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PHOTOLYSIS OF 2-PHENYLETHYL AND 4-PHENYL-1-BUTYL HALIDES IN ALCOHOLIC SOLVENTS**

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Abstract - Photolysis of 2-phenylethyl bromide in the lower alcohols gave the corresponding carbinols and ethers as the main products. With 2-phenylethyl iodide, the products were almost exclusively of the latter type, while 4-phenyl-1-butyl halides gave n-butylbenzene, 4-phenyl-1-butene and tetralin.

It is shown that each of these products may be assigned to an ionic or radical pathway and that both the nature of the solvent and the structure of the substrate affect the course of photolysis. There is a substrate dependent preference for specific reactions along pathways of both the radical and ionic types. The variations in product composition and distribution are rationalized in terms of the relative efficiencies furnished in these pathways for the relaxation of high energy intermediates produced in the initial stages of photolysis. Intervention by the phenyl group is more pronounced in the case of 2-phenylethyl halides than in the case of the higher homologues and more effective in the ionic pathway.

Recent work on the photolysis of alkyl halides in solution has shown that radical and ionic pathways generally compete with each other in these reactions[1-11]. The recognition of these types of pathways has been possible directly from the nature of the products formed in favourable cases. However, in others, this is not feasible and ambiguities of mechanism have remained. For instance, eliminations and cyclizations accompanying photolysis have been interpreted in terms of both ionic and radical pathways by different groups of workers. Thus, the preponderent formation of 3,7-dimethylocta-1,6-diene and p-menth-8-ene in the photolysis of citronellyl iodide in heptane has been rationalized in terms of an ionic pathway[7,8]. But, in the comparable study of 4-phenyl-1-butyl iodide in benzene and acetonitrile, where only an elimination product was observed, a radical pathway has been suggested on the basis of the consideration that the yield of the product was lowered in the presence of oxygen[10,11]. The authors felt that a similar pathway was most probably involved in the case of citronellyl iodide also, particularly in view of the hydrocarbon solvent employed and existing literature[12-15] on cyclization reactions proceeding through radical intermediates. The present work on 2-phenylethyl and 4-phenyl-1-butyl halides in the lower alcohols was undertaken for obtaining further clarification of the nature of this reaction. The results have not only clarified the nature of the elimination and cyclization reactions, but also given valuable information on details of the mechanisms involved. The individual reactions taking place along radical and ionic pathways have been found to show interesting variations depending upon the nature of the substrate and the solvent employed. Intervention by the aryl group seems to be an important factor affecting reactions through ionic pathways.

RESULTS

The photolyses of 2-phenylethyl halides (1a, 1b) and 4-phenyl-1-butyl halides (2a, 2b) were carried out in methanol, ethanol and isopropanol and the composition of the product mixture obtained for each substrate was determined

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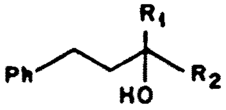
from GLC peak intensities. The results for 2a,2b and 1a,1b are shown in Tables 2 and 3 respectively.

1

1a : X = Br
1b : X = I

2

2a : X = Br
2b : X = I



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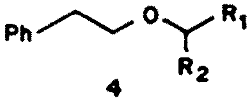

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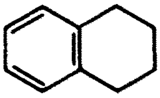

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The products obtained in significant amounts were of five types: ethers, carbinols and products of reduction, elimination and cyclization (Table 1). With the bromide, 1a, the main products were the corresponding ethers (4) and the carbinols (3). Ether formation was the dominant reaction in methanol and ethanol, and this was more so when the substrate was changed to 2-phenylethyl iodide, 1b, which gave exclusively the corresponding ethers.

TABLE 1 - PRODUCTS OF PHOTOLYSIS

Starting halides	Products	
	Radical pathway	Ionic pathway
1a (X=Br)	3	4
1b (X=I)	-	4
2a (X=Br)	5	6,7
2b (X=I)	5	6,7

The photolysis of 4-phenyl-1-butyl halides, however, furnished an altogether different set of products comprising n-butylbenzene (5), 4-phenyl-1-butene (6) and tetralin (7) in practically all cases except one. With the iodide as substrate and methanol as solvent, very small amounts of the methyl ether were formed. This, however, does not detract very much from the remarkable difference in the nature of the results obtained with these substrates. The main products here do not, unlike those from 1a and 1b, have incorporated in them moities coming from the solvent molecules.

