

One final comparison with experiment may be made. The polyatomic spectroscopic tabulation of Harmony et al. includes estimated error ranges (symbols A-E in Table I). For example, the symbol C attached to a bond length implies an error range of ± 0.005 to ± 0.01 Å. If we take the larger error estimate in each case, then 54 out of the 75 parameters (72%) so assessed (Table I) are calculated within the experimental range at the MP3/6-31G* level.

Conclusions

(1) For the wide range of molecules examined, MP3/6-31G* and CID/6-31G* equilibrium geometries are in good agreement with experimental data. A majority of the calculated lengths and angles lie within the error range associated with the experimental data.

(2) Systematic bond length deficiencies at HF/6-31G* (theory too short) and at MP2/6-31G* (theory too long) are largely

removed at the third-order level.

(3) Equilibrium geometries predicted by Møller-Plesset (MP3) and configuration interaction (CID) techniques are close.

Acknowledgment. We are indebted to Dr. J. S. Binkley for assistance with the computations. This research was supported by the National Science Foundation (Grant 81-01061-01).

Registry No. H₂, 1333-74-0; LiH, 7580-67-8; BeH, 13597-97-2; BH, 13766-26-2; BH₂, 14452-64-3; CH, 3315-37-5; CH₂, 2465-56-7; CH₃, 2229-07-4; CH₄, 74-82-8; NH, 13774-92-0; NH₂, 13770-40-6; NH₃, 7664-41-7; OH, 3352-57-6; OH₂, 7732-18-5; FH, 7664-39-3; Li₂, 14452-59-6; LiF, 7789-24-4; B₂H₆, 19287-45-7; BiO, 12505-77-0; BN, 10043-11-5; BF, 7637-07-2; C₂, 12070-15-4; C₂H₂, 74-86-2; C₂H₄, 74-85-1; HCN, 74-90-8; HNC, 6914-07-4; CH₃NH, 2053-29-4; CH₃NH₂, 74-89-5; CO, 630-08-0; H₂CO, 50-00-0; CH₃OH, 67-56-1; CF, 3889-75-6; CH₃F, 593-53-3; N₂, 7727-37-9; N₂H₂, 3618-65-1; N₂H₄, 302-01-2; NHO, 14332-28-6; H₂NOH, 7803-49-8; NF, 13967-06-1; O₂, 7782-44-7; HOF, 14034-79-8; F₂, 7782-41-4.

Metal Ion Photoinitiated Addition of Acetonitrile and Methanol to Olefins

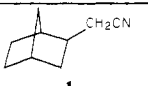
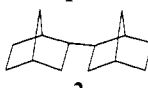
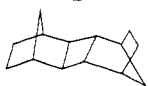
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Abstract: Irradiation of norbornene and silver or thallium trifluoromethanesulfonate in acetonitrile solution results in the efficient formation of *exo*-2-(cyanomethyl)bicyclo[2.2.1]heptane. Investigation of the scope of this reaction established that (a) copper(I or II) salts are not effective, (b) propionitrile and methanol give analogous norbornene-solvent adducts, and (c) acetonitrile addition is observed for several cyclic and acyclic olefins. Investigation of the mechanism of solvent addition indicates that the reaction is initiated by photoinduced electron transfer to silver(I) from coordinated norbornene. Reaction of the resulting norbornene cation radical with acetonitrile yields norbornyl cation and cyanomethyl radical. Free-radical chain addition of the cyanomethyl radical to norbornene then leads to product formation. In ethereal solvents, metal ion catalyzed photodimerization of norbornene has previously been reported for copper(I) salts. This reaction can also be effected by copper(II) and silver(I) salts, but not by Tl(I) salts.

Copper(I) salts are effective photocatalysts for olefin isomerization and cycloaddition reactions.¹ Among the most extensively investigated of these reactions is the photodimerization of norbornene to yield predominantly the *exo*-trans-*exo* dimer, a reaction first described by Trecker and co-workers.² The structure and bonding in Cu(I)-olefin complexes and the mechanism of photodimerization were subsequently investigated in detail by Salomon and Kochi.³ In contrast to the extensive investigations of Cu(I)-olefin photochemical reactions, there is but a single report of Ag(I)-assisted photodimerization⁴ and no reports of Tl(I)- or Cu(II)-olefin photochemistry. In addition, the effects of solvents on metal ion-olefin photochemistry have not been studied. We have investigated and report here the photochemical behavior of norbornene in the presence of Cu(I), Ag(I), Tl(I), and Cu(II) triflates in several solvents.⁵ In addition to the previously reported photocatalyzed dimerization of norbornene,¹ a novel and efficient photoinitiated free-radical chain addition of solvent (acetonitrile and methanol) to norbornene and other olefins is observed and its mechanism elucidated. It is seen that the intrinsic coordinative

Table I. Percent Yields of Photoproducts from Norbornene in Acetonitrile

product	AgOTf initiated ^a		xylene sensitized ^b	
	CH ₃ CN	CD ₃ CN	CH ₃ CN	CD ₃ CN
 1	93 ± 3 ^c	23 (<i>d</i> ₁)	86	18
 2	3 ± 0.5	38 (<i>d</i> ₂)	9	18
 3	1 ± 0.5	12 (<i>d</i> ₃)	1	8
 4	3 ± 0.5	27 (<i>d</i> ₄)	4	56

^a Percent yields determined by gas chromatography at ca. 1% conversion of norbornene (0.25 m) and AgOTf (0.02 m). ^b Reference 6. ^c Deviations in percent yield are typical of the data in Tables I and V.

preferences of the different metal ions profoundly influence the course and efficiency of the photochemical reactions.

(1) (a) Geoffroy, G. L.; Wrighton, M. S. "Organometallic Photochemistry"; Academic Press: New York, 1979; pp 205-215. (b) Fer-raudi, G.; Muralidharan, S. *Coord. Chem. Rev.* **1981**, *36*, 45-88.

(2) Trecker, D. J.; Foote, R. S.; Henry, J. P.; McKeon, J. E. *J. Am. Chem. Soc.* **1966**, *88*, 3021-3026.

(3) (a) Salomon, R. G.; Kochi, J. K. *J. Am. Chem. Soc.* **1973**, *95*, 1889-1897. (b) Salomon, R. G.; Kochi, J. K. *Ibid.* **1974**, *96*, 1137-1144.

(4) Leh, F.; Wong, S. K.; Wan, J. K. S. *Can. J. Chem.* **1971**, *49*, 2760-2762.

