

Survey of ^{13}C -H Splittings in Alkenes

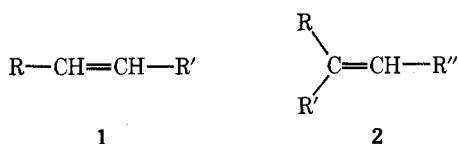
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Line separations due to splitting of the natural abundance ^{13}C signal by neighboring hydrogens are reported for a variety of di- and trisubstituted alkenes. For the trisubstituted alkenes, these line separations should be very close to true coupling constants. Qualitatively, the splittings conform to the prediction that carbon should show decreasing three-bond coupling constants in the order $sp^1 > sp^2 > sp^3$ with regard to the hybridization of the coupling carbon nucleus. However, the ranges of the coupling constants are not well separated for cis nuclei and also overlap for trans nuclei. The splittings are sufficiently regular in incidence that they are of use in assigning *E* or *Z* character to trisubstituted alkenes.

A number of papers have emphasized the parallelism between H-H NMR coupling constants and ^{13}C -H coupling constants.¹⁻⁴ Since proton coupling constants in alkenes such as 1 have been used for years to distinguish between *E* and *Z* isomers, the question arises whether ^{13}C -H coupling constants might not be of equal use with more highly substituted alkenes such as 2. DeHaan and Van de Ven and Roberts et al. have



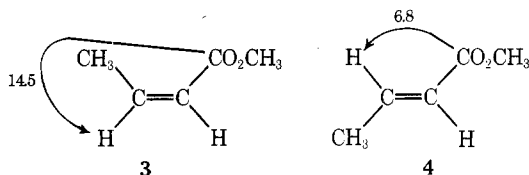
advanced a useful method of determining alkene configuration based on ^{13}C chemical shifts.⁵ However, this method seems best applied in cases where both the *E* and the *Z* isomers are available for comparison purposes. If only a single isomer is available the assignment of configuration would be difficult if unusual steric or electronic effects were present.^{6,7}

The use of additivity relationships, based on substituent effects on ^1H chemical shifts, seems to be an even more powerful method for determining alkene configuration.⁸ However, deviations from additivity predictions for carbonyl and other alkene substituents have been noted.

It was hoped that ^{13}C -H coupling constants would show sufficient regularity so that these data also could be used to identify *E* or *Z* isomers. Studies of chemical shifts and of coupling constants would complement one another, and provide the researcher with a battery of techniques for configuration assignment.⁸

Marshall and Seiwel have reported that a very large $^3J_{\text{CH}}$ value (14.5 Hz) is found between carbonyl and trans hydrogen in 3, and a smaller value (6.8 Hz) is found for cis nuclei in 4, rather similar to the variation in H-H coupling constants with geometry in other molecules.^{9,10} The coupling constant for trans ^{13}C -H nuclei was substantially higher than for certain α,β -unsaturated ketones briefly investigated in our laboratory.¹¹ A secondary objective of the present study was to observe the range in coupling constants as structure was varied.

In other studies, Karabatsos and Orzech suggested that bond angle variations imposed by steric constraints gave rise to sizable variations in ^{13}C -H coupling constants,¹ but electronegativity effects were not considered to be very important.^{1c} Perlin's data, however, could be interpreted in terms of a sizable electronegativity effect.¹² Lemieux and co-workers



also emphasized the importance of stereoelectronic factors on variations in $^3J_{\text{CH}}$.^{13,14}

In earlier studies, H-H coupling constants in alkenes were shown to vary over a twofold range for trans nuclei and over a fivefold range for cis nuclei, depending upon the type of alkene substitution.¹⁵ The effects of electronegativity, as determined by Banwell and Sheppard and by Schaefer, are given in eq 1 and 2, where E_X is an electronegativity parameter for the substituent X.¹⁶

$$J_{\text{cis}} = 11.71 (1 - 0.34E_X) \quad (1)$$

$$J_{\text{trans}} = 19.0 (1 - 0.17E_X) \quad (2)$$

If ^{13}C -H coupling constants indeed parallel H-H coupling constants, similar electronegativity effects would be expected.¹⁷

In considering the various factors that may affect the magnitude of $^3J_{\text{CH}}$, the hybridization of carbon deserves special mention. This factor, of course, is not present in H-H coupling constants. Karabatsos pointed out that $^3J_{\text{CH}}$ should decrease in the order $sp^1 > sp^2 > sp^3$ if the Fermi contact mechanism of spin coupling were dominant.^{16,18,19} A third objective of this study was to observe the effect of hybridization on $^3J_{\text{CH}}$, although these effects are hard to differentiate from electronegativity effects in certain cases.

Table I lists the ^{13}C NMR data for over 40 alkenes. The data quoted in Table I are line separation(s) (LS) measured directly from the spectra rather than true coupling constants ($^3J_{\text{CH}}$), which must be derived from the LS by computer simulation. The LS values should be of more use to the practicing chemist. In Table I, the data for trisubstituted alkenes are of foremost interest. In such alkenes, couplings between cyanide or carbonyl and hydrogen represent an AX spin system, and thus, LS and $^3J_{\text{CH}}$ are identical. For methyl substituted alkenes, an AM_3X spin system is present, where M are the methyl protons; LS should again be very close to $^3J_{\text{CH}}$.

The deviation of LS from $^3J_{\text{CH}}$ should be most serious for disubstituted alkenes. These alkenes were investigated in order to observe the variation of LS with structure in compounds whose configuration has been firmly established by other means. For disubstituted alkenes such as (*E*)-cinnamic acid (28), the carbonyl ^{13}C nucleus represents X of an ABX spin system, where the alkene hydrogens are A and B. Owing to the large difference in chemical shift of A and B, among other factors, the deviation of LS from $^3J_{\text{CH}}$ is small (-0.2 Hz). For propenylbenzene, the methyl ^{13}C represents X of an ABM_3X spin system. For the *Z* isomer 8, computer simulation shows that LS is again very similar to $^3J_{\text{CH}}$, within the error in data acquisition, ± 0.25 Hz. However, for the *E* isomer, LS does not correspond to $^3J_{\text{CH}}$ because of the small chemical shift difference between A and B, and large J_{AB} and $|J_{\text{AX}} - J_{\text{BX}}|$ terms.^{15b} For simplicity, all splittings will be termed LS whether or not they also correspond to true coupling constants.

