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THE REACTION OF 1,2,2-TRIMETHYLBICYCLO[1.1.0]BUTANE WITH EXCITED STATE 1-CYANONAPHTHALENE

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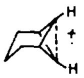
Abstract—1,2,2-Trimethylbicyclo[1.1.0]butane reacted with excited state 1-cyanonaphthalene at a diffusion-controlled rate in methanol to produce *cis*- and *trans*-1-methoxy-2,2,3-trimethylcyclobutane and 1-methoxy-2,2-dimethyl-3-methylenecyclobutane as simple methanol adducts of the starting bicyclo[1.1.0]butane. In addition, 1:1:1 adducts of the starting bicyclo[1.1.0]butane, 1-cyanonaphthalene, and methanol were isolated and characterized. Products were explained on the basis of a single electron transfer process from 1,2,2-trimethylbicyclo[1.1.0]butane to excited state 1-cyanonaphthalene to initially produce the cation radical of the bicyclo[1.1.0]butane and the anion radical of 1-cyanonaphthalene.

In 1979, we first demonstrated that a wide variety of highly strained polycyclic hydrocarbons had sufficiently high energy highest occupied molecular orbitals (HOMOs) that they were readily oxidized to cation radicals at $E_{1/2}$ vs SCE of 0.9–2.0 V.[1] Careful examination of a series of 15 bicyclo[1.1.0]butane derivatives indicated that electrons could be removed from this ring system at an $E_{1/2}$ vs SCE of 0.44–1.69 V.[2] Because the products of these electrochemical oxidations were always more easily oxidized than the starting materials, all electrochemical oxidations were two-electron, non-reversible processes.† In order to explore the one-electron oxidation of highly strained polycyclic molecules, we turned our attention to the use of excited state sensitizers as oxidizing agents, since it had been well established that such reagents would accept electrons from a wide variety of unsaturated systems.‡ Our initial efforts were devoted to the study of electron transfer from tricyclo[4.1.0.0^{2,7}]heptane (1) and its derivatives to excited state 1-cyanonapthalene (1-CN).[5] In the case of 1, very clean photochemistry was observed. Irradiation of 1 in methanol in the presence of 2 mol % of 1-CN gave a quantitative yield of 2 with a quantum yield for formation of 2 under these conditions of 0.22 vs a quantum yield for quenching of the fluorescence of 1-CN by 1 of 0.89. In contrast, irradiation of 1 in an inert solvent, such as benzene, using 1-CN as sensitizer gave a 95% yield of 3. Extensive evidence[6] suggests that 1 reacted with excited state 1-CN to yield a tight ion pair consisting of the cation radical 4 and the anion radical of 1-CN.

2 1 3



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Replacement of the proton at C-1 of 1 with a methyl group gave 5, whose photosensitized chemistry in nucleophilic solvents was similar to that of 1.[6] However, in non-nucleophilic solvents, 5 gave much more complex results than were observed with 1 under similar reaction conditions. These observations are illustrated by the high yield anti-Markovnikov addition of methanol to 5 to yield 6 and the dimerization of 5 to give 7 and the reduced dimers 8 and 9.

In contrast to the relatively straightforward electron-transfer photochemistry of 1 and 5, the related chemistry of 10 was quite complex.[6] While the need for 1-CN in the photochemistry of 1 and 5 was catalytic (1–5 mol %), it became a stoichiometric reagent in the photoinduced reactions of 10. Furthermore, 10 gave products which were different from those seen previously. This is exemplified by the conversion of 10 into equal proportions of 11 and 12 in 79% yield. Detailed studies demonstrated that 11 and 12 resulted from the disproportionation of a radical species. The change in mechanism was due to an increase in the stability of the cation radical derived from 10 as compared to 4 and to the cation radical formed from 5 (it was demonstrated through electrochemical oxidation that 10 had an $E_{1/2}$ which was 0.44 V less than that of 1). This increased stabilization by methyl substituents permitted solvent separation of the cation radical and anion radical pair. It would appear that the dramatic change in mechanisms was a result of such a separation process since a decrease in solvent polarity led to a decrease in the observed disproportionation and a return to the same reaction path as was exhibited by 1 and 5.

