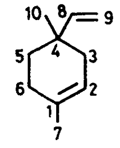
An Empirical Determination of ^{13}C Nuclear Magnetic Resonance Spectra of Terpene Isomers generated by Isoprene Cyclodimerisation

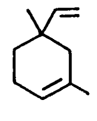
By **Roger Pétiaud** and **Younès Ben Taärit**,* C.N.R.S. Institut de Recherches sur la Catalyse, 2 avenue Albert Einstein, 69626 Villeurbanne Cédex, France

The ^{13}C n.m.r. spectra of 1,4- and 2,4-dimethyl-4-vinylcyclohexene and of 1- and 2-methyl-4-isopropenylcyclohexene have been calculated using the increment additivity method starting from 4-vinylcyclohexene. The calculated spectra fit well with the experimental values obtained for binary mixtures and all lines in the experimental spectra can be assigned to individual carbons.

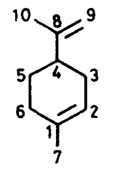
ISOPRENE oligomerisation has long been a subject of interest.[1-4] Much effort has been devoted to the search for effective catalysts and to the elucidation of the mechanism of the catalysed reaction and of the nature of the organometallic intermediates. Among the dimer products, isomers (A) and (A′) could not be distinguished by spectroscopic measurements and only destructive hydrogenation and subsequent aromatisation [1,5] could discriminate between the compounds. Thus we have sought a new means for performing both quantitative and qualitative determinations of the ratios and nature of various isomers using a particular catalytic system. ^{13}C N.m.r. spectroscopy proved a powerful and unique tool for simple, immediate, and non-destructive analyses of catalytic mixtures.



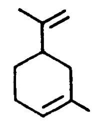
(A)



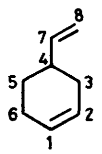
(A′)



(B)



(B′)



(C)

TABLE 1

Changes in ^{13}C n.m.r. chemical shifts for the transformation of octane into oct-1-ene

	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)
Octane [8]	14.0	23.0	32.4	29.7	29.7	32.4	23.0	14
Oct-1-ene [9]	115.0	139.2	35.0	31.1	31.1	33.8	24.3	15.4
Oct-1-ene — octane	+101.0	+116.2	+2.6	+1.4	+1.4	+1.4	+1.3	+1.4

EXPERIMENTAL

The catalyst $[Fe(NO)_2Cl]_2$ was prepared using the procedure reported by Petit *et al.*[3]

The catalyst was used immediately *in situ* by addition of purified isoprene and kept at room temperature for 48 h. A typical reaction mixture included dinitrosyliron chloride dimer (1 mmol), zinc (500 mg), and isoprene (200 mmol) in tetrahydrofuran (80 ml). Dimerisation products were separated by preparative g.l.c. after the excess of monomer was distilled off as described previously.[5,6]

Quantitative ^{13}C resonance intensities were determined by adding a relaxation agent, chromium acetylacetonate, Cr(acac) (0.1 mol^{-1}). The two terpene fractions collected by g.l.c. separation were identified by ^1H n.m.r.[1] as isomers of types (A) and (B). However ^1H n.m.r. does not allow identification of individual isomers. The only ^{13}C n.m.r. data available in the literature is for limonene (B). None of the other three isomers seemed to have attracted much attention possibly because of the difficulty of purification, Routine procedures for binary mixtures failed to achieve identification of the components of a given mixture. Therefore we attempted to carry out a semi-empirical *ab initio* determination of the chemical shift of the individual carbons of all four isomers so as to allow identification of a given isomer. This semi-empirical determination is based on additivity rules applied to chemical shift increments specific to various substituents. The final molecule was built starting from well known compounds. The applicability of the method was tested using 4-vinylcyclohexene (C), whose ^{13}C n.m.r. spectrum is well known.