Table I. Line Separations Due to Coupling of the ^{13}C Nucleus with the ^1H Nucleus Indicated

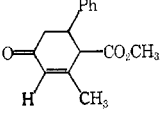
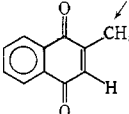
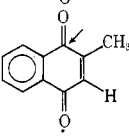
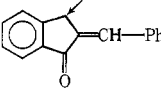
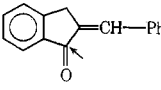
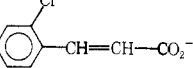
Registry no.	Compd	Isomer	Structure	Orientation of coupled nuclei	LS, Hz
674-76-0	5	<i>E</i>	$i\text{-C}_3\text{H}_7\text{CH}=\text{CH}-\text{CH}_3$	Cis	~6
690-08-4	6	<i>E</i>	$t\text{-C}_4\text{H}_9-\text{CH}=\text{CH}-\text{CH}_3$	Cis	6.9
4894-61-5	7	<i>E</i>	$\text{Cl}-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_3$	Cis	6.0
		<i>E</i>	$\text{Cl}-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_3$	Cis	~7
766-90-5	8	<i>Z</i>	$\text{Ph}-\text{CH}=\text{CH}-\text{CH}_3$	Trans	10.0
873-66-5	9	<i>E</i>	$\text{Ph}-\text{CH}=\text{CH}-\text{CH}_3$	Cis	6.6
104-54-1	10	<i>E</i>	$\text{Ph}-\text{CH}=\text{CH}-\text{CH}_2\text{OH}$	Cis	6.8
21087-29-6	11	<i>E</i>	$\text{Ph}-\text{CH}=\text{CH}-\text{CH}_2\text{Cl}$	Cis	8.0
833-81-8	12	<i>E</i>	$\text{Ph}-\text{CH}=\text{C}(\text{CH}_3)\text{Ph}$	Trans	8.3
98-83-9	13		$\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{Ph}$	Cis	6.6
				Trans	11.1
541-47-9	14		$\text{HO}_2\text{C}-\text{CH}=\text{C}(\text{CH}_3)_2$	Cis	7.1
				Trans	8.4
141-79-7	15		$\text{CH}_3-\text{CO}-\text{CH}=\text{C}(\text{CH}_3)_2$	Cis	7.0
				Trans	8.0
54435-79-9	16	<i>Z</i>	$\text{Ph}-\text{CO}-\text{CH}=\text{C}(\text{CH}_3)\text{Ph}$	Cis	6.7
22573-24-6	17	<i>E</i>	$\text{PhCO}-\text{CH}=\text{C}(\text{CH}_3)\text{Ph}$	Trans	7.8
23652-86-0	18	<i>Z</i>	$\text{CH}_3\text{CO}-\text{CH}=\text{C}(\text{CH}_3)\text{NHCH}_2\text{Ph}$	Cis	6.1
60135-00-4	19			Cis	6.2
58-27-5	20			Cis	5.7
				Trans	~10
17434-21-8	21	<i>E</i>		Trans	8.5
		<i>E</i>		Cis	~6
14182-01-5	22	<i>E</i>	$\text{Ph}-\text{CH}=\text{C}(\text{CH}_3)-\text{CO}-\text{Ph}$	Trans	8.5
		<i>E</i>	$\text{Ph}-\text{CH}=\text{C}(\text{CH}_3)-\text{CO}-\text{Ph}$	Cis	6.4
123-73-9	23	<i>E</i>	$\text{CH}_3-\text{CH}=\text{CH}-\text{CHO}$	Cis	6.0
		<i>E</i>	$\text{CH}_3-\text{CH}=\text{CH}-\text{CHO}$	Cis	8.8
104-55-2	24	<i>E</i>	$\text{Ph}-\text{CH}=\text{CH}-\text{CHO}$	Cis	8.8
33603-90-6	25	<i>Z</i>	$\text{Ph}-\text{CH}=\text{C}(\text{Br})-\text{CHO}$	Cis	7.8
584-45-2	26		$\text{Ph}-\text{CH}=\text{C}(\text{CO}_2^-)_2$	Cis	7.3
			$\text{Ph}-\text{CH}=\text{C}(\text{CO}_2^-)_2$	Trans	10.8
17041-60-0	27		$\text{CH}_3-\text{CH}=\text{C}(\text{CO}_2\text{CH}_3)_2$	Cis	7.0
			$\text{CH}_3-\text{CH}=\text{C}(\text{CO}_2\text{CH}_3)_2$	Trans	12.2
140-10-3	28	<i>E</i>	$\text{Ph}-\text{CH}=\text{CH}-\text{CO}_2^-(\text{D}_2\text{O})$	Cis	6.3
		<i>E</i>	$\text{Ph}-\text{CH}=\text{CH}-\text{CO}_2\text{H}(\text{CDCl}_3)$	Cis	7.0
704-96-1	29	<i>Z</i>		Trans	12.0
705-54-4	30	<i>Z</i>	$\text{Ph}-\text{CH}=\text{C}(\text{Cl})\text{CO}_2^-$	Cis	5.0
557-24-4	31	<i>Z</i>	$^-\text{O}_2\text{C}-\text{CH}=\text{CH}-\text{CONH}_2$	Trans	11.5
		<i>Z</i>	$^-\text{O}_2\text{C}-\text{CH}=\text{CH}-\text{CONH}_2$	Trans	12.2
498-23-7	32	<i>Z</i>	$^-\text{O}_2\text{C}-\text{C}(\text{CH}_3)=\text{CH}-\text{CO}_2^-$	Trans	10.8
		<i>Z</i>	$^-\text{O}_2\text{C}-\text{C}(\text{CH}_3)=\text{CH}-\text{CO}_2^-$	Cis	7.3
498-24-8	33	<i>E</i>	$^-\text{O}_2\text{C}-\text{C}(\text{CH}_3)=\text{CH}-\text{CO}_2^-$	Cis	6.7
		<i>E</i>	$^-\text{O}_2\text{C}-\text{C}(\text{CH}_3)=\text{CH}-\text{CO}_2^-$	Trans	8.3
584-99-6	34	<i>E</i>	$^-\text{O}_2\text{C}-\text{C}(\text{Br})=\text{CH}-\text{CO}_2^-$	Trans	9.5
644-80-4	35	<i>Z</i>	$^-\text{O}_2\text{C}-\text{C}(\text{Br})=\text{CH}-\text{CO}_2^-$	Cis	4.3
80-62-6	36		$\text{CH}_3\text{O}_2\text{C}-\text{C}(\text{CH}_3)=\text{CH}_2$	Cis	~6.5
			$\text{CH}_3\text{O}_2\text{C}-\text{C}(\text{CH}_3)=\text{CH}_2$	Trans	~12
60135-01-5	37	<i>E</i>	$\text{CH}_3\text{O}_2\text{C}-\text{C}(\text{CN})=\text{CH}-\text{CH}(\text{CH}_3)_2$	Cis	~6
		<i>E</i>	$\text{CH}_3\text{O}_2\text{C}-\text{C}(\text{CN})=\text{CH}-\text{CH}(\text{CH}_3)_2$	Trans	13.8
14533-86-9	38	<i>E</i>	$\text{CH}_3\text{O}_2\text{C}-\text{C}(\text{CN})=\text{CH}-\text{Ph}$	Cis	~7
		<i>E</i>	$\text{CH}_3\text{O}_2\text{C}-\text{C}(\text{CN})=\text{CH}-\text{Ph}$	Trans	14.0
1885-38-7	39	<i>E</i>	$\text{NC}-\text{CH}=\text{CH}-\text{Ph}$	Cis	8.7
2700-22-3	40		$(\text{NC})_2-\text{C}=\text{CH}-\text{Ph}$	Cis	8.4
			$(\text{NC})_2-\text{C}=\text{CH}-\text{Ph}$	Trans	14.4
53587-72-7	41	<i>E</i>	$\text{NC}-\text{C}(\text{CH}_3)=\text{CH}-\text{Ph}$	Cis	8.8
		<i>E</i>	$\text{NC}-\text{C}(\text{CH}_3)=\text{CH}-\text{Ph}$	Trans	8.2
13343-78-7	42	<i>Z</i>	$\text{Ph}-\text{C}\equiv\text{C}-\text{CH}=\text{CH}-\text{Ph}$	Trans	15.0
13343-79-8	43	<i>E</i>	$\text{Ph}-\text{C}\equiv\text{C}-\text{CH}=\text{CH}-\text{Ph}$	Cis	8.2

