New Furoxan Chemistry. 2.[1] Chemistry of Acyl Nitrile Oxides Generated in Situ by Thermolysis of Diacylfuroxans†

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Diacylfuroxans yield two types of nitrile oxides in situ when heated in solution. Uncrowded diacylfuroxans rearrange to α-acyloximino nitrile oxides; diacylfuroxans with bulky substituents give rise to the "half-molecule" acyl nitrile oxides. Intermediate cases give mixtures of both types of nitrile oxides. The nitrile oxides are characterized by trapping with dipolarophiles to yield substituted heterocyclic ketones. The cycloadducts of acyl nitrile oxides are uniformly the 5-substituted regio isomers, a result which is in accord with frontier orbital arguments using energy levels and coefficients derived from extended Hückel and CNDO/2 calculations.

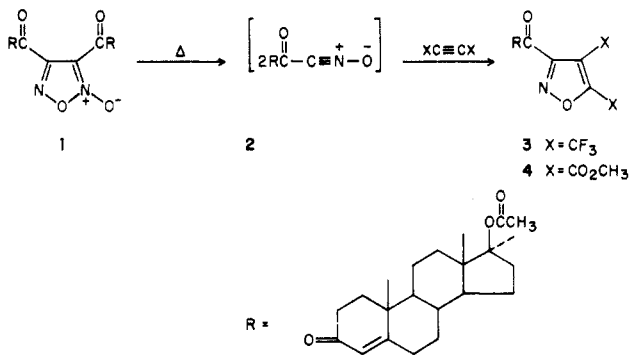
It has long been known that aliphatic and aromatic nitrile oxides dimerize to furoxans.[2] Nevertheless, the thermal regeneration of alkyl- and aryl-substituted nitrile oxides from the corresponding furoxans has been extensively investigated only in recent years. Only strained furoxans and furoxans bearing bulky substituents revert to nitrile oxides at moderate temperatures.[3,4] More generally, 3,4-disubstituted furoxans revert to nitrile oxides only at temperatures at which the nitrile oxides rapidly rearrange to isocyanates,[5a] although thermolysis of unstrained aliphatic and aromatic furoxans at 245 °C to afford the corresponding nitrile oxides (trapped in situ) has been described recently.[6]

In contrast, with the exception of acetyl and benzoyl fulmide, which have been generated in situ from hydroximic acid halides or nitrolic acids,[5b,7] the chemistry of acyl nitrile oxides (acyl fulmides) is unknown. As far as we are aware, only one study has been reported describing attempts to regenerate acyl nitrile oxides from the corresponding diacyl furoxan dimers.[8] Herein we describe the use of diacylfuroxans as in situ sources of acyl nitrile oxides and the behavior of the nitrile oxides thus generated, along with limitations of the method and some observations which offer a unifying explanation for the above[8] and some other previously observed diacylfuroxan chemistry.

Results and Discussion

In the previous paper of this series,[1] we described the conversion of α-ethynyl acetates to diacylfuroxans. The mass spectra of these furoxans lacked a parent ion; an ion corresponding to the "half-molecule" nitrile oxide was the highest mass fragment observed. This suggested that the cycloreversion of diacylfuroxans to α-keto nitrile oxides was unusually facile, since in the mass spectra of dialkyl- and diarylfuroxans the parent and several intermediate-mass fragments are typically observed in addition to the "nitrile oxide" ion.[4,9] In fact, reversion of these diacylfuroxans to α-keto nitrile oxides *is* unusually facile; furoxan 1[1] reacted with excess hexafluoro-2-butyne in toluene at 120 °C to afford the isoxazole 3.

Analogous results were obtained by using dimethyl acetylenedicarboxylate as the dipolarophile to afford 4. Clearly, cycloadducts resulted from the cycloreversion of 1 to two molecules of α-keto nitrile oxide 2 under mild thermolysis. Further probes into α-keto nitrile oxide chemistry were carried out with the readily available[1] camphor-derived furoxan 5. Furoxan 5 underwent extremely clean cycloreversion to the α-keto nitrile oxide 6



(Scheme I); very high yields of cycloadducts were isolated from reactions of 5 with various 1,3-dipolarophiles, e.g., 80% of dioxazole 7 from hexafluoroacetone and 96% of isoxazole 8 from hexafluoro-2-butyne.

Unlike their alkyl and aryl counterparts,[5a] acyl nitrile oxides show no tendency to undergo rapid thermal rearrangement to isocyanates. For example, furoxan 5 heated under reflux in toluene for three days was recovered unchanged; no trace of isocyanate 9 was detectable (IR spectroscopy).

