to **6** generated from racemic **3** and observing no line broadening (maximum mole ratio **6**/shift reagent 0.63:1; δ 8.72, H_a; 6.50, OCH_3). The enantiomeric purity of **6** generated from resolved **3** was determined by use of the chiral shift reagent $Eu(hfc)_3$ (mole ratio **6**/shift reagent 1.25:1, $\Delta\delta H_a = 0.27$; $\Delta\delta OCH_3 = 0.06$, $CDCl_3$) and was found to be 8:1 (downfield/upfield signal, respectively).

Thus, benzodihydrofuran **2a** undergoes a stereospecific photorearrangement to phenol **3**. Clearly, a long-lived diradical (or zwitterionic) intermediate such as **4** is incompatible with these experimental results. We suggest that photoexcited **2a** undergoes a concerted [1,3] sigmatropic rearrangement to **5**, and **5** rearranges (thermal, photochemical?) as shown.[20] Experiments designed to conclusively establish the intermediacy of cyclopropyl dienones are currently in progress.

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(19) ^1H NMR for **7:** δ 4.15 (H_a, sharp singlet), 6.19–6.68 (H_b, H_c, multiplet); irradiation at δ 2.08 causes a collapse of multiplet to AB quartet, $J_{bc} = 10$ Hz. We were delighted to find the high degree of stereoselectivity in the conversion **3** → **6;** presumably the neighboring carbomethoxy group is of importance in the stereochemical control of this reaction.
(20) The photoconversion of verbenone to chrysanthenone [J. J. Hurst and G. H. Whitham, *J. Chem. Soc.*, 2864 (1960)] involves the [1,3] migration of a quaternary carbon atom; in this case, stereochemical analysis [G. W. Shaffer and M. Pesaro, *J. Org. Chem.*, **39**, 2489 (1974)] demonstrates that a nonconcerted diradical mechanism operates. J. M. Burns, M. E. Ashley, G. C. Crockett, and T. H. Koch, *J. Am. Chem. Soc.*, **99**, 6924 (1977) report a "highly stereospecific" [1,3] rearrangement of 2-ethoxypyrrolin-5-ones to ethoxycyclopropyl isocyanates (98% retention of stereochemistry). These workers favor a mechanism involving "a short-lived singlet diradical intermediate which ring closes by a rate more than an order of magnitude faster than the rate for bond rotation."
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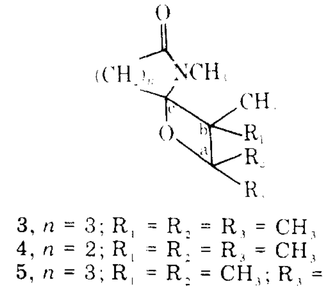
Photoaddition of Olefins to Cyclic Imides: Intermolecular Oxetane Formation and Ring Expansion[1]

Summary: Aliphatic cyclic imides undergo photochemical [2 + 2] addition with olefins to form "imide–oxetanes" whose structures and reactions are elucidated, whereas aromatic cyclic imide gave rise to ring-expanded products.

Sir: The photoreactions of cyclic imides have recently been the subject of considerable study.[2,3] Synthetic work has been concerned with structural variations of the imide substrates, mainly on the basis of the Norrish type II processes, leading to syntheses of a wide variety of nitrogen heterocycles which include even macrocycles.[3,4] Very recently the photoadditions of some olefin and diene systems to the cyclic imides have also been reported and the scope of such reactions involving either the imide carbonyl or the N-C bond is of current interest.[5-7] Earlier it was postulated that the photochemical behavior of the imide carbonyl, at least formally, closely parallels that of the simple ketone system.[3,8] However, this parallelism has been incomplete because the Paterno–Büchi reaction, one of the typical reactions of carbonyl compounds,[9] has not been observed except that intramolecular oxetane formation has recently been described.[5] We now wish to report that the intermolecular photochemical [2 + 2] addition reaction of the aliphatic cyclic imides **1** and olefins **2** lead to isolation of oxetanes, whereas similar reactions of aromatic imide lead to ring expansion as a result of additive incorporation of the olefinic unit.