RESULTS AND DISCUSSION

The ^{13}C n.m.r. spectrum of the binary mixture (A) and (A′) shown in Figure 1 exhibited 18 lines out of the expected 20 in the presence of Cr(acac). Thus a number of carbons have identical chemical shifts (probably two pairs). Moreover the total spectrum clearly appeared as the superposition of two patterns of uneven intensities reflecting the ratio of the two isomers in the mixture. The ^{13}C n.m.r. spectrum of (B) and (B′) is shown in Figure 2, exhibiting a particularly deshielded singlet.

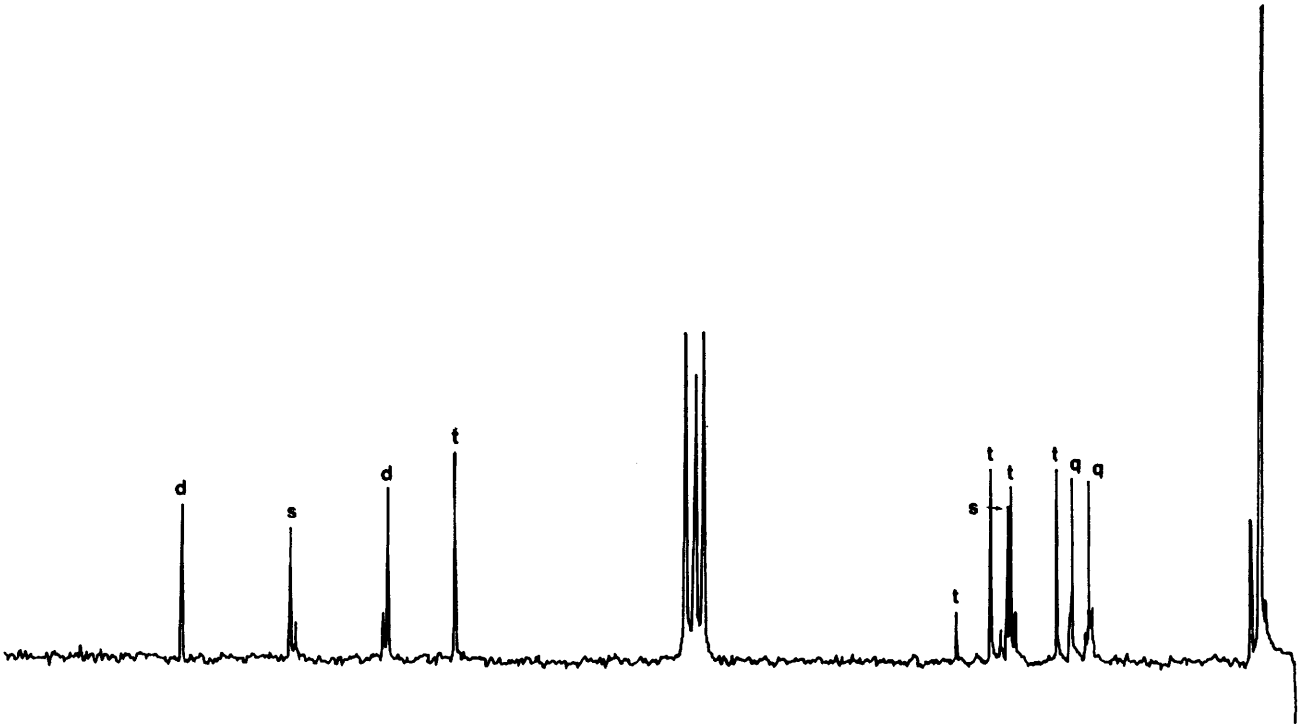


FIGURE 1 ¹H Decoupled ¹³C n.m.r. spectrum of (A) and (A′) with Cr(acac) added

The spectrum is that of an almost pure compound though a number of lines due to the other isomer appeared clearly

