The facile formation of **3** may be useful for preparation of some bicyclo[3.3.1]nonane derivatives and possibly of some homoadamantane derivatives.[10]

Experimental Section[11]

Beckmann Rearrangement of *anti*-Homoadamantan-4-one Oxime (1) with PPE.—The reaction was carried out similarly to the reported procedure[2] but by using a large excess of PPE. A mixture of 1 (900 mg, 5.02 mmol) and PPE (18 g) in chloroform (5 ml) was refluxed for 0.5 hr and the cooled mixture was poured onto ice–water (300 ml). The work-up and purification on a silica gel column eluting with chloroform afforded **7-cyanomethylbicyclo[3.3.1]non-2-ene (3)** as the first fraction (518 mg, 64%): mass spectrum *m/e* (rel intensity) 161 (52, M^+), 134 (100), and 119 (44).

Anal. Calcd for $C_{11}H_{15}N$: C, 81.93; H, 9.38; N, 8.69. Found: C, 82.18; H, 9.32; N, 8.50.

The second fraction gave 4-azatricyclo[5.3.1.$1^{3,9}$]dodecan-5-one (2) (189 mg, 21%) as colorless crystals, mp 184–185° (lit.[2] mp 184–185°).

Conversion of 2 to 3. A. With PPE.—A mixture of **2** (30 mg, 0.16 mmol) and PPE (540 mg) in chloroform (0.2 ml) was heated at 85° for 0.5 hr. Glpc analysis of the crude product after work-up revealed the formation of **3** in over 99% yield.

B. With PCl_5.—A mixture of **2** (30 mg, 0.16 mmol) and PCl_5 (80 mg, 0.38 mmol) in dry ether (5 ml) was stirred for 69 hr at room temperature. The mixture was poured onto ice–water, neutralized with 10% aqueous potassium hydroxide, and extracted with chloroform (3 × 10 ml). Dried ($MgSO_4$) extract was evaporated to give crude product, which was analyzed on glpc to reveal the formation of **3** in 8% yield and the recovery of **2** (92%).

Reduction of 2 to 4-Azatricyclo[5.3.1.$1^{3,9}$]dodecane (4).—A mixture of **2** (280 mg, 1.56 mmol) and lithium aluminum hydride (500 mg) in dry tetrahydrofuran (15 ml) was refluxed for 120 hr. Excess reagent was decomposed by adding water to the cooled mixture. The diluted mixture was extracted with ether (5 × 50 ml) and the combined extracts were dried (Na_2SO_4) and evaporated to give **4** (242 mg, 94%) which was purified by sublimation: mp 197–199°; ir (KBr) 3430, 2920, 1440, 1260, and 1160 cm^{-1}; nmr ($CDCl_3$) τ 6.0 (s, 1, NH), 6.34 (m, 1, C_3 H), 6.6–7.2 (m, 2, C_5 methylene), and 7.7–9.0 (m, 15, other ring protons); mass spectrum *m/e* (rel intensity) 165 (100, M^+), 164 (64), 150 (50), 136 (27), 122 (54), and 108 (57).

Anal. Calcd for $C_{11}H_{19}N$: C, 79.94; H, 11.59; N, 8.48. Found: C, 79.69; H, 11.56; N, 8.25.

Hydrolysis of 3.—A mixture of **3** (600 mg, 3.72 mmol), ethanol (12 ml), potassium hydroxide (12 g), and water (48 ml) was refluxed for 64 hr under nitrogen atmosphere. The cooled mixture was diluted with water (300 ml) and washed with *n*-hexane (3 × 30 ml). The water layer was acidified with 10% hydrochloric acid (pH *ca.* 5) and extracted with chloroform (7 × 50 ml). The combined extracts were dried (Na_2SO_4) and evaporated to give **bicyclo[3.3.1]non-6-ene-3-*endo*-acetic acid (5)** as an oil (555 mg, 82.7%): ir (neat) 3400–2500, 1695, and 1640 cm^{-1}; nmr (CCl_4) τ −1.79 (s, 1, COOH), 4.42 (m, 2, CH=CH), and 7.5–9.0 (m, 13, other protons); mass spectrum *m/e* (rel intensity) 180 (3.5, M^+), 179 (16), 161 (69), 142 (99), 129 (45), and 115 (100).

Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.60; H, 8.65.

