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STRAINED SYSTEMS. VI.[1]

SOME REACTIONS OF 5,6-DIPHENYLTRICYCLO-$[2.1.1.0^{5,6}]$HEXAN-2-ONE

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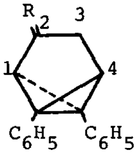
Previously (2) we described that diphenyltricyclo-$[1.1.1.0^{4,5}]$pentanone underwent facile carbon-carbon bond cleavage reactions even under mild conditions. Its homolog, 5,6-diphenyltricyclo$[2.1.1.0^{5,6}]$hexan-2-one, however, has been found to be relatively stable and to react with carbonyl reagents to afford normal reaction products useful for further studies on this strained system. We wish to discuss reactions in which the carbene and carbonium ion could be produced at position 2 of the system.

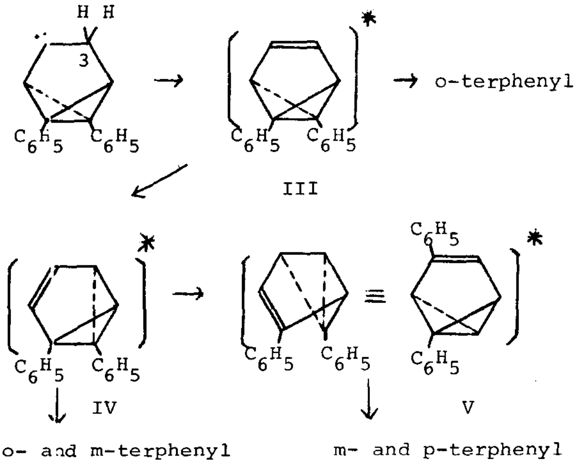


I. R = O

II. R=N-NH-TS

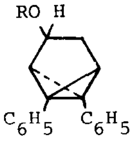
XII. R=H, NH_2.

The tosylhydrazone of ketone I was readily obtained in the usual manner, (II), m.p. 105-106°. A stirred suspension of finely powdered sodium salt of II in tetrahydrofuran was irradiated with ultraviolet light (>300 mμ). The theoretical amount of nitrogen evolved within one hour and the reaction mixture, after filtration of sodium sulfinate, was chromatographed first on silicic acid and then on silicon rubber at a column temperature of 215° (g.l.c.). The products consisted of *p*-terphenyl (23% yield), *m*-terphenyl (14%), *o*-terphenyl (8%) and ketone I (22%). The formation of the first three compounds is reasonably interpreted in the following fashion: The carbene generated photochemically first inserts the C_3-H bond (3) to provide vibrationally excited tricyclo[2.1.1.0^{5,6}]hexene (III). Since the three

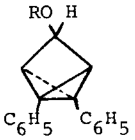


terphenyls are not isomerized under the photolytic conditions used, it is attractive to postulate the rearrangement of III to its isomers (IV) and (V). The possibility of phenyl migration is excluded in view of the recent finding (4a) that the apparent 1,2- or 1,3-shifts of benzene substituents under ultraviolet irradiation do not involve the direct migration of substituents but ring carbon interchange. The reduction of non-bonded interaction between the two phenyl groups in IV and V as compared to III would provide a driving force for the rearrangement. The relative stabilities of these intermediates would account for the increasing yield from o-terphenyl to m-terphenyl to p-terphenyl. The energy barriers of the rearrangement are expected to be very small. The above view is in accord with the recent report on the isolation of 2,5,6-tri-t-butyltricyclo[2.1.1.$0^{5,6}$]hex-2-ene from a photostationary mixture obtained by irradiation of 1,2,4- and 1,3,5-t-butylbenzene.(4b)

The lithium aluminum hydride reduction of I proceeded normally to afford the corresponding hydroxy compound, (VIa), m.p. 92°-93°, the tosylate (VIb), m.p. 84-86° (depending on the rate of heating). Similarly, 4,5-diphenyltricyclo-[1.1.1.$0^{4,5}$]pentan-2-ol (VIIa), m.p. 107.5-108.5 and p-nitrobenzoate (VIIb), m.p. 123-124° (decomp.), were prepared.



VIa R = H
VIb R = Ts

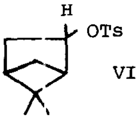


VIIa R = H
VIb R=p-NO_2-C_6H_5-CO

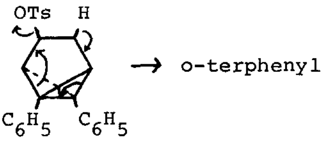
The ethanolysis of VIb occurred rapidly at 25°. The first-order rate constant was (10.7±0.5) x 10^{-4} sec.$^{-1}$. The only detectable reaction product from the ethanolysis in the presence of 2,6-lutidine (1.3 moles) was o-terphenyl.

This product was isolated in 88% yield and was estimated to have been produced in more than 93% yield by ultraviolet spectral analysis of the crude reaction products.