The regiospecificity of acyl nitrile oxides is also remarkable in comparison to that of alkyl and aryl nitrile oxides, which are known to give mixtures of 4- and 5-substituted cycloadducts in many cases,[10] especially in reactions with electron-deficient acetylenes.[11] By contrast, only 5-substituted isoxazoles have been isolated from the reactions of the acyl nitrile oxides studied in this work,

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(1) Part 1: D. R. Brittelli and G. A. Boswell, Jr., *J. Org. Chem.*, previous paper in this issue.
(2) A. Werner and H. Buss, *Chem. Ber.*, 27, 2193 (1894).
(3) J. Ackrell, M. Altaf-ur-Rahman, A. J. Boulton, and R. C. Brown, *J. Chem. Soc., Perkin Trans. 1*, 1587 (1972).
(4) A. Dondoni, G. Barbaro, A. Battaglia, and P. Giorgianni, *J. Org. Chem.*, 37, 3196 (1972).
(5) (a) C. Grundmann and P. Grünanger, "The Nitrile Oxides", Springer-Verlag, West Berlin, Heidelberg, New York, 1971, p 79, and references therein; (b) *ibid.*, pp 56, 215, 219.
(6) J. A. Chapman, J. Crosby, C. A. Cummings, R. A. C. Rennie, and R. M. Paton, *J. Chem. Soc., Chem. Commun.*, 240 (1976).
(7) Y. Otsuji, Y. Tsujii, A. Yoshida, and E. Imoto, *Bull. Chem. Soc. Jpn.*, 44, 223 (1971).
(8) M. Altaf-ur-Rahman, A. J. Boulton, and D. Middleton, *Tetrahedron Lett.*, 3469 (1972).
(9) (a) C. Grundmann, H.-D. Frommeld, K. Flory, and S. K. Datta, *J. Org. Chem.*, 33, 1464 (1968); (b) A. J. Boulton, P. Hadjimihalakis, A. R. Katritzky, and A. Majid Hamid, *J. Chem. Soc. C*, 1901 (1969).
(10) G. Bianchi, C. De Micheli, R. Gandolfi, P. Grünanger, P. Vita Finzi, and O. Vajna de Pava, *J. Chem. Soc., Perkin Trans. 1*, 1148 (1973).
(11) (a) J. Bastide and O. Henri-Rousseau, *Bull. Soc. Chim. Fr.*, 2294 (1973); (b) M. Christl and R. Huisgen, *Tetrahedron Lett.*, 5209 (1968).

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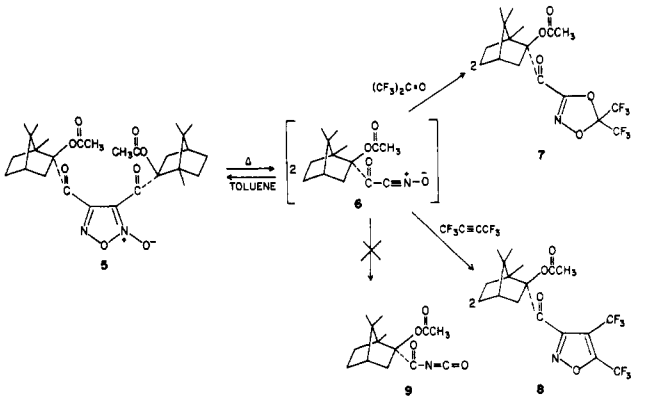
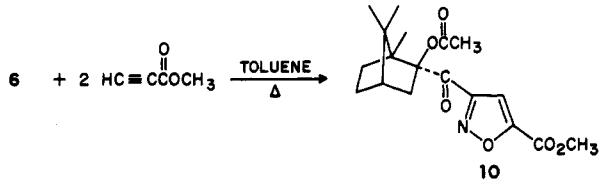
Scheme I

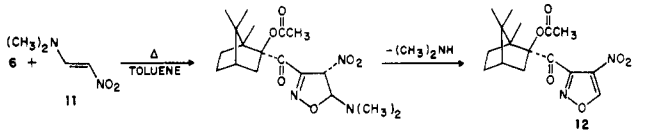


even in the case of the nefarious methyl propiolate,[12] which reacted with **6** to afford solely the 5-substituted compound



10 in high yield. None of the characteristic 5-H of the 4-substituted isomer was detectable in the NMR of the total crude reaction product.

Another interesting example is the cycloaddition to the nitro enamine **11**[13] to afford **12**, a convenient entry into



the 4-nitroisoxazole series. Amine substituents in push–pull conjugated ethylenes are known to control the regiospecificity of cycloaddition,[14] so it should be considered that here also the 5-substituted cycloadduct was formed and underwent subsequent loss of dimethylamine. It was demonstrated that **12** was not formed by cycloaddition of **6** to nitroacetylene formed in situ from **11** by recovery of **11** unchanged under identical reaction conditions in the absence of **6**. It should be noted that **11** is a nitroacetylene synthon complementary to 2-chloro-1-nitroethylene, which with nitrile oxides yields 5-nitroisoxazoles.[15]

The regiospecific formation of only 5-substituted products from acyl nitrile oxide cycloadditions is noteworthy. This regiospecificity has not been appreciated in previous work[7] in which the regiochemistry of benzoyl nitrile oxide cycloaddition was incorrectly assigned by analogy with benzonitrile oxide regiochemistry.[16] The regiospecificity phenomenon can be understood by consideration of acyl nitrile oxide energetics within the framework of the frontier molecular orbital theory of cycloaddition reactions.