Hydrogenation of 5.—A mixture of **5** (550 mg, 3.06 mmol), ethanol (30 ml), and 5% Pd/C (300 mg) was hydrogenated at room temperature under an atmospheric pressure for 13 hr. The catalyst was removed by filtration through Celite and the solvent was evaporated to give **bicyclo[3.3.1]nonan-3-*endo*-acetic acid (6)** (560 mg, 100%) as colorless crystals. Recrystallization from *n*-hexane afforded an analytical sample: mp 83–85.5°; ir (KBr) 3500–2400 and 1695 cm^{-1}; nmr ($CDCl_3$) τ 0.76 (s, 1, COOH), 7.87 (d, J = 7.5 Hz, *ca.* 2, $-CHCH_2COOH$), and 7.6–9.3 (m, 15, other protons); mass spectrum *m/e* (rel intensity) 182 (6, M^+), 164 (8), 123 (54), 122 (30), and 44 (100).

Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.96. Found: C, 72.75; H, 9.70.

Ethyl Bicyclo[3.3.1]nonan-3-*endo*-acetate (7). A. From 6.—A mixture of **6** (188 mg, 1.03 mmol), ethanol (12 ml), and 47% boron trifluoride etherate (300 mg) was refluxed for 1 day. The cooled mixture was poured onto 5% aqueous sodium carbonate (60 ml) and extracted with ether (5 × 20 ml). The combined extracts were washed with water and dried ($MgSO_4$). Removal of the solvent gave **7** as an oil (200 mg, 92%): ir (neat) 2920, 1730, and 1160 cm^{-1}; nmr ($CDCl_3$) τ 5.73 (q, J = 7.2 Hz, 2, CH_2CH_3), 7.80 (d, J = 7.80 Hz, 2, $CHCH_2COO-$), 8.01 (t, J = 7.2 Hz, 3, CH_2CH_3), and 7.7–9.2 (m, 15, other protons); mass spectrum *m/e* (rel intensity) 210 (10, M^+), 183 (13), 165 (76), 137 (36), 123 (85), 122 (90), and 95 (100).

Anal. Calcd for $C_{13}H_{22}O_2$: C, 74.24; H, 10.54. Found: C, 74.46; H, 10.32.

B. From Bicyclo[3.3.1]non-6-ene-3-*endo*-carboxylic Acid (8).—A mixture of **8**[6] (500 mg, 3.01 mmol), ethanol (10 ml), and platinum oxide (100 mg) was hydrogenated under an atmospheric pressure at room temperature for 1 day. The catalyst was removed by filtration through Celite and the solvent was removed to give colorless solid, which was recrystallized from ethanol to afford **bicyclo[3.3.1]nonan-3-*endo*-carboxylic acid (9)** as crystals (450 mg, 90%): mp 132–133°; ir (KBr) 3400–2500 and 1685 cm^{-1}; nmr ($CDCl_3$) τ −1.18 (s, 1, COOH) and 7.2–9.1 (m, 15, other protons).

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.20; H, 9.45.

To an ice-cooled solution of **9** (200 mg, 1.19 mmol) in dry *n*-hexane (4 ml) was added thionyl chloride (0.3 ml, 4.2 mmol) and the mixture was stirred for 1 day at room temperature. Evaporation of the solvent gave crude acid chloride **10** as an oil, ir (neat) 1800 cm^{-1}, which was dissolved in dry ether (7 ml) and treated with an excess ethereal diazomethane for 1 day. Removal of the solvent and the excess diazomethane afforded diazo ketone **11** as a yellowish oil, ir (neat) 2920, 2110, and 1720 cm^{-1}. The crude **11** was dissolved in ethanol (12 ml) and precipitates of polymethylene were removed by filtration. To the filtrate was added freshly prepared silver oxide (100 mg) and the mixture was refluxed for 5 min. Silver oxide was removed by filtration and the solvent was removed to leave crude product, which was purified on a silica gel column eluting with chloroform to afford a colorless oil (105 mg). Glpc analysis (3% silicone SE-30 on Varaport 30, at 180°) of this oil indicated the formation of **7**, homoadamantan-4-one, and methyl bicyclo[3.3.1]nonan-3-*endo*-carboxylate in a 63.3:25.4:11.3 ratio.

Registry No.—**1**, 26770-89-8; **2**, 29863-86-3; **3**, 36358-19-7; **4**, 33273-76-6; **5**, 36411-20-8; **6**, 36358-21-1; **7**, 36358-22-2; **9**, 19489-18-0.

(10) *Cf.* (a) D. J. Raber, G. J. Kane, and P. v. R. Schleyer, *Tetrahedron Lett.*, 4117 (1970); (b) M. A. McKervey, D. Faulkner, and H. Hamill, *ibid.*, 1971 (1970); (c) R. M. Black and G. B. Gill, *J. Chem. Soc. C*, 671 (1970).

