

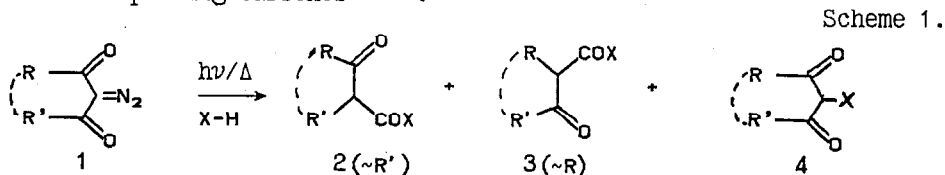
# Decomposition of 2-Diazo-1,3-diketones: Stereocontrol of the Mechanism.

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**Abstract:** Complete "inversion" of alkyl to aryl migratory tendency in Wolff rearrangement of diazodiketones with Z,Z-conformation was revealed by comparing decomposition behavior of the planar diazo tetralindione with its twisted acyclic analogues. Dramatic change in regioselectivity of this process was accompanied by the appearance of X-H insertion products in the reaction mixture. These data suggest that on the way from planar cyclic to highly skewed acyclic aroyldiazomethanes concerted Wolff rearrangement turns into a carbenic process.

Photolysis and thermolysis of unsymmetrically substituted diacyldiazomethanes **1** in the presence of nucleophilic reagents (alcohols, water and others) usually yields two regioisomers of  $\beta$ -keto esters, acids or their derivatives **2** and **3** owing to competitive migration of substituents R and R' during Wolff rearrangement (WR)<sup>1-5</sup> (Scheme 1). Apart from these products, X-H insertion products **4** and parent  $\beta$ -diketones **5** are usually formed in small amounts from the corresponding carbenes<sup>1,2,5</sup>.



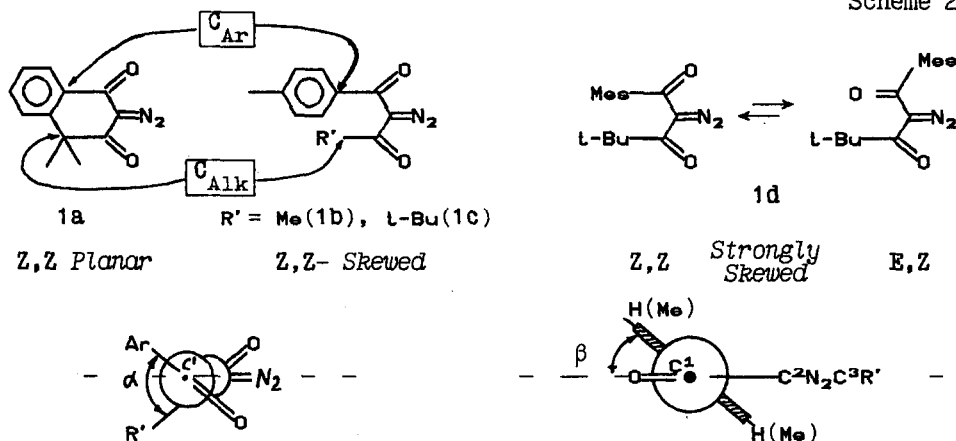
It is known that the ratio of keto esters **2** and **3** (relative migratory tendency of substituents, MT,  $\sim\text{R}/\sim\text{R}'$ ) as well as other reaction products **4** and **5** strongly depends on various parameters<sup>1,4,5</sup> but correlation between them is not firmly established yet.

In this research we tried to estimate the actual influence of stereochemistry of the aroyldiazomethanes **1a-d**, (which was established for the first time in our recent investigations<sup>6</sup>) on the MT of substituents and ratio of the other decomposition products.