Table 2 - Products of Photolysis of Ph-CH_2-CH_2-CH_2-CH_2-X

X	Solvent R_1R_2CHOH	Time of irradiation (hrs)	Composition of products (% of total,GLC)				Unidentified minor components
			5	6	7	4	
Br	R_1=R=H	27	11	48	40	Nil	
	R_1=H;R_2=Me	37	16	48	30	"	6
	R_1=R_2=Me	36	26	19	42	"	13
I	R_1=R_2=H	10	7	60	23	5	5
	R_1=H;R_2=Me	15	10	63	26	Nil	-
	R_1=R_2=Me	18	28	20	44	"	8

Table 3 - Products of photolysis of Ph-CH_2-CH_2-X

X	Solvent R_1R_2CHOH	Time of irradiation (hrs)	Composition of products (% of total, GLC)			Unidentified minor components
			3	4	1	
Br	R_1=R_2=H	50	25	65	9	-
	R_1=H;R_2=Me	50	27[a]	65	8	-
	R_1=R_2=Me	48	40[b]	40	17	3
I	R_1=R_2=H	23	-	80	-	20
	R_1=H;R_2=Me	20	-	64	10	25
	R_1=R_2=Me	20	-	55	30	15

[a] The NMR spectrum of this sample showed that it is not as pure as the product obtained in methanol. However, chromic acid oxidation of the material gave about 85% of the corresponding ketone.

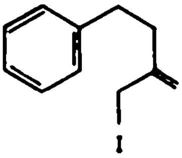
[b] The NMR spectrum of the product suggests that the impurity level in this sample is appreciable. It appears likely that isopropyl bromide gets formed in the reaction mixture and that secondary photolysis interferes with the results.

Another interesting aspect of these results is the formation of comparatively large amounts of tetralin from 2a and 2b, which is in sharp contrast to the behaviour observed earlier for 2b in benzene and acetonitrile[10,11].

DISCUSSION

Products and Pathways: The nature of the products obtained from 1a and 1b shows unambiguously the presence of both radical and ionic pathways for photolysis in the alcoholic solvents employed here and provides a basis for a qualitative grouping of products and pathways as shown in Table 1. The ethers, 4, are undoubtedly formed from the 2-phenylethyl cation intermediate. Similarly, only a radical pathway is feasible for the carbinols, 3. The predominant formation of ethers in methanol and ethanol in the case of the bromide and in all the three alcohols for the iodide shows that photolysis proceeds mostly through ionic pathways in these solvents. Consistency would, therefore, require that the same would be true in the case of 4-phenyl-1-butyl halides also, unless there are strong enough reasons for an abrupt change in mechanism. For the ionic path to be dominant for the latter group of halides, formation of 6 and 7 has to be through ionic pathways. *n*-Butylbenzene (5) is obviously formed through hydrogen abstraction by the 4-phenyl-1-butyl radical.

There are a number of other considerations which also point to the same conclusion. As already noted above, an earlier study on 2b gave 6 as the product and the formation of 7 was negligibly small[10,11]. On the basis of the consideration that the yield of 7 was reduced in presence of oxygen, it was regarded as arising through a radical pathway. This is merely a possibility and not a forcing conclusion. If the sequence of reactions accompanying photoexcitation involves the conversion of an initially formed radical pair into an ion pair as postulated by Kropp and coworkers[3], such a conclusion would not be tenable. With 4-phenyl-2-iodomethyl-1-butene (8) in acetonitrile, cyclization to 9 became an important reaction[11] with the concomitant formation of even larger amounts of a solvolysis product (10) suggesting that the factor responsible for this difference in the course of the reaction is the resonance stabilisation of the allylic cation, 11b, that would presumably be generated from the substrate. The conclusion of the authors was that there was a genuine mechanistic transition in



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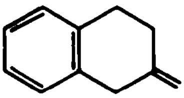

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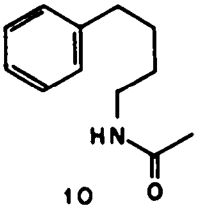

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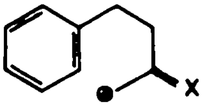

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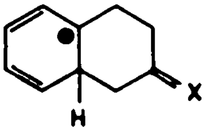