While the influence of substitution on 1 is far from being understood, it is of interest to note that strong carbocation stabilizing substituents at C-2 of 1 can produce unusual effects. This is illustrated by a com-

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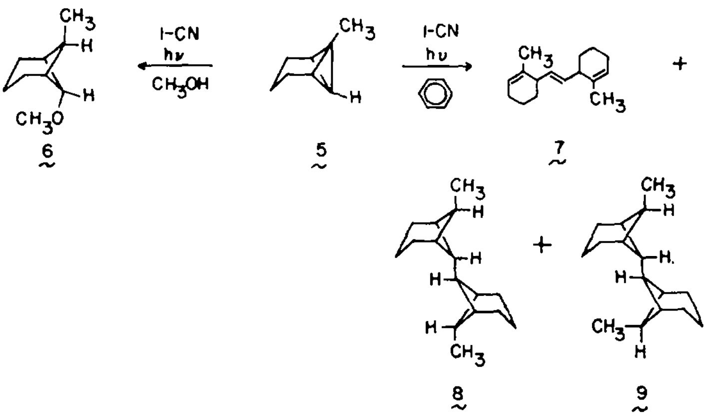
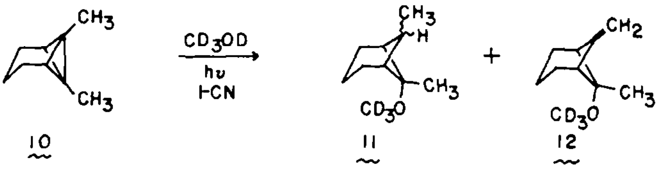
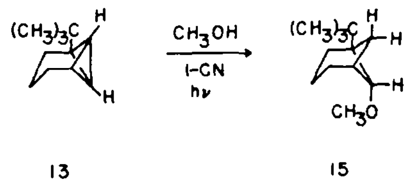
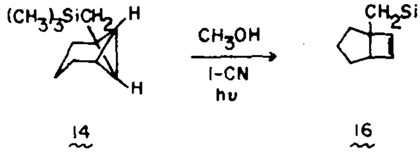
† For a detailed discussion see Ref. 3.

‡ It should be noted that isolated examples of fluorescence quenching by strained hydrocarbons have previously been reported. However, relatively little in the way of product-forming photochemistry has been observed. The major system which has been previously examined is quadricyclane (both bicyclo[2.1.0]pentane and tricyclo[4.1.0.0^{2,7}]heptane have also been evaluated as quenchers).[4]









parison of **13** and **14**. Whereas **13** resembled **1** and **5** in its photoinduced behavior in producing a high yield of **15**, **14** gave **16** as the only volatile product.[7]

In view of the intriguing behavior of a variety of derivatives of tricyclo[$4.1.0.0^{2,7}$]heptane, we became interested in evaluating the effect of the trimethylene bridge which joined the C-2 and C-4 positions of the bicyclo[1.1.0]butyl moiety of **1**. This prompted us to study the photochemical behavior of 1,2,2-trimethylbicyclo[1.1.0]butane (**17**)[8] under the same photosensitized conditions.

Irradiation of a 0.2 M solution of **17** in methanol† in the presence of 1.5 equiv of 1-CN gave four products with molecular weights ranging from 126 to 128, in addition to a large residue of higher molecular weight materials. The lower molecular weight components were identified as *c*-**18**, *t*-**18**, **19** and **20**. The *cis* and *trans* isomers, *c*-**18** and *t*-**18**, could not be separated on a preparative scale. Thus, they were treated as a single entity, which was isolated in 17% yield. Structural assignment was based on exact mass, elemental analysis, ^{1}H-NMR, and ^{13}C-NMR. The major isomer was assigned the *c*-**18** structure because the chemical shifts of the two geminal methyl groups differed by 0.17 ppm for the major isomer, but only by 0.07 ppm in the minor isomer (*t*-**18**). The structures of **19** and **20** were readily established through comparison of their spectral data with those of authentic samples.[3,8] The origin of **19**, which was isolated in 7% yield, is felt to be associated with a disproportionation reaction. Mechanisms similar to those discussed for the reactions of **1**, **5**, and **10** can be invoked. As shown below, **17**, which has an $E_{1/2}$ vs SCE of 1.27 V, should readily transfer an electron to excited state 1-CN to produce **21**. Simple addition of methanol to **21**, followed by back electron transfer from the 1-CN anion radical, and proton transfer would produce **18**. In contrast, addition of methanol to **21**, followed by loss of a proton would give radical **22** and the 1-CN anion radical. Disproportionation of **22** would yield an equimolar mixture of **18** and **19**. Since **18** and **19** were not formed in equivalent amounts, it seems likely that part of the yield of **18** resulted by the initially described procedure, which did not involve a disproportionation.

