and 5.72 (q, $J \cong 7$ Hz, $=CHCH_3$); mass spectrum m/e (calcd for $C_{10}H_{14}O_2$, 166.099) 166.100.

Mixture of lactams 35 and 42 was an oil: ir ($CHCl_3$) 3430 (NH), 1689 (C=O), and 1634 cm^{-1} (C=C); nmr ($CDCl_3$) (in addition to peaks of the major isomer **35**) δ 1.22 (d, J = 6.2 Hz), 1.63 (d, J = 7.2 Hz), 2.07 (s, CH_3), 2.43 (s, CH_3), 4.28 [q, J = 6.2 Hz, $-CH(CH_3)N-$], 5.73 (q, J = 7.2 Hz, $=CHCH_3$), and 6.82 (br s, 1 H, NH); mass spectrum m/e (calcd for $C_{10}H_{15}NO$, 165.116) 165.112.

Registry No.—**6**, 4544-23-4; **7a**, 37817-10-0; **7b**, 37817-11-1; **8a**, 37817-12-2; **8b**, 37817-13-3; **9a**, 37817-14-4; **9b**, 37817-15-5; **10a**, 37817-16-6; **10b**, 37817-17-7; **11**, 37817-18-8; **12**, 37817-19-9; **13**, 33530-27-7; **14**, 37817-21-3; **15**, 37817-22-4; **16**, 37817-23-5; **17**, 37817-24-6; **18a**, 37817-25-7; **18b**, 37817-26-8; lactam **19**, 37817-27-9; adduct **21**, 37817-29-1; **22**, 33530-26-6; **23**, 37817-31-5; **24**, 37817-32-6; **25**, 37817-33-7; **26**, 37817-34-8; **28**, 37817-36-0; **29**, 37817-37-1; **30**, 37817-38-2; **31**, 37817-39-3; **32a**, 37817-40-6; **32b**, 37817-41-7; **33a**, 37817-42-8; **33b**, 37817-43-9; **34**, 37817-44-0; **35**, 37817-45-1; **36**, 37817-46-2; **37**, 37893-77-9; **38a**, 37817-48-4; **38b**, 37817-53-1; **39**, 37817-47-3; **40**, 37817-51-9; **41**, 37817-49-5; **42**, 37817-28-0; CSI, 1189-71-5.

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Carbon-13 Nuclear Magnetic Resonance Spectroscopy. The Spectra of the Linear Alkynes[1]

DOUGLAS E. DORMAN, MANFRED JAUTELAT, AND JOHN D. ROBERTS*

Contribution No. 4509 from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California 91109

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The ^{13}C chemical shifts of a selection of linear alkynes are collected and correlated with structure. A system of empirical rules by which the ^{13}C nuclear magnetic resonance spectra of such compounds can be predicted is derived. The failure of the current point-dipole approximation to predict correctly the shifts due to the anisotropy of the triple bond is discussed.

Carbon-13 nuclear magnetic resonance (^{13}C nmr) spectra have been reported for a number of linear alkynes.[2–6] In most cases,[2–5] only the chemical shifts of the sp-hybridized carbons were reported, and in all cases spectra were measured using the adiabatic, rapid-passage technique, which generally yields experimental uncertainties of 0.5 ppm. While accuracy of this magnitude is adequate for many applications,[6] it is not sufficient to identify the more subtle chemical-shift differences associated with changes in substitution in remote sites in the molecule. Because such information is important in applications of ^{13}C nmr spectroscopy to problems in structure elucidation,[7] we have undertaken a brief survey of ^{13}C spectra of linear alkynes using the absorption mode and spectrum averaging. The present paper describes the results of this survey and compares them to those reported earlier.

