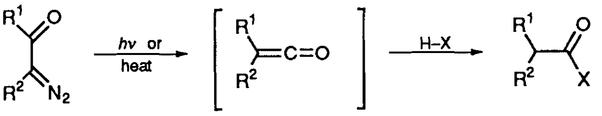
Stereochemistry and Thermal Stability of Diazodiketones

Vladimir V. Popik*,† and Valerij A. Nikolaev
Department of Chemistry, St. Petersburg State University, St. Petersburg, 199084 Russia

The thermal stability of diazodiketones strongly depends on the twisting of the molecular framework caused by steric interaction of substituents at the carbonyl groups. On going from planar cyclic 2-diazo-4,4-dimethyltetralin-1,3-dione to sterically congested mesitoylpivaloyldiazomethane the rate of decomposition increases 100 times. On the other hand, bulky substituents also decrease the reactivity of 2-ketoketenes formed in the Wolff rearrangement of these diazocarbonyl compounds.

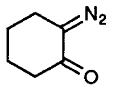
Diazoketones are widely used in organic synthesis and industrial photolithographic processes.[1] The main peculiarity of these compounds which is the basis of most of their applications is the Wolff rearrangement[2] (Scheme 1).



Scheme 1

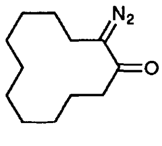
Photolytic or thermal decomposition of diazoketones usually leads to formation of very reactive ketenes which on further reaction with nucleophiles yield carboxylic acids or their derivatives. The high reactivity of diazocarbonyl compounds often is accompanied by their low thermal stability. This shortcoming is a very substantial obstacle for the application of photoresist resins with diazocompounds in microelectronics manufacturing. Partial thermal decomposition of them during storage, drying, reactive ion etching, and development decreases the sensitivity and resolution. Design of new deep UV resists systems based on diazoketones and diazodiketones requires information on the factors determining the thermal stability of these diazocompounds.

It is well-known that the rate of thermal decomposition of diazocarbonyl compounds depends on the nature of substituents at the diazo and carbonyl groups[4–6] as well as the electronic features of the substituents[4,7,8] and the concentration of the nucleophile in the reaction mixture.[4,8,9] The role of stereochemical factors on the thermal stability of these diazo compounds has not been investigated yet. At the same time analysis of literature data indicates that diazoketones with similar substituents often have dramatic differences in their thermal stability. Thus the rates of decomposition of three cyclic diazoketones **1–3** with alkyl substituents at diazo and carbonyl groups differ by two orders of magnitude.



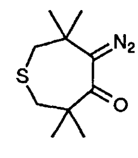
1

$\tau_{1/2}(100\ °C) = 32$ min[4]



2

$\tau_{1/2}(100\ °C) = 11$ min[4]



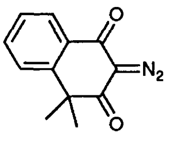
3

Fast decomposition
even at room temp.
$\tau_{1/2}(100\ °C) < 2$ s[10]

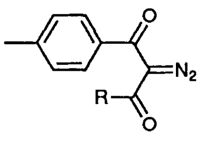
To our mind it is difficult to explain such differences in the thermal stabilities of the cyclic diazoketones **1–3** only in terms of electronic effects.

We chose diazodiketones as a model for the investigation of stereochemical factors in the thermal stability of diazocarbonyl compounds. The electronic influence of substituents on the diazo group in these diazo compounds is diminished by the carbonyl groups acting as 'electronic buffers' and therefore the steric influence of substituents on the reactivity of diazodiketones prevails. It was also mentioned in the literature that diazodiketones with bulky substituents such as Bu^t or mesityl are extremely unstable in comparison with their less sterically hindered analogues.[11–14]

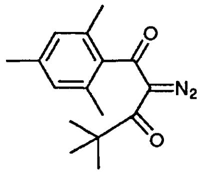
In this work we tried to estimate the actual influence of the stereochemistry of diazodiketones on their thermal stability. As a measure of relative thermal stability we chose the rate of thermal decomposition of acylaroyldiazomethanes **4–8**.