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11a : $X = H_2$, 11b : $X = CH_2$ 12a : $X = H_2$, 12b : $X = CH_2$

the change of substrate from 2b to its allylic analogue (8). It appears to us more likely that both the olefin formation and cyclization reactions are taking place through cationic intermediates. The 4-phenyl-1-butyl cation, 11a, would be expected to be a species of much higher energy and shorter life than its allylic analogue 11b. It is likely that it would, in the "hot" condition in which it is generated in photolysis, eliminate a proton from β-carbon long before cyclization to tetralin, which involves a substantial reorientation of the side chain with respect to phenyl ring, can take place. It is of interest to note that β-elimination is blocked in 11b and the only possible reaction with solvent is solvolysis. Cyclization would take place when the carbonium ion survives solvent attack long enough. When the present results are placed alongside with the earlier ones, it becomes clear that it is the change over to an alcoholic medium that has favoured the cyclization reaction in our experiments. It is this medium effect that enables us to distinguish between the ionic and radical pathways which are both, in principle, acceptable possibilities in this case. Although both routes are feasible, there is a difference between them in terms of the energetics involved. The presence of an alcohol will have little effect on radicals, while it will lower the energies of ionic intermediates by more effective solvation. Moreover, the stabilization that results in the conversion of 11a to 12a is much larger than for the corresponding set of radicals. For tetralin formation, an ionic pathway would therefore be the favoured one in an alcoholic medium. It is difficult to understand the observed medium effect in terms other than ionic. It will shortly be seen that the trends observable in the product composition can be rationalized satisfactorily only on the basis of the broad categorisation shown in Table-1.

Substrate Structure and Course of Reactions: A remarkable aspect of the results obtained here, which is indicative of mechanistic detail, is the apparent substrate dependent selectivity of reaction modes for each of the two types of pathways, ionic and radical. It will be convenient to discuss this along with variations in product proportion. While the specific ionic pathway preferred in the case of 2-phenylethyl halides is solvolysis, its place is taken over by elimination and cyclization in the case of the 4-phenyl-1-butyl halides studied. A similar difference is found for radical pathways also. With 1a, the products are the carbinols 3, while with 2, n-butylbenzene (5) seems to be the only product formed through the radical pathway. The increase in yield of 3 and 5 associated with change of solvent in the series from methanol to isopropanol is in accordance with the increasing capacity of the solvents to function as hydrogen donors.

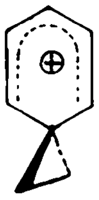
For a discussion of the significance of the susceptibilities or preferences for specific reaction modes, we shall first consider the ionic pathway. The cationic species generated from the first group of substrates (2-phenylethyl halides) seems to be highly prone to loss of energy through redistributive and dissipatory processes to reach the same level as that of the ion that would be involved in normal solvolytic reactions, for instance, solvolysis promoted by Ag^+ ions. This relaxation process is apparently the formation of the well known phenonium ion (13)[16] from the ion pair or the excited halide that is produced in the initial stages of photolysis. It appears most likely that the phenonium ion is formed at the intimate ion pair stage. It is obviously the proximity of the phenyl group that facilitates this process and prevents the formation of hot cations which can lead to elimination and rearrangement. It may be recalled here that formation of the phenonium ion as an intermediate has been explicitly demonstrated in the photolysis of 2-phenylethyl mesylate[17]. But, in this case, a larger number of possibilities in carbonium ion behaviour have actually been realized. With the corresponding halides as substrates in this study, energy loss from the excited species concerned seems to be more efficient.