The regiospecificity of alkyl, and especially aryl, nitrile oxides is heavily dependent upon the frontier orbital energies of the reacting dipolarophiles. Highest occupied molecular orbital (HOMO) nitrile oxide/lowest unoccupied

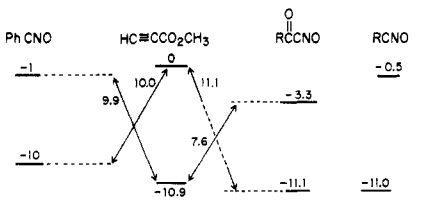


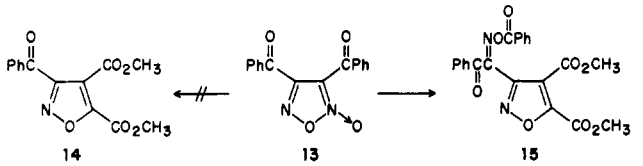
Figure 1. Frontier orbital energies (CNDO) for benzonitrile oxide, methyl propiolate, α-keto nitrile oxides and alkyl nitrile oxides (eV).

molecular orbital (LUMO) dipolarophile control produces 4-substituted isoxazole derivatives, while LUMO (nitrile oxide)/HOMO (dipolarophile) control yields instead 5-substituted isoxazoles.[17] Thus, for example, with electron-rich and conjugated dipolarophiles, the nitrile oxide LUMO is the controlling frontier orbital; however, with electron-poor dipolarophiles, especially methyl propiolate and other electron-poor acetylenic dipolarophiles, the dipolarophile frontier orbital energies are lowered, and the nitrile oxide HOMO now competes for dominance in determining the regioselectivity.

In the case of acyl nitrile oxides, preliminary calculations[18] indicate that the union of the carbonyl and nitrile oxide moieties has only a slight effect on the resulting acyl nitrile oxide HOMO but lowers the LUMO substantially (~3 eV). This substantially narrower HOMO–LUMO gap may also account for the observed higher dimerization reactivity of acyl nitrile oxides compared to nitrile oxides; unlike simple nitrile oxides, no acyl nitrile oxide has ever been isolated.

The energies of the acyl nitrile oxide frontier orbitals are such that it is difficult to conceive of a dipolarophile with frontier orbitals so situated energetically that the acyl nitrile oxide HOMO/dipolarophile LUMO could be the controlling interaction and give rise to 4-substituted products. Acyl nitrile oxides thus correspond to a "Type III" dipole in Sustmann's classification.[19] This comparison is summarized graphically in Figure 1. Further studies are in progress to more fully assess the scope of this interesting modification of nitrile oxide reactivity.

The ease of cycloreversion of the above-mentioned diacylfuroxans to acyl nitrile oxides led us to attempt the extension of this chemistry to simpler 3,4-diacylfuroxans. Reaction of 3,4-dibenzoylfuroxan (**13**), prepared by the

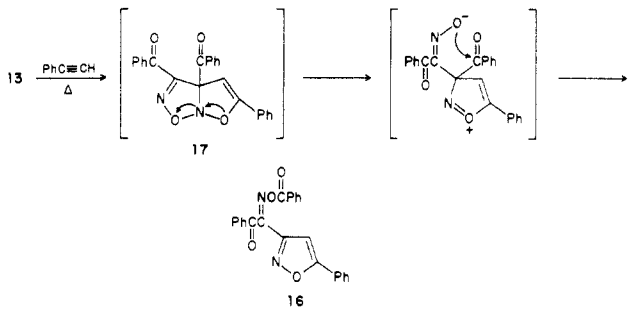


method of Boyer and Snyder,[20] with dimethyl acetylenedicarboxylate led not to the anticipated isoxazole **14**, but to a (formally) 2:1 adduct of nitrile oxide to dipolarophile.

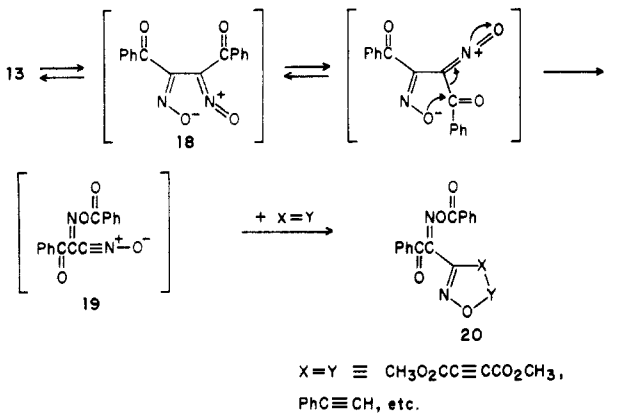
The structure **15** was assigned; in confirmation, the IR spectrum showed absorptions at 1770 cm^{-1} (characteristic of the carbonyl group of *O*-acyl derivatives of oximes),[21] 1755 cm^{-1} (ester carbonyl groups), and 1675 cm^{-1} (characteristic of the keto carbonyl of an ester of a monoxime of an α-diketone).[22] An analogous structural assignment

