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Mechanism of the Photochemical and Thermal Wolff Rearrangement of 2-Diazo-1,3-dicarbonyl Compounds

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Thermolysis and photolysis of 2-diazo-1,3-dicarbonyl compounds were investigated as a function of methanol concentration. As the methanol concentration decreased, methyl group migration increased concomitant with the suppression of O–H insertion into methanol, whereas aryl group migration was essentially unaltered with the methanol concentration. The results are interpreted as indicating that aryl migration occurs directly from the excited state of diazo compounds, but that methyl migration takes place in the singlet carbene in competition with O–H insertion.

The Wolff rearrangement of α-diazo carbonyl compounds has received continuous interests,[1] since the reaction has not only found wide use as the crucial step in the Arndt-Eistert synthesis, but also attracted much interests industrially as a photoresist process.[2] Although the Wolff rearrangement has been the subject of numerous mechanistic investigations,[1] a satisfactory rationalization of this reaction has been achieved only recently. Since Kaplan and Meloy[3] have shown that diazo ketones exist as an equilibrium mixture of *s-cis* and *s-trans* forms as a result of hindered internal rotation about central C–C bond, the crucial question related to the mechanism of the Wolff rearrangement seems to be whether the reactive intermediate is a free keto carbene or the diazo ketone itself. We have recently suggested[4] that the Wolff rearrangement to form ketene takes place directly from the diazo ketone in some cases, whereas singlet keto carbene undergoes either characteristic carbenic reactions, *e.g.*, insertion, or gives rise to ketene. The mechanisms have been shown[4] to account for the relative efficiency of other competing reactions of more complicated polyfunctional diazo compounds. The relative migratory aptitude established[5] with 2-diazo-1,3-dicarbonyl compounds should be re-examined in this respect since it has been generally assumed that only free keto carbene is involved in the migration. The relative migratory aptitudes of individual groups have been reported[1,5] to be sensitive to the method in which the reaction is conducted. Thus, the following series is generally valid for the thermal reaction:

$$\mathrm{H > Ph > Me > R_2N > RO.}$$

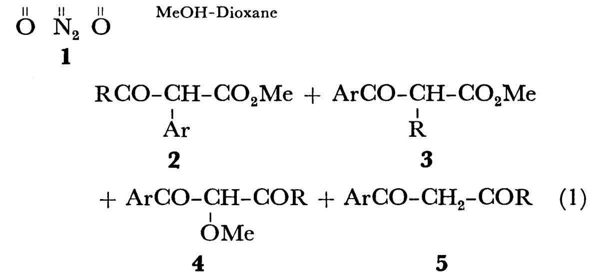
In the photochemical variant, Ph and Me change places:

$$\mathrm{H > Me > Ph > R_2N > RO.}$$

To date, no reasonable scheme to explain the difference has appeared. Thus, we have examined the thermolysis and photolysis of 2-diazo-1,3-dicarbonyl compounds in more detail in order to get deeper insight into the nature of migration.

Results and Discussion

A solution of 2-diazo-1-phenyl-1,3-butanedione (**1a**) in methanol-dioxane was decomposed in Pyrex tubes either photochemically or thermally as detailed in the Experimental section. GC analysis of the product mixture revealed the presence of two rearranged products (**2** and **3**) arising from the migration of both Ph and Me groups, O–H insertion (**4**) and double hydrogen-abstraction products (**5**) of carbene (Eq. 1). The product identifications and distributions were determined by GC and/or NMR using authentic samples. As summarized in Table 1, the product distributions were sensitive to the concentration of methanol. Thus,



$$\mathrm{Ar\text{-}\underset{O}{\underset{\|}{C}}\text{-}\underset{N_2}{\underset{\|}{C}}\text{-}\underset{O}{\underset{\|}{C}}\text{-}R \xrightarrow[\text{MeOH-Dioxane}]{h\nu/\Delta}}$$

1

$$\mathrm{RCO\text{-}\underset{Ar}{\underset{|}{CH}}\text{-}CO_2Me + ArCO\text{-}\underset{R}{\underset{|}{CH}}\text{-}CO_2Me}$$

