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PHENYLAZOALKENES FROM THE ALKALINE DECOMPOSITION OF PHENYLTOSYLHYDRAZONES

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Tosylhydrazones are versatile compounds,whose chemical behaviour has been largely investigated in these last years: the carbenic decomposition to olefins and insertion products (I) and the reduction to alkanes (2) open new ways to the organic chemist for the solution of particular problems.

We want to report shortly here some preliminary results we obtained in the course of our studies on the treatment with basic agents of phenyltosylhydrazones.

It is well known that tosylhydrazones,when treated with a basic agent,suffer an internal oxido-reduction process,the original sulphonate residue being reduced to the corresponding sulphinate,and the remaining moiety of the molecule resulting oxidized:p.toluensulphinic acid and diazocompounds are in such a way obtained:

$$\mathrm{Ts{-}NH{-}N{=}}\langle \longrightarrow \dot{\mathrm{T}}\mathrm{sH} + \bar{\mathrm{N}}{=}\overset{+}{\mathrm{N}}{=}\langle$$

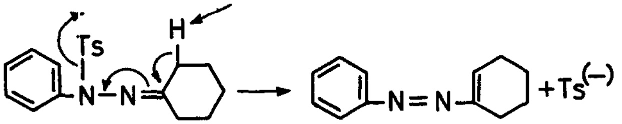
In the case of phenyltosylhydrazones the course of the reaction could be analogous,for what concerns the oxido-reduction process,but diazocompounds cannot in this case be formed:it is reasonable to expect from the decomposition of such compounds p.toluensulphinic acid,and a product whose oxidation level (3) is higher than the one of the original phenylhydrazone.

This has been the case:the treatment of the phenyltosylhydrazone of cyclohexanone (I) (4) with LiH in refluxing toluene (5),dioxane or I,2 dimethoxy ethane leads to the formation of a low-melting (30-40°) orange-yellow compound (II)that can be isolated in a yield variable (6) between 30 and 80%.Compound (II),b.p.II0-I20° (0,05 mm.),furnishes analytical data consistent for the formula $C_{I2}H_{I4}N_2$ (U.V.:λmax 222 mμ,ε=9400;227 mμ,ε=I0400; 233 mμ,ε=7300;300 mμ,ε=2I400;sh. at 3I0 and 325 mμ).

The I.R. spectrum of (II) indicates that no NH is present.The N.M.R. spectrum (CCl_4) confirms (7)the absence of NH,and shows the presence of one vinylic hydrogen (multiplet centered at 6,93 δ) and of five aromatic hydrogens (multiplet between 7,I5 and 8,0 δ) of a phenyl group.The signals of the remaining eight hydrogens lie as two separated complex absorptions,at 2,4 δ(four allylic hydrogens) and I,76 δ(four aliphatic hydrogens).

The origin and the physico-chemical constants of (II) suggest for this compound the structure of phenyl-azo-cyclohexene (8).

The formation of (II) from (I) under the action of basic agents can be rationalised as follows:



(I) (II)

As we have seen,the tosylation,followed by treatment with LiH in aprotic solvents,of the phenyltosylhydrazone of the cyclohexanone results in an oxidation of this compound:it is however noteworthy that this oxidation being conducted in particular conditions leads to the formation of a compound such as (II).

This compound,that is stable in the conditions of its formation,reacts rapidly with air and must be stored with caution (in vacuo,and in the cold) in order to avoid decomposition.

Work is in progress,in order to generalize this reaction,and to study the chemical behaviour of this unusual class of compounds (9).

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3. Oxidation levels are used in the sense suggested by R.Robinson,*The Structural Relations of Natural Products*,p.4,Oxford Univ.Press,London 1955.See also A.Nickon,A.S.Hill,*J.Amer.Chem.Soc.* **86**,1152 (1964).
4. Readily obtained from the treatment of the phenylhydrazone of cyclohexanone with TsCl in pyridine.
5. The reaction has been conducted under nitrogen atmosphere,for 24 hours.After working up with ether,the product has been chromatographed on Si-gel.Full details will be given elsewhere.
6. Intensive changements have been observed in the yield,probably due to the surface properties of LiH.
7. We are indebted to dr.R.Mondelli for discussions on the N.M.R. spectra.
8. Work is in progress,in order to establish the geometrical isomerism of (II).
9. Azoalkenes have been obtained,in a limited number of cases,from the reaction of aryl and alkyl hydrazines with α-halo ketones:J. van Alphen,*Rec.Trav.Chim.* **64**, 305 (1945);F.Ramirez and A.F.Kirby,*J.Amer.Chem.Soc.* **75**, 6026 (1953);B.T.Gillis and J.D.Hagarty,*Abstracts 148th A.C.S. Meeting*,p.87S