Semi-empirical Calculations of the ¹³C *Chemical Shift*.—Although the spectrum of 4-vinylcyclohexane has been reported [7] not all the lines were assigned to individual carbons. While lines were assigned to C(4) (doublet), C(7) (low-field olefinic doublet), and C(8) (olefinic triplet), lines due to C(1) and C(2) were left unassigned. The lines due to C(3), C(5), and C(6) were all triplets and could not be assigned. Therefore we attempted to predict the chemical shift of the individual

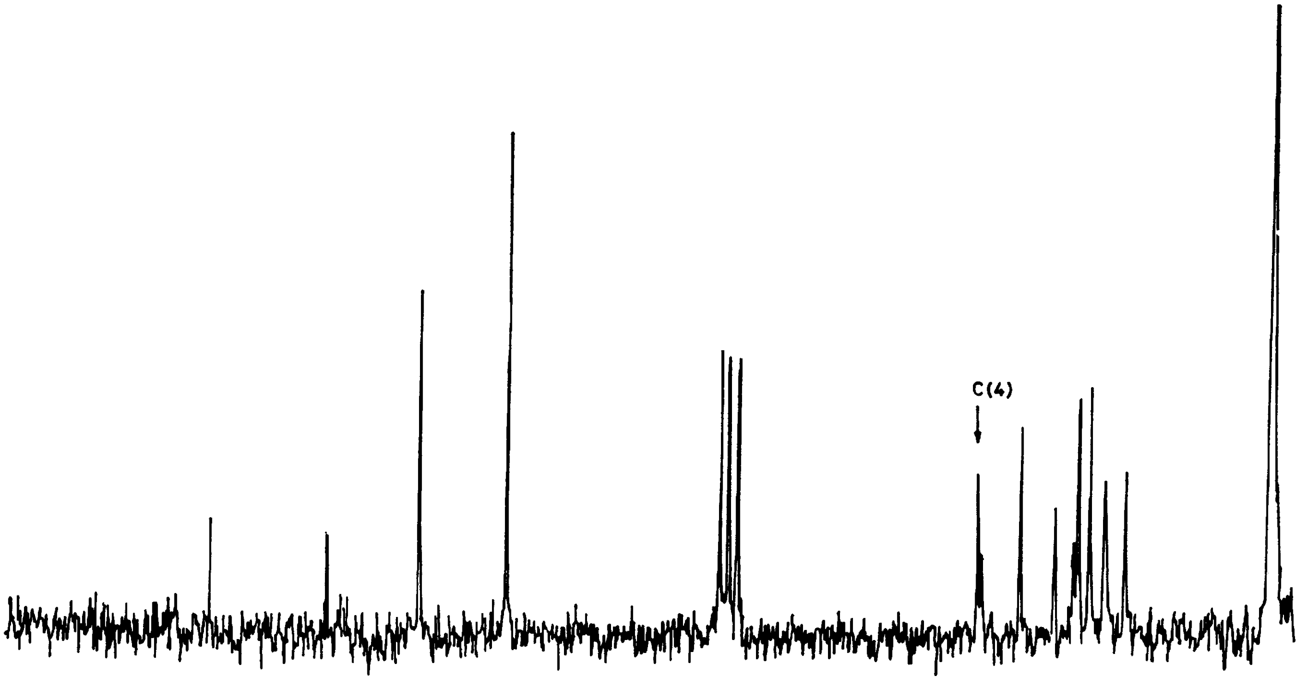


FIGURE 2 ¹H Decoupled ¹³C n.m.r. spectrum of (B) and (B′)

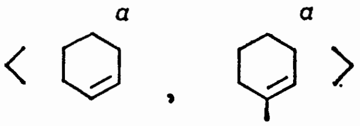
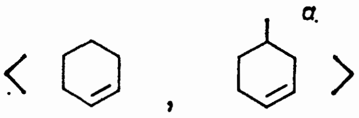
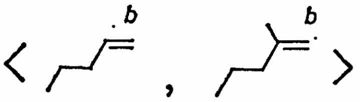
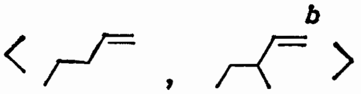
TABLE 2