Treatment of **17** with acidic methanol produces **20** in high yield.[8,9] Thus, it seems likely that **20** may arise from an acid-catalyzed addition of methanol to **17** under the photochemical conditions. However, the details of the formation of **18**–**20** appear to be more complex than might have been expected. As shown in Table 1, product ratios were critically dependent on the concentration of 1-CN. As can be seen from Table 1, the yield of **20** rapidly decreases as the concentration of 1-CN increases. This would appear to be due to the disappearance of most of the

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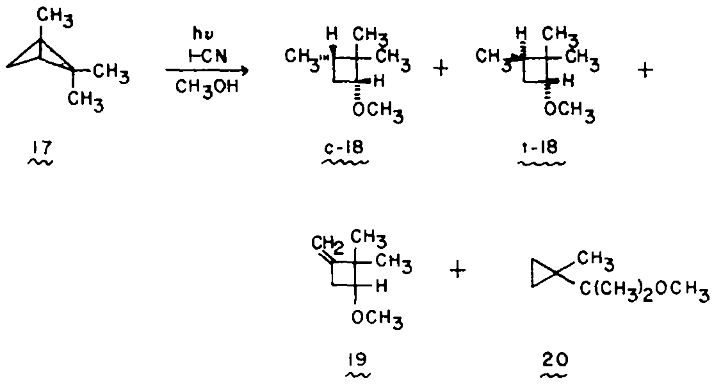
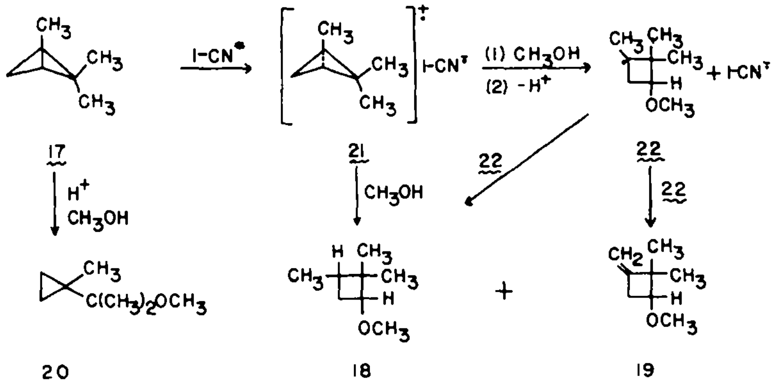
† Unless otherwise stated, all photochemistry was done in quartz tubes in a Rayonet Photochemical Reactor using a bank of 16 300 nm lamps. The methanol contained 0.1–0.2% potassium hydroxide in order to decrease acid-catalyzed rearrangements and acid-catalyzed addition of solvent to the bicyclo[1.1.0]butanes. The presence of potassium hydroxide gave no change in the quenching of 1-CN until the concentration of potassium hydroxide exceeded 10%. Electron transfer from **17** ($E_{1/2}$ vs SCE = 1.27 V)[2] to excited state 1-CN is a highly exothermic process.





1-CN at the lower concentration and subsequent acid-catalyzed rearrangement of **17**. In addition, the ratio of **18**:**19** decreases from 2.4 to 1.5 as the molar concentration of 1-CN increases from 1.5 to 10.0. Thus, it would appear that the amount of disproportionation was increased when the concentration of 1-CN was increased.

If a true radical–radical disproportionation was involved in the formation of **19** and part of **18**, it seemed likely that the addition of an efficient hydrogen atom source should decrease the yield of **19** and increase the yield of **18**. When a 0.07 M solution of **17** in methanol containing 1.0 equivalent of 1-CN and 0.5 equivalent of 1,4-cyclohexadiene (as hydrogen atom source) was irradiated, we obtained 26% of **18**, 7% of **19**, and 3% of **20** for an **18**:**19** ratio of 3.7. When the amount of 1,4-cyclohexadiene was increased to 2.0 equiv and all other concentrations were maintained as described above, 35% of **18**, 5% of **19**, and 4% of **20** were obtained. The ratio of **18**:**19** was 7.0. This indicated that the intermediacy of a radical such as **22** was highly probable.

Table 1. Product ratios as a function of 1-CN concentration in the photoconversion of 0.2 M **17** in methanol

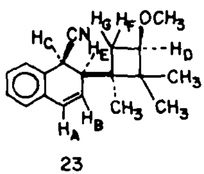
Concentration of 1-CN (M)	Time (h)	Percentage yield (%) **18**	**19**	**20**	Ratio of **18**/**19**
0.07	19.5	17	7	22	2.4
0.15[a]	20.0[a]	21	9	12	2.3
0.15	5.0	21	11	2	1.9
0.20	2.0	18	11	2	1.6
0.42	3.5	20	13	2	1.5

[a] The initial solution contained 0.35 equiv of 1-CN. After 2 h irradiation, an additional 0.35 equiv of 1-CN was added and the solution was irradiated for an additional 18 h.

The collective yield of **18**–**20** was generally in the range of 30–40%, depending on the exact reaction conditions. The remainder of the starting material appeared to be tied up in the dark brown, higher molecular weight residue. Analysis by TLC on both silica gel and alumina indicated the presence of a very large number of components. However, after a series of separations using gravity columns (silica gel), MPLC (both reverse phase and normal phase), and HPLC (both reverse phase and normal phase), six major components were isolated. The details of the separation sequence are described in the experimental section.

