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Nitrilimines

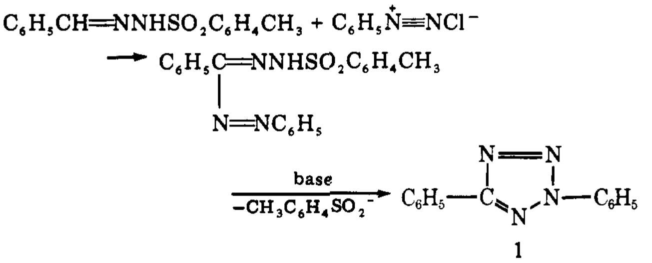
Sir:

Nitrilimines were first prepared by Huisgen and co-workers[1] by thermal decomposition of 2,5-disubstituted tetrazoles and by base-induced elimination of hydrogen halide from hydrazonoyl halides. Their formation was demonstrated by in situ addition to alkynes, alkenes, and nitriles. The synthetic usefulness of the addition reactions of nitrilimines has since then been described in numerous papers including recently reported examples of intramolecular 1,1- and 1,3-cycloaddition reactions[2,3] and intramolecular ring closure.[4] Irradiation of sydnones[5] and tetrazoles[6] investigated in great detail by Schmid and co-workers[7] also affords nitrilimines. However, in all cases the formation of these compounds has been demonstrated only by characteristic reactions. We now report the first preparation of nitrilimines under conditions where they are stable and can be spectrally characterized.

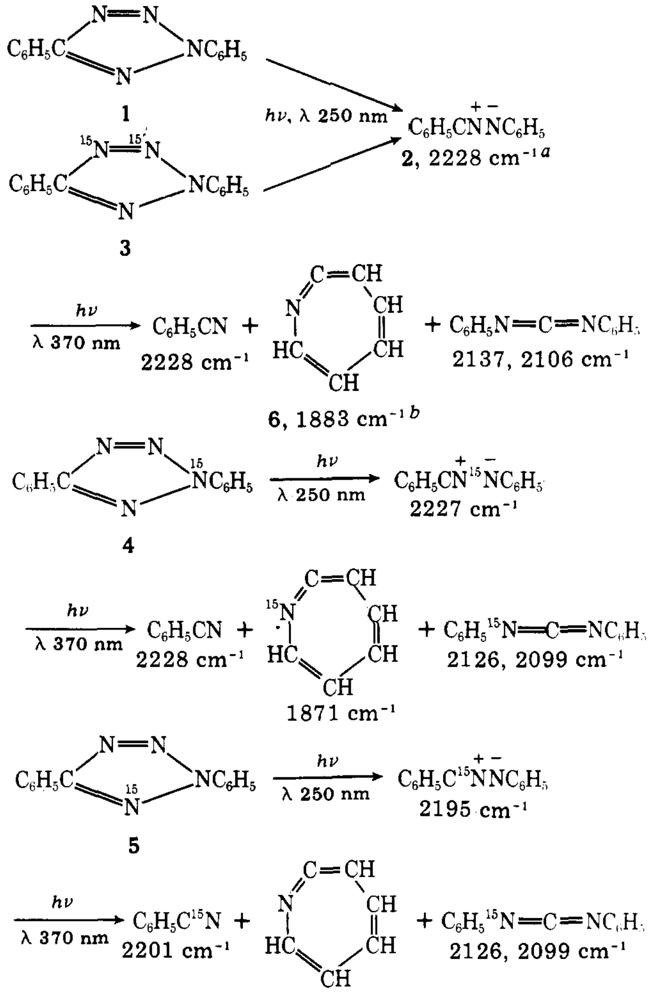
Irradiation (λ 250 nm) of 2,5-diphenyltetrazole (**1**) in EPA (ether–isopentane–ethanol, 5:5:2) or poly(vinyl chloride) (PVC)[8] at 85 K or PVC at 10 K gives, by loss of the N(3)–N(4) atoms (Scheme I), a thermally unstable product with a strong UV absorption at 377 nm (PVC, 85 K, Figure 1). Schmid et al.[9] recently reported a similar observation with the same substrate under similar conditions [2,2-dimethylbutane–pentane, 8:3 (DMBP), 85 K]. While monitoring the formation of products by IR spectroscopy in PVC at 85 K we observed the appearance of a band at 2228 cm^{-1} (Figure 2) which, in addition to a weak signal at 2137 cm^{-1}, assigned to diphenylcarbodiimide,[10] is the only new band in the region open for observation (~1500–2800 cm^{-1}). The 2228-cm^{-1} band is in the region characteristic of heterocumulenes and triple bonds (~1900–2400 cm^{-1}).[11] Among the possibilities for the substance which absorbs at 2228 cm^{-1}, benzonitrile (2228 cm^{-1})[10] can be excluded because it is thermally stable. Phenyl isocyanide (2125 cm^{-1}, CCl_4),[12] diphenyldiazomethane (2041 cm^{-1}, CCl_4),[13] and diphenylcyanamide (2223 cm^{-1})[10] can also be excluded because of their spectral properties as well as thermal stability, which leaves diphenylnitrilimine (**2**) and *N*-isocyanodiphenylamine for further consideration. The last compound is apparently unknown, but the corresponding dialkyl derivatives give rise to absorption bands at ~2100 cm^{-1}.[14] Since substitution with aryl groups is expected to give rise to absorption at lower wavenumbers, we exclude this type of compound and assign the structure of the new product to diphenylnitrilimine (**2**). Confirmation of this assignment is obtained from the results of irradiating the three differently labeled [^{15}N]-2,5-diphenyltetrazoles (**3–5**) shown in Scheme II. These were obtained by unequivocal syntheses[15] (Scheme I) from 1,2-di-^{15}N-labeled hydrazine (52.1%), ^{15}N-labeled aniline (95%), and ^{15}N-labeled sodium nitrite (95%), respectively.