In the photolysis of 4-phenyl-1-butyl iodide in methanol, only about 5% of the total of all products represents solvolysis. In ethanol and isopropanol, this reaction could not be detected. The same was the case with the corresponding bromide in all three alcohols. The formation of free, solvated and open chain cations (11a) from these substrates does not, presumably, take place at all or is reluctant at best under the conditions of the present study. It is obviously not through such an intermediate that the formation of tetralin, an important reaction here, takes place. The formation of olefin (6) seems to be distinctly greater from the iodide than from the bromide. The yield of 6 does not change much with the change of solvent from methanol to ethanol; but, in isopropanol, there is a sharp lowering. These variations are indicative of an ionic path for this product. An elimination reaction through an ionic pathway may, in principle, involve an ion pair or a free cationic intermediate. When these species are of high energy, the distinction between the two is not significant because dissociation of the ion pair would be followed so rapidly by proton elimination that it will be difficult to make out that the second process is separate from the first. But, as these species become stabler, either through interactions with solvent molecules or through internal interactions and accompanying redistributions of energy, the possibilities for alternative reactions tend to manifest. To what extent a competing reaction like cyclization would become manifest would depend upon the energy and entropy of activation involved. The energy of the species must be low enough for it to be sufficiently long lived, but, at the same time, it must be high enough for it to be able to go over the activation barrier for the reaction. As the energy decreases beyond an optimum value, the probability of such a reaction will decrease progressively. A fully solvated and free cation giving only solvolytic reactions would be at the lowest end of this energy scale. For the earlier study on 2b in benzene and acetonitrile, the reactive species concerned would presumably be towards the top of the scale. The region in which cyclization would compete with elimination is somewhere in between. This is the region of stability of ionic intermediates we are concerned with in the photolysis of 4-phenyl-1-butyl halides. Olefin formation is probably mostly through dissociated and free ions in which the C-H bonding electrons have yielded significantly to the pull of the cationic charge. The decreased olefin yield in isopropanol is best understood in terms of the reduced capacity of the solvent to support dissociation of ion pairs.

The situation with respect to tetralin formation is that the yields do not show any definite trend in the series of solvents employed. However, as already noted, the results in the alcoholic media are substantially different from those obtained in acetonitrile or benzene. The most probable source of this difference is the solvation that alcohols can furnish in an ionic pathway. We have already considered in general terms the behaviours that can be displayed by ionic intermediates of energies ranging from high to low. Species of very high energy would be too short lived to serve as intermediates in the cyclization reaction. A free 4-phenyl-1-butyl cation fully solvated by an alcohol is of too low an energy for cyclization. The alcohol molecule would be too closely associated with the cation in such a species[18]. We wish to suggest that an ion pair of intermediate energy is the most probable species through which tetralin is formed. In the alcoholic medium, the ion pair energy is lowered by solvation and the life time of the species becomes long enough for the cyclization reaction to be feasible. It is of interest to note that the conversion of 11a to 12a involves a spreading of charge which would be expected to be facilitated by lowering of the dielectric constant of the medium. This effect runs counter to that of solvation which decreases in the series from methanol to isopropanol. It is presumably the superposition of positive and negative effects that results in the absence of any definite trend in tetralin yield.

In the context of the present discussion, some comments on the results obtained for the photolysis of citronellyl and other terpene iodides in heptane referred to earlier[7,8] are called for. In these experiments, a molar equivalent or more of triethylamine was used for purposes of scavenging hydrogen iodide. It is presumably the presence of the amine which is responsible for the nature of the results obtained. It appears likely that there is association between the two dipolar species. It is of interest to note that cyclization yields were higher at higher temperatures. This behaviour is consistent with the mechanistic rationalization suggested above.

We shall now consider the peculiarities of the radical pathways and the possible significance of the observed preferences for specific reactions. Table 2 shows that while 2-phenylethyl iodide does not give any product assignable to radical pathway, the corresponding bromide does. With the latter, the preferred reaction along the radical pathway seems to be the formation of carbinols (3) and not reduction. This tendency seems to be reversed when the substrate is a 4-phenyl-1-butyl halide. When a dissociated and free 4-phenyl-1-butyl radical reacts with one of the abundant solvent molecules, the normally expected reaction is hydrogen abstraction from the latter. This is actually what is found. However, in the case of the 2-phenylethyl radical, there is an apparent reluctance to react with the solvent in this manner[20]. The species prefers, seemingly, to couple with the carbinyl radical produced from the solvent through hydrogen abstraction by the halogen atom (bromine). If the 2-phenylethyl radical is truly free from the influence of other species, this reaction would be unnatural and unlikely. The indication here is that the reaction is taking place at the radical pair stage, in which case the preferential hydrogen abstraction by the halogen atom can be understood. The generation of a carbinyl radical in close proximity to the alkyl radical would also facilitate coupling between the two. What is achieved is a radical double decomposition. However, there must be something special about the 2-phenylethyl - bromine radical pair since its behaviour seems to be different from that of the similar species from 4-phenyl-1-butyl halides. The former is apparently sufficiently long-lived to encounter a solvent molecule as a single entity, while the latter dissociates readily into its components which drift rapidly away from each other. In the case of the 2-phenylethyl - bromine radical pair, some internal interaction seems to have a stabilizing effect which is missing in the 4-phenyl-1-butyl analogues. What is required to be considered here is the possibility of formation of bicyclic intermediates. We have already noted that conversion of the 4-phenyl-1-butyl radical into the radical analogue of 12a is not a favoured process under the conditions of this study. Similarly, the conversion of an isolated 2-phenylethyl radical into the



