J. Org. Chem. 1991, 56, 7320–7322

A Kinetic Study of the Rearrangement of Triarylacetonitrile Oxides

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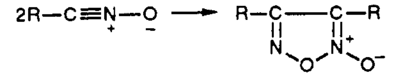
Received January 26, 1989 (Revised Manuscript Received July 18, 1991)

The thermal rearrangement of triphenylacetonitrile oxide (**1a**) to triphenylmethyl isocyanate (**2**) is a first-order process. Rate constants at five temperatures between 116 and 190 °C were determined giving $\Delta H^{\ddagger} = 9.3 \pm 1.1$ kcal/mol and $\Delta S^{\ddagger} = -58.2 \pm 2.4$ cal/mol·K. The rearrangement of substituted triarylacetonitrile oxides (**1b–d**) occur only slightly faster than that of **1a**. These results are interpreted in terms of a concerted single-step rearrangement in which the highly ordered transition state (**6c**) has a degree of radical character.

Although nitrile oxides generally dimerize to furoxans (eq 1), this process is inhibited when R is sterically bulky so that the competitive thermal rearrangement to the corresponding isocyanate can become the dominant process (eq 2).[1] The first dimerization-inhibited nitrile oxide reported was triphenylacetonitrile oxide (**1a**).[2] Since then a number of other sterically dimerization inhibited nitrile oxides have been prepared.[1,3,4]



(1)

$$R{-}C{\equiv}\overset{+}{N}{-}\overset{-}{O} \longrightarrow R{-}N{=}C{=}O \qquad (2)$$

We herein report our kinetic study of the rearrangement of triarylacetonitrile oxides (**1a–d**) and the consequential mechanistic implications. When **1a** is heated overnight in refluxing xylene in air, it smoothly rearranges to triphenylmethyl isocyanate (**2**) as confirmed by treatment of the resultant solution with excess aniline and isolation of *N*-(triphenylmethyl)-*N′*-phenylurea (**3**)[5] is near quantitative (99%) yield (eq 3).

$$\mathbf{1a} \xrightarrow[\Delta]{} \underset{\mathbf{2}}{Ph_3C{-}N{=}C{=}O} \xrightarrow{PhNH_2} \underset{\mathbf{3}}{Ph_3CNHCONHPh} \qquad (3)$$

The kinetics of this rearrangement were followed by infrared spectroscopy using carbon tetrachloride as the solvent. Compound **1a** shows strong bands characteristic of the nitrile oxide group[6,7] at 2280 and 1320 cm^{-1}. Since the isocyanate reaction product, **2**, has a strong absorption at 2250 cm^{-1} that interferes with the 2280-cm^{-1} band, the 1320-cm^{-1} peak of **1a** was chosen to follow the rearrangement. The intensity of this peak was shown to vary according to the Beer–Lambert law. The rearrangement of **1a** at 140.0 °C was shown to be cleanly first order. The plot of the log of the initial rates of disappearance of **1a** vs log [**1a**]$_0$ gave a slope of 1. First-order plots of the disappearance of **1a** over more than 5 half-lives showed no curvature. When the same data were plotted using the integrated second-order rate expression, curvature was observed.

The rearrangement kinetics of **1a** to **2** were studied at five different temperatures over the range of 116–190 °C. Using the first-order rate constants determined at the different temperatures (Table I), the Eyring equation gave values of $\Delta H^{\ddagger} = 9.3 \pm 1.1$ kcal/mol and $\Delta S^{\ddagger} = -58.2 \pm 2.4$ cal/mol·K calculated at 25 °C.

Substituted triarylacetonitrile oxides (**1b–d**) were prepared as shown in eq 4. The kinetics of their rearrangement were studied by following the 1320-cm^{-1} IR band. The first-order rate constants for the thermal rearrangements of the monosubstituted triarylacetonitrile oxides at 154.0 °C (Table II) are most noteworthy because of their similarity. 4-Methoxytriphenylacetonitrile oxide (**1b**), and 4-chlorotriphenylacetonitrile oxide (**1c**) rearrange only slightly faster than the unsubstituted triphenylacetonitrile oxide (**1a**). The 4-methyltriphenylacetonitrile oxide (**1d**) rearrangement occurs about 4 times as fast as that of **1a**.