Table II

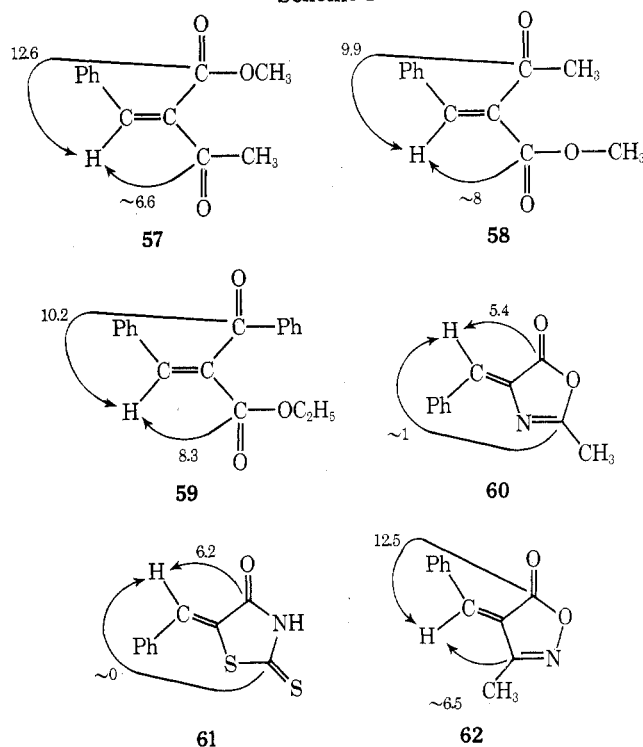
Hybridization of carbon	Ranges of LS values, Hz (common values)	
	Cis nuclei	Trans nuclei
sp^1 (CN, $\text{C}\equiv\text{C}$)	8.2–8.7 (~8)	14–15 (~14)
sp^2 (CO)	4.3–10	9.5–16.9
sp^3 (CH_2X)	5.7–8.0 (~6)	7.7–11.0 (~8)

In Table I, the compounds are loosely grouped in the order sp^3 , sp^2 , sp^1 with regard to the hybridization of the carbon coupled to the alkene proton. Table II shows a summary of these results. For cis nuclei, the range of LS between nuclei of different hybridization is not large. For trans nuclei, the LS roughly follow the predicted order sp^1 , sp^2 , sp^3 , although considerable overlapping of ranges occurs.^{19b}

Table III illustrates the effect of varying the type of ^{13}C nucleus coupled to H in an otherwise constant hydrocarbon skeleton. The acid chloride and aldehyde groups show the largest LS values for carbonyl groups. In Table I, the aldehydes **23**, **24**, and **65** exhibit similarly large values. Carboxylic acid, ester, and amide groups are not well differentiated (compare also **26–33**, **36–38**, and **57–59**). Ketones consistently have the smallest LS values (cf. Scheme I). The presence of a conjugating group such as phenyl substituted at carbonyl (e.g., **55**) has little effect compared to alkyl groups (e.g., **56**; also Scheme I). It is noteworthy that rigid (**21**) and nonrigid (**22**) ketone groups have similar LS values.²⁰ Except for the aldehyde group and oxime, the LS values are arranged such that ^{13}C nuclei that have large LS values lie upfield in chemical shift and vice versa.^{21,22} The LS values parallel $^1J_{\text{CH}}$ values for H–CO–X, again except for X = H.²³

As with H–H couplings, the effects of electronegative groups appears to be quite large. Comparison of bromomaleic acid (**34**) with citraconic acid (**32**) shows that the former has the lower LS (9.5 vs. 10.8 Hz). The difference between **35** and **33**

Scheme I



is even greater (4.3 vs. 6.7 Hz), similar to the case in H–H couplings where the electronegative substituent is trans to one proton (cf. eq 2 vs. eq 1). This series involves substituents of similar size, and thus differential steric effects are not likely to be important. The bromo aldehyde **25** shows a lower LS than **24** or **53**. Chlorocinnamic acid (**30**) has a lower LS than phenylcinnamic acid (**49**), although steric effects are variable in these compounds.

Table III. LS of Substituted Stilbenes

Z^a	Compd ^b	LS (trans)	Registry no.	Compd ^b	LS (cis)	Registry no.
CN	44 (Z)	14.2	6114-57-4	45 (E)	9.0	16610-80-3
$\text{C}=\text{O}-\text{Cl}$	46 (Z)	16.9	60135-02-6	47 (E)	9.9	51388-67-1
$\text{C}=\text{O}-\text{OH}$	48 (Z)	12.5	91-47-4	49 (E)	7.3	91-48-5
$\text{C}=\text{O}-\text{OCH}_3$		<i>c</i>		50 (E)	7.4	36854-27-0
$\text{C}=\text{O}-\text{N}(\text{Ph})\text{CH}_3$	51 (Z)	11.5	60135-03-7	52 (E)	6.8	60135-04-8
$\text{C}=\text{O}-\text{H}$				53 (E)	10.0	1755-47-1
$\text{C}=\text{N}-\text{OH}$				54 (E)	9.2	60135-05-9
$\text{C}=\text{O}-\text{Ph}$				55 (E)	6.0	7474-65-9
$\text{C}=\text{O}-\text{CH}_3$				56 (E)	~6	38661-88-0

^a Stilbene substituent. ^b The letter in parentheses refers to the configuration of the compound. ^c Data for a slightly impure compound are 12.5 Hz.