2 **3**

$$\mathrm{+ ArCO\text{-}\underset{OMe}{\underset{|}{CH}}\text{-}COR + ArCO\text{-}CH_2\text{-}COR} \quad (1)$$

4 **5**

a: Ar=Ph, R=Me, **c**: Ar=p-MeO-C_6H_4, R=Me,
b: Ar=p-Br-C_6H_4, R=Me, **d**: Ar=Ph, R=OEt

Table 1. Photolysis and thermolysis of 2-diazo-1-phenyl-1,3-butanedione (**1a**)[a]

hν or *Δ*	MeOH (%)	Additives	Yield/%[b]			
			2	**3**	**4**	**5**
hν[c]	100		12.5	23.9	27.4	h)
	100	Q[d]	11.5	26.2	27.2	h)
	100	S[e]	2.4	10.9	31.5	h)
	10		11.8	32.7	15.9	h)
	5		12.4	36.1	12.8	h)
	3		14.4	44.2	8.3	h)
	1		15.2	47.2	2.7	h)
Δ[f]	100		32.4	13.4	6.4	h)
	100	BPO[g]	1.9	h)	h)	82.0
	10		31.0	24.4	7.1	h)
	5		29.2	26.3	5.2	h)
	3		28.7	28.2	3.3	h)
	1		28.9	30.3	1.0	h)

a) Reactions were performed on a 10 mM solution of **1** in dioxane in sealed Pyrex tubes. b) Determined by GC. c) Irradiations were carried out at 10 °C with 300 W high-pressure Hg lamp. d) Ten-fold excess of 1,3-pentadiene was added as a triplet quencher. e) Five-fold excess of 4-methylbenzophenone was added. f) Thermolyses were carried out at 80±1 °C. g) One-fifth of benzoyl peroxide was added. h) Trace.

in both photolytic and thermal runs, as the methanol concentration decreased, Me group migration product **3** increased concomitant with the suppression of the O–H insertion product **4**, whereas phenyl group migration product **2** was essentially unaltered with the methanol concentration. Similar trends were also observed for other 2-diazo-1,3-diketones (**1b**, **c**) as summarized in Table 2. Although the high incidence of Me as opposed to Ar migration was generally observed for the photochemical Wolff rearrangement regardless of the methanol concentration, Ar and Me change places for the thermal run as the methanol concentration decreased. Consequently, at high methanol concentration where the Wolff rearrangement has been generally carried out, the apparent relative migratory aptitudes of Me and Ar groups are not same in the thermal and photochemical Wolff rearrangements, but the trends become similar at the lower concentration regardless of the way in which the reaction is conducted.

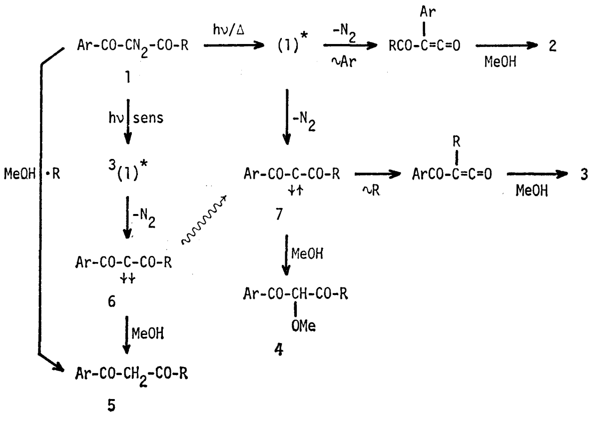
TABLE 2. PHOTOLYSIS AND THERMOLYSIS OF 2-DIAZO-1,3-DICARBONYL COMPOUNDS (**1**)[a)]