(11) *Cf.* footnote 27 in ref 6.

Thermal Cycloaddition of Cyanoallene and 1-(*N*-Morpholino)cyclohexene[1]

JOHN E. BALDWIN,* RONALD H. FLEMING,[2] AND DIANE M. SIMMONS

Department of Chemistry, University of Oregon, Eugene, Oregon 97403

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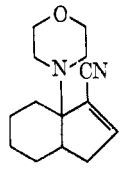
Cyanoallene and 1-(*N*-morpholino)cyclohexene combine thermally to produce a 1:1 adduct, mp 76°, formulated as 1-(*N*-morpholino)-9-cyanobicyclo[4.3.0]non-8-ene, **1**.[3] The morpholino enamine derived from cyclopentanone reacts with cyanoallene to give a similar

(1) Supported by the National Science Foundation and Hoffmann-La Roche Inc.

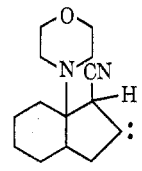
(2) National Science Foundation Trainee, 1968–1972.

(3) W. Ried and W. Käppeler, *Justus Liebigs Ann. Chem.*, **687**, 183 (1965).

cycloadduct, considered to be 1-(*N*-morpholino)-2-cyanobicyclo[3.3.0]oct-2-ene.[3]



1

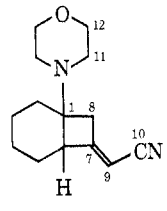


2

The structural assignment **1** for the 1:1 adduct rested on the interpretation of spectral evidence and hydrogenation of the adduct to a saturated nitrile, having the expected (but unreported) nmr spectrum. The mechanism proposed to account for the product assigned involved two-step addition of enamine to cyanoallene in a 1,3 sense to generate a carbene intermediate (**2**), which rearranged through a C–H insertion to afford **1**.

Our concern with allene–olefin cycloadditions[4] led us to reinvestigate the reaction between 1-(*N*-morpholino)-cyclohexene and cyanoallene, for, if the structural assignment **1** were indeed correct, thorough mechanistic scrutiny and numerous synthetic applications would be warranted.

Our study has shown, however, that the 1:1 adduct previously depicted as **1** should be re-formulated as the (2 + 2) cycloaddition product 1-(*N*-morpholino)-(*E*)-7-cyanomethylene-*cis*-bicyclo[4.2.0]octane (**3**).



3

The compound in question was synthesized according to the procedure of Ried and Käppeler.[3] The vinyl proton nmr absorption centered at δ 5.23 appeared as a quartet of lines, J = 2.2 Hz, with intensities in a 1:3:3:1 ratio, consistent with the vinyl hydrogen being coupled with equal or approximately equal constants to three allylic protons. The pattern is in all respects similar to those we have observed for the isomers of 1-ethylidene-2-methylcyclobutane,[5] and cannot be reconciled with structure **1**. The earlier report[3] described the vinyl resonance as a four-line pattern constituting a doublet of doublets centered at δ 5.15.

The natural abundance ^{13}C nmr spectrum of the cycloaddition product was obtained with broad-band proton decoupling and with no decoupling. The data and the assignments made are given in Table I.

It has been established for cyano-substituted ethylenes that the β-carbon resonance is shifted downfield, whereas the α-carbon resonance is shifted upfield.[6] Opposite behavior is observed for alkyl-substituted ethylenes.[6] Taken together, these two effects should cause the vinyl carbon singlet of structure **1** to occur upfield from the vinyl carbon doublet. On the other hand, the vinyl doublet of structure **3** would be expected substantially upfield from the singlet, in accord with the experimental data.

TABLE I

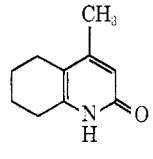
NATURAL ABUNDANCE ^{13}C NMR SPECTRUM OF ADDUCT **3**

Chem shift[a]	Multiplicity	J^{13}_{C-H}, Hz[b]	Assignment
−90.2	s		C-7
−38.4	s		C-10
−12.7	d	175	C-9
10.3	t	143	C-12
20.1	s		C-1
29.0	d	133	C-6
31.2	t	133	C-11
33.8	t	138	C-8
50.8	t	130	C-2,3,4,5
53.5	t	128	C-2,3,4,5
55.1	t	128	C-2,3,4,5
57.0	t	128	C-2,3,4,5

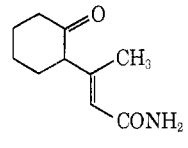
[a] Values given in ppm from deuteriochloroform as internal standard and solvent. [b] Coupling constants are given only for those protons attached directly to the carbon in question.