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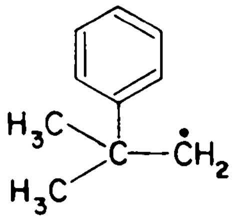

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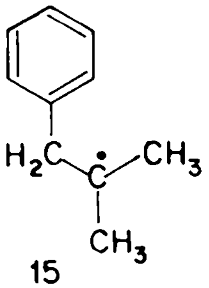

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radical analogue of 13, if it exists at all, would be more difficult than the formation of 13 itself. The isomerization of the neophyl radical, 14 to 15 is, of course, best visualized as taking place through a spiro radical stage[21], i.e. involving phenyl participation. But it is doubtful if this stage represents a true reaction intermediate rather than a transition state. There is no clear evidence for a radical species of this type. Even if it does exist, its stability may not be adequate for accounting for the behaviour observed. However, the situation in a radical pair can be different. Placing the odd electron of spiro radical in an orbital of appropriately mixed character can produce a complex in which there is partial charge transfer to the halogen. The development of some phenonium bromide character will tend to stabilize the species. On these considerations, it would appear that the 2-phenylethyl - halogen radical pair may have some ion pair character as well. This is of considerable interest in the context of the likelihood of "intimate ion-radical pair" intermediates first suggested by Walling[22] and later supported by Cristol and his colleagues[5] who have pointed out that ion pair formation in the photolysis of alkyl halides need not necessarily be through an initially formed radical pair of the conventional type and that both types of intermediates may have a common progenitor of mixed character. Further consideration of this issue would be justifiable only when more evidence is available.

CONCLUSION

The present study has not only confirmed that there is a competition between radical and ionic pathways in the photolysis of alkyl halides, but also obtained valuable additional information on how the structure of the substrate and the nature of the solvent can influence the reactions along these pathways. It has been possible to get a clear indication of the nature of the pathways for all major products. Elimination and cyclization here seem to take place through ionic intermediates. Although both groups of halides react through radical and ionic pathways, there is a striking difference between them in their preference for specific reactions of the radical and ionic types. The proximity of the aryl group in 2-phenylethyl halides makes it possible for the phenyl group to intervene in the reaction and bring about energy dissipation from excited species in both radical and ionic pathways, leading to the formation of 2-phenylethyl carbinols and ethers, respectively, as products. With the higher homologues, aryl intervention, which leads to tetralin formation, takes place only in the ionic path and is less effective because of the large negative entropy factor involved.

EXPERIMENTAL

General remarks: All b.ps are uncorrected. The following instruments were used for spectral/analytical data: Perkin-Elmer Model 137-E IR spectrophotometer (IR); Varian Associates T-60 NMR spectrometer (PMR); CEC mass spectrometer model 21-110B (Mass, 70 eV, direct inlet system); Aerograph model A-350B (GLC), columns: Analytical 180 cm x 0.6 cm Al column packed with FFAP (20% carbowax, 20M reacted with nitroterephthalic acid on chromosorb W 60-80 mesh). Preparative column: 300 cm x 1.0 cm Al column packed with 30% Hyprose S.P.80 on chromosorb W 30-60 mesh. PMR spectra were recorded in CCl_4 solution with TMS as an internal standard and the chemical shifts are expressed in ppm. The solvents employed in the present study were purified by standard procedures.

General procedure of irradiation: All irradiations were carried out with a Hanovia 200 Watt high pressure mercury lamp placed into an Ace double-walled, water cooled, quartz immersion well which was fitted in a pyrex reaction vessel equipped with a magnetic bar, condenser and a N_2 inlet tube. A minute steady flow of nitrogen was maintained for about 20 minutes before the irradiation. Approximately 1 to 1.5% solution of halide in an appropriate solvent along with an equivalent amount of zinc wool was irradiated till a photoequilibrium mixture was obtained (30-50 hrs). Zinc wool was removed by filtration, the excess solvent was stripped off under reduced pressure. The residue was taken in ether and was washed with 10% aq. Na_2CO_3, water and brine, dried over anhydrous Na_2SO_4. The crude product obtained on removal of solvent was distilled under reduced pressure. Each photolysis was repeated at least 3-4 times and the results given in the tables represent the averages. The GLC analyses were reproducible within 1%.