1	$h\nu$ or Δ	MeOH(%)	Yield/%[b)]		
			2	**3**	**4**
1b	$h\nu$[c)]	100	9.6	44.3	17.3
		10	7.9	47.3	12.1
		5	9.0	51.7	11.6
		3	9.3	53.0	7.6
		1	9.0	54.8	2.7
	Δ[d)]	100	21.3	20.0	5.7
		10	15.3	37.7	11.5
		5	14.6	40.6	9.7
		3	14.7	43.1	7.8
		1	15.3	45.9	2.7
1c	$h\nu$[c)]	100	6.6	26.0	22.5
		10	9.2	43.4	12.9
		5	9.1	49.6	10.1
		3	9.2	53.7	7.9
		1	10.2	65.5	3.1
	Δ[d)]	100	18.9	11.4	2.9
		10	17.9	31.4	f)
		5	17.0	32.7	f)
		3	17.0	36.0	f)
		1	16.9	38.3	f)
1d	$h\nu$[c)]	100	58.2	0	37.6
		100[e)]	12.1	0	45.4
		10	68.8	0	22.6
		5	76.3	0	2.5
		3	76.8	0	1.5
		1	80.1	0	f)
	Δ[d)]	100	23.8	0	5.4
		10	20.6	0	1
		5	20.3	0	1
		3	21.6	0	1
		1	18.5	0	f)

a)—d) They are defined in Table 1. e) Five-fold excess of 4-methylbenzophenone was added. f) Trace.

It is very important to examine the origin of the effect of the methanol concentration on the relative migratory aptitude. The above data indicate that Me migration **3** and O–H insertion products **4** arise from a common intermediate (A), while Ar migration product **2** is derived from a different intermediate (B). In order to obtain information on the multiplicity of the intermediates, the effects of triplet sensitizer and quencher were studied. When the photolysis of **1a** was carried out in the presence of 4-methylbenzophenone, formation of **2** was greatly reduced whereas **3** as well as **4** were still formed in moderate yields. One may propose that the intermediate A may be the triplet carbene, since it is generally accepted[6)] that photosensitized decomposition of a diazo compound circumvents the formation of the singlet carbene and generates exclusively the triplet carbene *via* energy transfer and loss of N_2 from the resulting triplet precursor diazo compound. The substantial formation of **3** and **4** in the direct irradiation, then, suggests that the triplet carbene would be formed either *via* a rapid intersystem crossing from the initially generated singlet carbene or *via* dissociation from the triplet diazo compound **1**, probably formed by the intersystem crossing from the singlet excited state. If this were the case, one would expect that the addition of 1,3-pentadiene, an efficient quencher for both triplet carbene and triplet excited states,[1)] should cause considerable suppression of the formation of **3** and **4**. No change in the product ratio was, however, observed even in the presence of a high concentration of this quencher. This clearly eliminates the triplet carbene as a possible intermediate A for **3** and **4**. It is generally accepted,[1,7)] on the other hand, that the key intermediate leading to the O–H insertion product (*e.g.*, **4**) is singlet carbene, and hydroxylic reagents have been shown[8)] to be efficient quenchers for singlet carbene. Thus, the structure for the intermediate A that best fits into these data is that of a singlet carbene.

What is then the intermediate B? It is quite important to note here that there has been accumulating evidence[3,4,9,10)] on the mechanism of the Wolff rearrangement which shows that there is a pathway which does not include the singlet carbene but favors the migration accompanied by loss of N_2 directly from the excited diazo compound. It is tempting to suggest the excited (either photochemically or thermally)

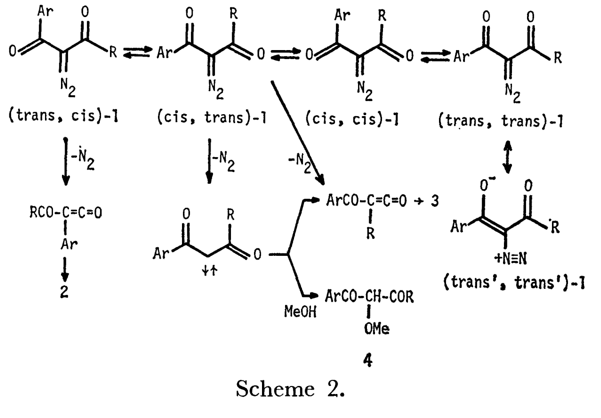


Scheme 1.