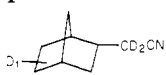
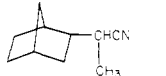
(5) For a preliminary report of a portion of this work, see: Bruno, J. W.; Marks, T. J.; Lewis, F. D. *J. Am. Chem. Soc.* **1981**, *103*, 3608-3609.

Table II. Relative Yields of Acetonitrile-Olefin Adduct Formation^a

olefin	K (Ag ⁺) ^b	adduct	relative yield
norbornene	62	1	(1.0)
cyclopentene	7.3	(cyanomethyl)cyclopentane	0.048
cyclohexene	3.6	(cyanomethyl)cyclohexane	0.017
2-ethyl-1-butene	3.0	1-cyano-3-ethylpentane	0.013
<i>trans</i> -2-pentene	1.1	1-cyano-2-methylpentane + 1-cyano-2-ethylbutane	0.0024
1-pentene	4.9	1-cyanoheptane	0.0016

^a Yields determined by gas chromatography for solutions of olefin (0.25 M) and AgOTf (0.02 M) irradiated simultaneously on a merry-to-round apparatus. ^b Equilibrium constants from ref 7.

Table III. Relative Yields of Norbornene-Solvent Adduct Formation^a

solvent	adduct	relative yield
CH ₃ CN	1	1.0
CD ₃ CN		0.014
CH ₃ CH ₂ CN		0.39

^a See Table II, footnote *a*.

Results

Irradiation of Olefins and Metal Salts in Acetonitrile. Irradiation of an acetonitrile solution of norbornene (0.25 M) and silver trifluoromethanesulfonate (AgOTf, 0.02 M), with a Vycor-filtered low-pressure or medium-pressure mercury lamp results in the formation of *exo*-2-(cyanomethyl)bicyclo[2.2.1]heptane (1), bi-(*exo*-2-norbornene) (2), and the *exo*-*trans*-*exo* and *exo*-*trans*-*endo* norbornene dimers 3 and 4. Relative product yields and structures are given in Table I along with yields for the formation of 1-4 in the triplet-sensitized (xylene) irradiation of norbornene in acetonitrile.⁶ Conversions of 35-40% of norbornene to adduct 1 can be achieved in preparative-scale reactions by periodically removing the deposit of silver metal that forms on the lamp well. Such conversions correspond to the formation of 5-6 product molecules per initial Ag(I) ion.

Acetonitrile-olefin adducts are also the major products formed upon irradiation of several monocyclic and acyclic olefins with AgOTf in acetonitrile. Relative yields obtained upon fixed-duration irradiation are given in Table II along with Ag(I)-olefin equilibrium constants previously determined by gas chromatography.⁷ Since the Ag(I)-olefin solutions do not have the same absorbance, the values in Table II are not indicative of relative quantum yields. No acetonitrile-olefin adducts were detected for 2,3-dimethyl-2-butene, *trans*-stilbene, 1,3-pentadiene, 1,5-hexadiene, or 1,4-cyclohexadiene. Irradiation of acetonitrile solutions containing norbornene and a terminal olefin results in the formation of both olefin adducts in a ratio similar to the initial olefin concentration ratio. Thus irradiation of an acetonitrile solution containing 0.2 M 2-ethyl-1-butene, 0.04 M norbornene, and 0.02 M AgOTf gives a 5.0:1 ratio of 1-cyano-3-ethylpentane:1.

Irradiation of norbornene and AgOTf in acetonitrile-*d*₃ results in a 71-fold decrease in the yield of adduct 1 (Table III) and a decrease in the relative yield of 1 vs. norbornene dimers 2-4 (Table I). Mass spectral analysis of the photoproducts indicates deuterium incorporation in adduct 1 ((cyanomethyl-*d*₂)norbornene-*d*) and dimer 2 (binorbornene-*d*₂) but no deuterium incorporation in dimers 3 or 4. Irradiation of norbornene and AgOTf in propionitrile solution also results in norbornene adduct formation (Table III); however, irradiation in isobutyronitrile solution does

Table IV. Solvent and Metal Ion Dependence of Norbornene Photoproduct Formation

solvent	metal ion ^a	major product	3/4	relative yield ^b
acetonitrile	Ag(I)	1	0.3	(1.0)
	Cu(I)	1	<i>c</i>	0.02
	Cu(II)	1	<i>c</i>	0.02
methanol	Tl(I)	1	<i>c</i>	1.5
	Ag(I)	6	3	0.15
	Cu(I)	3	>25	0.10
diethyl ether	Cu(II)	3	>25	0.04
	Ag(I)	3	6.5	0.04
	Cu(I)	3	>25	1.4
tetrahydrofuran	Cu(II)	3	13	1.7
	Tl(I)	<i>d</i>	<i>d</i>	<0.01
	Ag(I)	3	0.1	<i>e</i>
	Cu(I)	3	9.0	1.9
	Cu(II)	3	6.1	<i>e</i>

^a Triflate salts (0.02 M). ^b Yield of major product in fixed-duration irradiation relative to yield of 1 from 0.2 M norbornene and AgOTf in acetonitrile. ^c Yield of dimer too low for measurement. ^d No product formed, TlOTf only sparingly soluble. ^e Extensive solvent polymerization also occurs.

not yield a norbornene-solvent adduct. The major product detected by GC-MS is 2,2,3,3-tetramethylsuccinonitrile.

The yield of adduct 1 at low conversions of norbornene (<1%) is highly dependent upon oxygen concentration. No reaction is observed for either vacuum-line freeze-thaw degassed (10⁻⁵ torr) samples or fully oxygenated (1 atm) samples. Optimum yields are obtained by admitting 0.25-0.5 torr of oxygen above the frozen, degassed solutions, yielding solutions ca. 10⁻⁵ M in oxygen. Oxygen pressures in this range were used in quantitative experiments. Higher oxygen concentrations (1 atm) do not substantially inhibit preparative irradiations.

Quantum yields for formation of adduct 1 were measured at 313 nm, at which wavelength the Ag(I)-norbornene complex is the only absorbing species (vide infra). Least-squares fitting of a linear plot of Φ^{-1} vs. [norbornene]⁻¹ for 0.1-0.3 M norbornene, 0.1 M AgOTf, and 0.25 torr of oxygen in acetonitrile yields an intercept of 2.0 ± 0.2 , from which a limiting quantum yield of 0.5 ± 0.05 is calculated. The yields of all products increase with increasing norbornene concentration. Similar values were obtained with 254-nm irradiation; however, measurements at this wavelength are complicated by the absorption of light by both free and coordinated norbornene. Product yields are also dependent upon temperature. The yield of adduct 1 increases by a factor of 4.4 over the temperature range 5-50 °C, whereas the yield of dimers 3 and 4 decreases with increasing temperature.