Experimental Section

Carbon-13 chemical shifts were measured under conditions of full proton decoupling on the Varian digital frequency sweep spectrometer described previously.[8] Chemical shifts were measured relative to internal 1,4-dioxane and were then referenced to external carbon disulfide using the relation $\delta_{CS_2} = \delta_{1,4\text{-dioxane}} + 126.2$. Regression analyses were performed on an IBM 360/75 computer with the aid of a standard subroutine for stepwise multiple regression analysis.[9]

Results

The extant data for the linear alkynes and alkadiynes are presented in Table I. The spectrum of 1,7,13-tetradecatriyne[10] is also included for comparison. For the octynes, data from earlier workers and from these laboratories are both included in Table I. It is obvious that there are substantial differences between the spectra obtained by dispersion[6] and absorption modes. Indeed, the differences are often greater than the experimental errors of the two methods. These disparities are possibly partly due to solvent or concentration effects. The earlier data[6] were derived from neat solutions, while solutions in 1,4-dioxane were used in the present study. Throughout the remainder of this paper, only our own data for the octynes will be considered.

The spectra of the various alkynes are compared to those of the analogous alkanes in Table II. The values in this table were obtained by subtracting the shifts of the alkane from those of the alkyne in each case. From Table II it is evident that, within any particular subgroup of linear alkynes, the sp-hybridized carbons are shifted downfield from their positions in the saturated alkane by quite constant amounts. Thus, in the 1-alkynes, the terminal sp carbon is 54.5 ppm downfield from the corresponding methyl, while the other unsaturated carbon is about −61.0 ppm

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[1] Supported by the National Science Foundation.

[2] P. C. Lauterbur in "Determination of Organic Structures by Physical Methods," F. C. Nachod and W. D. Phillips, Ed., Academic Press, New York, N. Y., 1963.

[3] R. A. Friedel and H. L. Retcofsky, *J. Amer. Chem. Soc.*, **85**, 1300 (1963).

[4] K. Frei and H. J. Bernstein, *J. Chem. Phys.*, **38**, 1216 (1963).

[5] D. D. Traficante and G. E. Maciel, *J. Phys. Chem.*, **69**, 1348 (1965).

[6] (a) S. Rang, T. Pehk, E. Lippmaa, and O. Eisen, *Eesti NSV Tead. Akad. Toim. Keem., Geol.*, **16**, 346 (1967); (b) *ibid.*, **17**, 210, 294 (1968).

[7] R. E. Carhart, D. E. Dorman, and J. D. Roberts, in preparation.

[8] (a) F. J. Weigert and J. D. Roberts, *J. Amer. Chem. Soc.*, **89**, 2967 (1967); (b) F. J. Weigert, M. Jautelat, and J. D. Roberts, *Proc. Nat. Acad. Sci. U. S.*, **60**, 1152 (1968).

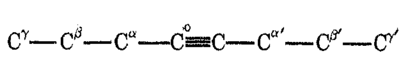
[9] A. Ralston and H. S. Wilf, "Mathematical Methods for Digital Computers," Wiley, New York, N. Y., 1965, Chapter 17.

[10] C. Charrier, D. E. Dorman, and J. D. Roberts, in preparation.

relative to its position in the alkane. The relative constancy of these shift differences suggest that the alkynes would yield a satisfactory regression analysis of the type noted earlier for the acyclic alkenes.[11] The effects of the triple bond upon the saturated carbons of the chain are, however, rather less regular than observed for the alkenes.[11] There is, of course, the large and relatively constant upfield shift which has been noted to occur at the α carbon,[6a] but the chemical-shift differences at the β, γ, $\cdots$ carbons are far less regular than observed for the alkenes.

The convention used in the regressional analysis is detailed in Figure 1. The chemical shift of each sp-hybridized carbon was expressed as a function of the number of α, β, γ, α', $\cdots$ carbons in the molecule. Thus, the expression for carbon 1 of 1-butyne is 125.5 $= \alpha' + \beta'$, while that of carbon 3 of 2-heptyne is 114.9 $= \alpha + \beta + \gamma + \alpha'$. It is important to note that because data are available only for linear alkynes, the coefficients of the substituent parameters α, β, $\cdots$ will be 1 or 0 in every case.