(12) M. D. Gordon, P. V. Alston, and A. R. Rossi, *J. Am. Chem. Soc.*, **100**, 5701 (1978).
(13) H. Meerwein, W. Florian, N. Schön, and G. Stopp, *Justus Liebigs Ann. Chem.*, **641**, 27 (1961).
(14) G. Stork and J. E. McMurry, *J. Am. Chem. Soc.*, **89**, 5461 (1967).
(15) R. Verbruggen and H. G. Viehe, *Chimia*, **29**, 350 (1975).
(16) NMR spectra presented in ref 7 are only consistent with formation of 5-substituted isoxazolines as cycloadducts of benzoyl nitrile oxide.
(17) K. N. Houk, J. Sims, C. R. Watts, and L. J. Luskus, *J. Am. Chem. Soc.*, **95**, 7301 (1973).
(18) T. Fukunaga, unpublished CNDO/2 and extended Hückel results.
(19) R. Sustmann, *Pure Appl. Chem.*, **40**, 569 (1974).
(20) N. E. Boyer and H. R. Snyder, *J. Am. Chem. Soc.*, **77**, 4233 (1955).
(21) W. P. Jencks, *J. Am. Chem. Soc.*, **80**, 458 (1958); W. F. Heldt, *ibid.*, **80**, 5880 (1958).
(22) J. H. Boyer and M. S. Chang, *Chem. Ind. (London)*, 730 (1959).

Scheme II



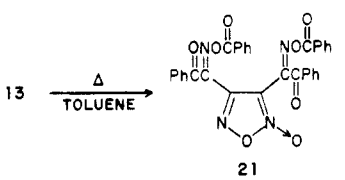
Scheme III



was made by Boulton and co-workers, who found a similar reaction of **13** with phenylacetylene afforded **16**.[8]

These workers suggested that **16** results from **13** reacting "as a nitrone" with phenylacetylene to yield initially **17**, which rearranges to afford the observed product, as formulated in Scheme II. We propose that cycloadducts of **13** arise by another mechanism (Scheme III).

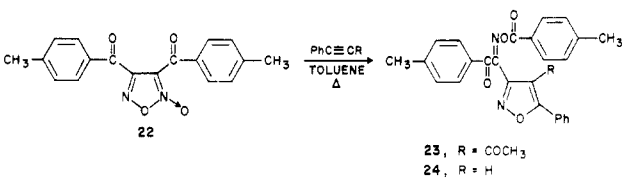
Under the reaction conditions, furoxan **13** is in thermal equilibrium with the ring-opened isomer **18**. (There is ample precedent for this equilibrium in studies of the thermal equilibration of unsymmetrically substituted furoxans.[9,23]) Rearrangement of **18** by intramolecular transfer of a benzoyl group affords nitrile oxide **19**, which cycloadds to dipolarophiles X=Y to afford the observed product **20**. Striking confirmation of this interpretation is obtained from heating **13** in toluene. In the absence of a trapping dipolarophile an 83% yield of **21**, the dimer of nitrile oxide **19**, is obtained.



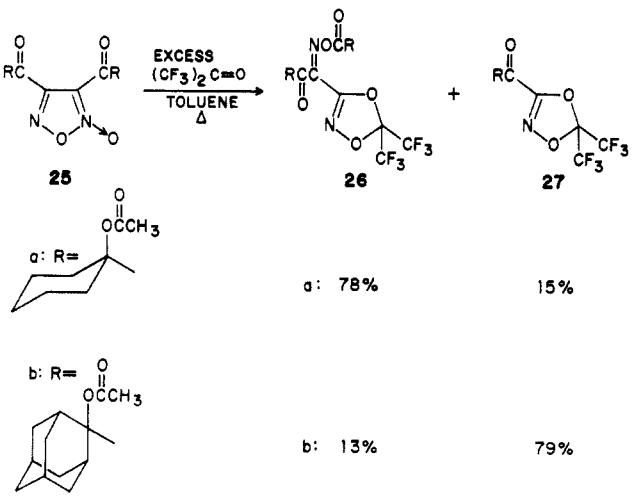
Furoxan **21** is a known substance, having previously been obtained as a byproduct (1–6% yield) in the nitric acid oxidation of acetophenone to dibenzoylfuroxan (**13**) at 100 °C.[22] We can now suggest that **21** probably arises as the byproduct by just such a rearrangement under these reaction conditions. The previously offered explanation[22] for the formation of **21** is effectively excluded since this requires the intermediacy of benzoyl nitrile oxide, no cycloadducts of which were detected in the reaction with dimethyl acetylenedicarboxylate which produced **6**.

(23) F. B. Mallory and A. Cammarata, *J. Am. Chem. Soc.*, 88, 61 (1966).

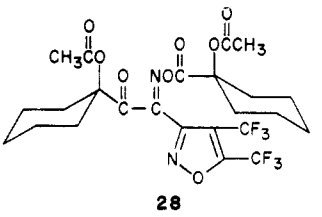
These results are general for 3,4-diaroylfuroxans. For example, mild thermolysis of **22** in the presence of 4-phenyl-3-butyn-2-one and phenylacetylene afforded isoxazoles **23** and **24**, respectively.



It remains to explain the disparity in behavior between furoxans **1** and **5**, which cleanly revert to two molecules of acyl nitrile oxide, and furoxans **13** and **22**, which rearrange to α-acyloximino nitrile oxides. The results of reactions of furoxans **25a** and **25b** with hexafluoroacetone suggest that a steric effect is responsible for this difference.