Electronegative substituents substituted on the carbon coupled to hydrogen appear to increase LS values. The series 9, 10, and 11 shows an increasing LS as the electronegativity of the substituent increases from H (LS 6.6 Hz), OH (6.8 Hz), to Cl (8.0 Hz). In 7, the chloromethyl group has an apparent larger LS than methyl.^{19b,24} Moving from 2-methyl-1,3-diphenyl-2-propen-1-one (22) to its bromomethyl analogue results in an increase in LS from 8.5 to 10 Hz. However, comparison of 39 and 43 indicates only a slightly larger LS for cyanide than alkyne.²⁵

With regard to the effect of substitution on the C=C double bond, disubstituted alkenes appear to have larger LS than trisubstituted alkenes for trans CH₃-H couplings (the difference would be still larger if ³J_{CH} values were calculated as ³J_{CH} > LS). Thus 8 and 13 show LS of 10–11 Hz, whereas 12, 14, 15, and 17 show LS of ca. 8 Hz. However, for CO-H couplings, disubstituted alkenes have larger LS in some cases but not in others.

The LS values discussed above show significant variation with structure, but these variations are by no means worse than variations in ³J_{HH} previously used to assign configuration in compounds of general structure 1.¹⁵ Using the data of Table I, certain molecules were investigated whose state of isomerism could not be assigned in any other way.²⁶ These compounds are shown in Scheme I. Compounds 57 and 58 were obtained as an inseparable mixture upon condensation of methyl acetoacetate with benzaldehyde. The major component, 57, showed a large LS for the ester carbonyl and a small LS for the ketone; 57 is thus the *Z* isomer. Compound 58 shows the reverse LS characteristics, and it is therefore the *E* isomer. Compound 59 (mp 89 °C) was obtained by condensation of ethyl benzoylacetate with benzaldehyde and it is clearly the *E* isomer.

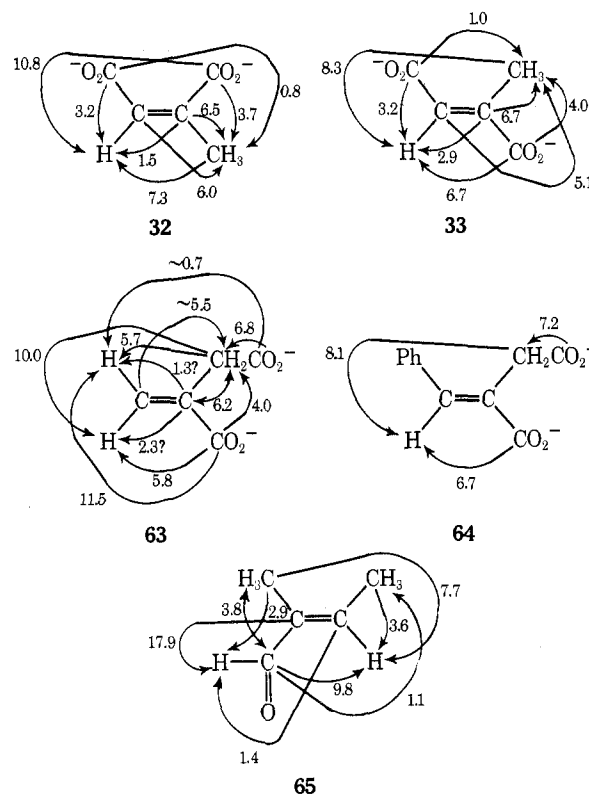
The configuration of the azlactone and rhodanine derivatives (60 and 61, Scheme I) was predictable on the basis that the maximum path for resonance between CO and Ph should be present.²⁷ In both cases, the CO and alkene proton are *cis*, as indicated by the low LS value, and CO and Ph are therefore *trans* as predicted. However, for the isoxazolinone 62, the CO and Ph are *cis* as shown by the large LS, thus confirming previous assignments.²⁸ In this case a steric effect between the ring methyl and phenyl probably destabilizes the *E* isomer.^{27c,29}

In citraconic, mesaconic, and itaconic acids (Scheme II), a relatively complete survey of all LS values was obtained. The two-bond coupling constants (i.e., line separations, strictly speaking) were not characterized by a particularly large variation in absolute magnitude, unlike a number of literature examples.^{30a,b}

For phenylitaconic acid (64), the LS values confirm the earlier assignment of configuration based on chemical transformations.³¹ In tigaldehyde (65) some uncertainty exists in the assignment of splittings, but generally the aldehyde group is seen to have large LS values not only to the alkene proton, but to other protons in the molecule. LS values for couplings to CHO are also sizable.

Certain experimental difficulties reduce the effectiveness of this technique for configurational assignment. The data acquisition is fairly time consuming, often requiring an overnight run. A sizable concentration of sample must be used (in our hands, a 10% w/v solution was near the minimum, in CDCl₃ or about 5% in D₂O). Alkyl groups other than methyl groups were difficult to study even using block acquisition due to extensively split signals. The disc data systems now coming into use may eliminate this difficulty, however. From the data in Table I, it is seen that the LS values for methyl groups *cis* or *trans* to an alkene proton are not sufficiently differentiated in some cases to warrant a firm assignment of configuration.

Scheme II



Experimental Section

Compounds 5, 6, 7, 10, 11, 13, 14, 23, 24, 28, 31, 32, 33, 36, 39, 63, and 65 were commercial products, mostly from Aldrich Chemical Co.; these were used without additional purification. Their ¹³C NMR spectra indicated a reasonable level of purity. Compound 20 was an undergraduate laboratory preparation, that was recrystallized several times, mp 104.5–106.0 °C (lit.³² 105–106 °C). Compound 21 was obtained from Dr. Henry Baumgarten. The remaining chemicals were synthesized by the method given in the literature reference given with the physical properties, except as noted.

(*E*)- and (*Z*)-Propenylbenzenes (8 and 9) were available from a previous study.^{33a} These were prepared by a Wittig reaction using the method of Shemyakin.^{33b}

(*E*)-1,2-Diphenyl-1-propene (12), mp 81–82 °C (lit.³⁴ 80–82 °C).

Mesityl oxide (15), bp 126–130 °C (lit.³⁵ 126–131 °C).

Dynpnone (16 and 17), bp 155 °C (1 mm) [lit.³⁶ 155 °C (1 mm)]; the product obtained was a mixture of about 85% the *E* isomer and about 15% *Z*. Despite the low concentration of the *Z* isomer, accurate NMR data could be obtained in this particular case.

Methyl 3-(*N*-benzylamino)-2-butenate (18) was prepared in situ by adding molar equivalent quantities of benzylamine and methyl acetoacetate,^{37a} followed by rapid NMR determination. Although ¹H NMR gave evidence for both isomers, the longer time period necessary for ¹³C NMR gave the mixture time to isomerize, and ¹³C NMR data for only the *Z* isomer could be obtained.^{37b}

4-Carbomethoxy-3-methyl-5-phenyl-2-cyclohexenone (19), mp 85 °C, was available from an earlier study.³⁸ The NMR for a related compound, 3,5-dimethyl-2-cyclohexenone, was very similar to that given for 19.