Irradiation (λ 250 nm) of **1** as well as **3** gives rise to the same product demonstrating loss of the N(3)–N(4) nitrogens, whereas irradiation of either **4** or **5** gives products that retain ^{15}N. Continued irradiation (λ 370 nm) of diphenylnitrilimine (**2**, 2228 cm^{-1}) leads to benzonitrile (2228 cm^{-1}) and a product absorbing at 1883 cm^{-1} (Figure 3). Although heating of **2** causes complete loss of the 2228-cm^{-1} band, irradiation of **2** brings about partial disappearance only. After the photochemical change, no further decrease in the intensity of the band is observed on heating, in agreement with the assignment of the band to benzonitrile. Upon irradiation of the nitrilimine generated from **4**, unlabeled benzonitrile is formed and the absorption formerly at 1883 cm^{-1} is shifted to 1871 cm^{-1} because of the presence of ^{15}N in the corresponding compound. On the other hand, irradiation of the nitrilimine from **5** gives rise to labeled benzonitrile (2201 cm^{-1}) and absorption at 1883 cm^{-1} as before. We identify the compound responsible for the absorption at 1883 cm^{-1} as 1-aza-1,2,4,6-cycloheptatetraene (**6**) (Scheme II), which has recently been observed by Chapman and co-workers as a product of irradiation of phenyl azide in an Ar matrix at 8 K.[16] Although this compound absorbs at 1895 cm^{-1} in an Ar matrix,[16] irradiation of phenyl azide in

Scheme I



Scheme II



[a] The band at 2228 cm^{-1} disappears on heating to ~230–240 K. [b] The band at 1883 cm^{-1} disappears on heating to ~160–170 K.

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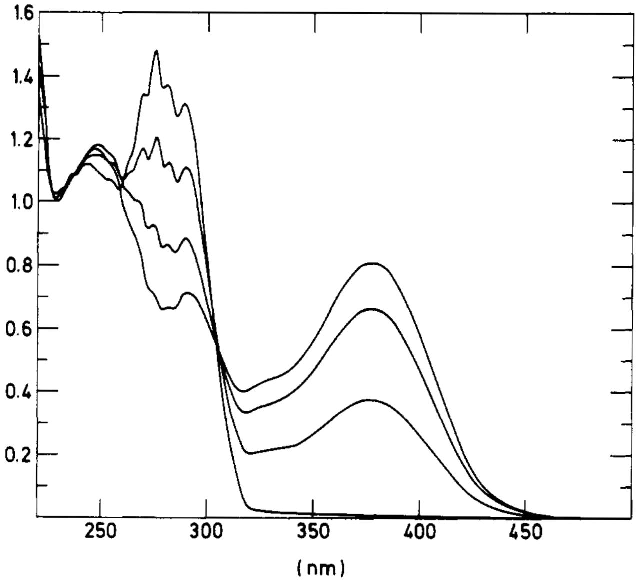

Figure 1. Irradiation (λ 250 nm) of 2,5-diphenyltetrazole (**1**) in PVC at 85 K with formation of diphenylnitrilimine (**2**, λ_{max} 377 nm) monitored by UV spectroscopy.