In a typical run, a solution of **1a** (0.1 M) and 2,3-dimethyl-2-butene (**2a**) (0.5 M) in acetonitrile was irradiated[10] for 10

Scheme I



1a, $n = 3$
b, $n = 2$

2a, $R_1 = R_2 = R_3 = CH_3$
b, $R_1 = R_2 = CH_3$; $R_3 = H$
c, $R_1 = CH_3$; $R_2 = R_3 = H$
d, $R_1 = R_3 = H$; $R_2 = CH_3$
e, $R_1 = R_2 = H$; $R_3 = CH_3$

3, $n = 3$; $R_1 = R_2 = R_3 = CH_3$
4, $n = 2$; $R_1 = R_2 = R_3 = CH_3$
5, $n = 3$; $R_1 = R_2 = CH_3$; $R_3 = H$
6, $n = 3$; $R_1 = H$; $R_2 = R_3 = CH_3$
7, $n = 3$; $R_1 = CH_3$; $R_2 = R_3 = H$
8, $n = 3$; $R_1 = R_2 = H$; $R_3 = CH_3$

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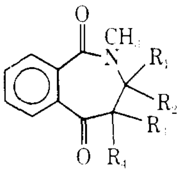
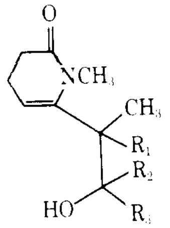
h. Alumina chromatography followed by recrystallization afforded **3** (mp 120–121 °C)[12] in 65% yield,[13] whose oxetane structure was determined based on spectral evidence: ^{13}C NMR ($CDCl_3$) 48 (C_b), 82 (C_a), 96 (C_c), 170 ppm (C=O); ^1H NMR ($CDCl_3$) five methyls and 1.6–2.6 ppm [m, 6 H, $(CH_2)_3$]; mass spectrum *m/e* 84 (dimethylbutene) (Scheme I). Similarly, **1b**[10b] gave the norhomologous oxetane **4** (mp 62–64 °C, 6 h, 71%): ^{13}C NMR ($CDCl_3$) 48 (C_b), 82 (C_a), 101 (C_c), 174 ppm (C=O); ^1H NMR ($CDCl_3$) five methyls and 1.7–2.8 ppm (m, 4 H, CH_2CH_2). The reaction of **1a** with 2-methyl-2-butene (**2b**) under similar conditions afforded a mixture (76%) which consists of mainly **5** [^1H NMR (CCl_4) 4.3 (q, 1 H, J = 6 Hz, C_a-**H**)] and small amount of **6**, suggesting that the oxygen is attached to the less-substituted carbon of the olefin. This regioselectivity was further confirmed by the reaction of **1a** with isobutene **2c**, which gave exclusively **7** in 71% yield:[13] ^1H NMR (CCl_4) 3.96, 4.20 (AB, 2 H, J = 6 Hz, C_a-H_2). The above results demonstrate that aliphatic cyclic imides undergo intermolecular oxetane formation in fairly good yields.

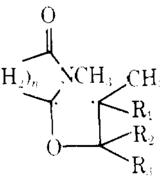
By contrast, *N*-methylphthalimide has been found to undergo addition to a series of alkenes, including **2c** and **2d**, to give ring-expanded products **9**[14,15] in place of oxetane. The structure of **9a** (mp 88.5–89.5 °C, 10 h, 81%[13]) was confirmed by comparison with an authentic specimen prepared from *N*-isobutylphthalimide by photolysis and subsequent methylation.[8b] It is of interest that the behavior of the excited aromatic cyclic imide toward olefin is distinct from that of the aliphatic counterparts. Mazzocchi et al. have recently found that *N*-alkylphthalimides undergo photochemical addition of dienes whereby the diene adds with its terminal carbon attached to nitrogen, suggestive of an addition to the N–C(O) bond.[6]



9a, $R_1 = R_2 = H$; $R_3 = R_4 = CH_3$
b, $R_1 = R_3 = H$; $R_2 = R_4 = CH_3$



10a, $R_1 = R_2 = H$; $R_3 = CH_3$
b, $R_1 = CH_3$; $R_2 = R_3 = H$



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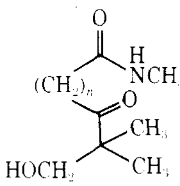