Calculated and experimental ^{13}C chemical shifts for 4-vinylcyclohexene

	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)
4-Ethylcyclohexene [7]	+126.6	126.6	31.7	35.8	29.0	25.3	29.5	11.5
Octane — oct-1-ene	1.4	1.4	1.4	2.6	1.4	1.4	116.2	101.0
4-Vinylcyclohexene (calc.)	128	128	33.1	38.4	30.4	26.7	145.7	112.5
4-Vinylcyclohexene (exp.)	126.0, 126.8	126.8, 126.0	31.1	37.7	28.5	24.9	143.7	112.3

TABLE 3

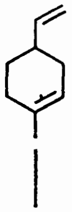
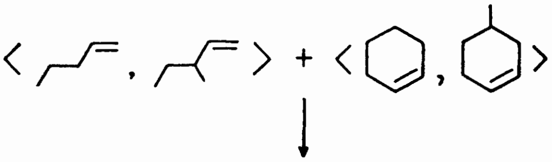
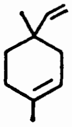
Operator elements

Operator / Carbon	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C(10)
	+7.1	−4.9	+1.2	+1.3	+1.3	+6.0	+23.8			
	−4.9	+7.1	+6.0	+1.3	+1.3	+1.2	+23.8			
	−0.6	−0.6	+9.4	+6.5	+9.1	+0.5				+23
								+6.0	−4.6	~23.4
								+6.4	−1.5	

[a] T. Pehk, S. Rang, O. Eisen, and E. Lippmaa, *Eesti NSV Tead. Akad. Toim. Keem. Geol.*, 1968, **17**, 296 (*Chem. Abs.*, 1969, **70**, 15,858e). [b] R. A. Friedel and H. L. Retcofsky, *J. Amer. Chem. Soc.*, 1963, **85**, 1300.

TABLE 4

Estimation of the spectrum of isomer (A) from that of 4-vinylcyclohexene

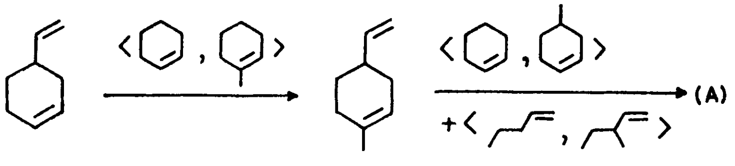
Compounds and operators / Carbon	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C(10)
	133.1	121.9	32.5	39.0	29.8	30.9	23.8	143.7	112.3	
	−0.6	−0.6	+9.4	+6.5	+9.1	+0.5		+6.4	−1.5	+23
	132.5	121.3	41.9	45.5	38.9	31.4	23.8	150.1	110.8	23

carbons of this molecule starting from 4-ethylcyclohexene and adding the appropriate increment to the chemical shift of a given carbon assuming the transformation of ethylcyclohexene into 4-vinylcyclohexene to have the same effect as the transformation of octane[8] into oct-1-ene[9] on the chemical shifts of the corresponding carbons. The various increments for the transformed molecule are termed operators and are assembled in Table 1. For the transformation of 4-ethyl- into 4-vinylcyclohexene the increments C(3)—C(6) have to be rearranged so as to be directly used in this transformation process and the arrangement in Table 1 becomes:

C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)
1.4	1.4	1.4	2.6	1.4	1.4	116.2	101.0

Hence the predicted chemical shifts for C(3)—C(6) in 4-vinylcyclohexene are given in Table 2 together with the experimental values.

The C(1), C(2), C(7), and C(8) chemical shifts are predicted to better than 2 p.p.m. while the more interesting C(3)—C(6) shifts also fit the experimental pattern with a general divergence of *ca.* 2 p.p.m. Furthermore while the experimental spectrum could not allow unambiguous assignments of the observed lines to particular carbons this method gives a general trend which fits the experimental values and provides a reasonable means of attributing signals to the appropriate carbons. The good fit also emphasises the applicability of the method.