The results of the regressional analysis are shown in Table III. As for the alkenes,[11] the α and β parameters are large and negative, while the γ shift is smaller and positive. In contrast to the α shift, α' is upfield in nature, again as observed for the alkenes. The only difference in the qualitative comparison of the results for the regressional analyses of the alkenes and alkynes is that of the β' parameter. This shift was found to be upfield in the alkenes, while for the present compounds it is small and deshielding. The analysis yields a standard error of 0.3 ppm and a multiple correlation coefficient of 0.998. It is of interest to note that the chemical shift of ethyne itself is predicted by the analysis to be 120.9 ppm. Apparently, the carbon shift of this compound has not yet been measured.



$$C^{\gamma}—C^{\beta}—C^{\alpha}—\overset{o}{C}\equiv C—C^{\alpha'}—C^{\beta'}—C^{\gamma'}$$

Figure 1.—The designation of the saturated carbons in the calculation of the chemical shift of C°.

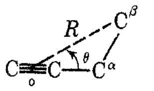


Figure 2.—A definition of the parameters in the McConnell equation, taking the β carbon as an example. The point o is the electrical center of gravity of the anisotropic group. The distance R is that between the point o and the nucleus in question, while θ is the angle between R and the axis of symmetry of the triple bond.

Discussion

Throughout the common hydrocarbons which have been studied by ^{13}C nmr spectroscopy, chemical shifts have been found to fall within three broad ranges, depending on the hybridization of the carbon. The chemical shifts of saturated carbons generally fall into a range of 140–190 ppm upfield from the resonance of carbon disulfide, while sp^2 carbons occur between 45 and 85 ppm. As seen from this and previous studies, the present range of chemical shifts of sp-hybridized carbons can be taken to be within the bounds of 105 and 125 ppm. Within these broad ranges, the largest variations have been shown[11,12] to correlate well with the extent of direct substitution by carbon, as well as the substitution on adjacent carbons (the so-called α and β effects[11,12]). Within the hydrocarbons, other effects, such as electronegativity, seem to be minor. Thus, a saturated carbon which is attached to a double bond is deshielded at most by 2 ppm. A shift of this magnitude is small in ^{13}C nmr spectroscopy, amounting to only about 1% of the general range of carbon chemical shifts. In fact, the small downfield shift observed for the α carbons in the alkenes is frequently entirely outweighed by opposing shielding effects which are considered to be steric in nature.[11,13] To demonstrate the differences between carbon and proton chemical shifts, we may consider the methyl carbon chemical shifts in methylcyclohexane, 1-methylcyclohexene, and toluene. The chemical shifts of the methyl carbons in these three compounds are 170.6,[14] 169.9,[6b] and 171.8 ppm,[15] respectively. Thus, the chemical shift of a carbon bonded to a double bond is relatively unaffected by the increased electronegativity of the unsaturated system.

The three examples above serve to demonstrate another curiosity regarding carbon chemical shifts. The methyl carbon resonance of toluene is upfield of the analogous absorption in 1-methylcyclohexene, while protons attached to aromatic rings are strongly deshielded by the ring-current effect.[16] Furthermore, the chemical shifts of sp^2-hybridized carbons in alkenes and aromatic carbons are not very different.

With this in mind, we may approach the interpretation of the ^{13}C nmr spectra of the alkynes. One of the most striking shifts observed in these compounds is that of the α carbon, which is shielded by *some 10 to 14 ppm* relative to the analogous alkanes (see Table II). While this shielding effect might be attributable to the diamagnetic anisotropy of the triple bond, it is clear that the point-dipole approximation,[17] which was derived to rationalize quantitatively the proton chemical shifts in such systems, fails to predict correctly the chemical shifts of the α carbons of linear alkynes.[6a] In terms of the spatial parameters defined in Figure 2, the McConnell equation takes the form

$$\sigma_g = \frac{\Delta\chi}{3R^3}(1 - 3\cos^2\theta)$$

where σ_g is the screening due to anisotropic group g, and $\Delta\chi$ represents the anisotropy of the diamagnetic susceptibility. Using general bond lengths and angles observed in alkynes,[18] and a value of $\Delta\chi$, which was derived from proton nmr studies,[19] the point-dipole approximation predicts a shielding effect of about 4 ppm at the α carbon. The empirical shift is at least three times this magnitude. Unless there is a second,

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(11) D. E. Dorman, M. Jautelat, and J. D. Roberts, *J. Org. Chem.*, **36**, 2757 (1971).