12a, *n* = 3
b, *n* = 2

The quantum yield of the oxetane formation is 0.19 in 0.5 M isobutene (**2c**) for **1a**, one order of magnitude higher than the value (0.03) for the addition of **2c** to *N*-methylphthalimide.[16] Irradiation in the presence of isoprene quantitatively quenched the reaction of **1a** and **2c**, indicative of an involvement of the triplet state.[17] The reaction of **1a** with **2d** and **2e** both produced the same mixture (1:1) of the two isomers **8**, as measured by ^1H NMR of their ring-opened products **10a**, to show scrambling of the olefinic geometry. Thus the mechanism of the oxetane formation may involve a nonconcerted addition of the imide carbonyl to the π system to form a biradical **11**, which will be a more stable one of the possible two; namely, the less-substituted carbon attached to the oxygen **7** in agreement with the observed regioselectivity.[18]

When heated at 170 °C for 0.5 h, **7** was transformed into an enamide **10b** in a good yield, which was also isolated from **7** on long standing at room temperature together with a hydrolyzed product **12a**. The amido keto alcohol **12a** was quantitatively obtained when **7** was treated with acid.[19] A similar keto alcohol **12b** was obtained in 80% yield when **1b** was irradiated with **2c** in acetonitrile–water (9:1). In view of recent general interests in chemical behavior of oxetanes,[20] it is worth noting that the thermal reactions of these "imide–oxetanes" follow this metathesis course and not the cycloreversion, although their mass spectra indicate the latter fragmentations. Systematic studies are required to elucidate chemical properties of these imide–oxetanes, formed inter- and intramolecularly, toward their possible synthetic utilization.

Since experiments with acrylonitrile gave no product, the cycloaddition is likely to occur only with electron-rich olefin, which may be a characteristic feature of the cross-conjugated imide carbonyl system involving nitrogen.[21] The different modes of addition between aliphatic and aromatic ones could be in part related to their possible different excited configurations.[22] This photocycloaddition described here completes the analogy between the photochemistry of simple carbonyls[25] and imides.[3]

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(10) (a) Irradiation was performed using a quartz immersion well in acetonitrile solution degassed with nitrogen with a 60-W low-pressure mercury lamp[11] and a 100-W high-pressure mercury lamp for the aliphatic imides and the aromatic imide, respectively, through quartz if not otherwise stated. (b) Only in this case the imide (0.01 M) and the olefin (0.1 M) were used.

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(12) All new compounds showed reasonable spectral properties (^1H NMR, IR, UV, and mass spectra) and elemental analytical data.

(13) This yield is based on the recovered starting material. Under the conditions in this work, the degree of conversion of imides was in the range of 60–70%.

(14) While this manuscript was in preparation, Mazzocchi et al. and Maruyama et al. reported the photoaddition of olefins to phthalimides; (a) P. H. Mazzocchi, S. Minamikawa, and M. J. Bowen, *J. Org. Chem.*, **43**, 3079 (1978); (b) K. Maruyama and Y. Kubo, *Chem. Lett.*, 769 (1978).

(15) Mazzocchi et al. have studied also the stereochemistry of the olefin addition: P. H. Mazzocchi, private communication.

(16) The light intensity was determined in Vycor and Pyrex tubes for aliphatic and aromatic imides, respectively, with a merry-go-round apparatus using potassium ferrioxalate as actinometer. The formation of **7** was monitored by acid-catalyzed transformation into **12a**[19] and the gas chromatographic determination of the latter.

(17) Since no substantial reaction was observed when **1a** was irradiated in acetonitrile containing isoprene, this quenching may primarily involve triplet–triplet energy transfer. The Stern–Volmer plots gave a linear slope up to 0.2 M of isoprene in acetonitrile from which the $k_q\tau$ value was found

to be 21 M^{-1}. Very weak fluorescence of **1** precluded fluorescence quenching studies.

(18) This interpretation is rather oversimplified and does not exclude the intermediacy of charge-transfer complexes or exciplexes.

(19) A solution of **7** in acetone containing toluenesulfonic acid (0.1 equiv) was stood overnight at room temperature. The transformation was quantitative as measured by ^{1}H NMR.

(20) G. Jones II and J. C. Staires, *Tetrahedron Lett.*, 2099 (1974); G. Jones II and H. H. Kleinman, *ibid.*, 2103 (1974); C. W. Funke and H. Cerfontain, *J. Chem. Soc., Perkin Trans. 2,* 1902 (1976).