The photochemical formation of adduct 1 can also be effected by using the Ag(I) salts of other poorly coordinating anions (PF₆⁻, BF₄⁻, and SbF₆⁻) or the triflate salts of Tl(I), Cu(I), and Cu(II). Relative yields of 1 in fixed-duration irradiations with 0.02 M metal triflates are reported in Table IV. The other anions gave yields of 0.20-0.25 relative to that for AgOTf. Metal precipitates are formed in all cases in yields roughly proportional to the yield of adduct 1 (Ag⁰ >> Cu⁰). Since the metal ion-norbornene solutions do not have the same absorbance, the reported relative yields are not indicative of relative quantum yields.

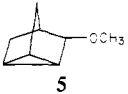
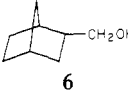
Irradiation of Norbornene and Metal Salts in Methanol. Irradiation of norbornene (0.25 M) and AgOTf (0.004 M) in methanol solution results in the formation of two norbornene-methanol adducts, 5 and 6, and norbornene dimers 2-4. Structures and percent yields are given in Table V along with previously reported results for the triplet-sensitized irradiation of norbornene in methanol.⁸ The formation of adduct 6 is significantly less efficient than the formation of adduct 1 in acetonitrile (Table IV). Irradiation in CH₃OD solution results in a decreased yield of 6 (O-D) but no deuteration of the carbon skeleton in any of the products (Table V). Irradiation in CD₃OD solution totally sup-

(6) Acetophenone sensitization yields products 1-4 as well as an oxetane: Schroeter, S. H. *Liebigs Ann. Chem.* **1974**, 1890-1894.

(7) Muhs, M. A.; Weiss, F. T. *J. Am. Chem. Soc.* **1962**, *84*, 4697-4705.

(8) Kropp, P. J. *J. Am. Chem. Soc.* **1969**, *91*, 5783-5791.

Table V. Percent Yields of Photoproducts from Norbornene in Methanol

product	Ag(I) ^a			sens ^b CH ₃ OH
	CH ₃ OH	CH ₃ OD	CD ₃ OD	
 5	23	30 (<i>d</i> ₀)	31 (<i>d</i> ₃)	
 6	32	15 (<i>d</i> ₁)	<1	24
2	7	7 (<i>d</i> ₀)	<1	11
3	29	40 (<i>d</i> ₀)	60 (<i>d</i> ₀)	3
4	9	8 (<i>d</i> ₀)	9 (<i>d</i> ₀)	26

^a See Table I, footnotes *a* and *b*. ^b Xylene-sensitization results from ref 8. Also formed were norbornane (8%) and ethylene glycol (28%).

presses the formation of both adduct **6** and dimer **2**. Adduct **5** is deuterated exclusively on the methoxy carbon while dimers **3** and **4** are undeuterated. Irradiation of norbornene with Cu(I) or Cu(II) triflates in methanol solution results in the formation of dimers **3** and **4** in a ratio of >25/1 (Table IV).

In view of conflicting reports on the photooxidation of alcohols by Ag(I) salts,^{9,10} the irradiation of AgOTf with cyclohexanol (neat and in dioxane, acetonitrile, and dimethyl sulfoxide solution) was investigated. While silver metal is slowly formed upon prolonged irradiation, no cyclohexanone is detected by gas chromatography. The failure of AgOTf to effect the photooxidation of cyclohexanol is in accord with the recent results of Macomber and co-workers.¹⁰

Irradiation of Norbornene and Metal Salts in Ethers. Irradiation of norbornene with Ag⁺OTf, Cu⁺OTf, or Cu^{II}(OTf)₂ in diethyl ether or tetrahydrofuran yields dimers **3** and **4** as the only norbornene-containing products. No photochemical reaction was observed with TlOTf, which is only sparingly soluble in ethereal solvents. Relative yields for the formation of dimer **3** are given in Table IV. The reaction of Ag(I) and Cu(II) salts in tetrahydrofuran is complicated by the formation of poly(tetrahydrofuran).¹¹ Silver metal also is formed upon irradiation in diethyl ether or tetrahydrofuran, in the presence or absence of norbornene. Little or no copper metal is formed from Cu(I) or Cu(II) under comparable reaction conditions. The CuOTf-catalyzed dimerization of norbornene does not require the presence of oxygen and proceeds in higher yield at -20 °C than at room temperature.

Absorption Spectra. Acetonitrile solutions of AgOTf are transparent at 254 nm, while norbornene displays end absorption at this wavelength. Addition of AgOTf (0.003 M) to an acetonitrile solution of norbornene (0.1 M) results in a 10–15-nm red shift in the onset of absorption and a weak long-wavelength tail that extends beyond 300 nm. From the slope and intercept of several Ketelaar plots¹² ([Ag⁺]/OD vs. [norbornene]⁻¹), the equilibrium constant and extinction coefficient of the Ag(I)–norbornene complex are estimated to be 0.3 ± 0.1 and 2300 ± 500 M⁻¹ cm⁻¹, respectively, assuming 1:1 complex formation. Addition of Cu^IOTf, Cu^{II}(OTf)₂, and Tl^IOTf to norbornene–acetonitrile solutions results in 5–10-nm red shifts in the onset of absorptions but no resolved ultraviolet absorption bands. Similar results were obtained for AgOTf and norbornene in ether solution.

Discussion

The present investigation has revealed that the salts of several metal ions classified as relatively soft Lewis acids¹³ can serve as

catalysts or initiators for the photochemical addition reactions of norbornene and other electron-rich alkenes. Two distinct photochemical reaction patterns have been identified for coordinated norbornene: photocatalyzed cyclodimerization and photoinitiated solvent addition. The distinction between catalyzed and initiated reactions is based upon the consumption (irreversible reduction) of metal ion in the latter but not in the former process. The relative efficiencies of metal triflates in the cyclodimerization reaction are Cu(II) > Cu(I) >> Ag(I), while for solvent addition the order is Tl(I) > Ag(I) >> Cu(I) ~ Cu(II). These reactions provide the first reported examples of Tl(I)– or Cu(II)–olefin photochemistry.