4



5 R = Me; **6** R = Pr^i; **7** R = Bu^t



8

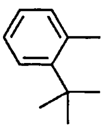
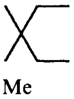
Diazodiketones **4–8** bear very similar substituents and their electronic influences on the diazo-group are practically the same as indicated by IR and ^{13}C NMR spectra.[14] Recent analysis of the conformational structure of acyclic acylaroyldiazomethanes **5–8** in solutions by low temperature ^{13}C NMR, IR spectroscopy and dipole measurements showed that the *Z,Z*-conformer predominates in *Z–E* conformational equilibrium of these compounds.[14] At the same time conformers of diazodiketones **5–8** have significant differences in stereochemistry due to the twisting of molecules forced by steric interaction of substituents.[14,15] Distortion of a molecular framework can be expressed by the angle α, the dihedral angle between planes of two carbonyl groups. 2-Diazo-4,4-dimethyltetralin-1,3-dione (**4**), chosen as a model compound, has a planar *Z,Z*-–CO–CN$_2$–CO– fragment of the molecule ($\alpha = 0°$). In the series of acyclic acylaroyldiazomethanes the twisting of –CO–CN$_2$–CO– increases with the size of the substituents: thus diazodiketones **5–8** have angles of 47°, 50°, 59° and 88°, respectively.[14,15]

Rates of thermal decomposition of diazodiketones **4–8** were measured in boiling dry dioxane (at $T = 101.5 \pm 0.2$ °C) and in the presence of 5% (v) of methanol (at $T = 93 \pm 0.5$ °C). Starting concentrations of diazodiketones **4–8** were 0.075 mol dm^{-3} and their decrease during thermolysis was monitored by HPLC. The measured decrease of these concentrations with

---

† *Present address:* Department of Chemistry, University of Toronto, Toronto, Ontario, Canada M5S 1A1.

Table 1 Rate constants and thermodynamic data for the decomposition of diazodiketones **4–8** R^1–CO–CN_2–CO–R^2

Diazodiketone	R^1	R^2	α^a/°	T/°C	$10^4\ k_{obs}/s^{-1}$	$\Delta G^{\ddagger}$/kJ mol^{-1}
4			0	101.5	3.9	116.9
				93	3.1[b]	
5	*p*-Tol	Me	47	101.5	26.7	110.9
				93	8.3	119
6	*p*-Tol	Pr^i	50	101.5	45.6[c]	109.3
7	*p*-Tol	Bu^t	59	101.5	101	106.8
				93	56	106.1
8	Mes	Bu^t	88	101.5	306	103.3
				93	115	103.9
9			0	101.5	1.06[d]	120.5
10	Me	Me	42	101.5	8.50[d]	114.5
11	Ph	Me	47	101.5	13.75[d]	113.0

[a] Distortion angles α were calculated using a molecular model program.[14,15] [b] This value is given only for qualitative comparison because experimental data did not fit the first-order law well. [c] Decomposition of diazodiketone **6** was monitored by IR spectroscopy. [d] These values were calculated from literature data.[4,5,9]

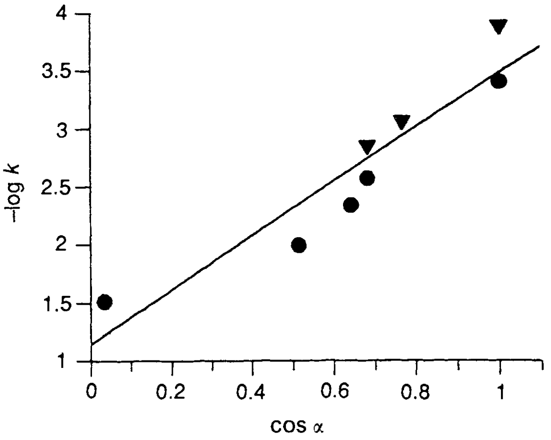


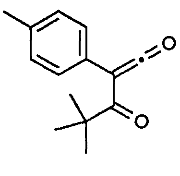
Fig. 1 Relationship between distortion of diazodiketone molecules (cos α) and the rate of decomposition of diazodiketones at 101.5 °C (−log k_{obs}): (●), experimental data; (▼), literature data[4,5,9]

reaction time fit the first-order rate law well, with only one exception in the case of decomposition of cyclic diazodiketone **4** in the presence of methanol. Observed first-order rate constants were obtained by least-squares fitting to an exponential function and are shown in Table 1. In further considerations we also used decomposition rates of diazodimedone (**9**), diazoacetylacetone (**10**), and acetylbenzoyldiazomethane (**11**) measured previously in mesitylene at 100 °C.[4,5,9] To compare these data with experimental results we have recalculated the rates at 100 to 101.5 °C assuming that differences of $\Delta G^{\ddagger}$ at these temperatures were negligible.