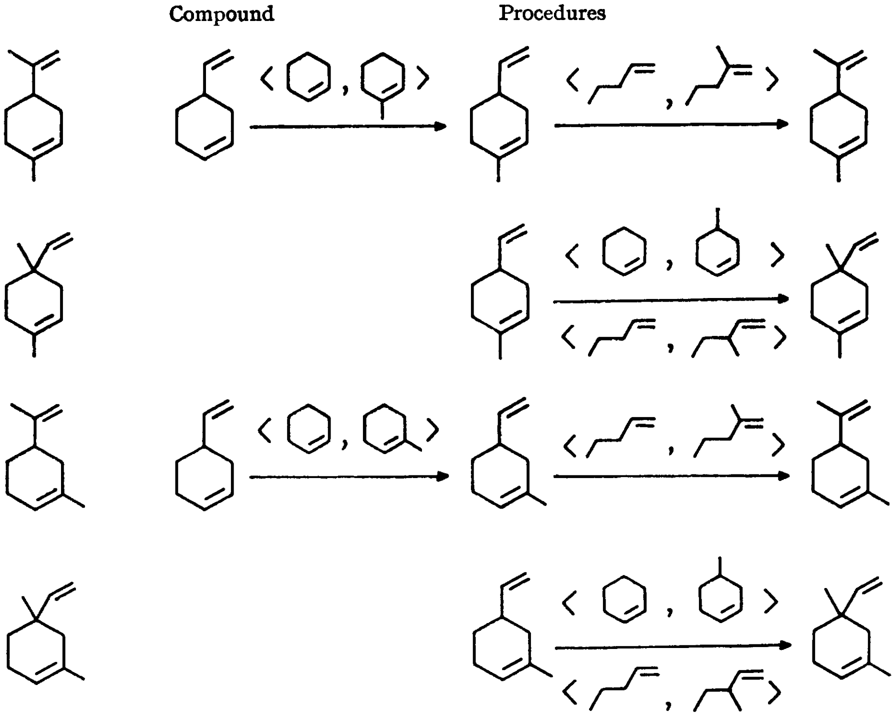
SCHEME 1

The spectra of the terpene isomers (A), (A′), (B), and (B′) are estimated by applying successively the appropriate operator corresponding to the attachment of a given substituent to the 4-vinylcyclohexene starting structure. The operators required for the construction of any given isomer were determined from literature data in the same way as the octane–octene operator. They are listed in Table 3 together with their elements. The arrangement of the elements was chosen with regard to the numbering of the carbons of the terpene molecules.

As an example the spectrum of isomer (A) could be estimated starting from 4-vinylcyclohexene (Scheme 1). The calculation is shown in Table 4. The other three isomers were dealt with following the same procedure (Table 5). Finally for comparison purposes the pre-

TABLE 5

Construction procedures for all isomers



dicted chemical shifts for all four isomers are gathered in Table 6 along with the experimental values.

From Table 6, it emerges that (A) and (A′) have similar predicted patterns with the following exceptions on which a distinction between the two isomers can be based: while C(4) is characterised by the same chemical shift in both isomers, C(3) of isomer (A) absorbs at significantly higher field than in (A′) and conversely the C(6) resonance of isomer (A) is shifted to significantly lower field than that of (A′). Thus, in principle, we have the means to distinguish between the two compounds.