(12) D. M. Grant and E. G. Paul, *J. Amer. Chem. Soc.*, **86**, 2984 (1964).

(13) D. M. Grant and B. V. Cheney, *ibid.*, **89**, 5315, 5319 (1967).

(14) J. D. Roberts, F. J. Weigert, J. I. Kroschwitz, and H. J. Reich, *ibid.*, **92**, 1338 (1970).

(15) K. S. Dhami and J. B. Stothers, *Can. J. Chem.*, **43**, 498 (1965).

(16) F. A. Bovey, "Nuclear Magnetic Resonance Spectroscopy," Academic Press, New York, N. Y., 1969, Chapter III.

(17) H. M. McConnell, *J. Phys. Chem.*, **27**, 226 (1956).

(18) J. Dale in "Chemistry of Acetylenes," H. Viehe, Ed., Marcel Dekker, New York, N. Y., 1968, Chapter 1.

(19) H. Heel and W. Zeil, *Z. Elektrochem.*, **64**, 962 (1960); W. Zeil and H. Buchert, *Z. Phys. Chem.*, **38**, 47 (1963).

TABLE I

^{13}C CHEMICAL SHIFTS OF CARBONS OF LINEAR ALKYNES IN PARTS PER MILLION WITH REFERENCE TO CS_2

Registry no.	Alkyne	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11	C-12	Ref
	1-Butyne	125.5	107.8											3
	1-Pentyne	125.5	110.1	173.6	171.6	180.6								6b
	1-Hexyne	125.1	107.4	175.1	162.6	171.3	179.6							6a
	1-Heptyne	125.1	109.6	174.8	164.4	161.8	170.1	178.5						6a
	1-Octyne	123.5	108.5	174.1	163.3	163.3	160.5	169.1	177.6					6a
629-05-0	1-Octyne	124.8	109.3	174.9	164.5	164.6	161.7	170.6	179.4					This study
	1-Dodecyne	124.9	109.0	174.4	163.5	163.5	163.5	163.5	163.5	163.5	160.9	170.2	178.9	6b
	2-Butyne		118.9	118.9										3
	2-Hexyne	190.8	118.8	115.6	172.9	170.9	180.4							6a
	2-Heptyne	190.2	118.3	114.9	174.8	161.3	170.7	179.0						6a
	2-Octyne	189.6	117.7	114.0	174.1	163.0	161.1	169.8	178.0					6a
2809-67-8	2-Octyne	190.7	118.5	114.5	174.6	164.2	162.0	170.9	179.6					This study
	2-Dodecyne	190.0	118.4	114.6	172.2	164.1	164.1	164.1	164.1	164.1	161.0	170.0	179.1	6b
	3-Hexyne	178.1	180.5	112.6										6a
	3-Heptyne	178.8	180.5	112.3	114.2	172.3	170.0	179.4						6a
	3-Octyne	177.4	179.5	111.5^a	112.8^a	173.8	160.6	169.7	177.9					6a
15232-76-5	3-Octyne	180.0	181.0	112.2	114.4	175.2	161.8	171.3	179.1					This study
	3-Dodecyne	178.6	180.3	112.0^a	113.8^a	174.0	163.4	163.4	163.4	163.4	160.9	170.1	178.6	
	4-Octyne	179.8	171.1	173.3	113.5									6a
1942-45-6	4-Octyne	180.2	170.6	173.6	113.6									This study
	4-Dodecyne	179.5	170.5	172.6	113.7	113.7	174.6	164.1	164.1	164.1	161.1	170.5	179.5	6b
	5-Dodecyne	179.4	171.1	161.6	174.6	113.7	113.7	174.6	164.0	164.0	161.6	171.1	179.4	6b
	6-Dodecyne	178.8	170.4	161.6	163.8	174.4	113.2							6b
871-84-1	1,7-Octadiyne	124.0	109.2	175.3	165.6									This study
16387-70-5	3,5-Octadiyne	180.0	180.6	115.2	128.3									This study
16287-71-6	4,6-Dicadiyne	180.1	171.1	172.2	117.0	127.3								This study
	5,7-Dodecadiyne					114.8	125.5							5
872-21-9	1,7,13-Tetradeca-triyne	124.6	109.6	175.2	165.1	165.5	174.9	112.7						This study

[a] The assignments of the indicated resonances have been reversed from those of the original study.