Data in Table 1 indicate that the rates of thermal decomposition of diazodiketones **4–8** strongly depend on the size of the substituents at carbonyl groups. The increase of the molecules' distortion angle α caused by steric interaction of substituents on going from diazotetralindione **4** to mesitoylpivaloyldiazomethane **8** resulted in growth of the decomposition rate. This fact is illustrated by good correlation between cos α and log k_{obs} (Fig. 1). Least-squares fitting gives the line $-\log k_{obs} = 2.35 \times \cos \alpha + 1.14$, with correlation coefficient $R = 0.93$.

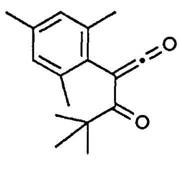
Data in Table 1 also show that the rates of decomposition of acylaroyldiazomethanes **5–8** are reduced 2–3 times by the addition of methanol. This was caused by a decrease in the boiling temperature of the dioxane–methanol mixture. But it is noteworthy that activation energies of decomposition of these diazodiketones in pure dioxane and in the presence of methanol are very similar. It means obviously that low concentrations of nucleophile do not change the mechanism of thermal decomposition of acyclic diazodiketones **5–8**. On the contrary 2-diazo-4,4-dimethyltetralin-1,3-dione (**4**) shows very different behaviour. The life-times of this cyclic diazodiketone in pure dioxane at 101.5 °C and in dioxane–methanol mixture at 93 °C are practically the same. Moreover experimental curves in the last case do not fit the first-order law and show an inflection point at 1 h. It was also reported previously that the difference in reactivity between cyclic and acyclic diazodiketones increased with the rise of alcohol concentration. In pure alcohols Wolff rearrangement of diazodiketone **4** and diazodimedone **9** is completely suppressed in favour of diketone formation.[15,16] These data indicate that even low concentrations of nucleophiles have an influence on the mechanism of decomposition of at least some cyclic diazodiketones.

The size of the substituents at carbonyl groups of diazodiketones controls not only the thermal stability of these diazo carbonyl compounds but also further reactivity of reaction products. 2-Ketoketenes which are formed or implied during Wolff rearrangement of diazodiketones (Scheme 1) are usually very reactive and react immediately after formation with nucleophiles or undergo rapid dimerization or polymerization. In most cases they are determined by capture with some nucleophilic reagents or by cycloaddition reactions. Only a few 2-ketoketenes protected by bulky substituents are stable enough to be observed by spectral methods and sometimes even to be isolated as individual compounds.[12,17] The family of relatively stable ketenes is now expanded by two new members, 4,4-dimethyl-2-*p*-tolylpent-1-ene-1,3-dione (**12**) and 4,4-dimethyl-2-mesitylpent-1-ene-1,3-dione (**13**).



12

$\tau_{\frac{1}{2}}$ = 1.5 h (room temp.)
ν_{CCO} = 2095 cm^{-1}



13

$\tau_{\frac{1}{2}}$ = 3 h (room temp.)
ν_{CCO} = 2096 cm^{-1}

These 2-ketoketenes containing bulky *tert*-butyl groups were observed after the thermal decomposition of diazodiketones **7** and **8** in pure dioxane. Ketenes **12** and **13** were identified by IR spectroscopy by the characteristic absorption band of the >C=C=O group at 2095 cm^{-1}. Decay of these species was also monitored by IR spectroscopy. Decomposition of diazodiketones **7** and **8** in the presence of methanol results in formation of methyl esters of 2-aryl-4,4-dimethyl-3-oxovaleric acids.[15] This fact confirms the structures of 2-ketoketenes **12** and **13**.

Conclusions

Experimental and literature data show that thermal stability of diazodiketones (and obviously diazoketones) depends mainly on the level of twisting of the planar structure of the diazocarbonyl fragment, –CO–CN_2–CO–. Distortion of the molecule increases on the way from cyclic diazodiketones **4** and **9** and to acyclic **5**, **6**, **10** and **11** and further to diazodiketones with bulky substituents **7** and **8** and the rate of thermal decomposition also dramatically increases in this series. The reason for the above mentioned decrease in thermal stability in this series is obviously due to the decrease in conjugation between the diazo and carbonyl groups. On the other hand bulky substituents reduce the reactivity of 2-ketoketenes.

Experimental

Instruments.—The samples of reaction mixture were analysed by analytical HPLC using a Milichrom-1V instrument equipped with a column packed with Silasorb 0.005 mm (Lachema) and a UV (236 nm) detector. IR spectra were recorded using a Specord IR 75 instrument.

Materials.—All diazodiketones were prepared using the modified diazo-transfer reaction[18] and were purified by recrystallization from diethyl ether. Dioxane and methanol were thoroughly dried and distilled just before use.