Table I. Temperature Dependence of the First-Order Rate Constant for the Rearrangement of Triphenylacetonitrile Oxide (1a)

temp	k (s^{-1})^a × 10^6	temp	k (s^{-1})^a × 10^6
116.3^b (389.5)^c	9.84 ± 0.11^d	170.2 (443.4)	37.3 ± 0.24
140.0 (413.2)	21.5 ± 0.17	189.8 (463.0)	74.0 ± 2.2
154.0 (427.2)	31.6 ± 1.6		

^{a} Determined by linear least-squares analysis. ^{b} Degrees centrigrade. ^{c} Kelvin. ^{d} Standard deviation.

Table II. First-Order Rate Constants for the Rearrangement of Substituted Triphenylacetonitrile Oxides (1a–d) at 154.0 °C

compound	k (s^{-1})^a × 10^5	compound	k (s^{-1})^a × 10^5
1a	3.16 ± 0.16^b	**1c**	4.63 ± 0.14
1b	3.96 ± 0.12	**1d**	13.6 ± 1.8

^{a} Determined by linear least-squares analysis. ^{b} Standard deviations.

$$\text{4-X-PhMgBr} + Ph_2CO \longrightarrow \underset{\mathbf{4a\text{–}d}}{\text{4-X-PhPh}_2\text{COH}} \xrightarrow{CH_3COCl}$$

$$\underset{\mathbf{5a\text{–}d}}{\text{4-X-PhPh}_2\text{CCl}} \xrightarrow{AgCNO} \underset{\mathbf{1a\text{–}d}}{\text{4-X-PhPh}_2\text{CCNO}} \qquad (4)$$

a, X = H; **b**, X = CH$_3$O; **c**, X = Cl; **d**, X = CH$_3$

These kinetic results with the substituted nitrile oxides clearly rule out the development of any significant charge on the benzylic carbon of the triphenylmethyl group in the transition state for the rearrangement reaction.[8a] The substituent effects,[8b] considered together with the highly negative $\Delta S^{\ddagger}$ for the first-order kinetics of the rearrangement, are consistent with a concerted process in which the transition state is highly ordered and which exhibits no significant charge separation. Our results are consistent with and are supported by work reported by Grundmann, Kochs, and Boal.[3] Their observation that no cross-over occurred when *p*-deuteriobenzonitrile oxide was rearranged

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[1] Grundmann, C.; Dean, J. M. *J. Org. Chem.* **1965**, *30*, 2809.

[2] Wieland, H.; Rosenfeld, B. *Ann.* **1930**, *484*, 236.

[3] Grundmann, C.; Kochs, P.; Boal, J. R. *Ann.* **1972**, *61*, 162.

[4] Ranganathan, S.; Singh, B. B.; Panda, C. S. *Tetrahedron Lett.* **1970**, 1225.

[5] Jones, L. W.; Hurd, C. D. *J. Am. Chem. Soc.* **1921**, *43*, 2422.

[6] Wiley, R. H.; Wakefield, B. J. *J. Org. Chem.* **1960**, *25*, 546.

[7] Beck, W.; Schwierer, E. *Ber.* **1964**, *97*, 3517.

[8] (a) For example see: Bachmann, W. E.; Ferguson, J. W. *J. Am. Chem. Soc.* **1934**, *56*, 2081. Burr, J. G.; Ciereszko, L. S. *J. Am. Chem. Soc.* **1952**, *74*, 5426. Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 3rd ed.; Harper and Row: New York, 1987; pp 633 and 798. (b) For measures of electron-donating and -withdrawing abilities, see: Hammett substituent constant (σ and σ^+) values, e.g., in Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 3rd ed.; Harper and Row: New York, 1987; p 144.

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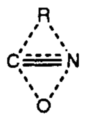
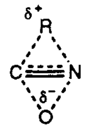
in the presence of rearranging [α-^{13}C]benzonitrile oxide established the intramolecular nature of the rearrangement. They also studied the nitrile oxide to isocyanate rearrangement in other systems, which all occurred with preservation of structural integrity and complete retention of configuration of the migrating group.

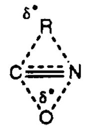
After extensive consideration of various possible mechanisms for the nitrile oxide to isocyanate reaction, Grundman, Kochs, and Boal[3] concluded that the mechanism which is most likely involves a one-step rearrangement in which bond breaking and making are concerted. Such a mechanism most simply and reasonably accounts for their results and our kinetic studies. A range of transition-state structures for the concerted rearrangement can be considered. Previously suggested[9] transition state **6b** is not consistent with our substituent effect results and can be ruled out. Either transition state **6a** or **6c** would be expected to show a negative $\Delta S^{\ddagger}$. However, our observed $\Delta S^{\ddagger}$ of -58.2 cal/mol·K is extraordinary. Significantly increased solvation of the rearrangement transition state by carbon tetrachloride relative to the nitrile oxide solvation is unlikely and could at most account only for a small portion of the observed $\Delta S^{\ddagger}$.



