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CONVENIENT PREPARATION OF 2-NORBORNEN-2-CARBONITRILES FROM 2-NORBORNENES

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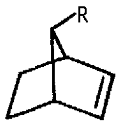
In the course of preparing new substrates for photochemical studies we were interested in the conversion of norbornenes (1) into the corresponding acids 2 or nitriles 3. A direct transformation of this sort is known and involves reaction of the vinyl anion derived from norbornene (1a) with carbon dioxide to form 2a,[2] but in our hands application of this procedure



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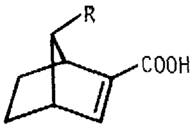

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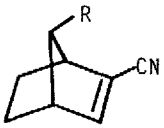

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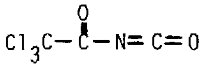
a, R=H
b, R=$CH_2CH(CH_3)_2$



$Cl_3C-\overset{O}{\overset{\|}{C}}-N=C=O$

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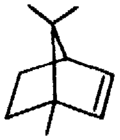

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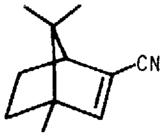

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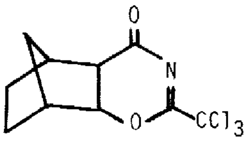
to an olefin of particular interest, syn-7-isobutylnorbornene (1b)[3] was slow and inconvenient. We then turned attention to other approaches and now report conditions under which norbornenes react with trichloroacetylisocyanate (4)[4] to yield unsaturated nitriles in a single operation. Heating of 1a or 1b with three equivalents of trichloroacetylisocyanate in p-xylene at reflux for five days, followed by dilution with ether and washing with aqueous base, gave the nitriles 3a and 3b directly in 70-90% yield. Similar treatment of 1,7,7-trimethylnorbornene (5, racemic bornylene)[5] furnished a lower yield of a single unsaturated nitrile 6. All three nitriles have ir, nmr, and high resolution mass spectral properties consistent with the structures assigned. In the nmr spectra of 3a and 3b the olefinic proton is coupled to the adjacent bridgehead hydrogen (J ∿ 4 Hz), while the olefinic proton of 6 appears as a slightly broadened singlet. The structure of 3a was further confirmed by independent preparation of this nitrile from norcamphor through formation of the cyanhydrin and subsequent elimination of water.

This conversion of norbornenes into the corresponding α,β-unsaturated nitriles poses an interesting mechanistic problem. At somewhat lower temperature norbornene (1a) and trichloroacetylisocyanate (4) yield a [4 + 2] adduct 7.[4] However, we found that treatment of independently prepared 7 with hot p-xylene containing either one or two equivalents of 4 and



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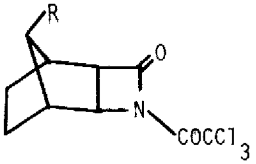

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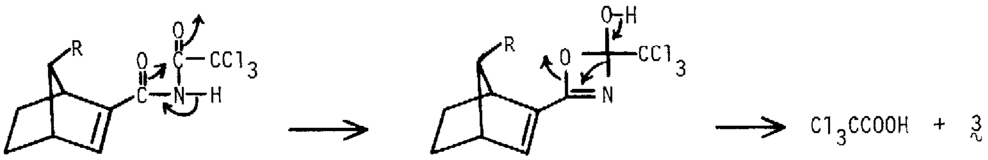

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then work-up with aqueous base furnished none of nitrile **3a**. A parallel experiment starting with bornylene (**5**) gave similar negative results. Suitable controls also showed that the nitriles were not formed during work-up with aqueous base but were already present in the xylene solution. Treatment with base appears simply to facilitate isolation of the neutral product. A plausible explanation for these observations is that at the higher reaction temperature that we employed the norbornene and **4** react to form an unsaturated imide **9**, possibly by way of [2 + 2] adduct **8**. Disproportionation of **9** *via* **10** then could lead to the observed nitrile **3**. The formation of both **8** and **9** has good precedent in the addition of trichloroacetylisocyanate (**4**) to various enol ethers and enol thioethers.[4,6] With these reactive olefins both [2 + 2] and [4 + 2] cycloaddition products, as well as unsaturated imides, are formed under quite mild conditions. The thermal disproportionation of imide **9** to **3** also has ample precedent,[7] although in the cases at hand the presence of excess trichloroacetylisocyanate may play a significant role. Experiments to test this suggested pathway are presently underway.[8]

Footnotes and References

(1) (a) The Rockefeller University; (b) Rutgers University; (c) please direct inquiries to this author.

(2) R. E. Finnegan and R. S. McNees, *J. Org. Chem.*, **29**, 3234 (1964).

(3) Preparation of this new compound will be described in our full publication.

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