(21) Presumable electron-deficient nature of the excited imide carbonyl does not permit forming exciplexes to electron-deficient olefins such as those considered for alkanones.[22]

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(23) Aliphatic cyclic imides appear to react from the n,π^* state, based on a preliminary wavelength dependency study,[2,3] whereas excited phthalimides are of largely π,π^* nature.[2,3,24]

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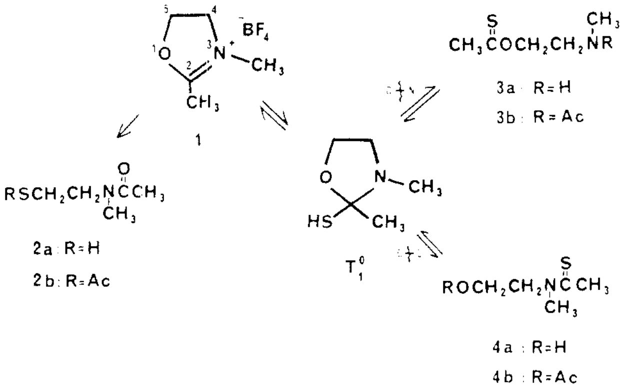
Breakdown of Hemiorthothioamide Tetrahedral Intermediates[1]

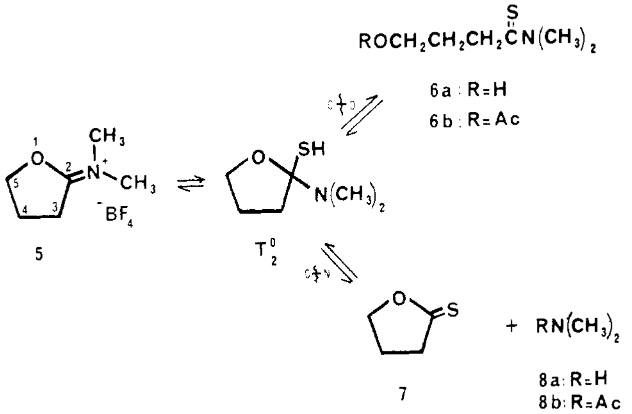
Summary: The sulfhydrolyses of 2,*N*-dimethyl-1,3-oxazolinium fluoroborate (1) and *N,N*-dimethyliminobutyrolactonium fluoroborate with anhydrous sodium hydrosulfide in solvent acetone at −78 °C were found to involve the preferential cleavage of the C–N bond rather than the C–O bond.

Sir: Tetrahedral intermediates play a central role in a wide variety of enzymatic and nonenzymatic reactions.[2] The involvement of such intermediates in enzymatic reactions, e.g. those involving α-chymotrypsin, carboxypeptidase, and lysozyme,[3] has been deduced by analogy with nonenzymatic intermolecular as well as intramolecular model reactions involving similar tetrahedral intermediates. Since the pioneering work of Bender,[4] transient tetrahedral intermediates have been invoked in the lytic reactions of carboxylic esters,[5] lactones,[6] amides,[7] thiolo[8] and thiono esters,[9] thioamides,[10] and amidines.[11] Tetrahedral intermediates have been detected spectroscopically,[12] trapped,[13] or isolated.[14] We report on the kinetic breakdown of hemiorthothioamide tetrahedral intermediates of the type $RC(SH)(OR)(NR_2)$ and on the first intramolecular O → N thionacyl transfer. These intermediates, which, in principle, may form during the alcoholysis of thioamides and aminolysis of thiono esters, were generated directly in an aprotic solvent (acetone) from anhydrous sodium hydrosulfide and two model imino ether salts (1 and 5).[15]