Mass spectral analyses showed that four of the six components were 1:1:1 adducts of **17**, 1-CN, and methanol. A fifth product was a dimer of 1-CN and the sixth was an adduct of 1-CN and naphthalene.

The four 1:1:1 adducts have been assigned structures **23**–**26** on the basis of spectral data, and in two cases, on chemical evidence. The mass spectral analysis of **23** established a molecular formula of $C_{19}H_{23}NO$. Infrared analysis showed the presence of a nitrile absorption as 2238 cm^{-1}, which indicated an alkyl nitrile. Eighteen different carbons could be accounted for by ^{13}C-NMR. Both ^{13}C- and ^{1}H-NMR indicated the presence of a single isomer. Extensive decoupling experiments gave the following ^{1}H-NMR data: δ 6.63 (H_A, dd, $J_{AB} = 9.9$ Hz, $J_{AE} = 1.6$ Hz), 5.78 (H_B, dd, $J_{AB} = 9.9$ Hz, $J_{BE} = 5.0$ Hz), 3.76 (H_C, d,



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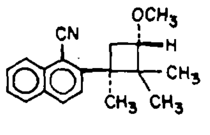

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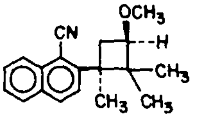

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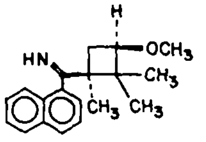

26

J_{CE} = 3.8 Hz), 3.41 (H_D, dd, J_{DF} = 6.9 Hz, J_{DG} = 3.6 Hz), 3.02–3.07 (H_E, m), 2.19 (H_F, dd, J_{FD} = 6.9 Hz, J_{FG} = 12.6 Hz), 1.53 (H_G, dd, J_{DG} = 3.6 Hz, J_{FG} = 12.6 Hz). These data are consistent with the assigned structure. The gem-dimethyl groups were tentatively assigned the peaks at δ 0.82 and 1.10. This, coupled with the 0.66 ppm shift between the geminal protons H_F and H_G, suggests, but does not prove, that the methoxyl group and the dihydronaphthalene moiety are *cis*.

Mass spectral analysis of **24** and **25** showed that each had a molecular formula corresponding to $C_{19}H_{21}NO$. In addition, both compounds exhibited almost identical fragmentation patterns in their electron impact mass spectra. Infrared analysis showed nitrile absorptions at 2210 and 2214 cm^{-1} for **24** and **25**, respectively, which indicated the presence of an aryl nitrile moiety in each molecule. Infrared analysis was also used to establish the substitution pattern. Both **24** and **25** showed IR bands at 830 and 750 cm^{-1}. This is consistent with the presence of either a 1,2- or 1,4-substitution pattern on the naphthalene substrate.[10] Since **23** could be converted to **25** under the reaction conditions, **25** was assigned the 1,2-substitution pattern. Of the four 1:1:1 adducts, **24** was present in the smallest quantity. The fact that **24** and **25** had identical mass spectral cracking patterns and IR bands at 830 and 750 cm^{-1} suggested that they were both 1,2-disubstituted naphthalene derivatives.† The difference between **24** and **25** would appear to be associated with the stereochemical relationship between the methoxyl group and the naphthalene moiety. Comparison of the ^{1}H-NMR peak positions of the gem-dimethyl groups of **23** and **25** show that they are shifted from each other by 0.28 and 0.39 ppm, respectively. For **24** this shift is only 0.51 ppm. Similarly, comparison of the ^{1}H-NMR peak positions of the geminal protons of the cyclobutyl groups of **23** and **25** shows that they are shifted from each other by 0.66 and 0.70 ppm, respectively. In contrast, the analogous protons of **24** exhibit a difference of only 0.2 ppm. This indicates that **24** has a different stereochemical relationship about the cyclobutyl ring than **23** and **25**, which can be chemically related. It appears probable that **24** has a *trans* relationship of the methoxyl group and the naphthalene skeleton.

Compound **26** showed an exact mass molecular weight consistent with a molecular formula of $C_{19}H_{23}NO$. It showed no nitrile band in the IR, but it did show bands at 3240 and 1610 cm^{-1}, which were consistent with the presence of an imine group.[11] The ^{13}C-NMR spectrum of **26** showed 19 carbons. This included eight peaks in the aliphatic region, ten peaks in the aromatic region, and one at δ 186.96 which corresponds to a ketimine quaternary carbon. This compound was surprisingly stable in that it resisted all attempts at hydrolysis and reduction. However, it was readily acetylated in 95% yield. The acetylated material showed IR absorptions at 1710 and 1650 cm^{-1}. In addition, the N—H stretch of **26** at 3240 cm^{-1} disappeared. The ^{1}H-NMR spectrum of **26** showed a typical pentasubstituted cyclobutyl pattern, which suggested that the methoxyl and imine substituents were *cis* on the cyclobutyl ring (Δδ for geminal protons was 1.0 ppm).