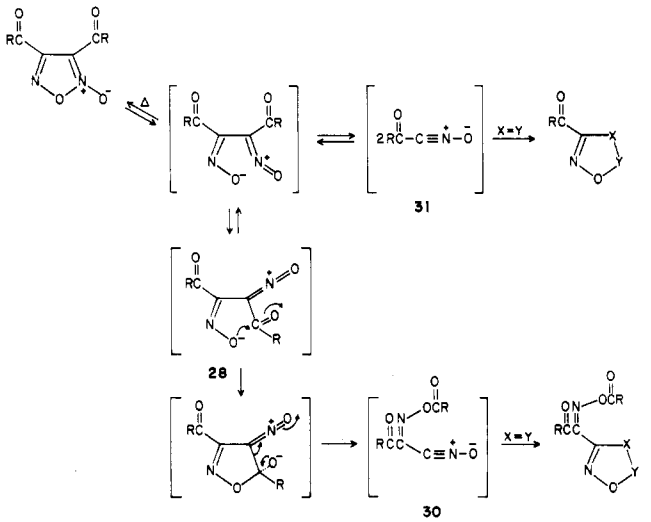


The more hindered (relative to furoxan **13**) acetoxy cyclohexyl compound **25a** yields 15% of **27a** derived from cycloreversion, while still giving as the major product (78%) the rearranged nitrile oxide adduct **26a**. Similar results are observed in the reaction of **25a** with hexafluoro-2-butyne to product **28**.



The even more hindered (acetoxyadamantyl)furoxan **25b** now affords as the major product the cycloadduct **27b** derived from cycloreversion, while a minor amount (13%) of the product of rearrangement **26b** is formed. Just how this steric bulk exerts its influence can be understood with reference to Scheme IV, which summarizes the thermal chemistry of diacylfuroxans. Under mild thermolysis, furoxans are in equilibrium with a ring-opened form, which can, in the case of uncrowded R substituents, undergo intramolecular rearrangement by acyl transfer via transition state **29** to afford products derived from nitrile oxide **30**. If the acyl transfer in **29** is made sterically difficult by a bulky R, then the second (and presumably more energetic in unbulky cases) cycloreversion pathway is available, yielding products derived from acyl nitrile oxide **31**. In furoxans **25a** and **25b**, these two pathways must be in close energetic balance, as both pathways are observed simultaneously.

Scheme IV



Experimental Section

Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were recorded in KBr disks or neat by using a Perkin-Elmer Model 21 spectrophotometer. Ultraviolet spectra were taken in absolute ethanol by using a Cary 14 spectrophotometer. ^{1}H NMR spectra were recorded on a Varian A-60 spectrometer with tetramethylsilane as the internal reference. ^{19}F NMR spectra were recorded on a Varian HR-60 spectrometer at 56.4 MHz with trichlorofluoromethane as the internal reference.

Thermal 1,3-Dipolar Cycloreversion of 3,4-Diacylfuroxans. General Procedure. A solution of the furoxan and at least 2 stoichiometric equiv of dipolarophile were heated in toluene under reflux for 18 h. Reactions with gaseous dipolarophiles were conducted in a Hastelloy bomb at 100 °C and autogenous pressure. The toluene solvent was removed in vacuo to afford the crude cycloadducts.

17α-[[4,5-Bis(trifluoromethyl)-3-isoxazolyl]carbonyl]-17β-acetoxyandrost-4-en-3-one (3). From 0.200 g of **1**[1] and 3 g of hexafluoro-2-butyne there was obtained 0.105 g (37%) of **3** after chromatography on Florisil with 1:9 acetone–hexane and recrystallization from acetone–hexane: mp 151–153 °C (from acetone–hexane); ν_{max} (KBr) 1740, 1680, 1625, 1610 cm^{-1}; λ_{max} (C_2H_5OH) 238 nm (ε 17 800), 315 (153); $[\alpha]^{25}_D$ (C_2H_5OH) +77° (*c* 0.20 g/100 mL); ^{1}H NMR ($CDCl_3$) δ 1.20 (s, 6 H, C-18 and C-19 CH_3), 2.03 (s, 3 H, $OCOCH_3$), 2.33 (m, 2 H, C-2 H), 5.74 (d, *J* = 1 Hz, 1 H, C-4 H).

Anal. Calcd for $C_{27}H_{29}F_6NO_5$: C, 57.85; H, 5.03; N, 2.50. Found: C, 57.63; H, 5.39; N, 2.56.

2-Acetoxy-2-bornyl 5,5-Bis(trifluoromethyl)-1,4,2-dioxazol-3-yl Ketone (7). Reaction of 1.59 g of **5**[1] and 10 g of hexafluoroacetone (**Caution**: mutagenic and fetotoxic agent)[24] afforded after chromatography on silica gel with $CHCl_3$ 2.0 g (80%) of **7**: bp 76 °C (0.2 mm); ν_{max} ($CHCl_3$) 1740, 1600 cm^{-1}; λ_{max} (C_2H_5OH) 239 nm (ε 3820), 320 (80); ^{1}H NMR ($CDCl_3$) δ 0.84 (s, 3 H, CH_3), 1.0–2.7 (br m, 7 H, bornane ring H), 1.07 (s, 3 H, CH_3), 1.10 (s, 3 H, CH_3), 2.04 (s, 3 H, $OCOCH_3$); ^{19}F NMR ($CDCl_3$) −4565 Hz.