1 as the most likely intermediate B for **2**. Suppression of **2** by the photosensitization which circumvents the formation of the excited singlet **1** also supports the above assignment.

On the basis of the above assignments, a reasonable mechanism which explains the data is given in Scheme 1. Thus, **1** is excited either thermally or photochemically to its excited state which can give rise to the Ph migration product directly or dissociate to give N_2 and singlet carbene (**7**). The singlet carbene **7** subsequently undergoes either Me migration or O–H insertion into alcohol. Appreciable formation of **3** and **4** from the singlet carbene **7** even in the sensitized decomposition can be interpreted as indicating that intersystem crossing of the triplet carbene to the singlet is possible, as has frequently been observed in other analogous carbene systems, *e.g.*, :$CHCOCH_3$,[9] :$CHCONEt_2$,[4] and :CHCN.[9] No prominent formation of the characteristic triplet product in the sensitized photolysis is interpreted as indicating that intersystem crossing of the triplet carbene to the singlet is significant and its rate is substantially greater than its overall rate. It has been generally accepted[1] that one of the characteristic product from the triplet carbene is the double hydrogen-abstraction product **5**. Thermolysis of **1** in the presence of benzoyl peroxide (BPO) resulted in almost exclusive formation of **5**. This indicates that **5** is formed mainly *via* radical-induced[11] decomposition of **1** itself, but not from the triplet carbene **6** in this case.

There remains the question of the factors which control the two competitive processes from the excited diazo compounds. One explanation must include Kaplan and Meloy's suggestion[3] that diazo ketones exist as an equibrium mixture of *s-cis* and *s-trans* forms as a result of hindered internal rotation about the central C–C bond. In the investigation of photochemical processes of several α-diazo monocarbonyl compounds, we have suggested[4] that the Wolff rearrangement to form ketene takes place directly from the singlet excited state of the *s-cis* conformer, whereas that of the *s-trans* conformer dissociates N_2 to generate singlet keto carbene which either undergoes characteristic carbenic reactions, *e.g.*, O–H insertion, or gives rise to ketene.



Scheme 2.

Thus, the ratio of the Wolff rearrangement to the competing carbenic processes is shown to be roughly proportional to the ground state population of *s-cis* and *s-trans* conformers. If one assumes here a coplanar molecule for **1** as a result of resonance contribution, one would expect four possible rotamers for **1** (Scheme 2). The influence of steric and electrostatic effects exerted between the Ar, R, C=O, and $C=N_2$ groups causes variations in the relative energy of four conformers and, therefore, in their populations.[12] Electrostatically, conformers (*trans, cis*), (*cis, trans*), and (*cis, cis*) are favorable as a result of electrostatic attraction, whereas (*trans, trans*) is less stable due to the repulsion between two C=O groups, as is predicted from the canonical form (*trans′, trans′*). Sterically, on the other hand, (*trans, trans*) would suffer from steric repulsion in the $Ar–N_2–R$ groups, all in a cis relationship, and in (*cis, cis*), the nonbonding repulsion between Ar and R would be severe. Thus, one would expect that conformers (*trans, cis*) and (*cis, trans*) would be more stable than (*trans, trans*) and (*cis, cis*). The conformer (*trans, cis*) presents a favorable situation for Ar migration to occur in its excited state, since migrating and leaving groups in this conformer are situated in positions with respect to each other which permit the migration. In the (*cis, trans*) conformer, on the other hand, Me migration accompanied by loss of N_2 would be expected to occur in its excited state. Experimental results suggest, however, that main pathway from this conformer is dissociation of N_2 to generate singlet carbene in which Me migration occurs in competition with the O–H insertion. The reason for this difference lies partly in the difference in inherent migratory ability between Me and Ph groups. A concerted process with Ph migration and loss of N_2 would be favored[13] by donation of more labile π-electron to the diazo carbon and by the stabilization of a transition state (or short-lived intermediate) through bridging delocalization. Since such stabilization is not attained in Me migration, dissociation of N_2 occurs before Me group shifts to the diazo carbon.