(*E*)-2-Methyl-1,3-diphenyl-2-propenone (22), bp 167 °C (0.6 mm) [lit.³⁹ 190 °C (28 mm)].

(*Z*)-2-Bromo-3-phenyl-2-propenal (25), mp 68–69 °C (lit.⁴⁰ 70.5 °C).

Benzylidenepropanedioic acid (26) was prepared by condensation of malonic acid with benzaldehyde, mp 196.5 °C dec (lit.^{41a} 195–196 °C). Compound 27 was similarly prepared, bp 110–112 °C (15 mm) [lit.^{41b} 110–112 °C (15 mm)].

(*Z*)-*o*-Chlorocinnamic acid (29) was prepared by irradiating the *E* isomer in a quartz flask with a 100-W Hanovia lamp for 1 week, and fractionally recrystallizing the resulting mixture of isomers. The higher melting isomer was sacrificially eliminated, plus any *Z* isomer carried along in the precipitation. The resulting product had mp 133–135.5 °C (lit.⁴² 136 °C).

(*Z*)-2-Chloro-3-phenyl-2-propenoic acid (30), mp 136–137 °C (lit.⁴³ 138–139 °C).

(*E*)-Bromobutenedioic acid (34), mp 146–147 °C (preheated oil bath, rapid heating) (lit.⁴⁴ 140–141 °C).

(*Z*)-Bromobutenedioic acid (35), mp 180–181 °C (lit.⁴⁵ 180–183 °C).

(*E*)-Methyl 2-Cyano-4-methyl-3-pentenoate, (37). A center cut of a large distillation was taken, bp 110 °C (20 mm). The compound was prepared as in ref 46: NMR (5% CDCl_3) δ 1.15 [d, 6, $\text{CH}(\text{CH}_3)_2$], ~3 [m, 1, $\text{CH}(\text{CH}_3)_2$], 3.88 (s, 3, $\text{CH}_3\text{O}_2\text{C}$), and 7.47 (d, 1, $J = 10.2$ Hz, $\text{CH}=\text{C}$); mass spectrum (70 eV) m/e (rel intensity) 153.06 (M^+ , 21.9), 138 (82.8), 125 (20.8), 121 (100), 110 (67.9), 106 (78.9), 94 (86.4), 67 (34), and 43 (25).

(*E*)-Methyl 2-cyano-3-phenyl-2-propenoate (38), mp 88–89 °C (lit.⁴⁶ 89 °C).

Benzylidenepropanedinitrile (40), mp 83–84 °C (lit.⁴⁷ 87 °C).

(*E*)-2-Methyl-3-phenyl-2-propenenitrile (41), bp 108–110 °C (4 mm) [lit.⁴⁸ 120 °C (14 mm)].

(*E*) and (*Z*)-1,4-Diphenyl-1-buten-3-yne (42 and 43) were prepared by the general procedure of Brandsma,^{49a} whereby phenylacetylide was added to styrene oxide, and the resulting alcohol was converted to the tosylate, and thence to the alkene using potassium *tert*-butoxide; from the resulting mixture of products, the *E* isomer could be obtained by crystallization, mp 94–96 °C (lit.^{49b} 97 °C). The remaining oil appeared to be roughly an equimolar mixture of *E* and *Z* isomers by NMR. In our hands, either isomerization or decomposition occurred on attempted distillation. The ^{13}C resonances of the two isomers were well separated and did not interfere with one another.

Z isomer: ^1H NMR (60 MHz, CDCl_3) δ 5.88 (d, 1, $J = 12.0$ Hz, $\text{PhC}=\text{C}-\text{H}$), 6.63 (d, 1, $J = 12.0$ Hz, PhCH), and 7.2 (m, 10, Ph).

E isomer: ^1H NMR (60 MHz, CDCl_3) δ 6.35 (d, 1, $J = 16.5$ Hz, $\text{PhC}=\text{C}-\text{H}$), 7.01 (d, 1, $J = 16.5$ Hz, PhCH), and 7.2 (m, 10, Ph).

(*Z*)-2,3-Diphenylpropenenitrile (44), mp 86–87 °C (lit.⁵⁰ 88 °C).

(*E*)-2,3-Diphenylpropenenitrile (45). This material was prepared by dehydrating the corresponding oxime. The literature⁵¹ preparation was a solid, mp 49–51 °C, but we were unable to crystallize this compound. The compound was purified by column chromatography on silica gel (eluted with a 1:9 mixture of ether and Skellysolve B). Thin layer chromatography showed only a single spot in eight solvent systems: NMR (5% CDCl_3) δ 7.0–7.4 (m, 11, Ph, and $\text{CH}=\text{C}$); mass spectrum (70 eV) m/e (rel intensity) 205.0893 (M^+ , 100), 204 (93.7), 203 (21.5), 202 (13.9), 191 (14.7), 190 (36.1), 178 (27.8), 177 (35.6), and 176 (27.53).

(*Z*)-2,3-Diphenyl-2-propenoic acid (48), mp 138–139 °C (lit.³² 136–137 °C). The *Z* acid chloride 46 was prepared from this acid using PCl_5 or SOCl_2 . Considerable difficulty was encountered upon attempts to purify and crystalline the acid chloride (isomerization and/or hydrolysis), and so in later runs, the crude acid chloride was run (NMR) immediately after synthesis: NMR (5%, CDCl_3) δ 6.87 (s, 1, $\text{CH}=\text{C}$) and 7.1–7.5 (m, 10, Ph).

(*E*)-2,3-Diphenyl-2-propenoic acid (49), mp 172–173 °C (lit.³² 173–174 °C). The acid chloride 47 was prepared similarly to 46. The ester 50 was prepared by Fischer esterification of 49, mp 75–76 °C (lit.³² 75–76 °C).

(*E*)-*N*-Methyl-*N*,2,3,-triphenylpropenamide (52). PCl_5 (3.0 g, 14.4 mmol) and 49 (3.0 g, 13.4 mmol) were added to 100 ml of CH_2Cl_2 and stirred overnight. The solvent and the POCl_3 side product were distilled off under reduced pressure. Pyridine (10 ml) and *N*-methylaniline (5 ml) were added and allowed to stand for several hours. The product was taken up with ether, and extracted with several portions of 1 M HCl until the aqueous layer was acidic. The ether was extracted with water and then with 5% NaHCO_3 , dried (MgSO_4), and evaporated, yielding a yellow solid, which was recrystallized from 95% ethanol giving 2.0 g (44% yield) of 52: mp 109–110 °C; ^1H NMR (5% CDCl_3) δ 3.32 (s, 3, NCH_3), 6.8–7.2 (m, 16, aryl and alkene protons); mass spectrum (70 eV) m/e (rel intensity) 313.1465 (M^+ , 58.5), 207 (65.1), 180 (25.2), 179 (100), 178 (48) and 77 (13).