Metal–Olefin Complexation and Excitation. Thermodynamic data for metal ion–olefin complexes are available for Cu(I) and Ag(I) but none of the other metal ions employed in this study.¹⁴ In general, Cu(I)–olefin complexes are more stable than those of Ag(I). Olefin complexes of Hg(II),¹⁵ Au(I),¹⁶ and Cu(II)¹⁷ are rare, and there are, to our knowledge, no reported examples of isolable Tl(I)–olefin complexes. To a first approximation, trends in the stability of metal ion–olefin complexes might be anticipated to be roughly related to the softness of the metal ion (Hg(II) > Au(I) > Ag(I) > Cu(I) > Tl(I) > Cu(II));¹⁸ however, the available data for Ag(I) and Cu(I) are contrary to this expectation. The stability of metal ion–olefin complexes is also dependent upon solvent. Hartley and co-workers^{19a} showed that the stability constants of Ag(I)–olefin complexes decrease as the strength of metal ion–solvent interaction increases in the order propylene carbonate < water < methanol < acetonitrile.^{19,20} Thus it appears likely that the metal ion–norbornene stability constants for all of the metal ions employed in the present study will decrease in the solvent order ether > methanol > acetonitrile.

The investigation of Salomon and Kochi³ established that the Cu(I)–photocatalyzed cyclodimerization of norbornene requires electronic excitation of a Cu(I)–bis(olefin) complex. The maximum of the moderately intense Cu(I)–norbornene absorption band is blue-shifted by strongly coordinating solvents. Trecker and co-workers² report band maxima for this complex at 262 nm in heptane, 239 nm in ether, and 234 nm in methanol. Silver(I)–olefin complexes²¹ absorb at shorter wavelengths than Cu(I) complexes. Thus the absence of absorption maxima at wavelengths longer than 230 nm for Cu(I) or Ag(I) in norbornene–acetonitrile is not surprising. Absorption spectra have not been reported for Cu(II)– or Tl(I)–olefin complexes.

The nature of metal ion–olefin excited states is not well understood.¹ On the basis of Hückel calculations on the Ag(I)–cyclohexene complex, Hosoya and Nagakura²¹ concluded that the lowest energy transition is of mixed olefin-to-metal and olefin Rydberg character. The 248-nm band of norbornadiene–CuCl has been described as a metal–olefin charge-transfer transition without specification of the direction of charge transfer.²² McIntosh, Ozin, and Messmer²³ have recently reported SCF Xα calculations for the metal atom–ethylene complexes of Cu, Ag, and Au. They assign a weak ultraviolet band present in both the metal atom and metal ion–ethylene complex to a 5a₁ → 6a₁ transition. The 5a₁ orbital (HOMO of the metal ion complex) is essentially nonbonding and of largely metal nd character, with more mixing of metal and ethylene orbitals for silver than for copper. The 6a₁ orbital is largely metal (*n* + 1)s in character and either nonbonding or weakly antibonding. Thus the lowest energy

(9) Rajan, S.; Ramesh, D. *J. Org. Chem.* **1979**, *44*, 138–140.

(10) Macomber, R. S.; Carr, S.; Boudjouk, P.; Kapfer, C. *J. Org. Chem.* **1980**, *45*, 356–357.

(11) (a) Woodhouse, M. E.; Lewis, F. D.; Marks, T. J. *J. Am. Chem. Soc.* **1978**, *103*, 996–998. (b) Woodhouse, M. E.; Lewis, F. D.; Marks, T. J., *Ibid.*, following article in this issue. (c) Woodhouse, M. E. Ph.D. Thesis, Northwestern University, 1981.

(12) Ketelaar, J. A. A.; van de Stolpe, C.; Goudsmit, A.; Dzcubas, W. *Recl. Trav. Chim. Pays-Bas* **1952**, *71*, 1104–1114.

(13) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533–3539.

(14) Hartley, F. R. *Chem. Rev.* **1973**, *73*, 163–190.

(15) Olah, G. A.; Clifford, P. R. *J. Am. Chem. Soc.* **1971**, *93*, 2320–2321.

(16) Komiya, S.; Kochi, J. K. *J. Organomet. Chem.* **1977**, *135*, 65–72.

(17) Zelinka, R. A.; Baird, M. C. *J. Organomet. Chem.* **1971**, *33*, 267–272.

(18) Klopman, G. *J. Am. Chem. Soc.* **1968**, *90*, 223–234.

(19) (a) Hartley, F. R.; Searle, G. W.; Alcock, R. M.; Rogers, D. E. *J. Chem. Soc., Dalton Trans.* **1977**, 469–477. (b) Cox, B. G.; Garcia-Rosas, J.; Schneider, J. *J. Am. Chem. Soc.* **1981**, *103*, 1384–1389.

(20) Isolable acetonitrile complexes of Cu(I) and Cu(II) are known: Storhoff, B. N.; Lewis, H. C. *Coord. Chem. Rev.* **1977**, *23*, 1–99.

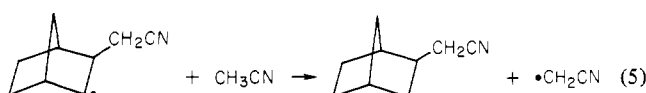
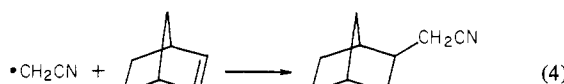
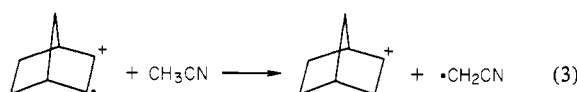
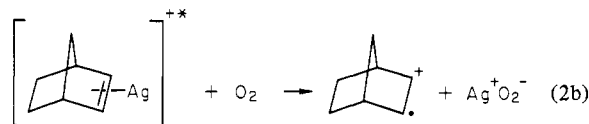
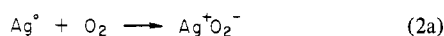
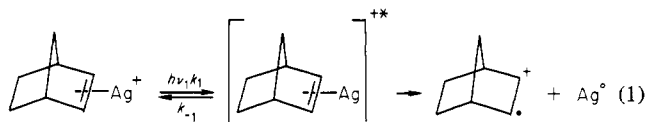
(21) Hosoya, H.; Nagakura, S. *Bull. Chem. Soc. Jpn.* **1964**, *37*, 249–265.

(22) Schwendiman, D. P.; Kutal, C. *Inorg. Chem.* **1977**, *16*, 719–721.

