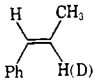
Table I. Photosensitized isomerization of 

Sensitizer (E_T)	Starting isomer (D/H)[a]	% convn	D/H[a] (recovered *trans*)	D/H[a] (*cis*)	$\phi_{t\rightarrow c}$[b]	$\phi_{c\rightarrow t}$[b]	% *cis* at photostationary state
Fluorenone (53.3)	*trans* (1.050 ± 0.003)	16.9	1.08 ± 0.02	0.91 ± 0.01	0.38 (0.5 *M*)		78[e]
		8.7	1.05 ± 0.005	0.93 ± 0.007	0.40 (0.5 *M*)		
Biacetyl (54.9)	*trans* (0.966 ± 0.005)	10.3	0.980 ± 0.008	0.85 ± 0.01	0.42	>0.39[f]	88[e,g]
Thioxanthone (65.5)					0.45	0.50	
Benzophenone (68.5)	*cis* (1.07 ± 0.02)	64[d]	1.06 ± 0.05	1.06 ± 0.06	0.51[c]	0.51[c]	65[c]
Propiophenone (74.6)					0.44	0.50	55[e]

[a] The ratio of *m/e* 119 to *m/e* 118, corrected for ^{13}C contribution to the *m/e* 119 peak. The precision represents the 95% confidence level for the mean of ten scans. [b] Quantum yields uncorrected for back-reaction, measured at about 5% conversion in solutions 0.05 *M* in β-methylstyrene, except as noted. [c] A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965). [d] Photostationary state. [e] At 0.06 *M*. Recovery of material was essentially quantitative for fluorenone, but in the region of 30–60% in other cases at photostationary state. [f] The photostationary state is so rich in *cis* isomer that back-reaction correction to this number is significant even at 5% conversion. It is accordingly a minimum value for the initial $\phi_{t\rightarrow c}$. [g] This number may be sensitive to the extent of decomposition of the sample.

clearly n–π*.[8] Addition of a biacetyl triplet to β-methylstyrene should occur in the β (labeled) position if Yang's[2] mechanism were operating, since only that mode of addition permits delocalization of an odd electron into the benzene ring. Consequently, an inverse deuterium isotope effect would be expected, contrary to our observation. It is possible that the isomerizations observed by Yang[2] did not involve free olefin triplets at all. We feel that our experiments probably do, since the constancy of $\phi_{t\rightarrow c}/\phi_{tc}$ at 0.43 ± 0.02 for all our data is readily interpretable on the basis that f_c of eq 1 = 0.43 (or slightly higher, since the back-reaction correction was not made).

The interpretation of the result that $k_H/k_D > 1$ must remain somewhat speculative until more is known about the details of energy-transfer mechanisms. Schmidt and Lee[9] have recently reported similar observations with benzene and acetone triplets as donors and C_2H_4 or C_2D_4 as quencher. Their explanation is based on the observation of Evans[10] that deuteration shifts the apparent onset of singlet–triplet absorption in ethylene to higher energies. Should it turn out that Evans' results relate to the true triplet energies (0–0 bands) of C_2H_4 and C_2D_4 *and* that energy transfer is in any of these cases a process involving the spectroscopic olefin triplet, then it would be expected that k_H/k_D would be greater than 1.

On the other hand, Hammond[11] has investigated "endothermic" triplet energy transfer and has presented results which strongly suggest that the donor–acceptor interaction can involve nonspectroscopic states of the acceptor. Simple olefin triplets are expected to have energy minima at geometries in which considerable twist around the double bond has occurred.[12] We consider it likely that relatively low-energy "twisted" states are available for β-methylstyrene. They may well be involved in these "endothermic" energy transfers (the triplet energy for *trans*-β-methylstyrene has been determined to be 59.8 kcal/mol[13]).

We believe an isotope effect in the observed direction can be rationalized equally well if spectroscopically inaccessible states of the acceptor are involved. The energy-transfer probability would be expected to depend upon Franck–Condon factors.[14] We feel there is reason to expect them to be larger when the substrate is undeuterated, and therefore to expect $k_H/k_D > 1$. The line of reasoning would be somewhat analogous to that conventionally used to explain the deuterium isotope effects, $k_H/k_D > 1$, on radiationless decay rates of triplet-state organic molecules.[15]

Much further work is needed to determine rate constants, temperature effects, and isotope effects in a variety of systems before very detailed understanding of endothermic energy transfer from organic sensitizer triplets will emerge.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research through Grant 3031-A4.