6a

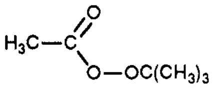


6b



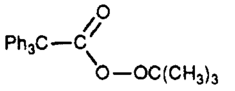
6c

A kinetic study of the thermal decomposition of a series of *tert*-butyl peresters by Bartlett and co-workers[10] is germane to the relation of the observed $\Delta S^{\ddagger}$ to the transition state structure. *tert*-Butyl peracetate (**7a**) undergoes a two-step decomposition, the slow step being homolytic oxygen–oxygen bond dissociation followed by the acyloxy radical losing carbon dioxide, with carbon–carbon bond cleavage, to give the methyl radical. Phenyl substitution stabilizes the carbon radical center causing both the carbon–carbon and oxygen–oxygen bonds to undergo homolysis simultaneously. This resonance interaction of phenyl with the methyl radical center lowers $\Delta H^{\ddagger}$ and simultaneously restricts phenyl rotation, decreasing $\Delta S^{\ddagger}$. In going from **7a** ($\Delta S^{\ddagger}$ = +20 cal/mol·K) to **7b** ($\Delta S^{\ddagger}$ = +4.9 cal/mol·K), the $\Delta S^{\ddagger}$ decreases by 15 cal/mol·K. This is in spite of the reverse $\Delta S^{\ddagger}$ trend being fostered by the fact that the kinetically important step for **7a** involves a dissociative cleavage of only one bond, whereas the thermolysis of **7b** involves a two-bond cleavage, forming three fragments instead of two.



$H_3C-C(=O)-O-OC(CH_3)_3$

7a



$Ph_3C-C(=O)-O-OC(CH_3)_3$

7b

The rearrangement of **1a** to **2** by way of transition state **6c**, in which radical character on the triphenylmethyl group is stabilized by phenyl conjugation, thus restricting the phenyl rotation and making a substantial negative contribution to $\Delta S^{\ddagger}$, is consistent with our experimentally determined highly negative $\Delta S^{\ddagger}$ for this rearrangement.

The rearrangement kinetics of substituted nitrile oxides **1b–d** are also consistent with transition state **6c**. It is generally observed that all *p*-phenyl substituents foster a small increase in rates of free-radical reactions such as aromatic substitutions and by implication increase the stability of the free-radical intermediates.[11] All of the substituted nitrile oxides (**1b–d**) rearrange slightly faster than **1a** (Table II), with **1d** showing the largest rate increase (4-fold).[12] Therefore, a stabilization of radical character in transition state **6c** by all substituents in **1b–d** accounts for their observed small rearrangement rate increases relative to **1a**. Although reaction of **1** involving an initial dissociation to a radical pair followed by rearrangement to the isocyanate entirely within a solvent cage is consistent with the substituent effect, a rate-limiting dissociation is not supported by the highly negative $\Delta S^{\ddagger}$. A noncage, free triphenylmethyl radical is clearly ruled out, since when the rearrangement of **1a** is carried out in air, no triphenylmethyl peroxide is formed.

The first-order kinetics, entropy of activation, and substituent effects on the rearrangement of **1a–d**, as well as all previous work on the nitrile oxide to isocyanate rearrangement, is most simply accounted for by a single-step concerted process in which the transition state has a degree of radical character (**6c**).

Experimental Section

General. Melting points are uncorrected. A Beckman IR-10 infrared spectrophotometer with an auxillary recorder was used to follow the kinetics of the nitrile oxide rearrangements which were carried out in a Haake Model FS constant temperature bath (temperature control rated at ±0.004 °C, observed ±0.05 °C). Temperatures reported for the kinetic runs were corrected by callibration against a standardized ASTM thermometer.