The *Z* amide 51 was prepared by adding a large excess of *N*-methylaniline to 1.1 g (4.4 mmol) of the *Z* acid chloride, followed by stirring for 1 h. Ether was added, and the mixture was extracted with 3 M HCl until the wash was acidic, followed by extractions with water and dilute NaHCO_3 and saturated NH_4Cl . The solution was dried (MgSO_4) and ether was evaporated. The resulting solid was recrystallized from ether–pentane, giving 0.6 g of product (48% yield): mp 132–133 °C; NMR (5%, CDCl_3) δ 3.33 (s, 3, NCH_3), 6.62 (s, 1, $\text{CH}=\text{C}$), and 7.3–7.4 (m, 15, Ph); mass spectrum (70 eV) m/e (rel intensity) 313.1453 (M^+ , 45), 207 (59), 179 (100), 178 (45), and 77 (4).

(*E*)-2,3-Diphenyl-2-propenal (53), mp 92–94 °C (lit.⁵² 94 °C). The 3-(4-tolyl) analogue of 53 gave very similar NMR results.

(*E*)-2,3-Diphenyl-4-propenal oxime (54), mp 164–166 °C (lit.⁵³ 165 °C).

(*E*)-1,2,3-Triphenyl-2-propen-1-one (55) was obtained in some runs as an oil, bp 144–146 °C (1.5 mm) [lit.⁵⁴ 136° (0.2 mm)]. In other runs, a solid was obtained, which was recrystallized to purity, mp 54–56 °C. The solid was used for the NMR run.

(*E*)- and (*Z*)-Methyl 2-aceto-3-phenyl-2-propenoates (57 and 58) were obtained as an inseparable mixture by condensing methyl acetoacetate with benzaldehyde, bp 110–115 °C (1.5 mm) [lit.⁵⁶ 158–162 °C (12 mm)].

(*E*)-Ethyl 2-benzoyl-3-phenyl-2-propenoate (59) was prepared similarly to 57 and 58, except that the isomer indicated could be obtained in a crystalline state, mp 98.5–99.5 °C (lit.⁵⁷ 95.0–96.5 °C).

4-Benzylidene-2-methyl-2-oxazolin-5-one (60) was prepared by condensation of the parent azlactone with benzaldehyde, mp 149–150 °C (lit.⁵⁸ 146–147 °C).

Benzylidenerhodanine (61) was similarly prepared, mp 197–200 °C (lit.⁵⁹ 200 °C).

4-Benzylidene-3-methyl-2-isoxazolin-5-one (62), mp 140–141 °C (lit.⁶⁰ 142 °C).

Phenylitaconic acid (64) was prepared by the Stobbe condensation, mp 191–192 °C (lit.⁶¹ 192 °C dec).

^{13}C NMR Spectra. Spectra were run on a Varian XL-100 instrument at normal probe temperature. The concentration of the samples was 0.3–1.0 g/3.0 ml of solvent. The higher concentration was used whenever possible to improve data acquisition statistics. Both coupled and decoupled spectra were run; the latter utilized 5K spectral width, and the former utilized a 1K spectral width or very infrequently a 2K spectral width. In runs using a 1K width, the error in LS indicated by the computer was 0.25 Hz. For runs in D_2O (mostly carboxylic acids in the form of their potassium salt), the level of base added (potassium carbonate) was just adequate to ensure solubility (pH usually 6–8). The gated mode of decoupler operation was used for coupled spectra.⁶²

In a typical run (for 30), 0.3 g of substrate was dissolved in 3 ml of CDCl_3 (plus 0.5 ml of $\text{Me}_2\text{SO}-d_6$ to improve solubility); a 1K spectral width was used with acquisition time of 4 s, pulse delay of 1.5 s, and a pulse width of 20 μs (ca. 30° tipping angle); 5K of transients were collected, and a 500-Hz filter was used.

In this particular study, the attempted use of $\text{Cr}(\text{acac})_3$ to enhance relaxation rates and reduce the time for data acquisition was unsuccessful, probably owing to the interaction of $\text{Cr}(\text{acac})_3$ with the protons of the molecule. However, in other studies, this reagent was successfully used to improve observations of ^{31}P - ^{13}C coupling constants.

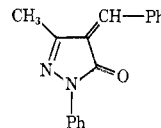
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Registry No.—Benzylamine, 100-46-9; methyl acetoacetate, 105-45-3; (*E*)-*o*-chlorocinnamic acid, 939-58-2; *N*-methylaniline, 103-67-3.

References and Notes

- (a) G. J. Karabatsos and C. E. Orzech, Jr., *J. Am. Chem. Soc.*, **87**, 560 (1965); (b) G. J. Karabatsos, C. E. Orzech, Jr., and N. Hsi, *ibid.*, **88**, 1817 (1966), and related papers; (c) see, however, G. J. Karabatsos and C. E. Orzech, Jr., *ibid.*, **86**, 3574 (1964).
- (a) F. J. Welgert, and J. D. Roberts, *J. Am. Chem. Soc.*, **91**, 4940 (1969); (b) F. J. Welgert, M. Winokur, and J. D. Roberts, *ibid.*, **90**, 1566 (1968).
- J. L. Marshall, D. Miller, S. Conn, R. Seiwel, and A. Ihrig, *Acc. Chem. Res.*, **7**, 333 (1974).
- For other studies see (a) G. Barbieri and F. Taddei, *J. Chem. Soc. B*, 1903 (1971); *J. Chem. Soc., Perkin Trans. 2*, 262 (1972); (b) D. M. McKinnon and T. Schaefer, *Can. J. Chem.*, **49**, 89 (1971); (c) K. R. Harris, *Spec. Period. Rep.*, **3**, 85 (1973), and references cited therein.
- (a) J. Dehaan and L. Van de Ven, *Org. Magn. Reson.*, **5**, 147 (1973); (b) J. D. Roberts, D. E. Dorman, and M. Jautelat, *J. Org. Chem.*, **36**, 2757 (1971).
- (a) U. Matter, C. Pascual, E. Pretsch, A. Pross, W. Simon, and S. Sternhell, *Tetrahedron*, **25**, 691 (1969); **25**, 2023 (1969), and related papers; (b) G. Decotes, Y. Bahurel, G. Pingeon, and R. Rostaing, *Bull. Soc. Chim. Fr.*, 282 (1970); (c) S. W. Tobey, *J. Org. Chem.*, **34**, 1281 (1969); (d) D. F. Ewing and K. Parry, *J. Chem. Soc. B*, 970 (1970).
- (a) W. Beckenbaugh, S. Wilson, and P. Leffler, *Tetrahedron Lett.*, 4281 (1972); (b) G. Ambruscato, P. D. Ellis, and T. T. Tidwell, *J. Chem. Soc., Chem. Commun.*, 988 (1972); (c) G. E. Maciel, P. D. Ellis, J. J. Natterstad, and G. B. Savitsky, *J. Magn. Reson.*, **1**, 589 (1969).
- Other methods used to identify configuration include the following. (1) Infrared spectroscopy: P. Duke and D. Boykin, Jr., *J. Org. Chem.*, **37**, 1436 (1972); J. Cason and M. Kalm, *ibid.*, **19**, 1947 (1954); Fr. Gasanov, *Opt. Spektrosk. (Akad. Nauk SSSR, Otd. Fiz.-Mat. Nauk)*, **3**, 76 (1967); *Chem. Abstr.*, **68**, 7788a (1968); J. Clark, *Appl. Spectrosc.*, **22**, 204 (1968); F.