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[8] (a) H. L. J. Bäckström and K. Sandros, *Acta Chem. Scand.*, **12**, 823 (1958); (b) H. L. J. Bäckström and K. Sandros, *ibid.*, **14**, 48 (1960), and references contained therein.

[9] M. W. Schmidt and E. K. C. Lee, *J. Am. Chem. Soc.*, **90**, 5919 (1968). These results appeared after initial submission of our manuscript.

[10] D. F. Evans, *J. Chem. Soc.*, 1735 (1960).

[11] (a) J. Saltiel and G. S. Hammond, *J. Am. Chem. Soc.*, **85**, 2515 (1963); (b) G. S. Hammond and J. Saltiel, *ibid.*, **85**, 2516 (1963); (c) G. S. Hammond, *et al.*, *ibid.*, **86**, 3197 (1964); (d) W. G. Herkstroeter and G. S. Hammond, *ibid.*, **88**, 4769 (1966).

[12] R. S. Mulliken and C. C. J. Roothaan, *Chem. Rev.*, **41**, 219 (1947).

[13] A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).

[14] G. W. Robinson and R. P. Frosch, *ibid.*, **38**, 1187 (1963).

[15] (a) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin and Co., New York, N. Y., 1965, pp 69–70; (b) G W. Robinson and R. P. Frosch, *J. Chem. Phys.*, 37, 1962 (1962); (c) G. W. Robinson, *J. Mol. Spectry.*, **6**, 58 (1961); (d) N. J. Turro and R. Engel, *J. Am. Chem. Soc.*, **90**, 2989 (1968).

[16] Procter and Gamble Fellow, 1968–1969.

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A Novel Synthesis of Isomerically Pure α,β-Unsaturated Nitriles *via* Hydroalumination of Alkynes[1]

Sir:

The facile reactions of vinylalanates with carbon dioxide and halogens, which provide stereoselective

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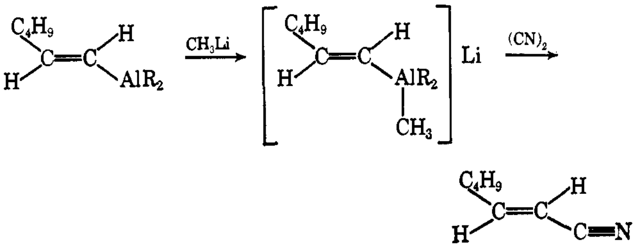
Table I. Physical Properties of α,β-Unsaturated Nitriles Derived from Vinylalanates

Vinylalanate from	Nitrile	Bp, °C (mm)	n^{23}D	Yield, %	Mp of amide, °C
1-Hexyne	*trans*-Hept-2-enenitrile	112–114 (20)	1.4397	87	123–124
Cyclohexylacetylene	*trans*-3-Cyclohexylprop-2-enenitrile	85–86 (4)	1.4825	78	156–158
Phenylacetylene	*trans*-2-Phenylethenenitrile	120–121 (3)	1.5986	64	146–147
1-Ethynylcyclohexene	*trans*-3-(1-Cyclohexenyl)-prop-2-enenitrile	87 (2)	1.5532	62	119–120
3-Hexyne	*trans*-2-Ethylpent-2-ene-nitrile	88–89 (15)	1.4383	76	113–114
3-Hexyne[a]	*cis*-2-Ethylpent-2-enenitrile	155–156 (760)	1.4305	65	108–109
3-Hexyne[b]	*cis,cis*-2,3,4-Triethylhept-2,4-dienenitrile	80 (1)	1.4703	63	

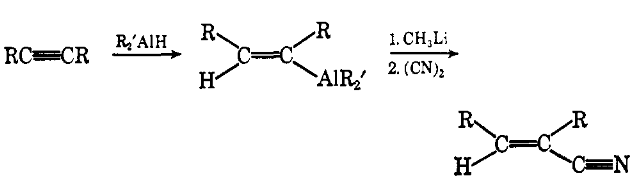
[a] Hydroalumination with lithium diisobutylmethylaluminum hydride. [b] The alkyne was treated with diisobutylaluminum hydride in a 2:1 ratio to give the dienylalane.

syntheses of α,β-unsaturated acids[2] and vinyl halides,[3] have now been extended to reactions with cyanogen which afford α,β-unsaturated nitriles of predictable stereochemistry.

