## NEIGHBORING GROUP PARTICIPATION IN THE ACETOLYSIS OF 1,1,1-TRIARYL-3-DIAZO-2-PROPANONES. AN UNPRECEDENTED 1,3 SHIFT OF AN ARYL GROUP VIA A FIVE-MEMBERED TRANSITION STATE.

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Summary. The acetolysis of diazo ketones 1a,b,c, leads to the corresponding indanones 3a,b,c, and to the rearranged acetates 4a,b,c. The formation of the acetates 4 can be explained in terms of a mechanism involving the same transition state responsible for the ring closure to 3.

The reaction of  $\alpha$ -diazo ketones with acids have been the object of several investigations, the acid catalyzed hydrolysis being mechanistically the most extensively studied one. $^1$ However, the acetolysis has received minor attention, presumably because the formation of lphaacetoxy ketones as the only products can in general be interpreted as proceeding <u>via</u> a preliminary reversible proton transfer, followed by the reaction of the diazonium ion with a second molecule of the acid or its conjugated base. Although opinions have differed about nucleophilic participation in the solvolysis, bimolecular displacement of the nitrogen by the acetate ion seems to be favoured. $^2$  However,  $\,$  lpha-diazo ketones lpha'-substituted by a hetero atom with lone electron pairs (S,O,N) have already been shown to undergo acetolysis through different and more complex pathways. Thus, cine substitution was occasionally observed and interpreted according to an alternative mechanism involving the intermediate formation of a conjugated enol and a delocalized carbonium ion.3,4 Neighboring group participation by the hetero atom was shown to intervene in the acetolysis of  $\alpha$ -diazo ketones  $\alpha$ '-arylthio-5,6,7, $\alpha$ 'benzhydryloxy-<sup>8,9</sup>,  $\alpha$ '-sulfonamido-substituted.<sup>10</sup> These reactions proceed via a four-membered transition state or intermediate, ultimately resulting in 1,3 shift of the  $\alpha$ '-substituted group or in ring closure. These results indicate that in different series of lpha-diazo ketones migration of sulfur, oxigen, nitrogen from the lpha'-C to the lpha-C is a process which may to some extent be independent from the nucleophilicity of the hetero atom incorporated in the parti~ cular function present on the lpha-carbon. This observation led us to explore whether neighboring group participation by a sp<sup>2</sup> carbon atom (e.g. an aryl group) might occur in the acetolysis of suitable  $\alpha'$ -substituted  $\alpha$ -diazo ketones.

Preliminary studies showed that the acetolysis of 1-diazo-3,3-diphenyl-2-propanone and 1diazo-3,3-diphenyl-3-methyl-2-propanone leads exclusively to normal substitution of the diazo group. We then turned to the acetolysis of a serie of  $\alpha$ -diazo ketones 1, in the assumption that a 1,3 anionotropic shift of an aryl group might reasonably depend on, or be facilitated by, an efficient delocalization of the incipient positive charge developing on the  $\alpha$ '-carbon in the transition state. The results, summarized in the Table, confirm the soundness of the above hypothesis. In fact, the acetolysis of 1a gave only minor amounts of the normal acetate 2a, the main product being the indanone 3a; however, some of the rearranged acetate 4a was also formed.



Normal substitution was instead absent in the acetolysis of both 1b and 1c, which afforded the corresponding indanones 3b,c along with considerable or equal quantities of the rearranged acetates 4b,c. On the other side, the acetolysis of 1d gave exclusively the indanone 3d. No traces of the acetates 2b,c,d, and 4d were detected by MS analysis of the final reaction mixtures.

Table. Acetolysis of  $\alpha$ -diazo ketones  $\begin{array}{c} C_{6}H_{5} \\ C_{6}H_{5} \\ I \\ Ar \end{array}$ 

Substrate	Ar			Products	(yield)		
la	C <sub>6</sub> H <sub>5</sub>	2a	(5%)	3a	(82%)	4a	(13%)
1b	C6H4.40CH3			3р	(64%)	4b	(36%)
lc	С <sub>6</sub> н <sub>4</sub> .40н			3c	(50%)	4c	(50%)
1d	C6H3.30CH3.40H			3đ	(100%)		

The structure of the new compounds have been unambigously assigned by  $^{1} ext{H-NMR}$  and MS data. In

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particular, the assignments relative to the rearranged acetates 4b,c are consistent with the finding that in their NMR spectra a sharp singlet is present at  $\delta$  6.65 (integrating for 3H); the latter signal is to be attributed to the three adjacent hydrogens present in the migrated aryl group.