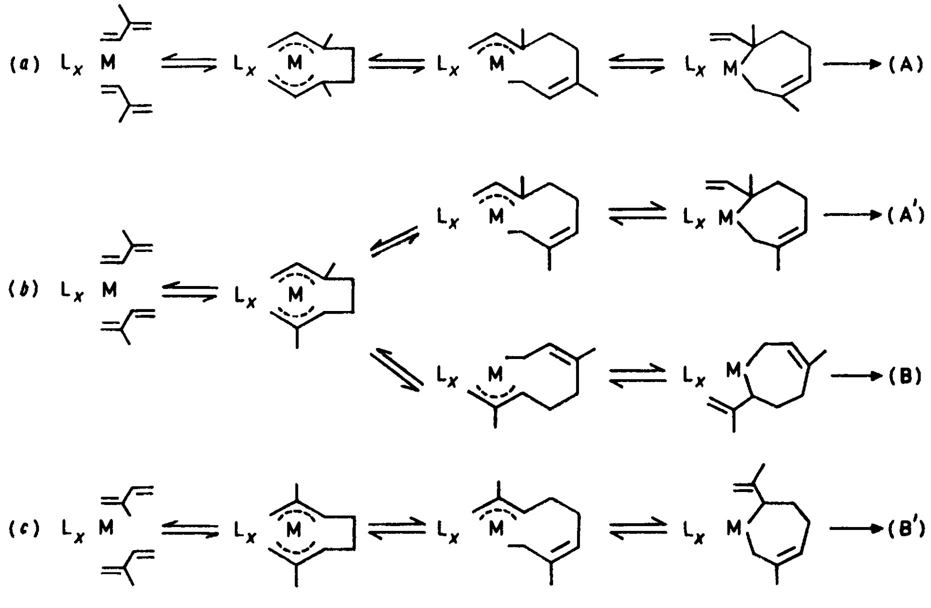
TABLE 6

Predicted and observed chemical shifts of terpene isomers

Compound		C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C(10)
(A)	P	132.5	121.3	41.9	45.5	38.9	31.4	23.8	150.1	110.8	23
	O	132.7	119.4	36.9	34.6	34.1	27.8	23.4	147.5	110.2	25.7
(A′)	P	120.5	133.3	46.7	45.5	38.9	26.6	23.7	150.1	110.8	23
	O	119.9	131.9	41.5	35.5	33.5	23.8 (26.0)	23	147.5	110.2	26.0 (23.8)
(B)	P	133.1	121.9	32.5	39.0	29.8	30.9	23.3	149.7	107.7	20
	O	133.4	120.6	30.7	41.2	28.0	30.9	23.7	150.0	108.3	20.8
(B′)	P	121.1	133.9	37.3	39.0	29.8	26.1	23.7	149.7	107.7	20
	O	120.6	133.4	35.6	41.7	27.4	25.8	23.7	150.0	108.3	20.8

P = Predicted, O = observed.

Similarly C(3) of limonene (B) clearly absorbs at higher field than in (B′) and the C(6) resonance of limonene is predicted to be significantly shifted to lower field than that in (B′). Thus again the C(6) and C(3) resonances should, in principle, provide a convenient means of discriminating between limonene and its isomer.



SCHEME 2

Identification of the Isomers.—The spectrum of the mixture of (A) and (A′) obtained upon addition of the relaxation agent yields two different patterns of lines with quite different intensities reflecting the relative concentrations of the two isomers. The more intense group including triplets at δ 27.8, 34.1, and 36.9 p.p.m. and a singlet at δ 34.6 p.p.m. on the one hand and the less intense group including lines at δ 26.0, 33.5, and 35.4 p.p.m. and a triplet at δ 41.5 p.p.m. on the other compare favourably with the predicted patterns of isomers (A) and (A′), respectively. Moreover, the fact that the less intense pattern includes a triplet at much lower field than any in the more intense pattern clearly indicates that the former corresponds to isomer (A′).

The low-field triplet can be assigned to C(3) which is predicted to resonate at lower field than in (A) by slightly <5 p.p.m. In fact the lowest field triplet of the other pattern arises at δ 36.9 p.p.m. which is at 4.2 p.p.m. upfield. Similarly the highest field triplet of the more intense pattern, presumably corresponding to isomer (A), resonates at δ 27.8 p.p.m. while the other pattern exhibits possible triplets at δ 23—26.0 p.p.m. at the most. The triplets at δ 27.8 and 23.8 p.p.m. (or 26 p.p.m.) probably result from the respective C(6) atoms thus confirming the assignment of both patterns since C(6) of isomer (A) is predicted to absorb at the lowest field.