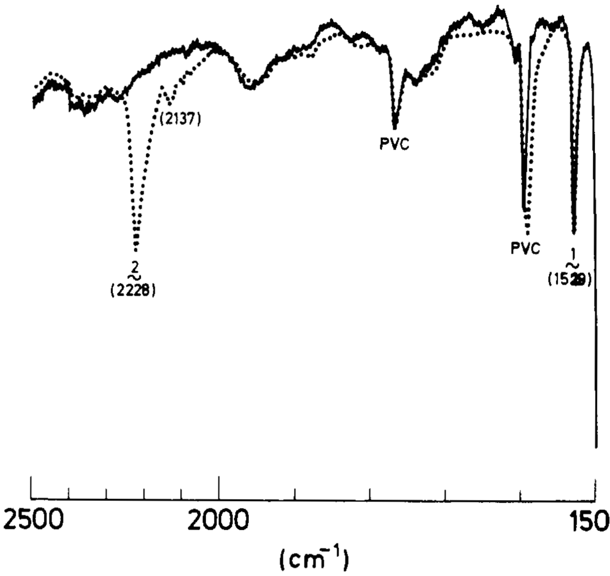

Figure 2. Irradiation (λ 250 nm) of 2,5-diphenyltetrazole (**1**, ν_{max} 1529 cm^{-1}) in PVC at 85 K with formation of diphenylnitrilimine (**2**, ν_{max} 2228 cm^{-1}) and diphenylcarbodiimide (ν_{max} 2137 cm^{-1}) monitored by IR spectroscopy.

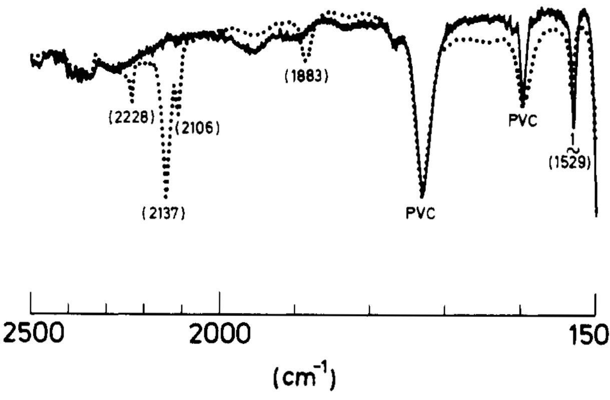

Figure 3. Irradiation (λ 370 nm) of diphenylnitrilimine (**2**) in PVC at 85 K with formation of benzonitrile (ν_{max} 2228 cm^{-1}), diphenylcarbodiimide (ν_{max} 2137, 2106 cm^{-1}), and 1-aza-1,2,4,6-cycloheptatetraene (**6**) (ν_{max} 1883 cm^{-1}) monitored by IR spectroscopy.

PVC gives rise to an absorption band at 1883 cm^{-1}, confirming the proposed assignment.

Besides the above-mentioned products, diphenylcarbodiimide is also obtained from **2** upon irradiation at 85 K. Its mode of formation is unknown at present.

Irradiation (λ 250 nm) of 2-phenyltetrazole at 85 K in PVC gives rise to *N*-phenylnitrilimine (2014 cm^{-1}, λ_{max} 310 nm) which on continued irradiation (λ 320 nm) forms hydrogen cyanide (2076 cm^{-1})[17] and 1-aza-1,2,4,6-cycloheptatetraene (**6**) (1883 cm^{-1}) as expected.

It is of particular interest to observe that introduction of ^{15}N in diphenylnitrilimine in position 2 gives rise to a frequency shift ($\Delta\nu$ = 33 cm^{-1}), while no shift is observed with ^{15}N in position 3. Furthermore, the observed shift compares favorably with that of the triple-bond frequency in [^{15}N]benzonitrile ($\Delta\nu$ 27 cm^{-1}). This demonstrates that N(2) participates in the stretching vibration at 2228 cm^{-1}, while N(3) does not. The ground-state structure of nitrilimines is therefore best described with a localized triple bond and a linear or almost linear array of the CNN atoms:

$$\underset{(1)}{-\mathrm{C}}\equiv\underset{(2)}{\mathrm{N}^{+}}-\underset{(3)}{\mathrm{N}^{-}}\diagdown$$

As suggested by the ab initio LCAO-MO-SCF calculations of Caramella and Houk,[18] only small amounts of energy input are required to provide bending. This is significant in understanding carbene reactions of nitrilimines[2,4] as well as their reactions with electrophilic and nucleophilic reagents.[18]

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