- Geise, F. Mijlhoff, G. Renes, and F. Rummens, *J. Mol. Strukt.*, **17**, 37 (1973).
- (2) Long-range NMR coupling constants: R. R. Fraser, *Can. J. Chem.*, **38**, 549 (1960); R. R. Fraser and P. McGreer, *ibid.*, **39**, 505 (1961). (3) Ultraviolet spectroscopy (and NMR): K. Nilsson and S. Sternhell, *Acta Chem. Scand.*, **19**, 2441 (1966). (4) NMR chemical shifts: (a) V. Watts and J. H. Goldstein, *Chem. Alkenes*, **2**, 1 (1970); (b) A. Bahl and W. Kemp, *J. Chem. Soc. C*, 1583 (1971); (c) J. Elguero and C. Marzin, *Bull. Soc. Chim. Fr.*, 3401 (1973); (d) D. Kevill, E. Weiler, and N. H. Cromwell, *J. Org. Chem.*, **29**, 1276 (1964). (5) Shift reagents: M. Zinic, M. Stromar, and D. Kolbach, *Hem. Ind.*, **28**, 15 (1974); C. Beaute, 2. Walkowski, Z. Merda, and J. Lelandais, *Tetrahedron Lett.*, 2473 (1971). (6) Truly unique methods include clathrate inclusion: W. Schlenk, Jr., *Justus Liebigs Ann. Chem.*, **7**, 1179 (1973); M. Nicolaidis and F. Laves, *J. Am. Chem. Soc.*, **76**, 2596 (1954). (7) A general discussion of NMR methods: F. A. L. Anet, *Determination Org. Struct. Phys. Methods*, **3**, 343 (1971).
- (9) J. A. Marshall and R. Seiwel, *J. Magn. Reson.*, **15**, 150 (1974).
- (10) K. Creceley, R. Creceley, and J. H. Goldstein, *J. Mol. Spectrosc.*, **37**, 251 (1971), reported greater ^{13}C coupling constants for trans nuclei than for cis nuclei in molecules such as acrolein.
- (11) Our determination for (*E*)-crotonic acid, however, agrees well with that of Marshall and Seiwel⁹ for 4.
- (12) A. S. Perlin and J. Schwarcz, *Can. J. Chem.*, **50**, 3667 (1972).
- (13) R. U. Lemieux, T. Nagabhushan, and B. Paul, *Can. J. Chem.*, **50**, 773 (1972), and later papers.
- (14) In studies of proton coupling constants in alkenes, several other factors have been shown to affect the magnitude of the coupling constant. Thus, Rummens and DeHaan, *Org. Magn. Reson.*, **2**, 351 (1970), discussed certain J_{HH} variations in terms of rehybridization of the sp^2 carbon atoms. Schliebe, Seiffert, Hohlneicher, Jutz, and Springer, *Tetrahedron Lett.*, 5053 (1966), showed that increasing sp^2 - sp^2 single bond length in butadienes gave smaller values of $^3J_{\text{HH}}$. Yalyimova and Samitov, *Zh. Org. Khim.*, **6**, 1945 (1970), also considered electronegativity effects. M. Cooper and S. L. Manatt, *Org. Magn. Reson.*, **2**, 511 (1970), considered the effect of bond angle variations on $^3J_{\text{HH}}$.
- (15) (a) F. A. Bovey, "Nuclear Magnetic Resonance Spectroscopy", Academic Press, New York, N.Y., 1969, p 358.
- (16) (a) C. Banwell and N. Sheppard, *Discuss. Faraday Soc.*, **34**, 115 (1962); (b) T. Schaefer, *Can. J. Chem.*, **40**, 1 (1962).
- (17) J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, N.Y., 1972, pp 348-362, presents a general discussion of the topic.
- (18) G. J. Karabatsos, J. Graham, and F. Vane, *J. Phys. Chem.*, **65**, 1657 (1962); (b) see also F. J. Weigert and J. D. Roberts, *J. Am. Chem. Soc.*, **89**, 2967 (1967); (c) G. Binsch, J. Lambert, B. Roberts, and J. D. Roberts, *ibid.*, **86**, 5564 (1964); (d) G. Miyazima, T. Utsumi, and K. Takahashi, *J. Phys. Chem.*, **73**, 1370 (1969).
- (19) (a) The combination of π and σ pathways for spin coupling in alkenes, in comparison to only the σ pathway in Karabatsos' cases,¹⁸ represents an unknown factor. J. Murrell and R. Ditchfield, *Mol. Phys.*, **15**, 533 (1968), suggested that π contributions to $^3J_{\text{HH}}$ are small. See also G. Gray, P. Ellis, D. Traficante, and G. Maciel, *J. Magn. Reson.*, **1**, 41 (1969). (b) W. von Philipsborn and R. Hollenstein, *Helv. Chim. Acta*, **55**, 2030 (1972); **56**, 847 (1973); report LS values of 9-10 Hz for trans $\text{C}=\text{C}-\text{C}=\text{CH}$ couplings.
- (20) The *s*-cis conformer is preferred in simple (nonrigid) chalcones: B. Arbuzov, Y. Yuldasheva, I. Anonimova, R. Shagidullin, A. Chernova, and D. Fazliev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1258 (1969); *Chem. Abstr.*, **71**, 80535 (1970); however in α -substituted chalcones, a mixture of *s*-cis and *s*-trans forms seems more likely.
- (21) G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists", Wiley-Interscience, New York, N.Y., 1972, p 110.
- (22) R. L. Lichter and J. D. Roberts, *J. Am. Chem. Soc.*, **93**, 5218 (1971), and references cited therein, have emphasized the possible importance of changes in excitation energy on coupling constants. Parallel changes occurred in *J* and chemical shift in the system studied. See also ref 17, p 104, for a general discussion.
- (23) Reference 17, p 353.
- (24) A. M. Ihrig and J. L. Marshall, *J. Am. Chem. Soc.*, **94**, 1756 (1972).
- (25) For previous configuration studies on alkenyl cyanides, see R. Heilmann and J. Bonnier, *C. R. Acad. Sci.*, **248**, 2442 (1959).
- (26) The difference in ketone carbonyl chemical shift was -7.5 ppm ($\delta_{57} - \delta_{58}$), whereas the difference in ester carbonyl chemical shift was $+3.3$ ppm. Thus, the carbonyl cis to phenyl was the most "deshielded". A steric shift such as discussed by DeHaan and Van de Ven⁹ for alkyl groups cannot explain the chemical shift data. Matter et al. noted a fairly large difference in ^1H chemical shift for protons cis to ester compared to protons cis to a ketone function, but in other cases irregularities involving carbonyl groups were noted.⁶ Thus, the ^1H chemical shift method for isomer identification should be applied with caution to 57 and 58.
- (27) (a) G. Stewart and H. Eyring, *J. Chem. Educ.*, **35**, 550 (1958), state that electrons do not like to go "around corners"; (b) R. C. Bingham, *J. Am. Chem. Soc.*, **98**, 535 (1976); (c) H. Zimmerman and L. Ahranjian, *ibid.*, **81**, 2086 (1959).
- (28) H. Price, K. Williamson, and K. Brocklehurst, *Chem. Commun.*, 884 (1968).
- (29) Determination of configuration in the pyrazolone derivative