TABLE II

^{13}C SHIFT DIFFERENCES BETWEEN LINEAR ALKYNES AND ALKANES WITH THE SAME NUMBER OF CARBONS

	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11	C-12
1-Butyne	−54.8	−60.7										
1-Pentyne	−54.3	−60.8	+14.6	+0.7	+0.8							
1-Hexyne	−54.5	−60.9	+13.6	+1.1	+0.7	0						
1-Heptyne	−54.5	−60.9	+13.7	+0.4	+0.7	−0.4	−1.1					
1-Octyne	−54.8	−61.2	+13.8	+0.7	+0.8	+0.6	+0.1	−0.2				
1-Dodecyne	−54.0	−61.4	+13.5	+0.3	+0.3	+0.3	+0.3	+0.3	+0.3	0	−0.2	0
2-Butyne		−49.6										

2-Hexyne	+11.2	−51.8	−45.9	+11.4	+0.3	+0.8						
2-Heptyne	+10.6	−52.2	−46.2	+10.8	+0.2	+0.2	−0.6					
2-Octyne	+11.1	−52.0	−46.6	+10.8	+0.4	+0.9	+0.4	0				
2-Dodecyne	+11.1	−52.0	−46.3	+9.0	+0.9	+0.9	+0.9	+0.9	+0.9	+0.1	−0.4	+0.2
3-Hexyne	−1.5	+9.9	−48.9									
3-Heptyne	−0.8	+9.6	−48.8	−49.8	+11.2	−0.5	−0.2					
3-Octyne	+0.4	+10.5	−48.9	−49.4	+11.4	+0.7	+0.8	−0.5				
3-Dodecyne	−0.3	+9.9	−48.9	−49.4	+10.8	+0.2	+0.2	+0.2	+0.2	0	−0.3	−0.3
4-Octyne	+0.6	+0.1	+12.5	−50.2								
4-Dodecyne	+0.6	+0.1	+11.7	−49.5	−49.5	+11.4	+0.9	+0.9	+0.9	+0.1	+0.1	+0.6
5-Dodecyne	+0.5	+0.7	+0.7	+11.4	−49.5	−49.5	+11.4	+0.8	+0.8	+0.7	+0.7	+0.5
6-Dodecyne	−0.1	0	+0.7	+0.6	+11.2	−50.0						

TABLE III

CHEMICAL-SHIFT PARAMETERS IN PARTS PER MILLION OBTAINED FROM REGRESSIONAL ANALYSES[a]

Parameter	Value	F level	Parameter	Value	F level
α	−6.7	2.5	α′	+5.3	2.5
β	−6.3	2.5	β′	−0.6	0.6
γ	+1.6	2.0	γ′	−0.4	0.5

[a] Standard error of fit = ±0.3. Multiple correlation coefficient, 0.998; constant term, 120.9. The standard error of the parameters were uniformly ±0.2 ppm.

unrecognized shielding mechanism at the α carbon of these alkynes, these results indicate a clear failure of the point-dipole approximation. Further experiments designed to clarify this problem are in progress and will be reported separately.[10]

The shielding effect at the β and γ carbons is less regular and, in many instances, shows variations greater than expected from experimental errors. In the case of the γ carbons, as well as those more remote from the triple bond, these differences could be due to conformational differences. Thus, changes in the dihedral angles between the triple bond and the γ carbon could change the R and θ of Figure 2 significantly. The same is not true of the β carbon, the R and θ values of which are fixed. The variation at these centers cannot be explained in terms of neighboring-group effects. It is possible that some form of self-association of alkyne units is responsible for these variations, and a study of a more extended range of dilutions using pulse Fourier transform spectroscopy is badly needed.