Preparation of the halides: The halides 1a, 1b were prepared by known methods^{23a,b}.

4-Phenyl-1-butyl bromide (2a): This was also prepared by a reported method which involved the Clemmensen reduction of β-benzoylpropionic acid to γ-phenylbutyric acid^{24}. The methyl ester of the above acid on treatment with LAH afforded 4-phenyl-1-butanol which could be converted to its bromo derivative using PBr_3.

4-Phenyl-1-butyl iodide (2b): Treatment of 4-phenyl-1-butanol^{24} with iodine and red phosphorus furnished the required compound.

All the halides gave satisfactory spectral data and elemental analyses.

Photoirradiations:

(i) 2-Phenylethyl bromide, (1a) in methyl alcohol: A solution of 1a (6.1 g, 0.033M) in methanol (400 ml) along with zinc wool (2.0 g) was irradiated for 50 hrs (90% conversion, GLC). The product isolated as described in the general procedure was distilled, b.p. 110-160°(bath)/15 mm (4.10 g). A fractional distillation with a Vigreux column followed by preparative GLC (FFAP, 30%, 170°, H_2 50 ml/min) afforded the following pure compounds.

Methyl 2-phenylethyl ether (4, R_1=R_2=H): b.p. 121-3°/14 mm; IR: 1124 cm^{-1}; PMR: 7.13 (s, 5H), 2.76 (t, 2H), 3.50 (m, 2H) and 3.23 (s, 3H). (An authentic sample of 4 was also prepared by the reaction of sodium salt of 2-phenylethanol with CH_3I in refluxing benzene)[25].

3-Phenyl-1-propanol (3, R_1=R_2=H): b.p.95-103°/4 mm, IR: 3279 cm^{-1} and 1064 cm^{-1}; PMR[26]; 7.16 (s, 5H), 2.66 (t, 2H), 1.83 (m, 2H), 3.53 (t, 2H) and 3.76 (bs, 1H exchanges with D_2O).

(ii) Photolysis of 1a in ethyl alcohol: A solution of 1a in ethanol (4.74 g, 0.025M, 400 ml) when irradiated in presence of zinc wool (~2 g) for 50 hrs afforded a product (3.20 g), b.p. 122-160°/10-12 mm. The total product was found to comprise essentially ethyl 2-phenylethyl ether 4 (R_1=H, R_2=Me) and methyl-2-phenylethyl carbinol 3 (R_1=H, R_2=Me). A fractional distillation furnished two fractions, the first one being rich in 4 while the second one was enriched in 3. These fractions were separately loaded on Al_2O_3 and eluted with pentane to yield 4 and 3 in pure form.

Ethyl 2-phenylethyl ether (4) b.p. 115-20(bath)/20 mm, IR: 1099 cm^{-1}; PMR: 7.1 (s, 5H), 2.8 (t, 2H), 3.1 to 3.8 (m, 4H) and 1.2 (t, 3H); m/e 150 (28%, M^+), 91 (100%, $C_6H_5CH_2$), 105 (63%, $M-OCH_2CH_3$) and 59 (70%, $M-C_6H_5CH_2$).

Methyl-2-phenylethyl carbinol (3) b.p. 130-2°/14 mm. IR: 3250 and 1100 cm^{-1}; PMR: 7.13 (s, 5H); 2.70 (m, 2H); 3.73 (q, 1H); 1.5 (m, 2H) and 1.16 (d, 3H).

(iii) Irradiation of 1a in Isopropanol: A solution of 1a in isopropanol (4.74 g, 0.025M, 400 ml) containing zinc wool (~2 g) was photolyzed for 48 hrs. The product obtained (3.5 g), b.p. 110-150°/15 mm, was found to comprise 4, 3 (R_1=R_2=CH_3) and 1a in a 2:2:1 proportion. A fractional distillation using a Vigreux column afforded two cuts, Fr.I b.p. 110-120 (bath)/15 mm (1.5 g) and Fr.II b.p. 120-130 (bath)/15 mm (1.38 g).