The nmr spectral data indicate the 1:1 adduct is a single isomer. The cis geometry for the bicyclic ring system is assigned primarily on grounds of mechanistic plausibility; the *E* configuration for the cyanomethylene function is suggested tentatively, for it seems in better accord with the ^{13}C chemical shifts.

Further confirmation of structure **3** was obtained by chemical correlation with a known compound. Treatment of the adduct **3** with mild base leads to a white crystalline solid identified as 4-methyl-5,6,7,8-tetrahydrocarbostyril (**4**) through direct comparisons with an authentic sample prepared by the method of Sakurai and Midorikawa.[7]



4



5

Formation of the tetrahydrocarbostyril **4** from **3** under these conditions is easily rationalized as proceeding through intermediates such as **5** derivable through simple hydrolysis; no change in the carbon skeleton is involved in the **3** → **4** conversion. By contrast, the transformation **1** → **4** would be awkward to formulate in straightforward terms.

Thus we conclude on the basis of proton and carbon nmr data, and of a chemical correlation, that the 1-(*N*-morpholino)cyclohexene cycloadduct with cyanoallene should be assigned structure **3**, not **1**,[3] and the cycloaddition process itself presents no unique mechanistic problems.

Experimental Section

Melting points were determined on a Kofler hot stage and are uncorrected. Proton and carbon nmr spectra were measured with a Varian XL-100-FT spectrometer acquired through NSF and NIH-HSAA grants to the University of Oregon. The mass

(4) J. E. Baldwin and R. H. Fleming, *Fortschr. Chem. Forsch.*, **15**, 281 (1970).

(5) J. E. Baldwin and R. H. Fleming, *J. Amer. Chem. Soc.*, **94**, 2140 (1972).

(6) G. B. Savitsky, P. D. Ellis, K. Namikawa, and G. E. Maciel, *J. Chem. Phys.*, **49**, 2395 (1968).

(7) A. Sakurai and H. Midorikawa, *Bull. Chem. Soc. Jap.*, **41**, 165 (1968).

spectrum was determined on a CEC-110-21B spectrometer by Dr. Susan Rottschaefer.

4-Methyl-5,6,7,8-tetrahydrocarbostyril (4).—Sodium carbonate (100 mg, 0.94 mmol), adduct **3** (201 mg, 0.865 mmol), and 80% ethanol (5 ml) were heated at reflux for 1 hr. Chloroform (20 ml) was added, and the mixture was washed with water (2 × 20 ml) and brine (1 × 20 ml), dried ($MgSO_4$), filtered, and concentrated to yield 127 mg of solid residue (about 60% **4** by nmr). Recrystallization from acetone gave 30.8 mg (22%) of compound **4**. A portion after further purification by recrystallization from chloroform had mp 256°: nmr ($CDCl_3$) broad signal δ 12.76 (1 H), singlet 6.26 (1 H), broad signal 2.68 (2 H), broad signal 2.39 (2 H), singlet 2.11 (3 H), complex multiplet 1.77 (4 H); mass spectrum *m/e* (rel intensity) 163 (100), 148 (10), 135 (42), 107 (47). The compound was identical with an authentic sample of 4-methyl-5,6,7,8-tetrahydrocarbostyril as judged by nmr spectral, melting point, and mixture melting point criteria.

Registry No.—**3**, 36286-99-4; **4**, 36287-00-0; cyanoallene, 1001-56-5; 1-(*N*-morpholino)cyclohexene, 670-80-4.

Electron Impact Induced Fragmentations Mimicking Retro-1,3-dipolar Cycloadditions

STEEN HAMMERUM* AND PEDER WOLKOFF

Department of General and Organic Chemistry, The H. C. Ørsted Institute, The University of Copenhagen, Universitetsparken 5, DK-2100, Copenhagen, Denmark