Some additional insight regarding the effect of a triple bond upon neighboring carbon nuclei is available from the data for the diynes and single triyne in Table I. It is noteworthy, for example, that in the spectra of 3,5-octadiyne and 5,7-dodecadiyne the interior sp-hybridized carbons are upfield by 12 to 14 ppm from their positions in the corresponding monoalkynes. Hence, the effect of a triple bond at the neighboring α position is broadly independent of the hybridization of the α carbon. In the spectra of 1,7-octadiyne and 1,7,13-tetradecatriyne, the chemical shifts of the β and γ carbons are 0.6–1.1 ppm upfield from their positions in the spectrum of 1-octyne. It appears then that the magnitude of the shielding effect in these compounds is dependent upon the number of triple bonds present, even if these effects cannot be put in accurate quantitative terms.

The sp-hybridized carbons fall into a range intermediate between those of saturated carbons and alkene and aromatic carbons. It has been pointed out that the range of shifts for acetylenic carbons is more limited than those of the other two hybridizations,[6a] but it should be recognized that this results primarily from the lack of data regarding examples of alkynes which are branched at the α carbon. Thus, because both the α and β parameters are large and negative (see Table III), it would be expected that alkynes branched at the α position could show more extended ranges of shifts. There are, unfortunately, no data available for a branched alkyne at the present time.

It was pointed out above that the chemical shifts of sp-hybridized carbons are relatively constant within a given subgroup of alkynes. Thus, the shifts of carbons 1 and 2 of 1-alkynes are quite consistently about 124 and 109 ppm, respectively. It has been suggested[5] that the differences between the chemical shifts of the sp-hybridized carbons of an alkyne will be a diagnostic tool which allows differentiation of 1-alkynes, 2-alkynes, and midchain alkynes. Unfortunately, our results again indicate that these generalizations will break down when alkynes with chain branching at the α position are taken into account.

The γ parameter (Table III) for the alkynes is of the same sign and magnitude as observed for the alkenes.[11] This fact would seem to argue against the earlier conclusion[11] that the γ effect is at least partially steric in nature, because the steric interactions of sp^2- and sp-hybridized carbons must surely be different. Except for the alkanes, the γ effect remains an important but poorly rationalized phenomenon. Further research into the mechanism of this effect is underway.[20]

Regardless of the origin of the γ effect, its identification has allowed us to assign the sp resonances uniquely in the spectra of 3-alkynes. In previous work, the unsaturated carbon resonances of such alkynes as 3-octyne were incorrectly assigned, or left unassigned.[6a] The derivation of the γ parameter, however, allows specific assignment in such examples. Alkynes which possess triple bonds which are removed by more than three sp^3-hybridized carbons from the end of a linear chain cannot, however, be assigned using our method. Fortunately, the chemical shifts of the sp-hybridized carbons in such systems are frequently so similar as to preclude the resolution of the peaks.[6a]

The similarities of the α' shifts of alkenes and alkynes tends to confirm the hypothesis[11] that this effect is derived in part from polarizations of the π electrons. Certainly, large chemical-shift differences have been demonstrated for unsaturated species and, where mesomeric polarizations can be expected, these lead to very large polarizations of both double[21,22] and triple[23] bonds. In the hydrocarbons, in which the polarizing effect can be due only to inductive and hyperconjugative effects, the polarizations lead to much smaller differences in the shifts of the unsaturated carbons. Thus, the chemical shifts of carbons 1 and 2 of ethoxyethyne are 104.6 and 170.8 ppm,[23] respectively. These shifts may be directly compared to those of 1-pentyne, in which the chemical shifts of the sp-hybridized carbons differ by only 15.4 ppm.

Both the β' and γ' shifts are small and negative. Furthermore, the lower F levels[9] indicate that these parameters are less important to the regressional analysis. In the alkenes,[11] the analogous β' effect was found to be approximately +2 ppm, and its origin was considered to be of a steric nature. The present results are consistent with such a formulation. In the rigidly linear alkynes, the β' carbon is precluded from coming into the proximity of the more distant sp-hybridized carbon and a steric effect would therefore be suppressed. Without such an influence, the presence of the β' effect becomes less important.