Kinetics.—Initial diazodiketone concentrations were 0.075 mol dm^{-3}. For rate determination 9–12 samples of the reaction mixture were extracted from the reaction flask into glass tubes precooled to −30 °C during diazodiketone decomposition. These samples were then warmed to room temp. and analysed by HPLC. At least three independent measurements were performed for every sample. The UV detector was calibrated before experiments using solutions of diazodiketones (**4**–**8**) of six different concentrations for each to check the linearity of the peak area–concentration relation. For elution of the column a hexane–THF (19:1) mixture was used at a flow rate 100 mm^3 min^{-1}; injection volumes were 10 mm^3. The experimental rate data fit the first-order law well, and observed first-order rate constants were obtained by least-squares fitting to a single exponential function.

2-*Ketoketenes.*—The solutions containing 2-ketoketenes **12** and **13** were prepared by thermolysis of the corresponding diazodiketones **7** and **8** in boiling dioxane. When reaction was completed (7 min for **7** and 3 min for **8**) the reaction mixture was cooled rapidly to room temp. The samples at that time were free of diazocompounds as indicated by HPLC. The decay of ketenes was monitored by IR spectroscopy by observation of the absorption band at 2095 cm^{-1}. Rate data fit the second-order law by ketene concentration alone.

References

1 *Polymers for Electronic and Photonic Applications*, ed. C. P. Wong, Academic Press, San Diego, 1993; E. Reichmanis and L. F. Thompson, *Chem. Rev.*, 1989, **89**, 1273; W. M. Moreau, *Semiconductor Lithography*, Plenum Press, New York, 1988.

2 D. Whittaker, in *Chemistry of Diazonium and Diazo Group*, ed. S. Patai, Wiley, New York, 1978, part 2, 593.

3 Y. Tani, M. Endo, M. Sasago and N. Nomura, in *International Symposium on Carbene-Type React. Intermediates*, Book of Abstracts, Kyoto, 1989, 116; J.-U. Thurner, M. Ulbricht, R. Donau and G. Z. Tomaschewski, *Z. Chem.*, 1988, **28**, 145; C. G. Wilson, R. D. Miller, D. P. McKean, L. A. Pederson and M. Regitz, *Proc. SPIE-INT. Soc. Opt. Eng.*, 1987, 771, 2.

4 M. Regitz and G. Maas, *Diazo Compounds*, Academic Press, Orlando, 1986, 72.

5 M. Regitz and W. Bartz, *Chem. Ber.*, 1970, **103**, 1477.

6 R. Munschaner and G. Maas, *Angew. Chem.*, 1991, **103**, 312.

7 A. Melzer and E. F. Jenny, *Tetrahedron Lett.*, 1968, 4503.

8 W. Juglet and D. Schmidt, *Tetrahedron*, 1969, **25**, 969.

9 W. Bartz and M. Regitz, *Chem. Ber.*, 1970, **103**, 1463.

10 A. de Groot, J. A. Boerma, J. de Valk and H. Wynberg, *J. Org. Chem.*, 1968, **33**, 4025.

11 H. Meier, H. Wengenroth, W. Lauer and W. Vogt, *Chem. Ber.*, 1988, **121**, 1643.

12 V. A. Nikolaev, Yu. Frenkh and I. K. Korobitsyna, *Zh. Org. Khim.*, 1978, **14**, 1147; V. A. Nikolaev, Yu. Frenkh and I. K. Korobitsyna, *Zh. Org. Khim.*, 1978, **14**, 1433.

13 W. Lauer, V. Krause, H. Wengenroth and H. Meier, *Chem. Ber.*, 1988, **121**, 465.

14 V. A. Nikolaev, V. V. Popik and I. K. Korobitsyna, *Zh. Org. Khim.*, 1991, **27**, 505.

15 V. A. Nikolaev and V. V. Popik, *Tetrahedron Lett.*, 1992, **33**, 4483; V. V. Popik, Ph.D. Thesis, Leningrad State University, 1989.

16 H. Veshambre and D. Vocelle, *Can. J. Chem.*, 1969, **47**, 2853.

17 R. Leung-Toung and C. Wentrup, *J. Org. Chem.*, 1992, **57**, 4850.

18 V. V. Popik, S. M. Korneev, V. A. Nikolaev and I. K. Korobitsyna, *Synthesis*, 1991, 195.

Paper 3/02955G
Received 24*th May* 1993
Accepted 2*nd July* 1993