Mechanistically, the formation of **23**–**26** could be viewed as occurring in a variety of ways.[12] One could speculate on whether they were derived from a combination of **21** with the anion radical of 1-CN, or whether **22** was first formed and subsequently underwent a radical combination reaction with the anion radical of 1-CN. Lastly, it should be noted that either **21** or **22** could react with 1-CN itself. In the absence of specific facts, we cannot make a choice between these various possibilities.

As noted above, in addition to the four 1:1:1 adducts, two additional components were isolated. One was a dimer of 1-CN. Chemical ionization mass spectrometry established the molecular formula as $C_{22}H_{16}N_2$ while electron impact mass spectrometry showed a base peak of formula $C_{11}H_8N$. This suggested the presence of a dimer which readily fragmented to the parent components. Two nitrile absorptions at 2233 and 2241 cm^{-1} were observed by IR spectroscopy. The ^{1}H-NMR spectrum showed aromatic, olefinic and aliphatic protons (Experimental).

Lastly, an adduct of naphthalene and 1-CN was identified through its molecular formula, $C_{21}H_{13}N$, and its spectral data. The ^{1}H-NMR spectrum showed only aromatic protons in a complex pattern at δ 7.60–8.36. The ^{13}C-NMR showed 21 peaks, eight of which corresponded to quaternary carbons and 13 to methines. All, including the nitrile carbon, were in the aromatic region. In addition, the IR spectrum showed the presence of a nitrile group.

In summary, the photoinduced reactions of **17** in the presence of 1-CN and methanol appear to be much more complex than the analogous photochemistry of **1** and **5**. The exact cause of these differences is currently under study.

EXPERIMENTAL‡

1,2,2-Trimethylbicyclo[1.1.0]butane (**17**). The preparation of **17** was carried out according to the lit. procedure.[8]

Photoreaction of **17** *in methanol containing* 1-*cyanonaphthalene*. Six 15 mm quartz phototubes were charged with a soln prepared from 2.00 g of **17**, 3.82 g of 1-CN, and 105 ml of MeOH containing 0.16% KOH. After degassing with

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† We cannot unequivocally rule out the possibility that **24** might be a 1,4-disubstituted naphthalene, but we feel that the spectral data makes this the less likely of the two possibilities.

‡ All m.ps are uncorrected. Microanalyses were carried out by the Scandinavian Microanalytical Laboratory, Herlev, Denmark. NMR data were collected on a Varian CFT-20/HFT-80 Nuclear Magnetic Resonance Spectrometer and on a Nicolet NT-300 Nuclear Magnetic resonance Spectrometer.

argon, the tubes were placed in a merry-go-round and irradiated in a Rayonet Photochemical Reactor equipped with 16 300 nm lamps for 24 h. A second sample of 2.00 g of **17** was treated in the same manner and the two mixtures were combined. At this point the solvent and volatile products were vacuum transferred and the distillate and residue were worked up by two independent pathways.

Water was added to the distillate to generate a soln which was approximately 10% MeOH–90% water. This soln was continuously extracted with CH_2Cl_2 for 2 days. The CH_2Cl_2 extracts were fractionally distilled through a 12 in glass helices packed column to remove the CH_2Cl_2. The pot residue was subjected to HPLC separation using 1 : 1 acetonitrile : water and a preparative Alltech Affordable C-18 column. The unsaturated ether, **19**, eluted first. Three recycles of **19** through the HPLC gave reasonably pure material. An analytically pure sample of **19** was obtained by preparative GLC of a sample of **19**, obtained by HPLC, on a 10 ft Carbowax 20 M on Chromosorb W packed glass column with an oven temp of 60°. This colorless liquid had the following spectral properties: ^{1}H-NMR ($CDCl_3$) δ 4.83 (2H, m), 3.54 (1H, t, J = 7.8 Hz), 3.38 (3H, s), 2.85 (2H, m), 1.19 (3H, s), 1.17 (3H, s); ^{13}C-NMR ($CDCl_3$) δ 152.32 (s), 103.28 (t), 79.79 (d), 59.95 (q), 49.14 (s), 36.19 (t), 26.02 (q), 20.70 (q); IR (neat) 3070, 2955, 2920, 2860, 2820, 1675, 1460, 1426, 1382, 1365, 1354, 1221, 1125, 1005, 875 cm^{-1}; exact mass calc for $C_8H_{14}O$: 126.1045; found: 126.1049. (Found: C, 75.98; H, 11.17. Calc for $C_8H_{14}O$: C, 76.14; H, 11.18%.)