Anal. Calcd for $C_{17}H_{19}NO_5F_6$: C, 47.31; H, 4.41; N, 3.25. Found: C, 47.73; H, 4.40; N, 3.30.

2-Acetoxy-2-adamantyl 4,5-Bis(trifluoromethyl)-3-isoxazolyl Ketone (8). From 1.59 g of **5** and 5.0 g of hexafluoro-2-butyne there was obtained 2.50 g (96%) of **8**: mp 88–88.5 °C (from pentane); ν_{max} ($CHCl_3$) 1725, 1640, 1250–1200 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.90 (s, 3 H, CH_3), 0.9–3.0 (br m, 7 H, ring H), 1.03 (s, 3 H, CH_3), 1.13 (s, 3 H, CH_3), 2.03 (s, 3 H, $OCOCH_3$); ^{19}F NMR ($CDCl_3$) −3222 Hz (q, *J* = 8 Hz, 3 F, CF_3); λ_{max} (C_2H_5OH) 225 nm (sh, ε 2100), 322 (76).

Anal. Calcd for $C_{18}H_{19}NO_4F_6$: C, 50.58; H, 4.45; N, 3.28; F, 27.60. Found: C, 50.12; H, 4.36; N, 3.22; F, 27.23.

2-Acetoxy-2-bornyl 5-(Carbomethoxy)-3-isoxazolyl Ketone (10). From 0.270 g of **5** and 0.286 g of methyl propiolate there was obtained 0.350 g (100%) of **10**: mp 110–111 °C (from pentane); ν_{max} ($CHCl_3$) 1740, 1590 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.93 (s, 3 H, CH_3), 1.02 (s, 3 H, CH_3), 1.15 (s, 3 H, CH_3), 1.0–3.0 (br m, 7 H, bornane ring H), 2.07 (s, 3 H, $OCOCH_3$), 4.00 (s, 3 H, CO_2CH_3), 7.23 (s, 1 H, isoxazole 4-H); λ_{max} (C_2H_5OH) 245 nm (ε 4400), 322 (125).

Anal. Calcd for $C_{18}H_{23}NO_6$: C, 61.88; H, 6.64; N, 4.01. Found: C, 61.86; H, 6.60; N, 3.96.

2-Acetoxy-2-bornyl 4-Nitro-3-isoxazolyl Ketone (12). From 2.65 g of **5** and 1.16 g of **23**[13] was obtained after chromatography on silica gel with $CHCl_3$ 1.89 g (50%) of **12**: mp 137–138 °C (from methanol); ν_{max} ($CHCl_3$) 1740, 1570, 1540, 1300 cm^{-1}; λ_{max} (C_2H_5OH) 245 nm (ε 4100), 309 (336); ^{1}H NMR ($CDCl_3$) δ 0.92 (s, 3 H, CH_3), 0.95 (s, 3 H, CH_3), 1.12 (s, 3 H, CH_3), 0.8–2.3 (br m, 7 H, bornane ring H), 9.33 (s, 1 H, isoxazole 5-H).

Anal. Calcd for $C_{16}H_{20}N_2O_6$: C, 57.14; H, 5.99; N, 8.37. Found: C, 57.14; H, 5.98; N, 8.27.

Dimethyl 3-(*O*-Benzoylbenzoylformaldoximino)isoxazole-4,5-dicarboxylate (15). From 1.47 g of **13**[20] and 1.42 g of dimethyl acetylenedicarboxylate there was obtained a mixture which was chromatographed on silica gel with $CHCl_3$. Fractions 5–13 were recrystallized from benzene–cyclohexane to yield 0.937 g (43%) of **15**: mp 96.5–98 °C; ν_{max} ($CHCl_3$) 1755, 1675, 1600 cm^{-1}; λ_{max} (C_2H_5OH) 224 nm (ε 23 500), 242 (22 400); ^{1}H NMR ($CDCl_3$) δ 3.65 (s, 3 H, CO_2CH_3), 4.03 (s, 3 H, CO_2CH_3), 6.3–6.7 (br m, 6 H, meta and para C_6H_5H), 6.92 (m, 2 H, *o*-C_6H_5H), 7.32 (m, 2 H, *o'*-C_6H_5H).

Anal. Calcd for $C_{22}H_{16}N_2O_8$: C, 60.55; H, 3.70; N, 6.42. Found: C, 60.43; H, 3.58; N, 6.49.