With the present analysis of the ^{13}C nmr spectra of alkynes, procedures are now available for the prediction of the spectra of all three major groups of acyclic hydrocarbons. We are therefore prepared to establish a set of rules through which the interpretation of carbon-13 chemical-shift data can lead to elucidation of structures. The development of such rules and their applications to compounds other than hydrocarbons are currently under investigation in these laboratories and will be reported later.[7]

Registry No.—^{13}C, 14762-74-4.

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[20] C. Marzin, D. E. Dorman, and J. D. Roberts, unpublished results.

[21] G. E. Maciel, *J. Phys. Chem.*, **69**, 1947 (1965).

[22] T. Higashimura, S. Okamura, I. Morishima, and T. Yonezawa, *J. Polym. Sci., Part B*, **7**, 23 (1969).

[23] D. Rosenberg, J. W. deHaan, and W. Drenth, *Recl. Trav. chim. Pays-Bas*, **87**, 1387 (1968).

Cycloaddition. XV. Competing Mechanisms in the Reaction of Cyclopentadiene with Trifluoroethylene and 2-Chloro-1,1-difluoroethylene

BARRY M. JACOBSON AND PAUL D. BARTLETT*

Converse Memorial Laboratory of Harvard University, Cambridge, Massachusetts 02138

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Thermal cycloaddition of trifluoroethylene to cyclopentadiene competes unfavorably with diene dimerization (about 1:600 at 8°). At 210°, where the dimer dissociates thermally, a cross-cycloadduct is obtained consisting of about 99% of the two norbornenes (exo H/endo H, 2:1). 2-Chloro-1,1-difluoroethylene appears to be about four times as reactive a dienophile as trifluoroethylene, yielding a cycloadduct at 170° that is 99.5% norbornenes (exo H/endo H, 5:3). Photosensitized cycloaddition of trifluoroethylene to cyclopentadiene yields mixtures of six cross-cycloadducts, whose structures and configurations were established by proton and fluorine nmr spectroscopy and by independent synthesis. The product composition did not depend on the nature or triplet excitation energy of the sensitizer, but reflected competition, even at 2°, between slow thermal cycloaddition and the relatively inefficient photosensitized process. When thermal reaction was minimized, the photosensitized product consisted of 15.5% norbornenes and 84.5% bicyclo[3.2.0]heptenes from (2 + 2) cycloaddition. The latter showed major/minor regioselectivity of about 2.3, and in the major orientation the ratio of endo H/exo H was ~ 2. The photosensitized adduct of 2-chloro-1,1-difluoroethylene to cyclopentadiene differed from that of trifluoroethylene chiefly in showing a much greater regioselectivity in the bicyclo[3.2.0]-heptenes: the major/minor orientation = 42 and endo H/exo H = 3.2–3.4. These results are consistent in detail with competition in the thermal cycloaddition such that about 98.5% is concerted in the case of trifluoroethylene and 99.4% in the case of 2-chloro-1,1-difluoroethylene. The endo preference of halogen in the concerted (2 + 4) cycloaddition mechanism is absent or slightly reversed in the (2 + 4) products of the photosensitized reaction and is strongly reversed in the (2 + 2) product.

Photosensitized cycloadditions, proceeding through an excited triplet state of one of the reactants, have been used successfully as models indicating what may be expected of a *bona fide* biradical mechanism.[1,2] When one of the reactants is a conjugated diene and the other is unsymmetrically substituted, the product mixture is characterized by its relative content of

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[1] Part XIII: P. D. Bartlett, B. M. Jacobson, and L. E. Walker, *J. Amer. Chem. Soc.*, in press.

[2] P. D. Bartlett, XXIIIrd International Congress of Pure and Applied Chemistry, Boston, Mass., July 26–30, 1971, Vol. 4, Butterworths, London, 1971, pp 281–305.