(23) McIntosh, D. F.; Ozin, G. A.; Messmer, R. P. *Inorg. Chem.* **1980**, *19*, 3321–3327.

electronic transition in the metal ion complexes is described as largely metal centered and weakly antibonding, with some olefin-to-metal charge transfer for silver and less for copper.

Mechanism for Silver(I)-Initiated Acetonitrile Addition. A plausible mechanism for the formation of the norbornene-acetonitrile adduct **1** is presented in eq 1–5. Since the ground-state



Ag(I)–norbornene complex is the only absorbing species in reactions employing 313-nm irradiation, an excited-state metal–olefin complex must be an intermediate in the addition reaction. The essential role of molecular oxygen may involve reaction with either a silver atom formed in a light-initiated redox process (eq 2a) or a long-lived excited-state complex (eq 2b), yielding in either case Ag^+O_2^- and the norbornene cation radical. Silver atoms are known to react rapidly with oxygen to yield Ag^+O_2^- , even at 10 K.^{24,25} The efficiency of various metal ions in this reaction (Table IV) may be determined by the stability of the metal superoxides, which will determine the efficiency of initiation (eq 1 and 2). On the basis of atomic one-electron ionization potentials,¹⁸ the predicted order of metal superoxide stability ($\text{Ti} > \text{Ag} > \text{Cu}$) is the same as the observed yield order for photoinitiated solvent addition (Table IV). Oxygen also serves as an essential electron carrier in the charge-transfer-initiated photodimerization of *N*-vinylcarbazole and other electron-rich olefins.²⁶

Abstraction of a hydrogen atom from acetonitrile by norbornene cation radical (eq 3) is an approximately thermoneutral process, based on the most recent value for the acetonitrile C–H bond dissociation energy.^{27,28} Precedent for hydrogen atom abstraction from acetonitrile by organic cation radicals is provided by the recent report of Whitten and co-workers.²⁹

The two final steps in the mechanism for addition of acetonitrile to norbornene (eq 4 and 5) constitute a free-radical chain-transfer process. This process finds precedent in the radical addition of aldehydes, alcohols, and amines to olefins, reactions investigated over 30 years ago by Karasch, Urry, and co-workers.^{30–32} While the chain-transfer addition of nitriles to olefins has not previously

been reported, the chain-transfer constant for acetonitrile in the free-radical polymerization of ethylene (0.011) is larger than the values for methanol (0.0021) or methylamine (0.0053).³³ The abstraction of a hydrogen atom from acetonitrile in the second step of the chain-transfer process (eq 5) should be approximately thermoneutral, as is the case for the initiation step (eq 3), whereas the first chain-transfer step (eq 4) should be exothermic.^{27,28} The abstraction of a hydrogen atom from solvent in both the initiation (eq 3) and chain-transfer (eq 5) steps should be more exothermic for propionitrile and isobutyronitrile than for acetonitrile. The formation of tetramethylsuccinonitrile upon irradiation of AgOTf and norbornene in isobutyronitrile indicates that the α -cyanoalkyl radical is indeed formed but does not add efficiently to norbornene, presumably for steric reasons. The failure of tetrasubstituted and conjugated olefins (including stilbene) to form acetonitrile adducts plausibly reflects the endothermic nature of hydrogen atom abstraction from acetonitrile by more stable free radicals.

In support of a free-radical chain-transfer mechanism (eq 4, 5), the yield of adduct **1** at low conversions is found to be substantially reduced in the presence of oxygen (>1 torr), in the presence of added terminal olefin, and in acetonitrile-*d*₃ solvent. The yield of Ag(I)-photoinitiated addition of acetonitrile to 2-ethyl-1-butene is only 1.3% of the value for addition to norbornene (Table II). Yet when mixtures of 2-ethyl-1-butene and norbornene are irradiated in the presence of AgOTf, the ratio of solvent addition products equals the initial olefin concentration ratio. This result is compatible with nearly random interception of cyanomethyl radicals by the two olefins. Since the copolymerization reactivity ratios of polyethylene radical with ethylene vs. 1-butene, 2-butene, and isobutene are similar,³⁴ the large variation in olefin–acetonitrile adduct yields when the olefins are irradiated separately with AgOTf (Table II) cannot be due entirely to variations in the chain length of the radical addition process. In view of the approximate correlation between adduct yield and Ag(I)–olefin equilibrium constant⁷ (Table II), it appears likely that the yield of adduct when the olefins are irradiated separately is determined primarily by the efficiency of complex formation and light absorption. The failure of tetrasubstituted olefins, dienes, and stilbene to yield acetonitrile adducts is consistent with the known stability of their cation radicals in acetonitrile solution.³⁵ Thus, acetonitrile addition is restricted to mono- and disubstituted olefins that form relatively unstable (reactive) cation radicals.

The remarkable 70-fold decrease in the yield of adduct **1** upon solvent deuteration (Tables I, III) provides further support for a free-radical chain process in the formation of **1**. Comparably large isotope effects have been reported for autooxidation of alkylbenzenes.³⁶ For a long-chain process with a primary isotope effect in both the initiation (k_i) and propagation (k_p) steps, the isotope effect on product yield is given by eq 6. An isotope effect

$$\text{Yield-H/Yield-D} = k_i^H k_p^H / k_i^D k_p^D \quad (6)$$

of 4.0 has been reported for chain transfer from 1-butanethiol S–H vs. S–D for free-radical polymerization of styrene.³⁷ Larger values (ca. 7) expected for the thermoneutral abstraction of a hydrogen atom from acetonitrile³⁸ would provide a calculated isotope effect of ca. 49, smaller than the observed value. This discrepancy may result from the experimentally observed short chain length. Inclusion of termination processes for both the cyanomethyl and (cyanomethyl)norbornyl radicals in the kinetic scheme precludes a simple steady-state solution.

Mechanism of Silver(I)-Initiated Methanol Addition. Irradiation of AgOTf and norbornene in methanol solution results in the formation of solvent–norbornene adducts **5** and **6** and norbornene dimers **2–4** (Table V). The mechanism for formation of adduct **6** is probably analogous to that for formation of adduct **1** (eq 1–5).

(33) Mortimer, G. A. *J. Polym. Sci., Polym. Chem. Ed.* **1966**, *4*, 881–900.

(34) Mortimer, G. A. *J. Polym. Sci., Part B* **1965**, *3*, 343–344.