Isopropyl-2-phenyl ethyl ether (4): Fraction I was passed through a short column of Al_2O_3 to afford a pure compound (98%). IR: 1150 cm^{-1}; PMR: 7.06 (s, 5H); 2.73 (t, 2H); 3.3 - 3.7 (m, 3H) and 1.1 (d, 6H). An authentic sample of 4 was prepared by solvolysis of the tosylate from 2-phenyl-ethyl alcohol with isopropanol.

1,1-Dimethyl-3-phenyl-n-propanol (3): Fraction II from the above described fractional distillation was passed through a short column of Al_2O_3 to furnish pure 3, b.p. 124°/15 mm. IR 3450 and 1140 cm^{-1}; PMR: 7.0 (s,5H), 2.6 (m, 2H), 1.7 (m, 2H), 1.23 (s, 6H) and 3.0 (br.s, 1H, exchanges with D_2O). This spectral data agreed well with those of an authentic sample of 3 prepared by the Grignard reaction of 1a with acetone.

(iv) Photolysis of 1b in methyl alcohol: When a solution of 1b (5.8 g, 0.025M) in methanol (400 ml) along with zinc wool (2 g) was irradiated for 23 hrs, the product obtained (2.70 g) comprised essentially 4 (80%) and three minor products.

(v) Photolysis of 1b in ethyl alcohol): A solution of 1b (3.48 g, 0.015M) in ethanol (400 ml) containing $NaHCO_3$ (1 g) was photolysed for 20 hrs to yield a product (1.35 g) which comprised a major component (64%) and a few minor products (together constituting 20% of the total) along with unreacted 1b. The major product was separated as described in (ii) and was identified as 4.

(vi) Irradiation of 1b in isopropanol: Similar irradiation of 1b (3.48 g) in isopropanol (400 ml) for 20 hrs furnished a product (1.3 g) which comprised 4 (55%) and unreacted 1b (30%).

(vii) Irradiation of 2a in methanol: A solution of 2a (1.08 g 0.005 mole) in methanol (230 ml) and zinc wool (~1 g) when photolysed for 27 hrs yielded a product (0.58 g), b.p. 100-120°(bath)/30 mm. The total product was found to consist of 5, 6 and 7 approximately in a 1:4:3 ratio. Preparative GLC (FFAP 30%, 160°, H_2 50 ml/min) furnished three components in pure form.

n-Butylbenzene (5): b.p. 78-80°/24 mm; IR: 705, 750 cm^{-1}; PMR: 7.13 (s, 5H), 2.6 (t, 2H), 1.5 (m, 4H) and 0.96 (ill-defined triplet, 3H).

4-Phenyl-1-butene (6): b.p. 64-66°/10 mm; IR: 1640, 925 cm^{-1}; PMR: 7.1 (s, 5H), 2.2 - 2.9 (m, 4H) and 4.73 - 5.13 (m, 3H). Mass: m/e 132 (18%, M^+), 91 (100%, C_6H_5 CH_2) and 42 (12%, allyl cation).

Tetralin (7): b.p. 90-1°/17 mm; PMR: 6.96 (s, 4H), 2.73 (m, 4H) and 1.80 (m, 4H); Mass: m/e 132 (65% M^+), 104 (100%, $M-C_2H_4$) and 91 (49%, $C_6H_5CH_2$).

Irradiation of 2a in ethyl and isopropyl alcohols: Photolyses of 2a in ethyl and isopropyl alcohols furnished the products 5, 6 and 7 in varying proportions (Table 2).

Irradiation of 2b in methyl, ethyl and isopropyl alcohols: Photolyses of 2b were carried out separately employing methyl, ethyl and isopropyl alcohols as described in the general procedure. The products 5, 6 and 7 were separated by preparative GLC (FFAP 30%, 160-5°, H_2 50 ml/min) and have been shown in Table 2.

4-Phenylbutyl methyl ether: b.p. 108°/11 mm. PMR: 7.10 (s, 5H), 2.60 (m, 2H), 1.60

(m, 4H), 3.23 (m, 5H).

Oxidation of Methyl-2-phenylethyl carbinol (3, R_1=H, R_2=CH_3): The alcohol 3 (250 mg) taken in ether (25 ml) was treated with chromic acid reagent[27] under stirring for 0.5 hr, maintaining the temperature at about 0°C. The product isolated after a standard work-up was distilled, b.p. 100-120°(bath)/20 mm (212 mg, 85%). IR: 1710 cm^{-1}; PMR: 7.16 (s, 5H), 2.73 (m, 4H) and 2.06 (s, 3H).

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