The second component to elute upon HPLC separation was a mixture of the *cis* and *trans* ethers represented by **18**. The *cis* isomer could not be separated from the *trans* isomer by any preparative technique which we attempted. Thus, the mixture of *cis* and *trans* isomers was treated as a single component. Analytically pure **18** was obtained by preparative GLC on a 10 ft Carbowax 20 M on Chromosorb W packed glass column with an oven temp of 60°. The colorless product had the following spectral data: ^{1}H-NMR[†] ($CDCl_3$) δ 3.54 (t, J = 7 Hz), 3.30* (t, J = 7.5 Hz), 3.25* (s), 3.20 (s), 2.20–2.30 (m), 1.95–2.05 (m), 1.70–1.80 (m), 1.35–1.58 (m), 1.08* (s), 1.07 (s), 1.00 (s), 0.95 (d, J = 6 Hz), 0.91* (s), 0.87* (d, J = 6 Hz); ^{13}C-NMR ($CDCl_3$) δ 81.05 (d), 80.53* (d), 56.34* (t), 42.90* (s), 41.20 (s), 32.77* (t), 31.81 (t), 32.19 (d), 31.00* (d), 28.55* (q), 22.94 (q), 22.49 (q), 16.46 (q), 14.90* (q), 13.65* (q); IR 2960, 2860, 1460, 1390, 1370, 1330, 1220, 1210, 1170, 1120, 1100, 1080, 1070 cm^{-1}. (Found: C, 74.66; H, 12.59. Calc for $C_8H_{16}O$: C, 74.94; H, 12.58%.)

The third component to elute in the HPLC separation was **20**. It was identified through spectral comparison with an authentic sample.[3,8,9]

The residue from the vacuum transfer of the volatile products of the original mixture was purified using gradient elution MPLC (C-18 and silica gel columns), and HPLC (C-18 and silica gel columns). Initially the residue was chromatographed on a gravity silica gel column to produce two fractions weighing 7.82 and 1.60 g, respectively. The larger fraction was subjected to preparative MPLC using 70:30 CH_2Cl_2: hexane as solvent and a silica gel column. This produced a separation into two major fractions, one containing 1-CN and the adduct of 1-CN and naphthalene, and a second fraction containing **23**–**25** and the dimer of 1-CN. The fraction containing 1-CN and the adduct of 1-CN and naphthalene was rechromatographed using MPLC with 7:93 CH_2Cl_2–hexane and a silica gel column. This gave 1-CN as the major component which eluted. Rinsing the column with CH_2Cl_2 gave a second component which was contaminated with small amounts of 1-CN. This second component was further purified by preparative HPLC using 20:80 CH_2Cl_2: hexane on a preparative Alltech silica gel column to give a broad melting, white solid: ^{1}H-NMR ($CDCl_3$) δ 8.00–7.12 (m); ^{13}C-NMR ($CDCl_3$) δ 137.69 (s), 135.81 (s), 133.40 (s), 133.15 (s), 132.74 (s), 132.04 (d), 131.18 (s), 130.80 (d), 128.83 (d), 128.74 (d), 128.36 (d), 128.11 (d), 127.77 (d), 127.53 (d), 126.55 (d), 126.42 (d), 126.12 (d), 124.81 (d), 124.73 (d), 117.63 (s), 110.71 (s); exact mass molecular weight calc for $C_{21}H_{13}N$: 279.1063; found: 279.1055.

The second fraction described above, which contained mainly **23**–**25**, and the dimer of 1-CN, was first chromatographed using MPLC with a Merck RP8 reverse phase column with 75 : 25 acetonitrile : water. The major components were isolated as a single fraction (1.92 g). This fraction was rechromatographed using HPLC on an Alltech preparative C-18 column and 65 : 35 acetonitrile–water as eluent. This produced four major fractions, A–D, each of which contained one major component and several minor components.

Fraction A was further purified by HPLC on an Alltech Affordable preparative silica gel column using 80:20 CH_2Cl_2–hexane which gave 130 mg of a dimer of 1-CN: ^{1}H-NMR ($CDCl_3$) δ 7.43 (dd), 7.20–6.85 (m), 6.70 (d), 6.58 (d), 4.12–4.08 (dd), 4.10–3.90 (m), 3.80–3.68 (m), 3.45–3.30 (m), 3.20–2.75 (m), 2.48 (dd), 2.15 (s), 2.00 (d); ^{13}C-NMR ($CDCl_3$) δ 135.69 (s), 132.62 (s), 131.74 (s), 130.08 (d), 128.62 (d), 128.31 (d), 128.08 (d), 126.97 (d), 126.48 (d), 125.14 (d), 124.28 (s), 121.15 (s), 52.18 (d), 48.98 (s), 45.53 (d), 41.53 (d), 40.38 (t), 39.69 (s), 36.25 (d), 26.07 (t); IR (KBr) 3026, 2983, 2242, 2233, 1684, 1559, 1506, 1423, 1345, 1335, 1243, 1216, 1127, 1057, 1021, 984 cm^{-1}; exact mass molecular weight calc for $C_{11}H_8N$ (base peak): 154.0656; found: 154.0650. Chemical ionization base peak (NH_3) *m/e* 326 (m + 18).