(35) Lewis, F. D.; DeVoe, R. J. *Tetrahedron* **1981**, *38*, 1069–1077.

(36) Krumbiegel, P. Z. *Chem.* **1968**, *8*, 328–333.

(37) Wall, C. A.; Brown, D. W. *J. Polym. Sci.* **1954**, *14*, 513–520.

(38) Pryor, W. A.; Kneipp, K. G. *J. Am. Chem. Soc.* **1971**, *93*, 5584–5586.

(24) McIntosh, D.; Ozin, G. A. *Inorg. Chem.* **1977**, *16*, 59–63.

(25) Shimizu, N.; Shimakoshi, K.; Yasumori, I. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 2929–2932.

(26) Ledwith, A. *Acc. Chem. Res.* **1972**, *5*, 133–139.

(27) Gonen, Y.; Rajleenbach, L. A.; Horowitz, A. *Int. J. Chem. Kinet.* **1977**, *9*, 361–369.

(28) Egger, K. W.; Cooks, A. T. *Helv. Chim. Acta* **1973**, *56*, 1516–1536.

(29) DeLaive, P. J.; Giannotti, C.; Whitten, D. G. *J. Am. Chem. Soc.* **1978**, *100*, 7413–7415.

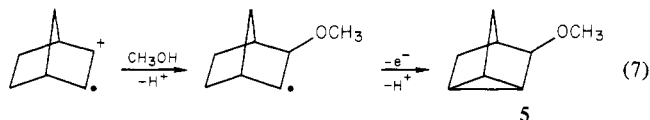
(30) Karasch, M. S.; Urry, W. H.; Kuderna, B. M. *J. Org. Chem.* **1949**, *14*, 248–253.

(31) Urry, W. H.; Stacey, F. W.; Juveland, O. O.; McDonnell, C. H. *J. Am. Chem. Soc.* **1954**, *76*, 450–455.

(32) Urry, W. H.; Juveland, O. O.; Stacey, F. W. *J. Am. Chem. Soc.* **1952**, *74*, 6155.

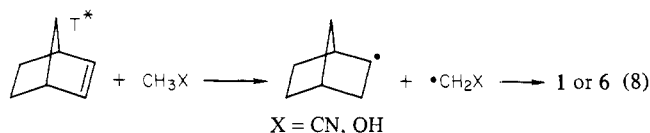
The large isotope effect on the formation of adduct **6** observed in CD_3OD but not in CH_3OD supports a free-radical chain-transfer mechanism. The lower yield for formation of **6** vs. **1** (Table IV) may reflect the higher bond dissociation energy^{27,28} and smaller chain-transfer constant for methanol vs. acetonitrile.³³ The reported average chain length for addition of ethanol to 1-octene is 2.4,³¹ approximately half the value observed for acetonitrile addition to norbornene. Alternatively, chain transfer may be disrupted by the oxidation of hydroxymethyl radicals to formaldehyde by Ag(I) .³⁹

The formation of methanol-norbornene adduct **5** has previously been observed in the electrochemical oxidation of norbornene.⁴⁰ A possible mechanism for the photochemical and electrochemical reaction is shown in eq 7. There is ample precedent for nu-



cleophilic trapping of olefin cation radicals by methanol.⁴¹ The second one-electron oxidation is probably a nonphotochemical reaction, with Ag(I) serving as the oxidizing agent.

Mechanism of Triplet-Sensitized Solvent Addition. Triplet-sensitized irradiation of norbornene in acetonitrile⁶ or methanol⁸ is known to result in the formation of adducts **1** and **6**, respectively, along with norbornene dimers **2–4** (Tables I and V). The proposed mechanism for triplet addition involves hydrogen atom abstraction from solvent by the norbornene π, π^* triplet state followed by radical coupling (eq 8) or short-chain-length addition reactions.^{6,8}



Quenching of the singlet state of aromatic hydrocarbons by silver perchlorate has been shown to result from enhanced intersystem crossing to the triplet state.⁴² That formation of triplet norbornene is not involved in the AgOTf -initiated solvent addition reactions is supported by the following evidence: (a) The AgOTf -initiated reaction occurs for acyclic and medium-ring olefins whereas the triplet-sensitized reaction does not. (b) Low-oxygen concentrations are required for the AgOTf -initiated reaction but are known to quench the triplet-sensitized reaction. (c) The product ratios are different for the two types of reaction (Table I and especially Table V).

Mechanism of Norbornene Dimer Formation. Salomon and Kochi³ established that excitation of a bis(olefin) complex is necessary for Cu(I) -catalyzed photodimerization and proposed that a possible role for Cu(I) is to serve as a template for the allowed $[2 + 2]$ -cycloaddition process. The observed decrease in cyclodimerization efficiency with increasing strength of metal ion-solvent coordination (Table IV, ether < methanol < acetonitrile) is consistent with the requirement of a bis(olefin) complex for this reaction. The yield of dimer upon irradiation of AgOTf in acetonitrile solution increases with increasing norbornene concentration and decreasing temperature, conditions that would favor the formation of a bis(olefin) complex. Support for the proposal that the metal ion serves as a template for the cyclodimerization process³ is also provided by the observation that the efficiency of metal ion photocatalyzed cyclodimerization decreases with increasing ionic radius of the metal ion ($\text{Cu(II)} < \text{Cu(I)} < \text{Ag(I)} < \text{Tl(I)}$) although other factors (e.g., π -bonding capacity) are also certainly operative.¹⁸ The proximity of the coordinated olefin molecules is also likely to be influenced by preferred co-

ordination geometry. For example, Cu(II) and Cu(I) have a far greater tendency toward tetra- vs. dicoordination than does Ag(I) .⁴³ Differences in norbornene and solvent coordination may also account for the metal ion and solvent dependence of the ratio of dimers **3/4** (Table IV).

Alternative mechanisms that might be considered for dimer formation include (a) addition of triplet norbornene (free or complexed) to ground-state norbornene and (b) addition of the norbornene cation radical to norbornene to yield a dimeric cation radical, which upon one-electron reduction (by Ag^0 or O_2^-) would yield dimers **3** and **4**. The former mechanism should yield **4** as the major dimer by analogy to the results of triplet sensitization in acetonitrile (Table I) and methanol (Table V) solution. The latter mechanism is analogous to that proposed by Ledwith²⁶ for charge-transfer-initiated photodimerization of several electron-rich olefins and would be expected to yield the less hindered dimer **3**. Thus neither alternative mechanism can account for the solvent dependence of the dimer ratio.