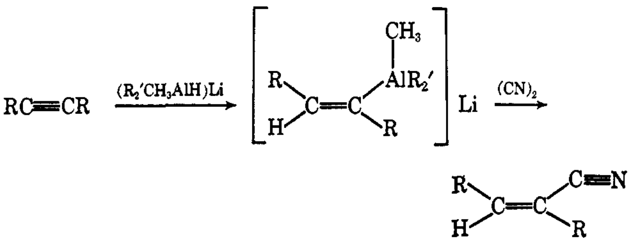
Hydroalumination of 1-hexyne in a hydrocarbon solvent with diisobutylaluminum hydride in a 1:1 ratio produces *trans*-1-hexen-1-yldiisobutylalane in 90% yield. The vinylalane unfortunately does not react with cyanogen at room temperature. However, after conversion of the vinylalane into the corresponding *ate* complex with methyllithium in ether, addition of cyanogen yields 87% *trans*-hept-2-enenitrile.



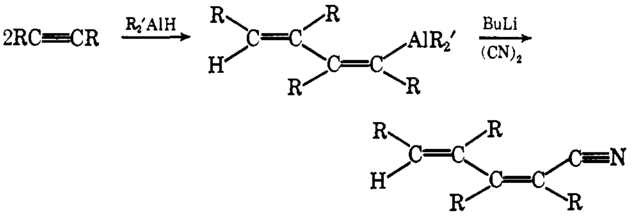
Vinylalanates derived from the hydroalumination of disubstituted alkynes with diisobutylaluminum hydride followed by treatment of the intermediate vinylalanes with methyllithium also react readily with cyanogen to give *trans*-α,β-unsaturated nitriles. Thus, 3-hexyne is converted by this procedure to *trans*-2-ethylpent-2-enenitrile.



Synthesis of the corresponding *cis* nitriles entails only a slight modification of the procedure leading to the *trans* derivatives. Thus, treatment of diisobutylaluminum hydride in monoglyme with methyllithium results in the formation of lithium diisobutylmethylaluminum hydride. In contrast to the behavior of diisobutylaluminum hydride, this reagent adds *trans* to the triple bonds of disubstituted alkynes.[2] The intermediate *cis*-vinylalanate formed in the case of 3-hexyne reacts readily with cyanogen to give *cis*-2-ethylpent-2-enenitrile.



The synthetic potentialities of this novel procedure are further illustrated by the conversions of disubstituted alkynes and enynes into dienenitriles. Thus reaction of diisobutylaluminum hydride with 3-hexyne in a 1:2 ratio in a hydrocarbon solvent at 70° affords tetraethyl-1,3-butadienylalane.[4] By successive treatment of the dienylalane with butyllithium and cyanogen, 2,3,4-triethylhept-2,4-dienenitrile is obtained in 63% yield. Hydrolysis of the dienylalane derived from 3-hexyne affords *cis,cis*-4,5-diethyl-3,5-octadiene.[5] Also, the reaction of vinylalanates with cyanogen appears to be another example of an electrophilic substitution reaction involving an organoalane which proceeds with retention of configuration.[2,3,6] Therefore, the *cis,cis* structure is tentatively assigned to the dienenitrile.



Diisobutylaluminum hydride exhibits a high selectivity for the triple bonds of enynes. However, in reactions involving a terminal triple bond which is conjugated with a vinyl group, partial metalation of the enyne is also observed. Thus, 1-ethynylcyclohexene reacts with diisobutylaluminum hydride at 50° to produce 80% of the dienylalane contaminated with 20% of the corresponding metalation product. Conversion of the dienylalane to the *ate* complex with butyllithium followed by the addition of cyanogen yields, after fractional distillation, 62% of the *trans*-dienenitrile.