It is difficult to choose a model system for estimating the rate of unassisted ionization of compound VIb. Two rough model systems may be considered. These are cyclopentyl *p*-toluenesulfonate and 5,5-dimethylbicyclo[2.1.1] hec-2-yl *p*-toluenesulfonate, (VIII). Meinwald et al. have suggested (5) that VIII undergoes acetolysis with neighboring carbon participation. The ethanolysis of VIII has not been reported, however, the first-order rate constants for acetolysis of VIII and cyclopentyl *p*-toluenesulfonate are the same within a factor of two at 75°. If this is also true for ethanolysis at 25°, then we estimate (6) the first-order rate constant for ethanolysis of either compound at 25° would be 2.5 x 10^{-6} sec.$^{-1}$. Compound VIb solvolyses over two powers of ten faster in ethanol than either model system. The results indicate that solvolysis of VIb is accelerated. However, they do not provide evidence as to the nature of any assumed intermediates. A portion, if not all, of the driving force for the reaction could arise from relief of angle strain on ring opening. At present we only express the reaction as shown below.



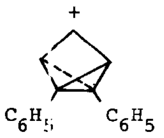
VIII

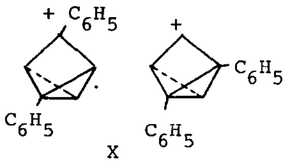


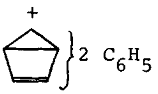
Solvolysis of VIIb in 70% acetone is rapid. The first-order rate constant at 25° was (1.96 ± 0.21) x 10^{-4} sec.$^{-1}$. An estimate of the rate of ethanolysis of the corresponding p-toluenesulfonate (VIIc, R=Ts-) can be made in the following way. Using (i) a factor of 10^7 as an estimate of the ratio of rates of solvolysis of the p-toluenesulfonate and p-nitrobenzoate (7) and ii) a value of 10^{-2} for the ratio of rates of solvolysis of the p-toluenesulfonate in ethanol and 70% acetone, one can conclude that the ethanolysis of compound VIIc would proceed 2 x 10^4 times as fast as VIb at 25°.

No structure has been assigned with certainty to the products of the solvolysis of VIIb. However, the product is not VIIa. A control experiment showed that VIIa would survive the reaction conditions.

The results obtained from the study of VIIb suggest a marked acceleration of ionization but provide little information on the nature of the ionic species. The absence of VIIa in the reaction products indicates that ion (IX) in which the cationic center is symmetrically disposed between the two cyclopropyl rings and which reacts to afford VIIa cannot be the precursor of products. Products may arise from ions of types X and XI. There is some indication that both X and XI type ions may be involved in the solvolysis. If ion XI forms directly from VIIb, the rate enhancement must be due to the relief of strain on ring opening.


IX

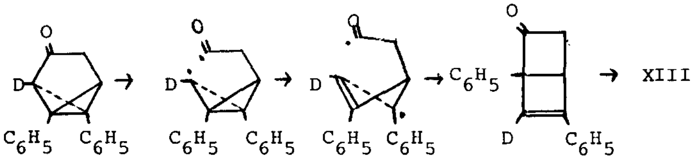

X


XI

The oxime, m.p. 143-144° of I was prepared readily and converted with lithium aluminum hydride to the corresponding amino compound (XII), m.p. 64-65°. The study of deamination of XII, however, was unsuccessful due to the facile ring opening reaction of the bicyclobutane with nitrous acid.

Finally we wish to discuss the mechanism of the photochemical rearrangement of I to 2,4-diphenylphenol. (11) For this purpose we have prepared ketone I, monodeuterated at position 1. 1-(Δ^2-5,6-Diphenylcyclopropenyl)-3-diazopropan-2-one was monodeuterated at carbon 3 with sodium methoxide and deuterium oxide (n.m.r. analysis). The copper-catalysed cyclization of the deuterodiazoketone provided ketone I, deuterated at carbon 1 (n.m.r. analysis). The photolysis of this ketone under identical conditions with those for the non-deuterated compound I afforded 2,4-diphenylphenol (XIII), which was washed with water several times. The mass spectral analysis revealed that this phenol (XIII) contained one deuterium atom (the peak (molecular ion) at 247 was 15 times as intense as that at 246) and the n.m.r. spectrum and decoupling experiments indicated that the deuterium was located at carbon 3 of 2,4-diphenylphenol. Apparently no scrambling of the deuterium atom occurred.

This result led us to propose the following mechanism.



The first step, the α-cleavage of the carbonyl group is a well-documented process and the photo-induced rearrangement of the above type has several precedents. (13)

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(7) Isopropyl p-toluenesulfonate reacts 3500 times as fast as isopropyl chloride in 80% ethanol (8) at 50°.

Benzhydryl chloride (9) can be calculated to react 7×10^3 times as fast as benzhydryl *p*-nitrobenzoate (10) in 90% acetone at 114.6°. Using these two factors a rough estimate of 10^7 is obtained for the ratio of rate of solvolysis of a *p*-toluenesulfonate and a *p*-nitrobenzoate.

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