The final aspect of the metal ion catalyzed photodimerization reaction that requires discussion is the relative efficacy of the different metal ions. The stability constants of Cu(I) -olefin complexes are greater than those of Ag(I) -olefin complexes,¹⁴ in accord with the higher yields of dimer formation using Cu(I) vs. Ag(I) salts in poorly coordinating ether solvents (Table IV). The higher yield of dimer with Cu(II) vs. Cu(I) in diethyl ether solution is surprising, in light of the absence of previous examples of Cu(II) -olefin photochemical reactions. The Cu(II) -initiated dimerization reaction might be attributed to photoreduction of Cu(II) to the catalytically active Cu(I) ion. While Cu(I) is undoubtedly formed and responsible for part of the observed dimerization, it cannot be the exclusive catalytic species in view of the higher yield of dimer and lower **3/4** ratio observed with Cu(II) vs. Cu(I) . Since Cu(I) disproportionates thermally to Cu(0) and Cu(II) , the formation of more than one equivalent of Cu(I) from Cu(II) is thermodynamically impossible.

Less evidence is available pertaining to the mechanism of bis(norbornene) (**2**) formation in acetonitrile and methanol solution. The formation of binorbornene- d_2 in acetonitrile- d_3 solution is consistent with free-radical combination of two norbornyl radicals, which could be produced by reduction of the norbornyl cation by either Ag^0 or O_2^- . Since the norbornyl cation is produced by the reaction of norbornene cation radical with solvent (eq 3), a larger isotope effect on the yield of **2** would be expected for $\text{CD}_3\text{OD}/\text{CH}_3\text{OH}$ vs. $\text{CD}_3\text{CN}/\text{CH}_3\text{CN}$, as is observed (Tables I and V).

Experimental Section

General Procedures. For typical photochemical reactions, metal salts were weighed out in an inert-atmosphere glove box. Ten-milliliter solutions were prepared containing 0.020–0.20 mmol of metal salt and 2.5 mmol of olefin and were manipulated with nitrogen-flushed syringes by using standard Schlenk techniques. The solutions were transferred to 12-mm quartz tubes equipped with Teflon brand vacuum valves and were irradiated on a merry-go-round apparatus with a Hanovia 450-W medium-pressure mercury lamp in a water-cooled Vycor brand lamp well. Care was taken to ensure solutions were totally immersed in a water bath of the appropriate temperature (ca. 25 °C unless otherwise specified). The same light source and a 500-mL Ace glass photochemical reaction vessel were employed in preparative irradiations. Quantum yields (313-nm irradiation) were determined on 3-mL solutions with higher metal salt concentrations (0.10–0.14 M) in square cells with a Bausch and Lomb high intensity monochromator. Light intensities were monitored by using ferrioxalate actinometry.⁴⁴ Solutions contained hexadecane internal standard and were analyzed by gas chromatography with a Hewlett-Packard 5750 dual-flame gas chromatograph on a 5% FFAP on Chromosorb G 6 ft $\times$ $\frac{1}{8}$ in. column. NMR spectra were recorded on either a Perkin-Elmer R20B or Varian EM360 60-MHz spectrometer, optical absorption spectra on a GCA-McPherson EU707 spectrophotometer, IR spectra on a Perkin-Elmer 267 spectrophotometer, and mass spectra on a Hewlett-Packard GC (HP-5700A)-MS (5930A) spectrophotometer with a Data General Nova 840 computer.

(43) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley: New York, 1980; Chapters 21-H and 22-I.

(44) Parker, C. A. *Proc. R. Soc. London, Ser. A* **1953**, 220, 104–116.

(39) Kumar, A. *J. Am. Chem. Soc.* **1981**, 103, 5179–5182.

(40) Shono, T.; Ikeda, A. *J. Am. Chem. Soc.* **1972**, 94, 7892–7898.

(41) Maroulis, A. J.; Shigemitsu, Y.; Arnold, D. R. *J. Am. Chem. Soc.* **1978**, 100, 535–541.

(42) Saito, T.; Yashoshima, S.; Masuhara, H.; Mataga, N. *Chem. Phys. Lett.* **1978**, 59, 193–196.

Solutions for oxygen-dependence studies were prepared in the usual manner and transferred to quartz tubes. They were then vacuum line degassed with four or five freeze-pump-thaw cycles and kept frozen. A controlled amount of oxygen was admitted to the manifold, one tube opened, and the pressure recorded with a mercury manometer. Each tube was closed and allowed to thaw completely prior to irradiation.

Materials. Spectroquality acetonitrile (Burdick and Jackson) was distilled from calcium hydride under nitrogen. Spectroquality methanol (Burdick and Jackson) was distilled from magnesium methoxide under nitrogen. Gold Label tetrahydrofuran and ether (Aldrich) were distilled from Na/K-benzophenone under nitrogen. Metal salts were synthesized via literature methods.^{11b,c} Norbornene (Aldrich) was distilled from sodium under nitrogen and sublimed prior to use. Cyclohexene and cyclopentene (Aldrich) were distilled from sodium hydroxide under nitrogen. 2-Ethyl-1-butene, *trans*-2-pentene, and 1-pentene (Chemical Samples Co.) were used as received.

The identities of the photoproducts were established by comparison of spectral properties with those of commercial or independently synthesized samples. Authentic samples of 2,2'-binorbornene (**2**) and exo-*trans*-endo norbornene dimer (**4**) were prepared by the method of Kropp⁸ and displayed mass⁸ and ¹H NMR⁴⁵ spectra similar to those previously reported. Exo-*trans*-exo norbornene dimer (**3**) was prepared via the method of Salomon and Kochi;³ mp 64–66 °C (lit.⁴⁵ mp 63–64 °C); ¹H NMR was identical with a previously reported spectrum.⁴⁵ 2-(Hydroxymethyl)bicyclo[2.2.1]heptane (**6**) was a commercial sample (Aldrich).