The dependence of the product ratio, **2**/(**3**+**4**), on the method of reaction reflects, at least in part, the influence of the temperature on the relative population of each conformer. It has been reported,[14] for example, that photolysis of diazo ketone $RCOC(CH_2R')N_2$ yields the α,β-unsaturated ketone as the major product at room temperature; however, at higher temperature, the ketene rearrangement product is obtained. The results are similarly explained by assuming that the higher energy conformations are more populated as the temperature is raised. The product distributions in Tables 1 and 2 indicate that (*cis, trans*) conformers are preferred for **1a**—**c**. Apparent decrease in this conformer for **1d** can be attributable to a finite activation energy to migration of the alkoxyl group which is known[1] to be an inefficient migrating group. This group did not migrate at all either in the excited diazo compound or in the singlet carbene even in the absence of an efficient trap for the singlet carbene, *i.e.*, methanol. It is also important to note that the singlet carbene generated thermally undergoes Me migration more readily than that generated photolytically as opposed to the O–H insertion. This is explained in terms of the activation energy difference between two processes. Alternatively, a part of Me migration would occur directly in the excited state in thermal run.

From the data, we propose a reasonable reaction scheme to explain why Me and Ph migrations take place in the trend of relative migratory aptitude as the method of reaction is changed. We wish to point out that the ground state population of rotational isomers and nature of migration (carbenic or diazo) are definitely related to the apparent relative migratory aptitude in 2-diazo-1,3-dicarbonyl compounds. These factors have not been taken into account in the literature.

Experimental

Instrumentation. UV spectra were recorded on a Hitachi 220-S spectrophotometer. IR spectra were measured on a JASCO IR-G recording spectrometer, and ^{1}H NMR spectra were determined with a JEOL JNM-MH-100 NMR spectrometer in $CDCl_3$ with Me_4Si as an internal reference. GC analyses were performed on a Yanagimoto Model G-180 instrument with flame ionization detector using 80 cm×4.0 mm column packed with (A) 5% PEG 20 M and (B) 5% Silicone SE-GE on 60—80 mesh Diasolid L.

Materials. 2-Diazo-1,3-dicarbonyl compounds **1a**—**d** were conveniently prepared[13] by diazo-group transfer from *p*-toluenesulfonyl azide to the appropriate dicarbonyl compounds and purified through a short silica-gel column. Authentic samples for product identification were prepared according to the literature procedures. Thus, Ar migration products **2a**—**c** were prepared by the condensation[15] of ethyl acetate with the corresponding benzyl cyanides, followed by methanolysis[16] of the resulting cyanide. Phenylmalonate **2d** was obtained by stepwise esterification of phenylmalonic acid.[17] Me migration products **3a**—**c** were synthesized[18] by the reaction of methyl propionate with the corresponding methyl benzoates. OEt migration product **3d** was obtained in the photolysis of methyl diazobenzoylacetate in ethanol. O–H insertion products **4a**—**c** were obtained in the reaction[19] of acetic anhydride with the corresponding α-methoxyacetophenone in the presence of $BF_3 \cdot OEt_2$. **4d** was isolated in the irradiation of **1d** in methanol.

Photolysis and Thermolysis of 1. All irradiations were carried out with a Halos 300 W high-pressure mercury lamp with a water-cooled jacket. In a typical procedure, 0.05 mmol of **1** was added to 5.0 cm^3 of a mixture of methanol and dioxane in Pyrex tubes. The sample was then degassed, sealed, and irradiated until all of the diazo compound was destroyed. Thermolysis was done in a sealed Pyrex tube in an oil bath thermostated at 80±1 °C. Control experiments ruled out the interconversion of the products during the reaction. Product identification and yields were determined mainly by GC. The product ratio was also determined by NMR. CF_3CO_2H was used as solvent for NMR to prevent the enolization of products. The product ratios determined by both methods were generally in good agreement.

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