Scheme I



Scheme II



TLC analysis (at room temperature) of the reaction mixture obtained from equimolar amounts of 2,*N*-dimethyl-1,3-oxazolinium fluoroborate[16] (1) and anhydrous sodium hydrosulfide[17] in acetone at −78 °C revealed **4a** (Scheme I) as the only organic product ($2R_f$ 0.48, $CHCl_3$–MeCN (1:1 v/v)): IR($CHCl_3$) 3500–3200, 1510 cm^{-1}; NMR ($CDCl_3$) δ 2.69–2.75 (3 H, 2 s, $CH_3C{=}S$), 3.38, 3.53 (3 H, 2 s, $C\mathbf{H}_3N$), 3.92 (1 H, s, O**H**), 4.05, 4.35 (4 H, m, OCH_2CH_2N). However, TLC analysis of the latter reaction mixture *after* low-temperature trapping (AcCl/pyridine, −78 °C) showed **3b** as the major product along with **4b** (**3b/4b** ~9:1). **3b:** R_f 0.32, $CHCl_3$–MeCN (3:1 v/v); IR ($CHCl_3$) 1660, 1280 cm^{-1}; NMR ($CDCl_3$) δ 2.20, 2.25 (3 H, 2 s, CH_3CO), 2.72 (3 H, s, $CH_3C{=}S$), 3.13, 3.23 (3 H, 2 s, CH_3N), 3.83–4.05 (2 H, m, CH_2N), 4.76–4.95 (2 H, m, CH_2O). **4b:** R_f 0.61, $CHCl_3$–MeCN (3:1 v/v); IR ($CHCl_3$) 1760, 1540, 1300 cm^{-1}; NMR ($CDCl_3$) δ 2.12 (3 H, s, CH_3CO), 2.71, 2.78 (3 H, 2 s, $CH_3C{=}S$), 3 40, 3.54 (3 H, 2 s, CH_3N), 4.36–4.54 (4 H, m, OCH_2CH_2N). At room temperature, the reaction of **1** and NaSH led to **4a,** along with **2a** (**4a/2a** ratio ~3:2). **2a:** R_f 0.35, $CHCl_3$–MeCN (1:1 v/v); IR ($CHCl_3$) 3450, 2520, 1640 cm^{-1}; NMR ($CDCl_3$) δ 1.34 (1 H, t, J = 8.0 Hz, S**H**), 2.08, 2.13 (3 H, 2 s, CH_3CO), 2.67–2.91 (2 H, m, CH_2N), 2.91, 3.05 (3 H, 2 s, CH_3N), 3.40–3.66 (2 H, m, CH_2S).[18]

TLC analysis of the reaction mixture from equimolar amounts of anhydrous NaSH and *N,N*-dimethyliminobutyrolactonium fluoroborate[16] (**5**) in acetone at room temperature revealed **6a** (Scheme II) as the exclusive sulfur-containing component:[20] R_f 0.46, $CHCl_3$–MeCN (1:1 v/v); IR ($CDCl_3$) 3400, 1525, 1395, 1280, 1050 cm^{-1}; NMR ($CDCl_3$) δ 1.72–2.24 (m, 2 H, CCH_2C), 2.96 (m, 2 H, $CH_2C{=}S$), 3.38 (s, 3 H, NMe), 3.53 (s, 3 H, NMe), 3.74 (t, J = 6.5 Hz, 2 H, CH_2O). However, when the reaction was run at −78 °C and the mixture acetylated at −78 °C (AcCl/pyridine), compounds **7** and **8b** were the major detectable products. **7:** R_f 0.36, $CHCl_3$–MeCN (99.5:0.5 v/v); IR (neat) 1460, 1380, 1270, 1180, 920, 740 cm^{-1}; NMR ($CDCl_3$) δ 2.36 (2 H, q, J = 6.5 Hz, CCH_2C), 3.10 (2 H, t, J = 6.5 Hz, $CH_2C{=}S$), 4.70 (2 H, t, J = 6.5 Hz, CH_2O).

As shown in Scheme I, the nucleophilic attack on **1** at −78 °C is exclusively at C-2, and the resulting transient tetrahedral intermediate T_1^0,[21] under kinetic control, breaks down by cleavage of the C_2–N bond to yield **3a.** The latter, at −78 °C, is efficiently trapped as the acetamide **3b;** in the absence of an acetylating agent, as the temperature is increased from −78 °C to room temperature, **3a** undergoes an unprecedented intramolecular O → N thionacyl transfer, most probably through the intermediate T_1^0, to yield the more stable isomer **4a.**[22]

Similarly, the initially formed intermediate T_2^0 [21] undergoes kinetic breakdown by cleavage of the C_2–N bond (in preference to C_2–O) to yield **7** and **8a** (Scheme II); after acetylation (−78 °C) the products are **7** and **8b.** In the absence of acetylating agent at room temperature the more stable

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