Authentic samples of *exo*-2-(cyanomethyl)bicyclo[2.2.1]heptane (**1**) and *exo*-2-(1-cyanoethyl)bicyclo[2.2.1]heptane were prepared by the method of Schroeter.⁶ Observed for **1**: bp 80–85 °C/(6 torr) [lit.⁶ bp 72 °C (3 torr)]; ¹H NMR (CDCl₃) δ 2.2 (2 H), 2.1 (2 H, αCN), 0.9–1.8 (9 H); IR CN 2248 cm⁻¹; mass spectrum, *m/e* 135 (4), 95 (73), 68 (100). Observed for *exo*-2-(1-cyanoethyl)bicyclo[2.2.1]heptane: ¹H NMR (CDCl₃) δ 2.2 (2 H), 2.1 (1 H), 0.9–1.8 (12 H); mass spectrum matched the reported spectrum.⁶

Authentic samples of all other cyanoalkanes except 1-cyano-3-ethylpentane were prepared by standard synthetic procedures and spectral data compared to those of photochemical products. Hydrogenation (40 psi of H₂) of 1-(cyanomethyl)cyclopentane (Aldrich) in ethyl acetate with 10% Pd/C yielded (cyanomethyl)cyclopentane;⁴⁷ bp 102–105 °C (50 torr) [lit.⁴⁷ bp 88 °C (27 torr)]; ¹H NMR (CDCl₃) δ 2.4 (2 H), 1.95 (1 H), 1.10–1.70 (8 H); IR nitrile 2245 cm⁻¹; mass spectrum, *m/e* 108 (4), 69 (100), 41 (34). Treatment of (chloromethyl)cyclohexane (Aldrich) with NaCN in Me₂SO⁴⁶ yielded (cyanomethyl)cyclohexane;⁴⁸ bp 102–105 °C (30 torr) (lit.⁴⁸ bp 200–205 °C); ¹H NMR (CDCl₃) δ 2.2 (d, 2 H) 0.90–1.90 (m, 11 H); IR 2250 cm⁻¹; mass spectrum, *m/e* 96

(38), 83 (98), 82 (37), 81 (66), 67 (56), 55 (100), 41 (32). Substitution of 1-bromohexane (Aldrich) in the same manner resulted in 1-cyano-hexane;⁴⁹ bp 174–177 °C [lit.⁴⁹ bp 98 °C (39 torr)]; ¹H NMR (CDCl₃) δ 2.2 (t, 2 H), 1.0–1.7 (m, 8 H), 0.80 (t, 3 H); IR 2250 cm⁻¹; mass spectrum, *m/e* 124 (5), 110 (18), 97 (21), 96 (55), 83 (44), 82 (100), 69 (45), 55 (38), 54 (41), 43 (28), 41 (44). Treatment of 2-ethyl-1-butanol (Aldrich) with SOCl₂⁵⁰ resulted in formation of 3-(chloromethyl)pentane (bp 120 °C). Reaction of this chloride with NaCN in Me₂SO afforded 3-(cyanomethyl)pentane;⁵¹ bp 68–70 °C (20 torr) (lit.⁵¹ bp 164–166 °C); ¹H NMR (CDCl₃) δ 2.40 (d, 2 H), 1.30–1.80 (m, 5 H), 0.97 (t, 6 H); IR 2245 cm⁻¹; mass spectrum, *m/e* 110 (5), 96 (11), 82 (15), 71 (100), 68 (28), 55 (29), 54 (22), 43 (84), 41 (26).

Preparative Irradiation. The following examples are illustrative of the preparation of olefin-acetonitrile photoadducts.

exo-2-(cyanomethyl)bicyclo[2.2.1]heptane (1). A solution of 1.75 g of AgOTf (6.8 mmol) and 9.5 g of norbornene (0.1 mol) in 0.4 L of acetonitrile was irradiated for several days with periodic removal of plated silver. The solution was added to water and extracted with ether. The organic layer was concentrated and chromatographed with 5% ethyl acetate/hexane on silica gel to yield 4.4 g (35%) of **1**.

1-Cyano-3-ethylpentane was isolated from a preparative-scale photolysis of an acetonitrile (300 mL) solution containing 1.02 g of AgOTf (4.0 mmol), 12.6 g of 2-ethyl-1-butene (150 mmol), and 4.70 g of norbornene (50 mmol). The solution was concentrated and chromatographed with 5% ethyl acetate/hexane on silica gel and the product isolated via preparative gas chromatography (10% FFAP, 7.5 ft × 0.5 in. column, 155 °C): ¹H NMR (CDCl₃) δ 2.25 (t, 2 H), 1.31–1.7 (m, 7 H), 0.8–0.9 (t, 6 H); IR 2240 cm⁻¹; mass spectrum, *m/e* 124 (5), 110 (12), 96 (73), 71 (34), 69 (78), 55 (100), 54 (31), 43 (39), 41 (32).

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Registry No. **1**, 27108-25-4; **1**(*d*₃), 82598-75-2; **2**, 82637-91-0; **2**(*d*₂), 82614-05-9; **3**, 1624-14-2; **4**, 1624-16-4; **5**, 21516-65-4; **6**, 5240-72-2; CH₃CH₂CN, 107-12-0; CH₃OH, 67-56-1; AgOTf, 2923-28-6; TiOTf, 73491-36-8; Cu(OTf)₂, 34946-82-2; CuOTf, 42152-44-3; CH₃CN, 75-05-8; CD₃CN, 2206-26-0; **6**(*d*₁), 82598-76-3; norbornene, 498-66-8; cyclopentene, 142-29-0; cyclohexene, 110-83-8; 2-ethyl-1-butene, 760-21-4; *trans*-2-pentene, 646-04-8; 1-pentene, 109-67-1; (cyanomethyl)cyclopentane, 5732-87-6; (cyanomethyl)cyclohexane, 4435-14-7; 1-cyano-3-ethylpentane, 82598-77-4; 1-cyano-2-methylpentane, 53783-89-4; 1-cyano-2-ethylbutane, 5631-83-4; 1-cyano-hexane, 766-05-2.

(45) Arnold, D. R.; Trecker, D. J.; Whipple, E. B. *J. Am. Chem. Soc.* **1965**, *87*, 2596–2602.

(46) Friedman, L.; Shechter, H. *J. Org. Chem.* **1960**, *25*, 877–879.

(47) Moureau, H.; Chovin, P.; Bloch, G.; Rivoal, G. *Bull. Soc. Chim. Fr.* **1949**, 475–477.

(48) Braun, C. E.; Randall, W. M. *J. Am. Chem. Soc.* **1934**, *56*, 2134–2136.

(49) Pattison, F. L. M.; Brown, G. M. *Can. J. Chem.* **1956**, *34*, 879–884.

(50) Gerrard, W.; Hudson, H. R. *J. Chem. Soc.* **1963**, 1059–1064.

(51) Rhinesmith, H. S. *J. Am. Chem. Soc.* **1936**, *58*, 596–597.