Bis(*O*-benzoylbenzoylformaldoximino)furoxan (21). From 5.88 g of **13**[9] there was obtained 5.1 g (87%) of **21**, mp 184–186 °C (from benzene–pentane) (lit.[21] mp 187 °C). The IR spectrum was superimposable with an IR spectrum of authentic **21**.[22]

α-[(*p*-Tolyloxy)imino]-α-(4-acetyl-5-phenyl-3-isoxazolyl)-4-methylacetophenone (23). From 3.22 g of **22**[20] and 2.88 g of 4-phenyl-3-butyn-2-one[25] there was obtained, after chromatography on silica gel with $CHCl_3$, 3.05 g (50%) of **23**: mp 147–148 °C (from pentane); ν_{max} ($CHCl_3$) 1765, 1667, 1600, 1575 cm^{-1}; λ_{max} (C_2H_5OH) 259 nm (ε 26 100); ^{1}H NMR ($CDCl_3$) δ 2.18 (s, 3 H, $COCH_3$), 2.36 (s, 3 H, CH_3), 2.44 (s, 3 H, CH_3), 7.1–8.4 (br m, 13 H, phenyl H).

Anal. Calcd for $C_{28}H_{22}N_2O_5$: C, 72.09; H, 4.75; N, 6.01. Found: C, 72.14; H, 4.76; N, 6.04.

α-[(*p*-Tolyloxy)imino]-α-(5-phenyl-3-isoxazolyl)-4′-methylacetophenone (24). From 1.61 g of **22** and 1.02 g of phenylacetylene there was obtained, after chromatography on silica gel with benzene, 0.62 g (29%) of **24**: mp 132.5–133.5 °C (from pentane); ν_{max} ($CHCl_3$) 1755, 1680, 1600, 1575 cm^{-1}; λ_{max} (C_2H_5OH) 262 nm (ε 38 200); ^{1}H NMR ($CDCl_3$) δ 2.42 (s, 6 H, *p*- and *p'*-CH_3), 7.06 (s, 1 H, isoxazole 4-H), 7.2–8.2 (br m, 13 H, aromatic H).

Anal. Calcd for $C_{26}H_{20}N_2O_4$: C, 73.57; H, 4.75; N, 6.60. Found: C, 73.34; H, 4.76; N, 6.41.

2,2-Bis(trifluoromethyl)-5-[(1-acetoxycyclohexyl)carbonyl]-1,3,4-dioxazole (27a). From 8.44 g of **25a**[7] and 16.0 g of hexafluoroacetone there was obtained a liquid which was chromatographed on silica gel with $CHCl_3$. Fractions 9–15 contained a liquid which was 2.30 g (15%) of **27a**: bp 62 °C (0.25 mm); ν_{max} (liquid film) 1740, 1620, 1250–1200 cm^{-1}; ν_{max} (C_2H_5OH) 235 nm (ε 3400), 313 (60); ^{1}H NMR ($CDCl_3$) δ 2.05 (s, 3 H, $OCOCH_3$), 1.5–2.15 (br m, 10 H, ring H); ^{19}F NMR ($CDCl_3$) −4555 Hz (s, CF_3); mass spectrum (70 eV), calcd *m/e* 377.0698, found 377.0707.

Anal. Calcd for $C_{13}H_{13}NO_5F_6$: C, 41.44; H, 3.48; N, 3.75; F, 30.49. Found: C, 41.67; H, 3.76; N, 3.72; F, 29.85.

2,2-Bis(trifluoromethyl)-5-[[(1-acetoxycyclohexyl)carbonyl][[[(1-acetoxycyclohexyl)carbonyl]oxy]imino]methyl]-1,3,4-dioxazole (26a). Fractions 11–15 from the chromatography described in the preparation of **27a** above were combined and recrystallized from pentane: yield 9.07 g (78%);

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mp 83–84 °C; ν_{max} ($CHCl_3$) 1815, 1740, 1250–1200 cm^{-1}; λ_{max} (C_2H_5OH) 214 nm (ϵ 9820), 325 (70); ^1H NMR δ 1.7 (br m, 20 H, ring H), 2.05 (s, 3 H, $OCOCH_3$), 2.10 (s, 3 H, $OCOCH_3'$); ^{19}F NMR ($CDCl_3$) −4553 Hz.

Anal. Calcd for $C_{23}H_{26}N_2O_9F_6$: C, 46.90; H, 4.42; N, 4.75; F, 19.35. Found: C, 46.99; H, 4.45; N, 4.75; F, 19.38.

2,2-Bis(trifluoromethyl)-5-[2-acetoxy-2-adamantyl)carbonyl]-1,3,4-dioxazole (27b). From 1.32 g of **25b**[7] and 16 g of hexafluoroacetone there was obtained 1.97 g of a liquid. Bulb-to-bulb distillation afforded 1.28 g [60%, 79% on the basis of **25b** consumed (vide infra)] of **27b**: bp 90–100 °C (0.1 mm); ν_{max} (liquid film) 1740, 1620, 1250–1200 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.6–2.8 (br m, 13 h, adamantyl H), 2.18 (s, 3 H, $OCOCH_3$); ^{19}F NMR (94.1 MHz, $CDCl_3$) −84885 Hz.