Fraction B was purified by HPLC on an Alltech Affordable preparative C-18 column using 60:40 acetonitrile–water, followed by a second purification by MPLC on a Merck silica gel column using 75:25 CH_2Cl_2–hexane to afford 12 mg of **23**: ^{1}H-NMR ($CDCl_3$) δ 7.30–7.07 (4H, m), 6.63 (1H, dd, J_{AB} = 9.9 Hz, J_{AE} = 1.6 Hz), 5.78 (1H, dd, J_{AB} = 9.9 Hz, J_{BE} = 5.0 Hz), 3.76 (1H, d, J_{CE} = 3.8 Hz), 3.41 (1H, dd, J_{DF} = 6.9 Hz, J_{DG} = 3.6 Hz), 3.02–3.07 (1H, m), 2.19 (1H, dd, J_{FD} = 6.9 Hz, J_{FG} = 12.6 Hz), 1.53 (1H, dd, J_{DG} = 3.6 Hz, J_{GF} = 12.6 Hz), 1.33 (3H, s), 1.10 (3H, s), 0.82 (3H, s); ^{13}C-NMR ($CDCl_3$) δ 132.50 (s), 125.92 (d), 128.46 (d), 127.84 (s), 127.74 (d), 127.04 (d), 126.29 (d), 120.97 (s), 81.12 (d), 56.90 (q), 44.68 (s), 43.27 (s), 35.52 (t), 31.96 (d), 25.36 (q), 19.48 (q), 17.96 (q); IR (CCl_4) 3055, 2986, 2964, 2931, 2238, 1680, 1560, 1507, 1491, 1473, 1463, 1454, 1436, 1377, 1260, 1125, 1108, 1079, 1058, 896 cm^{-1}; exact mass molecular weight calc for $C_{19}H_{23}NO$: 281.1779; found: 281.1777.

Fraction C was purified by HPLC on an Alltech Affordable preparative silica gel column using CH_2Cl_2 as eluent with recycling to give 23 mg of **24** as a clear oil: ^{1}H-NMR ($CDCl_3$) δ 8.27–7.28 (6H, m), 3.72 (1H, t, J = 7.8 Hz), 3.35 (3H, s), 2.60–2.80 (1H, br dd), 2.45–2.55 (1H, br s), 1.50 (3H, s), 1.43 (3H, s), 0.92 (3H, s); ^{13}C-NMR ($CDCl_3$) δ 133.35 (s), 131.71 (d), 130.93 (s), 128.28 (d), 128.05 (d), 126.66 (d), 125.68 (d), 124.92 (d), 119.00 (s), 78.87 (d), 56.74 (q), 42.88 (s), 39.07 (s), 38.23 (t), 27.33 (d), 25.55 (q), 24.48 (q), 19.85 (q); IR (neat) 3060, 2970, 2930, 2875, 2825, 2710, 1625, 1595, 1505, 1478, 1392, 1378, 1335, 1265, 1243, 1228, 1180, 1130, 1109, 1095, 1010, 939, 828, 753 cm^{-1}. Electron impact mass spectrometry failed to give a parent ion; chemical ionization mass spectrometry (NH_3), *m/e* = 297 (m + 18).

Fraction D was purified by MPLC on a Merck silica gel column using CH_2Cl_2 as eluent followed by HPLC on an Alltech Affordable preparative silica gel column using CH_2Cl_2 as eluent with recycling. This gave 161 mg of **25** as a white solid: ^{1}H-NMR ($CDCl_3$) δ 7.20–8.40 (6H, m), 3.43 (1H, dd, J = 6.4 Hz, J = 1.0 Hz), 3.36 (3H, s), 3.10 (1H, dd, J = 12.9 Hz, J = 6.5 Hz), 2.40 (1H, br d), 1.68 (3H, s), 1.39 (3H, s), 1.00 (3H, s); ^{13}C-NMR ($CDCl_3$) δ 154.98 (s), 133.29 (s), 132.03 (d), 130.75 (s), 128.16 (d), 127.98 (d), 126.50 (d), 125.27 (d), 124.74 (d), 117.60 (s), 106.29 (s), 82.01 (d), 56.29 (q), 47.54 (s), 45.76 (s), 36.64 (t), 27.59 (q), 26.94 (q), 18.40

[†] The resonances corresponding to the major isomer are indicated by an asterisk. In complex multiplets (^{1}H-NMR) containing both the major and minor isomers no indication is made of the presence of the major isomer.