With the exception of C(4) whose predicted chemical shift is far too large compared with the experimental value, the trend and order of the predicted values rigorously fit the observed values.

Further confirmation of the assignment arises from the quantitative determination of the relative concentration of the isomers. Using eight of the ten pairs of carbons, the ratio of A to A′ was 4 : 1.

Isomers (B) and (B′) are easier to identify since the former has been isolated and its spectrum reported.[10] Comparison of the reported values as well as those obtained in this study with the predicted figures shows a reasonable fit between the anticipated and observed chemical shifts, thus providing evidence for the applicability of the method, the departure of the predicted from observed values not exceeding 2.1 p.p.m. Moreover, the chemical shifts of the most characteristic carbons, namely C(3) and C(6), were accurate to within 1.8 p.p.m. The spectrum of (B′) could therefore be analysed easily. Again, the expected and assigned chemical shifts of the individual carbons are listed in Table 6.

As can be seen from Table 6, semi-empirical calculations may often provide a useful means of assigning lines and thus identifying products in catalytic mixtures when conventional non-destructive methods fail to achieve the separation of closely related isomers. The need for an unambiguous means of identification has been clearly illustrated in recent reports. Billard [6] and Tkachenko and his co-workers [4] could only list a number of mechanistic schemes presumably because they lacked a method of obtaining the final isomer distribution.

Billard [6] suggested three possible co-ordination processes of isoprene to the activated metal centre L_xM [Scheme 2, (*a*)—(*c*)]. Route (*a*) is sterically favoured and gives rise to isomer (A). According to our data the predominant product is certainly compound (A) and thus we favour route (*a*) which is sterically less demanding than the other two.

Clearly the reaction paths cannot be easily accessible unless the necessary spectroscopic data are available. We have shown in this study that predictions of ^{13}C chemical shifts are possible provided the correct basis is available and the right procedure applied (choice of operators). Thus tedious and destructive procedures for product identification can be avoided. Furthermore, even in the case of readily available pure compounds, this procedure proves a useful aid to line assignment.

We are indebted to Dr. C. Naccache, Dr. P. C. Gravelle, and Professor B. Imelik for helpful advice and encouragement, and to Mr. J. Ravier for technical assistance.

[9/943 *Received, 19th June, 1979*]

REFERENCES

[1] J. P. Candlin and W. H. Janes, *J. Chem. Soc.* (*C*), 1968, 1856.

[2] C. W. Bird, 'Transition Metal Intermediates in Organic Synthesis,' Logos, London, 1967, p. 35.

[3] (*a*) E. Leroy, F. Petit, J. Hennion, and J. Nicole, *Tetrahedron Letters*, 1978, **27**, 2403; (*b*) D. Huchette, B. Thery, and F. Petit, *J. Mol. Catalysis*, 1978, **4**, 433.

[4] D. Ballivet, C. Billard, and I. Tkatchenko, *Inorg. Chim. Acta*, 1977, **25**, L58.

[5] E. Le Roy, Dissertation, Université de Lille, 1978, p. 17.

[6] C. Billard, Dissertation, Université Claude Bernard Lyon, 1977, pp. 99—100.

[7] Le Roy, F. Johnson, and W. C. Jankowski, 'Carbon-13 NMR Spectra,' Wiley, New York, 1972, spectrum 306.

[8] D. M. Grant and E. G. Paul, *J. Amer. Chem. Soc.*, 1964, **86**, 2984.

[9] E. Lippmaa, S. Rang, O. Eisen, and T. Pehk, *Eesti NSV Tead. Akad. Toim. Keem. Geol.*, 1967, **16**, 351 (*Chem. Abs.*, 1968, **69**, 23491z).

[10] F. J. Weigert, M. Jautelat, and J. D. Roberts, *Proc. Nat. Acad. Sci. U.S.A.*, 1968, **60**, 1152.