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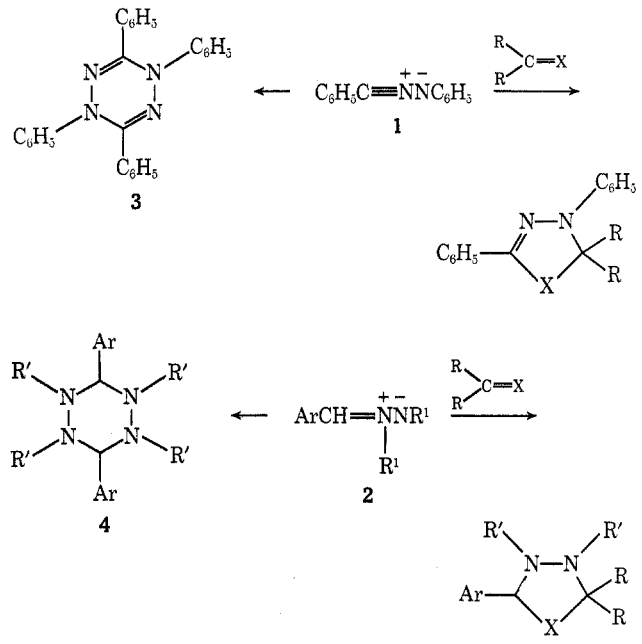
Correlation of thermal and photochemical processes with reactions that occur after electron impact has received considerable attention. The best known examples of successful analogies are the similarity of the mass spectrometric McLafferty rearrangement–decomposition process and the Norrish type 2 photofragmentation, and the occurrence of thermal, photochemical, and mass spectrometric retro-Diels–Alder reactions.[1] Recently, Nomura, Furusaki, and Takeushi[2] have proposed that retro-1,3-dipolar cycloadditions also have mass spectrometric counterparts, since 4- and 5-aminoisoxazolidines formed by 1,3-dipolar cycloaddition of enamines to nitrones yield ionized enamines upon electron impact. Earlier, at least one other well-established mass spectrometric retro-1,3-dipolar cycloaddition has been reported,[3] namely, the elimination of *tert*-butyl isocyanide from the molecular ion of the 3-(*N*-*tert*-butylimino)-1,2-diazetidine formed by addition of *N*-(*p*-nitrophenylimino)-1,2,3,4-tetrahydroisoquinoline to *tert*-butyl isocyanide.

We wish here to report the preliminary results of an investigation of the mass spectrometric behavior of heterocyclic compounds formed by 1,3-dipolar cycloaddition reactions of nitrile imines and azomethine imines, to show that such compounds upon electron impact may fragment by way of a cycloelimination reaction corresponding, formally, to the reverse process of their formation.

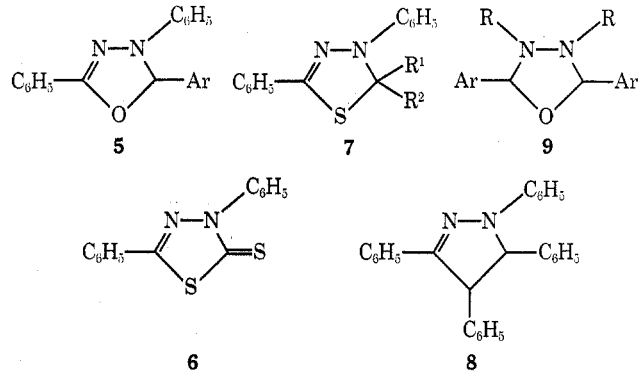
Addition of compounds incorporating C=C, C=O, or C=S double bonds to diphenylnitrileimine (**1**) or azomethine imines (**2**) usually yields five-membered ring compounds,[4] as illustrated in Scheme I.

SCHEME I



In the absence of dipolarophiles the 1,3-dipolar species dimerize to give dihydro-1,2,4,5-tetrazines (**3**) or hexahydro-1,2,3,4-tetrazines (**4**).[4] We have examined the mass spectra of several compounds formed in such reactions, **3**–**9**[5] (Scheme II).

SCHEME II



The mass spectrometric decomposition of the five-membered ring compounds **5**–**8** leads in all cases to ions corresponding in elemental composition to the parent 1,3 dipole (**1**, *m/e* 194), usually accompanied by minor peaks corresponding to the ionized dipolarophile. The most pronounced example of such retro-1,3-dipolar cycloaddition is found in the fragmentation of **5**, where more than 60% of Σ_{50} is carried by the three ions shown in Scheme III. Metastable ion peaks corresponding to both processes are observed in the spectra and have also been observed by metastable

(1) T. W. Bentley and R. A. W. Johnstone, *Advan. Phys. Org. Chem.*, **8**, 151 (1970), and references cited therein.

(2) Y. Nomura, F. Furusaki, and Y. Takeushi, *J. Org. Chem.*, **37**, 502 (1972).

(3) J. A. Deyrup, *Tetrahedron Lett.*, 2191 (1971).

(4) R. Huisgen, *Angew. Chem., Int. Ed. Engl.*, **2**, 565 (1963).

(5) Formulas **4**, **5**, **7**, and **9** each represent several compounds of the class in question. A full discussion of the mass spectra of these compounds will appear elsewhere.