(q); IR (neat) 3051, 2955, 2925, 2870, 2820, 2214, 1630, 1600, 1510, 1470, 1462, 1392, 1378, 1361, 1219, 1130, 1105, 1084, 1060, 910, 829, 750, 734 cm^{-1}; chemical ionization mass spectrum (NH_3), *m/e* 297 (m + 18). (Found: C, 81.47; H, 7.56. Calc for $C_{17}H_{21}NO$: C, 81.68; H, 7.58%.)

The original 1.60 g fraction from the initial chromatography was rechromatographed using MPLC on a silica gel column using 1.5% isopropyl alcohol–98.5% CH_2Cl_2 as eluent and one major peak was collected. This major peak was subjected to HPLC on an Alltech Affordable preparative silica gel column using 1 : 99 isopropyl alcohol–CH_2Cl_2. After two recycles, 77 mg of **26** was obtained as a colorless oil: ^{1}H-NMR ($CDCl_3$) δ 8.00–7.20 (7H, m), 3.58 (1H, dd, J = 7.0 Hz, J = 4.4 Hz), 3.30 (3H, s), 2.70 (1H, br s), 1.71 (1H, dd, J = 12 Hz, J = 4.4 Hz), 1.40 (3H, s), 1.34 (3H, s), 1.21 (3H, s); ^{13}C-NMR ($CDCl_3$) δ 186.96 (s), 137.95 (s), 133.59 (s), 130.02 (s), 128.29 (d), 128.12 (d), 126.32 (d), 125.81 (d), 125.30 (d), 124.40 (d), 121.94 (d), 80.75 (d), 56.58 (q), 47.91 (s), 46.68 (s), 36.01 (t), 26.60 (q), 23.77 (q), 18.29 (q); IR (neat) 3235, 3050, 2960, 2925, 2860, 2815, 1608, 1591, 1504, 1465, 1380, 1365, 1346, 1260, 1220, 1170, 1121, 1100, 1073, 1056, 1040, 1010, 973, 945, 925, 798, 778 cm^{-1}; exact mass molecular weight calc for $C_{19}H_{23}NO$: 281.1779; found: 281.1778.

Numerous attempts to hydrolyze or reduce the imine linkage of **26** were unsuccessful.

Acetylation of **26**. A small test tube was charged with 10.2 mg of **26** and cooled to 0°. Ac_2O (300 μl) was added and the mixture was allowed to warm to room temp and stirred for 18 h. After the addition of 1 ml of water, the resulting mixture was extracted with CH_2Cl_2. The organic extracts were washed with water and sat $NaHCO_3$ aq, followed by drying of the soln over anhyd K_2CO_3. After filtration, the solvent was removed *in vacuo*. This afforded 11.1 mg (95%) of monoacetylated **26**: ^{1}H-NMR ($CDCl_3$) δ 7.80–7.10 (7H, m), 3.40–3.60 (1H, m), 3.28 (3H, s), 2.40–2.70 (1H, dd), 1.82 (3H, s), 1.27 (3H, s), 1.18 (3H, s); IR (neat) 3060, 2980, 2940, 2880, 2840, 1710, 1650, 1600, 1515, 1480, 1470, 1390, 1375, 1365, 1250, 1220, 1120, 1090, 1060, 1020, 970, 950, 860, 845 cm^{-1}; exact mass molecular weight calc for $C_{21}H_{25}NO_2$: 323.1885; found: 323.1885.

GLC yield data for the formation of **18**–**20**. A 2 mm quartz photolysis tube was charged with 18.3–21.0 mg of **17**, 10.1–63.9 mg of 1-CN, 19.6–21.1 mg of octane (as internal standard) and 1 ml of MeOH containing 0.2% of KOH. These solns were then irradiated for the time specified in Table 1 in a Rayonet Photochemical Reactor equipped with 16 300 nm lamps. Yields were determined vs the internal standard by GLC analysis on an 8 M OV-101 capillary column. The results are tabulated in Table 1.

The effect of added 1,4-*cyclohexadiene on the yields of* **18**–**20**. A 2 mm quartz photolysis tube was charged with 7.1 mg of **17**, 14.0 mg of 1-CN, 3.0 mg of 1,4-cyclohexadiene, 4.0 mg of octane as an internal standard, and 1 ml of MeOH containing 0.2% of KOH. The soln was irradiated as described above for 9 h. Analysis as described above gave 26% of **18**, 7% of **19**, and 3% of **20**.

When the same reaction was run except with 7.0 mg of **17**, 11.2 mg of 1-CN, and 11.7 mg of 1,4-cyclohexadiene, the yields were 35% of **18**, 5% of **19**, and 4% of **20**.

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