

completely and *p*-nitroanisole and *p*-anisidine were obtained as an equimolar mixture. The yield of both compounds was 80%.

Reaction of *N*-*p*-Anisylaziridine (13) in Microsomal Suspension. The solution of *N*-*p*-anisylaziridine in ethanol (20 μ l, 0.01 mmol) was added in the complete system and incubated for 60 min at 37 °C with moderate shaking. NaOH (2 N, 2 ml), 2 ml of CH₂Cl₂, and *n*-C₁₄H₃₀ and *n*-C₁₈H₃₈ as internal references were added. After vigorous shaking and centrifuge, CH₂Cl₂ solution was supplied to VPC analysis. The recovered aziridine (71%), 0.7% of *p*-nitroanisole, and 0.7% of *p*-anisidine were observed.

Reactions of Aziridines and *m*-Chloroperbenzoic Acid. Aziridine (1 mmol) in 10 ml of CH₂Cl₂ was cooled at 0 °C and 2 mmol of *m*-chloroperbenzoic acid was added. After 1 h, the reaction mixture poured on 30 g of Merck standard Al₂O₃ column was eluted with pentane to obtain the olefin fraction. VPC analysis showed that the reactions proceeded with retention of the configuration and the yields of olefins were usually 30–40%.

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Communications to the Editor

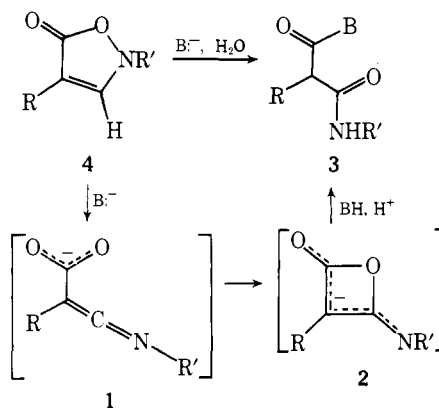
Observation of Ketenimine Carboxylates and Their Conversion to Four-Membered Heterocycles

Sir:

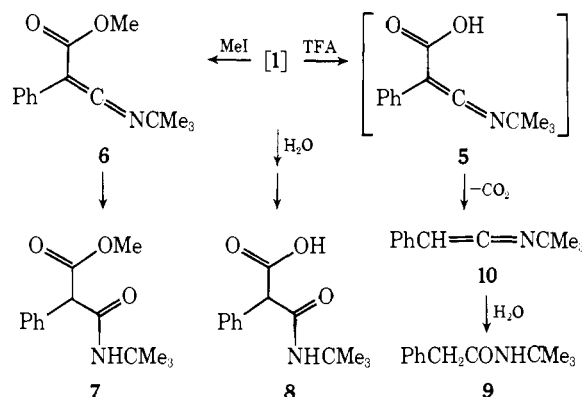
Monoimino derivatives of cyclic malonic anhydrides previously have been proposed as unstable intermediates in heterocumulene cycloadditions.¹ We have now established that ring closure of ketenimine carboxylates (**1**) provides a new, anionic entry to this reactive heterocyclic system. Elimination with ring cleavage, followed by cyclization to give the four-membered ring **2** (Scheme I), was suggested earlier to account for the formation of products of type **3** from isoxazolones having the substitution pattern **4**.² The present results confirm the essential mechanistic features of Scheme I and bring to light an additional rearrangement leading to malonimides.

To demonstrate that the postulated intermediates **1** can be generated by an elimination about the C–N bond of **4**, ring opening studies were conducted with 4-phenyl substituted compounds (**4**, R = Ph) and strong bases in nonnucleophilic media. Definitive infrared spectral evidence for **1** (R' = CMe₃, Ph, or Me; absorptions at 4.95, –C=C=N–, and 6.3 μ , –CO₂[–]) was obtained when the respective starting materials were treated with BuLi or hexamethyldisilazane anion in THF. In the case of the *N*-*tert*-butyl compound, further characterization included the transformations of Scheme II.³ Consistent with Scheme I, the anions **1** were found to undergo conversion to type **3** products. In the reaction of **4** with methoxide, in one case (R = Ph, R' = CMe₃) **1** was detected (ir) as a transient species during the formation of **3** (–B = –OMe). Moreover, when THF solutions of **1** were added to aqueous solutions of diethylamine, the corresponding diamides were obtained in 70–80% yield. However, clean diamide formation did not take place upon addition of amines or amine salts to THF solutions of **1**, apparently because of competing decarboxylation in that solvent.

Scheme I

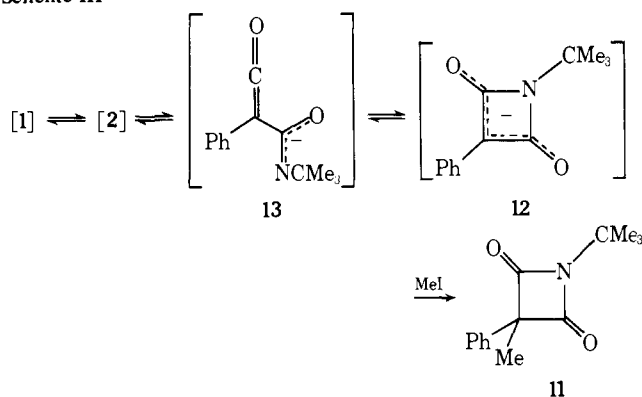


Scheme II



Attempts to utilize nonnucleophilic solvents more polar than THF, in the hope of favoring the pathway of Scheme I over