Preparation of Triarylmethanols (4b–d). A Grignard solution, under nitrogen, prepared from 0.10 mol of the appropriate substituted bromobenzene and 2.4 g (0.10 g-atom) of Mg in 100 mL of anhyd ether was treated with a solution of 18.2 g (0.10 mol) of benzophenone in 75 mL of anhyd benzene. It was then washed successively with dilute H_2SO_4, $NaHCO_3$, and water, and steam distilled to remove solvents and unreacted starting materials. The 4-substituted triphenylmethanols were recrystallized from benzene and petroleum ether (30–60 °C) giving **4b** (69%), mp 84–84.5 °C (lit.[14] mp 84 °C); **4c** (40%, mp 83–84.5 °C (lit.[15] mp 85 °C); **4d** (62%), mp 97–98 °C (lit.[16] mp 98 °C).

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(12) Attempts to isolate bis(4-methoxyphenyl)(3-(trifluoromethyl)-phenyl)acetonitrile oxide and (4-methoxyphenyl)bis(3-(trifluoromethyl)phenyl)acetonitrile oxide for use in other studies by the same method used to synthesize **1a–d** (eq 4) proved unsuccessful. When the triarylmethyl chlorides were reacted with silver fulminate, the crude products showed appropriate nitrile oxide peaks in the IR. Substantial IR absorption for the isocyanate group was also always observed. In fact, even when these crude nitrile oxides were stored under refrigeration, the IR showed that the nitrile oxide to isocyanate rearrangement was occurring. Since the triarylmethyl group of both of these trisubstituted nitrile oxides contain both strong electron-donating and -withdrawing groups, it is likely that the extreme ease with which these compounds rearrange is a manifestation of a captodative stabilization[13] of radical character on the triarylmethyl group in the transition state (**6c**). Attempts to isolate 4-(trifluoromethyl)triphenylacetonitrile oxide prepared by eq 4 also led to observations that the crude product was rearranging to the isocyanate. It is possible that captodative stabilization of radical character in the transition state is also operative here, since the unsubstituted phenyls would be electron donating relative to the strongly electron withdrawing 4-(trifluoromethyl)phenyl group. To examine the possibility that the nitrile oxide to isocyanate rearrangement of the above substituted triarylacetonitrile oxides might be catalyzed by a Lewis acid, for example by traces of magnesium halide carried over from the triarylmethanol preparations, triphenylacetonitrile oxide (0.2 M, 10 mL of a CCl_4 solution) with 0.1 g of added $MgBr_2$ was rearranged at 140 °C. When compared to the control (identical conditions except no added $MgBr_2$), no difference in rearrangement rate was observed.

(13) Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry, Part A: Structure and Mechanisms*, 2nd ed.; Plenum: New York, 1984; pp 650–651. Viehe, H. G.; Merenzi, L. S.; Janousek, Z. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 917.

(14) Kauffman, H.; Pannwitz, P. *Ber.* **1912**, *45*, 766.

(15) Gomberg, M.; Cone, L. H. *Ber.* **1906**, *39*, 3274.

Preparation of Triarylmethyl Chlorides (5b–d). To a solution of 0.01 mol of the 4-substituted triphenylmethanol under nitrogen in 20 mL of anhyd benzene, 1.96 g (0.025 mol) of acetyl chloride was added, and the mixture was refluxed for 1.0 h. The solvent and unreacted acetyl chloride were removed under reduced pressure, and the product was set aside in a dessicator to crystallize. The following triarylmethyl chlorides were prepared: **5b** (89%), mp 84.5–86 °C. Anal. Calcd for $C_{20}H_{17}OCl$: C, 76.89; H, 5.77; Cl, 11.95. Found: C, 77.13; H, 5.53; Cl, 11.80. **5c** (85%), mp 88–88.5 °C (lit.[17] mp 88–88.5 °C); **5d** (90%), mp 99–100 °C (lit.[18] mp 99 °C).

Preparation of Triarylacetonitrile Oxides (1a–d). (a) Preparation of Silver Fulminate. (Note: Silver fulminate (AgCNO) is shock sensitive and must be handled with extreme care.) All preparations and subsequent reactions of silver fulminate were carried out in a hood behind an explosion shield. We found that it can be handled safely if one always keeps the solid moist and uses a solvent slurry for transfers. Plastic ware was used in all reactions, and transfers were facilitated with plastic or wood spatulas.