2,2-Bis(trifluoromethyl)-5[[(2-acetoxy-2-adamantyl)carbonyl][[[(2-acetoxy-2-adamantyl)carbonyl]oxy]imino]methyl]-1,3,4-dioxazole (26b). The residue from the distillation described in the isolation of **27b** above was chromatographed on silica gel with $CHCl_3$. In addition to 0.32 g of starting furoxan **25b**, there was obtained 0.165 g (9.5%, 13% on the basis of **25b** consumed) of **26b**: mp 184.5–186 °C (from pentane); ν_{max} (KBr) 1835, 1740, 1665, 1610, 1250–1200 cm^{-1}; λ_{max} (C_2H_5OH) 213 nm (ϵ 10 000), 335 (83); ^1H NMR ($CDCl_3$) δ 1.8–2.65 (br m, 28, adamantane ring H), 2.06 (s, 3 H, $OCOCH_3$), 2.13 (s, 3 H, $OCOCH_3'$); ^{19}F NMR ($CDCl_3$) −4500 Hz (s, CF_3).

Anal. Calcd for $C_{31}H_{34}N_2O_9F_6$: C, 53.85; H, 4.96; N, 4.05; F, 16.50. Found: C, 53.74; H, 4.94; N, 3.99; F, 16.51.

3-[[(1-Acetoxycyclohexyl)carbonyl][[[(1-acetoxycyclohexyl)carbonyl]oxy]imino]methyl]-4,5-bis(trifluoromethyl)isoxazole (28). From 4.22 g of **25a** and 5.0 g of hexafluoro-2-butyne there was obtained from fractions 4–8 of silica gel/$CHCl_3$ chromatography 2.63 g (45%) of **28**: mp 89.5–90 °C (from pentane); ν_{max} ($CHCl_3$) 1800, 1740, 1625 cm^{-1}; ν_{max} (C_2H_5OH) 220 nm (sh, ϵ 7000), 327 (55); ^1H NMR ($CDCl_3$) δ 1.4–1.8 (br m, 20 H, cyclohexane ring H), 1.94 (s, 3 H, $OCOCH_3$), 2.16 (s, 3 H, $OCOCH_3$); ^{19}F NMR ($CHCl_3$) −3230 (q, J = 6 Hz, 3 H, CF_3), −3560 Hz (q, J = 6 Hz, 3 H, CF_3).

Anal. Calcd for $C_{24}H_{26}N_2O_8F_6$: C, 49.30; H, 4.46; N, 4.79. Found: C, 49.42; H, 4.51; N, 4.70.

Registry No. 1, 75768-35-3; 3, 75768-36-4; 5, 75768-37-5; 7, 75768-38-6; 8, 75768-39-7; 10, 75768-40-0; 12, 75768-41-1; 13, 6635-54-7; 15, 75768-42-2; 21, 75768-42-3; 22, 21443-49-2; 23, 75768-44-4; 24, 75768-45-5; 25a, 75768-46-6; 25b, 75768-47-7; 26a, 75768-48-8; 26b, 75768-49-9; 27a, 75768-50-2; 27b, 75768-51-3; 28, 75768-52-4; hexafluoro-2-butyne, 692-50-2; hexafluoroacetone, 684-16-2; methyl propiolate, 922-67-8; dimethyl acetylenedicarboxylate, 762-42-5; 4-phenyl-3-butyn-2-one, 1817-57-8; phenylacetylene, 536-74-3.

Reaction of Some 1-(*p*-Tolylsulfonyl)-2,3,3-trialkyldiaziridines with Aryl Isocyanates and Benzoyl Isocyanate

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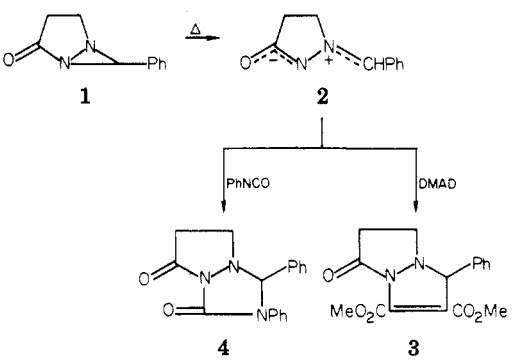
1-(*p*-Tolylsulfonyl)-2-alkyl-3,3-pentamethylenediaziridines react with aryl isocyanates and benzoyl isocyanate to form 1-alkyl-2-(*p*-toluenesulfonyl)-4-aryl-5,5-pentamethylene-1,2,4-triazolidin-3-ones. The structure of one of the latter compounds was established by a single-crystal X-ray diffraction study. 1-(*p*-Tolylsulfonyl)-2,3-dialkyldiaziridines fail to react with isocyanates.

Diaziridines substituted in the 1- or 1,2-positions with electron-withdrawing groups are prone to form azomethine imines which undergo reactions typical of 1,3-dipoles. For example, heating **1** neat affords a 78% yield of **2**.[1,2] Compound **2** reacts with dimethyl acetylenedicarboxylate (DMAD) and phenyl isocyanate to give **3** and **4**, respectively[3] (Scheme I).

In many cases the formation of the azomethine imine from the diaziridine must be inferred by trapping experiments with 1,3-dipolarophiles[4] or nitrones,[5] isomerizations to ring-expanded products,[6-8] interaction with neighboring groups,[9,10] and rearrangements to open-chain isomeric hydrazones.[9,11,12]

Scheme I



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