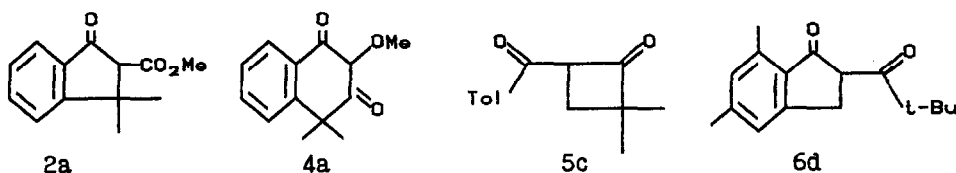
We used unsymmetrically substituted 2-diazo-1,3-diketones **1a-d**<sup>7</sup> which have well defined differences in their stereochemistry (Scheme 2): Z,Z-planar 2-diazo-4,4-dimethyl-1,3-tetralindione **1a** ( $\alpha \approx \beta \approx 0$ ),

Z,Z-nonplanar diazodiketones **1b**, **1c** ( $\alpha \approx 50$  and  $59^\circ$ ,  $\beta \approx 33$  and  $40^\circ$ ), and mesytoylypivaloyldiazomethane **1d**, which exists as an equilibrium mixture of Z,Z- and E,Z-conformers (2 : 1) ( $\alpha \approx 88$  and  $81^\circ$ ;  $\beta \approx 60$  and  $52^\circ$ )<sup>6</sup>.

Scheme 2.



The sole pathway of the thermolysis and photolysis<sup>8</sup> of cyclic diazodiketone **1a** is WR, which results in formation of keto ester **2a** (83-88%). In this case exclusive migration of  $\text{C}_{\text{Alk}}$ -atom occurs ( $\sim \text{C}_{\text{Alk}}/\sim \text{C}_{\text{Ar}} > 50/1$ ). Appearance of significant amounts of O-H insertion product **4a** (up to 60%)<sup>9</sup> takes place only under catalytic decomposition<sup>8</sup> of diazodiketone **1a**.



Relative MT of  $\text{C}_{\text{Alk}}$ -atom rapidly diminishes when the degree of skewing of the molecule rises during transition from **1a** to acyclic **1b** ( $R, R' = \text{Tol, Me}$ ; yields of **2b** and **3b** are 49 and 21% respectively). In the case of diazo diketones **1c** ( $R, R' = \text{Tol, t-Bu}$ ) and **1d** ( $R, R' = \text{Mes, t-Bu}$ ) with the most twisted structures exclusive migration of aryl group (**3c**, 43%; **3d**, 90%) occurs. It is interesting to note that MT is practically insensitive to considerable difference in population of the Z-E conformers of the compounds **1c** and **1b**<sup>6</sup> (in both cases  $\sim \text{C}_{\text{Alk}}/\sim \text{C}_{\text{Ar}} < 1/50$ ).

As a side process during decomposition of p-toluoylpivaloyl diazomethane **1c** C-H insertion of the corresponding diacylcarbene into

the C-H bond of the pivaloyl methyl group occurs with the formation of cyclobutanone **5c** (48%)<sup>9</sup>. In the case of diazodiketone **1d** similar insertion but into the C-H bond of the mesitoyl methyl group affords 5,7-dimethyl-2-pivaloyl-indanone-1 **6d** (2-4%)<sup>9,10</sup>

Deviation of  $C_{Alk}$ ,  $C_{Ar}$  atoms from  $C^1C^2(N_2)C^3$  plane of diazodiketones **1a-d**, MT of substituents and yields of insertion products.