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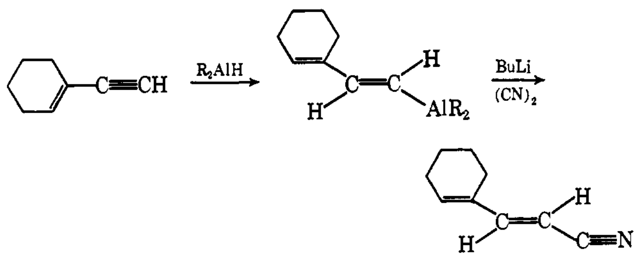
(2) G. Zweifel and R. B. Steele, *J. Am. Chem. Soc.*, **89**, 2754 (1967); **89**, 5085 (1967).

(3) G. Zweifel and C. C. Whitney, *ibid.*, **89**, 2753 (1967).

(4) G. Wilke and H. Müller, *Ann.*, **629**, 222 (1960); G. Zweifel and N. L. Polston, to be published.

(5) G. Zweifel, N. L. Polston, and C. C. Whitney, *J. Am. Chem. Soc.*, **90**, 6243 (1968).

(6) It is conceivable that the reaction may proceed *via* the vinyllithium derivative resulting from disproportionation of the vinylalanate.



Finally, hydroalumination of phenylacetylene with diisobutylaluminum hydride at 50° affords 70% vinylalane and 30% alkynylalane.[7] Successive treatment of the reaction mixture with butyllithium and cyanogen gives, after fractional distillation, a 64% yield of *trans*-2-phenylethenenitrile.

The experimental results are summarized in Table I.

Since the nitrile group is readily converted into other functional groups (amides, amines, aldehydes, etc.), the present procedure provides a valuable tool for the preparation of numerous vinyl derivatives of defined stereochemistry. The simplicity of the procedure for the conversion of alkynes into *trans*-α,β-unsaturated nitriles is illustrated by the following example.

A dry 200-ml flask equipped with a side arm capped with a rubber septum, a thermometer well, and a magnetic stirrer was flushed with nitrogen. To the flask, which was kept under a static pressure of the gas, was added 4.1 g (50 mmol) of 1-hexyne, 20 ml of *n*-hexane, and 9.3 ml (50 mmol) of diisobutylaluminum hydride. The temperature during the addition was maintained at 25–30° by means of a water bath. The solution was stirred at room temperature for 30 min, then heated slowly to 50°. After remaining for 2 hr at this temperature, the reaction mixture was cooled to −20° (CCl$_4$–CO$_2$ bath) and 31 ml (50 mmol) of methyllithium in ether was added. Cyanogen (3 ml, 60 mmol) was condensed at −30° using a small cold trap.[8] The cooling bath was then removed and the cyanogen was allowed to pass into the vinylalanate solution while the temperature was maintained between −10 and +10°.[9] In order to avoid the escape of excess cyanogen, the reaction flask was connected to a wash bottle containing 6 *N* sodium hydroxide.[9] After addition of the cyanogen was completed the dark reaction mixture was stirred for an additional 30 min at room temperature before being poured into a well-stirred slurry of 3 *N* sodium hydroxide (100 ml) which had been precooled in a Dry Ice–acetone bath. The hydrolysate was allowed to come to room temperature and then was extracted with pentane. Distillation gave 4.7 g of *trans*-hept-2-enenitrile (87%); bp 112–114° (20 mm), $n^{23}\mathrm{D}$ 1.4397 (lit.[10] bp 186–187 (759 mm), $n^{23}\mathrm{D}$ 1.4399).

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(7) J. R. Surtess, *Australian J. Chem.*, **18**, 14 (1965).

(8) Cyanogen was obtained from the Matheson Co.

(9) In view of the fact that the reactions of cyanogen with vinylalanates or sodium hydroxide result in the formation of precipitates, the use of sintered-glass dispersion tubes should be avoided.

(10) P. Bruylants, *Bull. Soc. Chim. Belges*, **41**, 336 (1932).