Scheme III



decarboxylation, led to the detection of a second intermediate. Infrared spectral assay of the reaction of **4** (where R' = Ph or Me) with dimsyl anion in Me₂SO showed new peaks in the carbonyl region,⁴ but no cumulene absorption for **1**. The new bands can be assigned to a second anion formed reversibly from **1**, on the basis of the following results with the *N*-*tert*-butyl substituent. Upon dilution of THF solutions of **1** with HMPA, the ir peak at 4.95 gradually disappeared as absorption for the second anion built up. In accord with a solvent-dependent equilibrium, the spectral change was reversed when more THF was added. In Me₂SO-*d*₆ concurrent ir and NMR assays indicated an apparent equilibrium mixture (1:1 in **1** and the second anion) was achieved within a few hours.⁵ The second anion also formed diamide when solutions were poured into aqueous diethylamine and is more reactive than **1**, as expected for a subsequent intermediate such as **2** of Scheme II. Addition of amine salts to the *N*-*tert*-butyl anion mixture in Me₂SO resulted in the immediate reaction of the second anion, while consumption of **1** requires a few hours. In the same solvent, the reaction of the starting isoxazolone **4** with amines is on the time scale of weeks.

While decomposition of the second anions has prevented their thorough characterization to date, a trapping experiment has revealed that additional transformations beyond the reversible cyclization of Scheme I are accessible to this reactive system. The second anion, where R' = CMe₃, in HMPA was converted to a stable derivative by methylation (MeI).⁶ The molecular weight of the product ruled out a methylated dimer of **1**, and a high-field *C*-methyl signal in the ¹H NMR spectrum was indicative of a delocalized carbanionic precursor such as **2**. However, the methylation product was not sensitive to moisture or even amines, in contrast to the expectation for the *C*-methyl derivative of **2**. Rearrangement to the relatively stable malonimide system⁷ would account for the results, and the presence of a single, low-field, carbonyl carbon signal (173 ppm downfield from Me₄Si) in the ¹³C NMR spectrum (C₆D₆) confirmed that the methylation product was **11**.

The simplest mechanistic rationale for the formation of **11** would be the reversible anionic rearrangement of Scheme III. The second observed anion may well, then, be **12** rather than **2**, although the present evidence does not permit a rigorous conclusion. The absence of new infrared bands in the cumulene region in the polar solvents used excludes substantial concentrations of the free ketene **13**, but solvent-intercepted derivatives remain an additional possibility. Regardless of the structure of the predominant form of the anion in polar solvents, the rearrangement to the malonimide system in the trapping experiments raises the possibility of the ketene **13** as the actual intermediate leading to products of type **3**.

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- (3) The NMR and ir spectra were in accord with all structures shown. For **6**–**9** the properties also either agreed with reported values for the known compounds or satisfactory elemental analyses were obtained.
- (4) In addition to peaks near 6.1 and 6.25 μ where R' = Ph or Me, both anions show an unexpectedly short wavelength band at about 5.65 μ. In the case of R' = CMe₃, only the 5.65 μ absorption is not masked by solvent (HMPA) or remaining **1** (in Me₂SO).
- (5) The composition was invariant over a ninefold concentration range (keeping total ion concentration constant with added NaNO₃), providing possible support for intramolecular cyclization as opposed to an intermolecular reaction.
- (6) Mp 46–47°. Anal. Calcd for C₁₄H₁₇NO₂: C, 72.70; H, 7.41; N, 6.06. Found: C, 72.78; H, 7.63; N, 6.03. Molecular weight: theory, 231; Osmometric, 244; CI M S, 231. NMR (CDCl₃): 1.50 (s, 9), 1.66 (s, 3), 7.2–7.6 (m, 5).
- (7) Infrared carbonyl absorption at 5.75 μ (CHCl₃) agrees with values reported for compounds assigned the malonimide structure.⁸
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Rearrangements of Free Radicals. 5.¹ Sigmatropic and Electrocyclic Reactions of Bicyclo[3.1.0]hexenyl Radical

Sir:

Rearrangements of free radicals have been observed mainly in reactions with small activation energies.² Under these conditions a rearrangement can compete with recombination and disproportionation reactions. Recently¹ we have shown that matrix ESR spectroscopy, which allows the investigation of free radicals as isolated moieties over longer periods of time, provides a tool for studying such reactions even with substantial activation energies. It therefore becomes possible to compare the behavior of analogous closed and open shell molecules and to delineate the special properties of radicals in such reactions. We wish to report a sigmatropic and an electrocyclic reaction of the bicyclo[3.1.0]hexenyl radical (**1**). The properties of **1** in solution were studied previously.³ **1** was obtained by hydrogen abstraction from bicyclo[3.1.0]hex-2-ene⁴ (**2**) with photolytically generated *tert*-butoxy radicals. Its ESR spectrum could be recorded from –100 to +70 °C without appearance of a signal due to a rearranged radical. A thermolysis of **2** in the presence of di-*tert*-butyl peroxide in chlorobenzene at 130 °C yielded 35% benzene as a consequence of an electrocyclic ring opening of **1** to cyclohexadienyl radical.

Bicyclo[3.1.0]hex-2-ene in adamantane as matrix was x-ray irradiated at –196 °C.⁵ At temperatures below –60 °C one observes the ESR spectrum of **1**. Heating the sample in the cavity of the ESR spectrometer above –60 °C produces gradually the spectrum of the cyclohexadienyl radical which had been generated by x-ray irradiation of benzene in adamantane.⁶ The free energy of activation for the rearrangement which could be determined by recording the growth of the signal for the cyclohexadienyl radical as a function of time and temperature amounts to Δ*G*[‡] = 14.5 kcal/mol at –50 °C. Because of competing reactions with very small activation energies it was not possible to observe this rearrangement in solution. The concentration of cyclohexadienyl radical never becomes sufficient for detection by ESR. As a consequence one should be cautious to conclude that the nonobservance of a rearrangement in solution is a sufficient proof against its occurrence.