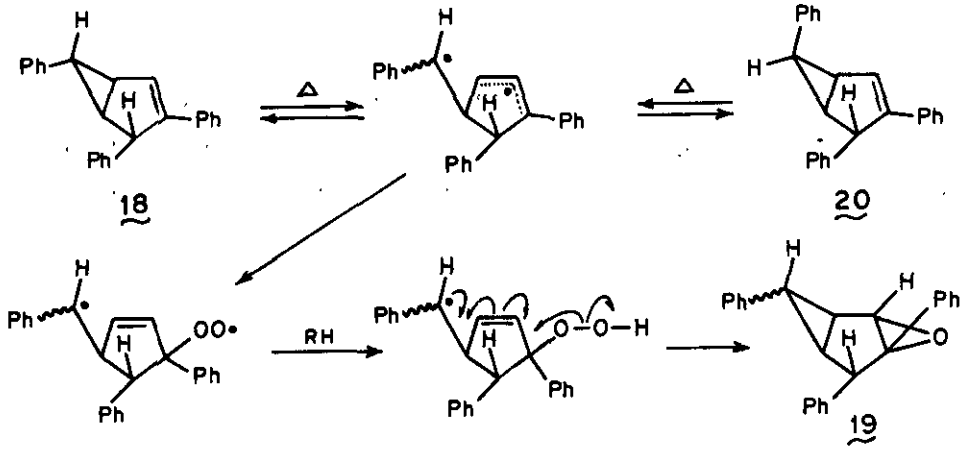
20 , $R_1 = H, R_2 = Ph$



19 , $R_1 = Ph$, $R_2 = H$

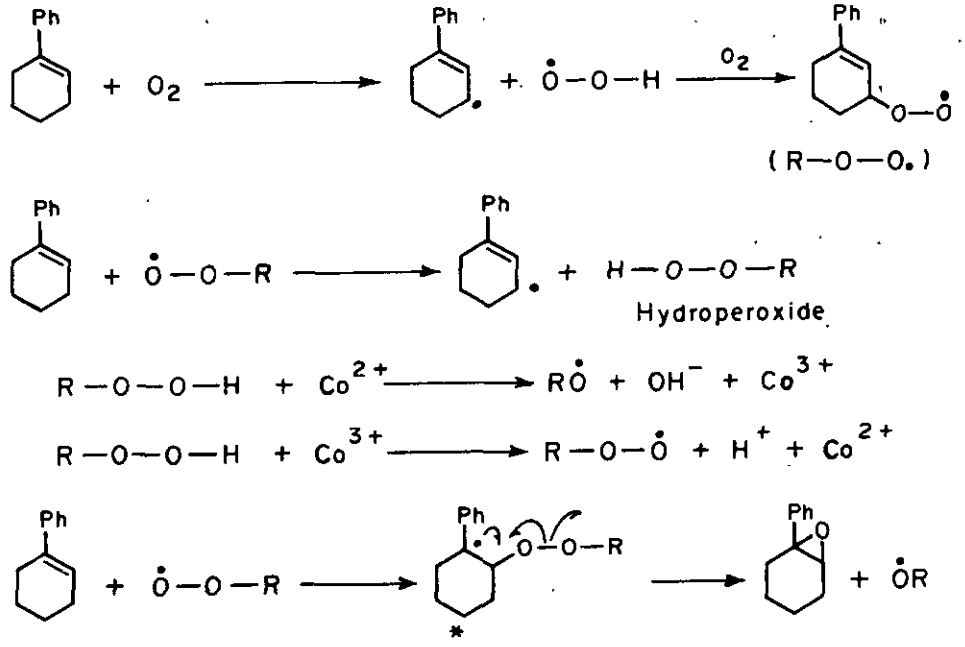
21 , $R_1 = H$, $R_2 = Ph$

In an interesting paper on thermal epoxidation of 18 by molecular oxygen (xylene solution, refluxed for 48 hrs) Padwa and Brodsky[15] have reported the formation of the epoxide 19. Furthermore, similar reaction on 20 gave besides 21 the isomerised olefin 18 and its epoxide 19. To account for these results they suggested the following mechanism.



The above mechanism indicates that the cyclopropane ring is taking part in the epoxidation. In our studies on 1-phenylcycloalkenes (1-4) obviously no such cyclopropane participation is possible. Hence, we feel, that even if in the above example (18) cyclopropane participation does occur it is not a necessary requirement for epoxidation.

The mechanism for epoxidation in our case can be given as follows.



*This radical being on a tertiary carbon and also in conjugation with the benzene ring, is more stabilised and preferntially formed.

ACKNOWLEDGEMENTS : This communication is dedicated in humble tribute to Prof. H. C. BROWN (on his seventieth birthday) with whom one of us (S.C.S.) had the privilege of working from 1963 to 1966. A.D.N. is grateful to University Grants Commission, New Delhi, for the grant of a teacher fellowship.

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