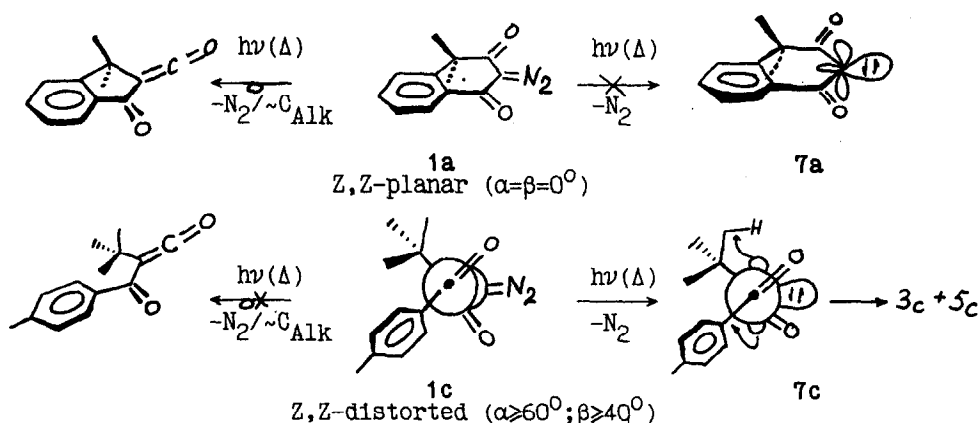
Diazodiketone, №	<b>1a</b> (Z,Z)	<b>1b</b> (Z,Z)	<b>1c</b> (Z,Z)	<b>1d</b> (Z,Z-E,Z)
$\alpha^6$	0	50	59	88 81
$\beta^6$	0	33	40	60 52
$\sim C_{Alk}/\sim C_{Ar}(\Delta, h\nu)$	> 50/1	2-3/1	< 1/50	< 1/50
X-H Insertion products ( $\Delta, h\nu$ ), %	0	2-4	45-60	2-4

On the basis of the given data we can conclude that the main stereochemical reason of the observed MT inversion and formation of carbenic products in this process is considerable deviation of the  $C_{Alk}$  and  $C_{Ar}$  atoms from a planar  $C^1C^2(N_2)C^3$  framework in the molecules **1b-d** ( $\alpha \geq 60^\circ$ ;  $\beta \geq 40^\circ$ ), and not the difference in Z-E stereochemistry of conformers or their ratio in an equilibrium mixture<sup>5</sup>.

Furthermore, preliminary mechanistic analysis of stereochemical aspects and features of known WR schemes<sup>1,5,11</sup>, applied todiazodiketones **1a-d**, shows that in the case of the planar cyclic diazotetralindione **1a** elimination of dinitrogen and migration of substituent is apparently a concerted process, while decomposition of its nonplanar acyclic analogues includes generation of the intermediate diacylcarbene **7** (Scheme 3).

Really, migration of  $C_{Alk}$ ,  $C_{Ar}$  atoms in diacylcarbene **7a** (and so its participation in WR of diazotetralindione **1a**) is unlikely, since  $C_{Alk}-CO$ ,  $C_{Ar}-CO$  bonds and vacant p-orbital of this intermediate would be located in orthogonal planes<sup>11</sup> (Scheme 3) and conformational rigidity of its cyclic structure would prevent their synperiplanar position which is necessary for a 1,2-shift.

In the case of acyclic diazodiketones **1c,d** the  $C_{Alk}-CO$  and  $C_{Ar}-CO$  bonds are strongly located out of the  $C^1C^2(N_2)C^3$  plane and in corresponding intermediate carbenes **7c,d** these bonds are "approaching" the plane of the vacant p-orbital. So their position is favoring the realization of stereochemical condition of the carbenic WR mechanism (Scheme 3).



Appearance in the reaction mixtures of characteristic "carbenic" X-H insertion products such as 4b (R,R'= Tol, Me; X= OMe), 5c, 6d is also evidence in favor of this conclusion.

The causes of the diametrically opposite **MT** behavior of the aryl and alkyl groups ( $C_{Ar}$  and  $C_{Alk}$  atoms) in the concerted process and carbenic **WR** are under investigation.

#### References and Notes

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- Diazodiketones **1a-d** were prepared according to the modified procedure of diazotransfer reaction: Popik, V.V.; Korneev, S.M.; Nikolaev, V.A.; Korobitsyna, I.K. *Synthesis* **1991**, 195-198.
- Thermolysis and photolysis of diazodiketones **1** were carried out in dioxane solution with 5% vol. MeOH<sup>5,6</sup> at 95-97°C ( $\Delta$ ) and  $\lambda > 280$  nm ( $h\nu$ ). Catalytic decomposition by  $Rh_2(OAc)_4$  - in THF/MeOH mixture 4/1 at 50°C.
- All compounds were characterized by IR, N.M.R. spectroscopy and microanalytical data.
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(Received in UK 4 March 1992)