From a mechanistic point of view, not a single citation of a 1,3 shift of an aryl group, to our knowledge, is found in the literature, while a 1,4-phenyl migration has been reported to occur in a base catalyzed reaction (but not during solvolysis) of 4,4-diphenylcyclohexyl p-toluenesulfonate, very probably in the boat conformation.<sup>1</sup>

The question concerning the migration of a group R with its electron pair from A to C in a R-A-B-C system has been much debated. Although claims have been made about groups migrating in this way,<sup>11</sup> the evidence is that such migration are extremely rare, if they occur at all; they may eventually be the result of two successive 1,2 shifts. However, by no means this can be the case under discussion.

Our proposed mechanism, reported in the following Scheme, postulates that the competitive formation of the indanones and the rearranged acetates proceeds <u>via</u> a common, five-membered

Scheme. Proposed mechanism for the acetolysis of  $\alpha$ -diazo ketones 1.



transition state of type **A**, which has to collapse to the Wheland intermediate **B**, clearly responsible for the formation of indanones **3**. The rearrangement of the latter intermediate to the isomeric cation **C**, involving a 1,2 hydride shift, may well be the alternative pathway leading to  $\alpha$ -acetoxy ketones **4**, possibly through the benzhydryl cation **D**.

The driving force of the above rearrangement, which is particularly favoured in the case of **lb** and **lc**, is to be found in the more efficient delocalization of the positive charge of **C**, due to the strong, electron donating power of the para substituent. In the case of **ld**, the corresponding Wheland intermediate **B** does not necessitate any further stabilization, and consequently the reaction proceeds entirely towards the indanone formation.

The data reported in the present paper and the proposed mechanism suggest that in the acetolysis of 1,1,1-triaryl-3-diazo-2-propanones the product distribution is under the control of electronic factors. On the other side, the hypothesis can be made that steric (<u>i.e</u>. conformational) factors might also be important in allowing the rearrangement observed for  $\alpha$ 'triaryl-substituted  $\alpha$ -diazo ketones. This is suggested by the above mentioned finding that the acetolysis of 1-diazo-3,3-diphenyl-3-methyl-2-propanone resulted simply in normal substitution.

The study of the electronic as well as steric factors at work in the above rearrangements is, at present, under investigation.

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## REFERENCES

- See references reported in "Organic reaction mechanism", Chapter 2. Capon, B.; Rees, C.W.; Editor Wiley Interscience, London, New York, Sydney, 1968-1972.
- 2) Lane, J.F.; Feller, R.L.; J.Am.Chem.Soc. 1951, 73, 4230.
- 3) Rosnati, V.; Pagani, G.; Sannicolo', F.; Tetrahedron Letters, 1967, 1241.
- 4) Rosnati, V.; Sannicolo', F.; Paganí, G.; Gazz.Chim. Ital., <u>1969</u>, 99, 152.
- 5) Gladiali, S.; Pusino, A.; Rosnati, V.; Saba, A.; Soccolini, F.; Selva, A.; Gazz.Chim.Ital. <u>1977</u>, 107, 535.
- 6) Pusino, A.; Rosnati, V.; Saba, A.; Soccolini, F.; Selva, A.; Gazz.Chim.Ital. <u>1978</u>, 108, 557
- 7) Flowers, W.T.; Freitas, A.M.; Holt, G.; Purkiss, S.C.; J.Chem.Soc. Perkin Trans. <u>1981</u>, 1, 1119.
- 8) Pusino, A.; Rosnati, V.; Solinas, C.; Vettori, U.; Tetrahedron, 1983, 39.
- 9) Rosnati, V.; Soccolini, F.; Gazz.Chim.Ital. 1979, 109, 623.
- 10) Pusino, A.; Saba, A.; Desole, G.; Rosnati, V.; Gazz.Chim.Ital. <u>1985</u>, 115, 33.
- 11) Abdun-Nur, A.R.; Bordwell, F.G.; J.Am.Chem.Soc.; 1964, 5695, 24.

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