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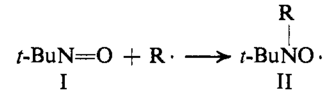
A Probe for Homolytic Reactions in Solution. II. The Polymerization of Styrene[1]

Sir:

There are now several examples in the literature of the observation by electron spin resonance of nitroxide radicals formed by the addition of reactive free radicals to C-nitroso compounds.[2] We wish to point out the potential value of this reaction as a probe for exploring the mechanisms of free-radical reactions in solution. This suggestion is based on the very large bimolecular rate constants estimated[3] for these additions, coupled with the exceptional stability of nitroxide radicals; consequently, sufficient nitroxide concentrations can readily be achieved for direct esr observation to be possible without recourse to flow-system techniques.

The nitroso compound of choice is 2-methyl-2-nitrosopropane (I), since nitroxides (II) derived from I exhibit hyperfine couplings due only to nitrogen and to the scavenged radical. Two disadvantages in the use of I are that unresolved coupling with the *t*-butyl protons gives rather broad lines and that red light is sufficient to effect photolysis of I (→ *t*-Bu· + NO),[4] and light must therefore be excluded during the preparation of samples.[5] Figure 1a shows a typical spectrum, obtained in this case by warming a dilute solution of lauryl peroxide and I in deoxygenated[6] benzene. Each of the nine principal lines, attributable to coupling with nitrogen plus two equivalent α-methylene protons (a_N = 15.0 G, a_H = 9.9 G), is further split into a partially resolved triplet, presumably by the β-methylene protons.



$$\underset{\text{I}}{t\text{-BuN=O}} + \text{R}\cdot \longrightarrow \underset{\text{II}}{t\text{-Bu}\overset{\text{R}}{\overset{|}{\text{N}}}\text{O}\cdot}$$

Application to a more complex reaction is illustrated in Figures 1b–e, which show spectra of radicals generated during the polymerization of styrene initiated by *t*-butyl peroxyoxalate (*ca.* 15 mg of peroxyoxalate/ml of styrene) at room temperature in the presence of I. The highest concentrations of I (*ca.* 0.05 *M*) gave the spectra shown in Figures 1b,c. In Figure 1b the two outermost lines are part of the known three-line spectrum of *t*-BuO(*t*-Bu)NO·[7] which results from scavenging of the

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(1) G. R. Chalfont and M. J. Perkins, *J. Am. Chem. Soc.*, **89**, 3054 (1967), is regarded as part I of this series.

(2) For recent examples see ref 1 and A. Mackor, T. A. J. W. Wajer, and T. J. de Boer, *Tetrahedron*, **24**, 1623 (1968).

(3) For example, the "methyl affinity" of nitrosobenzene at 65° is greater than that of benzene by *ca.* 10^5: W. J. Heilman, A. Rembaum, and M. Szwarc, *J. Chem. Soc.*, 1127 (1957); the rate constant for reaction of ·CH$_3$ with benzene has been estimated at 50 l. mol^{-1} sec^{-1} at 80°: D. F. DeTar, *J. Am. Chem. Soc.*, **89**, 4058 (1967); these figures put the rate of reaction of ·CH$_3$ with C$_6$H$_5$NO within 2–3 orders of magnitude of the diffusion-controlled limit. (It is, however, not certain that all of this reaction occurs at nitrogen.)

(4) A. Mackor, T. A. J. W. Wajer, T. J. de Boer, and J. D. W. van Voorst, *Tetrahedron Letters*, 2115 (1967); J. G. Calvert and S. S. Thomas, unpublished work quoted in J. G. Calvert and J. N. Pitts, "Photochemistry," John Wiley & Sons, Inc., New York, N. Y., 1966, p 476.

(5) The *t*-butyl radicals are readily scavenged to give di-*t*-butyl nitroxide,[3] the spectrum of which may mask that of radicals under investigation. In some instances, on the other hand, this photolysis may constitute a useful radical initiation.

(6) A solution of lauryl peroxide (*ca* 0.4 ml, 5%) was added to the solid nitroso dimer (*ca* 0.1 mg) in a quartz esr tube, and the solution was deoxygenated by a stream of oxygen-free nitrogen. The tube was capped to exclude air and heated in the cavity of the spectrometer. All samples were similarly deoxygenated before spectroscopic examination.

(7) A. Mackor, T. A. J. W. Wajer, T. J. de Boer, and J. D. W. van Voorst, *Tetrahedron Letters*, 385 (1967).