A 3.83-g (22.6-mmol) portion of silver nitrate was dissolved in aqueous HNO_3 ($d = 1.34$, 60.7 mL of HNO_3 (concd), 14.3 mL of H_2O). The cooled solution was then added by means of a dropping funnel into a 1.0-L plastic beaker containing 112.5 mL of 95% ethanol. This was kept cold (20 °C) as the nitric acid solution was being added. Approximately two-thirds of this mixture was then transferred to another beaker, and it was heated on a water bath until the temperature reached 85 °C. It was heated at this temperature for approximately 1 h when the material began to foam and brown NO_2 gas was emitted. The remaining cold solution was quickly added to the hot solution, and the mixture was transferred to an ice bath. The reaction was controlled by adding small portions of 95% ethanol until the reaction was complete as evidenced by the cessation of foaming. The material was handled with great care from this point. The solid was transferred to a plastic Buchner funnel where it was washed successively with water, 95% ethanol, absolute ethanol, anhyd diethyl ether, and anhyd toluene. The slightly moist solid was quickly weighed, and the material was transferred as a slurry in toluene to a 1.0-L plastic beaker equipped with a Teflon-covered magnetic stirrer and containing 100 mL of anhyd toluene and 5.0 g of anhyd magnesium sulfate. The beaker was sealed with a plastic cover containing a nitrogen inlet and an addition funnel. After being stirred under nitrogen for 0.5 h, the silver fulminate was ready for the addition of the triarylmethyl chlorides (6a–d).

(b) Triarylacetonitrile Oxides (1a–d). The following preparation of **1a** is illustrative. A solution of 8.6 g (0.031 mol) of triphenylmethyl chloride in 50 mL of toluene was added under nitrogen to 6.0 g (0.04 mol) of a stirred silver fulminate suspension in toluene at 5 °C. After being stirred for 0.5 h, it was allowed to stand overnight at room temperature. The light yellow solution was filtered, and the solid was washed with toluene. Evaporation under reduced pressure yielded a yellow, semicrystalline mass that was washed with small portions of ether yielding an off-white solid, 4.9 g, mp 148–150 °C. Recrystallization from a minimum amount of benzene gave 1.7 g of white crystalline solid, mp 152–153 °C (lit.[2] mp 153–154 °C). The filtrate was evaporated to about one-fourth volume and a second crop of light yellow crystals was obtained (1.9 g), mp 149–151.5 °C. **1b–d** were prepared in the same manner. When the toluene reaction solvent was removed under reduced pressure, only oils were obtained. Attempts to crystallize these materials proved futile. All compounds showed the characteristic nitrile oxide infrared bands at 2280 and 1320 cm^{-1} and were used for the kinetic studies without further purification.

***N*-(Triphenylmethyl)-*N*′-phenylurea (3).** A solution of **1a** (0.61 g, 2.15 mmol) in xylene (20 mL) was refluxed overnight in air. To the hot xylene solution, 0.43 g (4.2 mmol) of aniline was added, whereupon **3** crystallized on cooling. A second fraction was obtained on concentration of the mother liquor. Recrystallization of the combined solid from aqueous acetic acid gave **3** (0.81 g (99%), mp 243.5–245 °C (lit.[5] mp 242–243 °C)).

Kinetic Measurements of the Rearrangement of 1a–d to Triarylmethyl Isocyanates. A 0.2 M solution (10 mL) of triarylacetonitrile nitrile oxide in spectrograde carbon tetrachloride was prepared. Pyrex reaction tubes (10 mm o.d.) were charged with 1.0-mL aliquots of this solution, cooled (−80 °C), and sealed. The tubes were simultaneously placed in the constant-temperature bath which had been preheated to the desired temperature. Tubes were withdrawn at intervals and quenched in an ice bath. The infrared spectrum from 1400 to 1250 cm^{-1} was determined for each sample using 0.1-mm path length matched KBr cells. Nitrile oxide concentration was followed by observation of the 1320-cm^{-1} peak which was shown independently to obey the Beer–Lambert Law over the concentration range of the kinetic experiments.

Registry No. **1a**, 13412-55-0; **1b**, 137003-25-9; **1c**, 137003-26-0; **1d**, 137003-27-1; **3**, 24308-39-2; **4a**, 76-84-6; **4b**, 847-83-6; **4c**, 6922-89-0; **4d**, 5440-76-6; **5a**, 76-83-5; **5b**, 14470-28-1; **5c**, 27023-37-6; **5d**, 23429-44-9; AgCNO, 5610-59-3; CH_3COCl, 75-36-5; PhMgBr, 100-58-3; p-$CH_3OC_6H_4MgBr$, 13139-86-1; p-ClC_6H_4MgBr, 873-77-8; p-$CH_3C_6H_4MgBr$, 4294-57-9; Ph_2CO, 119-61-9; silver nitrate, 7761-88-8; ethanol, 64-17-5.

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