- was hampered by insolubility (TFA was added to improve solubility). The LS between CO and alkene H is ca. 8.5 Hz, whereas for $\text{C}=\text{N}-\text{H}$, the LS is ca. 6 Hz, which suggests the *Z* configuration. G. Desimoni, A. Gamba, P. Righetti, and G. Tacconi, *Gazz. Chim. Ital.*, **102**, 491 (1972), also assigned configuration as *Z*.
- (30) (a) F. J. Weigert and J. D. Roberts, *J. Phys. Chem.*, **73**, 449 (1969); (b) K. L. Servis, J. Casanova, Jr., and M. Geisel, *Org. Magn. Reson.*, **1**, 209 (1969); (c) O. Yamamoto, W. Watanabe, and K. Kikuchi, *Mol. Phys.*, **17**, 249 (1969).
- (31) H. Stobbe and O. Horn, *Chem. Ber.*, **41**, 3983 (1908).
- (32) L. F. Fieser and K. L. Williamson, "Organic Experiments", D. C. Heath, Boston, Mass., 1975, pp 335, 278. See also C. Koelsch and P. Johnson, *J. Am. Chem. Soc.*, **65**, 565 (1943).
- (33) (a) G. M. Underwood, A. Chan, T. Green, and C. A. Kingsbury, *J. Org. Chem.*, **38**, 2735 (1973); (b) L. Bergelson and M. Shenyakin, *Tetrahedron*, **19**, 149 (1963).
- (34) D. J. Cram and F. A. Abd Elhatez, *J. Am. Chem. Soc.*, **74**, 5828 (1952).
- (35) A. I. Vogel, "Practical Organic Chemistry", 3d ed, Longmans, Green and Co., New York, N.Y., 1956, p 353.
- (36) "Organic Syntheses", Collect. Vol III, E. Horning, Ed., Wiley, New York, N.Y., 1955, p 367.
- (37) (a) M. Conrad and L. Limpach, *Chem. Ber.*, **21**, 525 (1888); (b) A. Sanchez, T. Aldave, and U. Scheidegger, *J. Chem. Soc. C*, 2570 (1968).
- (38) C. Kingsbury, R. Egan, and T. Perun, *J. Org. Chem.*, **35**, 2913 (1970).
- (39) E. P. Kohler, *Am. Chem. J.*, **31**, 642 (1904).
- (40) T. Zincke and D. von Hagen, *Chem. Ber.*, **26**, 651 (1884). Beilstein (Drittes Ergänzungswerke) lists the configuration as *E*, but recent *Chemical Abstracts* show apparently the same isomer as *Z*. See also A. Robert, J. Pommeret, and A. Foucaud, *Tetrahedron*, **28**, 2085 (1972).
- (41) (a) W. Rodionow, *J. Am. Chem. Soc.*, **51**, 847 (1929); (b) F. Goss, J. Thorpe, and C. K. Ingold, *J. Chem. Soc.*, **123**, 3342 (1923).
- (42) R. Stoermer, *Chem. Ber.*, **44**, 637 (1911).
- (43) R. Stoermer and P. Heymann, *Chem. Ber.*, **46**, 1249 (1913).
- (44) R. Fittig and C. Petri, *Justus Liebigs Ann. Chem.*, **195**, 56 (1879).
- (45) A. Michael, *J. Prakt. Chem.*, **52**, 289 (1895).
- (46) J. Sudborough and L. Lloyd, *J. Chem. Soc.*, **73**, 81 (1898).
- (47) R. Heuck, *Chem. Ber.*, **28**, 2251 (1895).
- (48) P. Pfeiffer, J. Engelhardt, and W. Alfuss, *Justus Liebigs Ann. Chem.*, **467**, 158 (1928).
- (49) (a) L. Brandsma, "Preparative Acetylenic Chemistry", Elsevier, Amsterdam, 1971, p 60; (b) F. Straus, *Justus Liebigs Ann. Chem.*, **342**, 190 (1905).
- (50) C. Kingsbury, *J. Org. Chem.*, **33**, 1128 (1967).
- (51) P. Pfeiffer, I. Engelhardt, and W. Alfuss, *Justus Liebigs Ann. Chem.*, **467**, 158 (1928).
- (52) G. Payne and P. Williams, *J. Org. Chem.*, **26**, 651 (1961).
- (53) H. Meerwein and H. Dott, *J. Prakt. Chem.*, **97**, 225 (1918).
- (54) Reference 36, p 156.
- (55) H. Zimmermann, L. Singer, and B. Thyagarajan, *J. Am. Chem. Soc.*, **81**, 108 (1959).
- (56) J. Erickson, *J. Am. Chem. Soc.*, **67**, 1382 (1945).
- (57) J. Postma and J. Arens, *Recl. Trav. Chim. Pays-Bas*, **75**, 1385 (1956).
- (58) E. Erlenmeyer, Jr., *Justus Liebigs Ann. Chem.*, **337**, 265 (1904).
- (59) M. Nencki, *Chem. Ber.*, **17**, 2277 (1884).
- (60) E. Gilbert, *J. Am. Chem. Soc.*, **59**, 1074 (1937).
- (61) H. Stobbe, *Chem. Ber.*, **41**, 4350 (1908).
- (62) O. A. Gansow and W. Schiltensheim, *J. Am. Chem. Soc.*, **93**, 4294 (1971).