Tetrahedron Vol. 27, pp. 2811 to 2821 Pergamon Press 1971. Printed in Great Britain

ISOTOPIC STUDY OF DUAL REACTIVITY AND TAUTOMERISM OF TRIAD A=B—AX SYSTEMS—II

THE USE OF ^{13}C FOR THE DETERMINATION OF SUBSTITUTION MECHANISMS IN ALLYLIC AND METHYLENEAZOMETHINE SYSTEMS

M. M. SHEMYAKIN,* L. A. NEIMAN,† S. V. ZHUKOVA, YU. S. NEKRASOV

Institute for Chemistry of Natural Products of the USSR Academy of Sciences, Moscow, USSR

T. J. PEHK and E. T. LIPPMAA

Institute of Cybernetics of the Estonian Academy of Sciences, Tallinn, USSR

(Received in the UK 26 May 1970; Accepted for publication 9 March 1971)

Abstract—A general isotopic method for discriminating between S2, S'2 and S1 (S_R) substitutions reactions and tautomerism in triad systems of the type A=B AX (allylic, methyleneazomethine, triazene, etc) has been proposed. The method is particularly effective if stable isotopes, such as ^{13}C or ^{15}N, are used. Its application is illustrated in the reactions of 1,3-diphenylpropene and N-benzylidenebenzylamine with azodicarboxylic ester. Both reactions proceed by at least two competitive mechanisms, of which one (predominant in the case of 1,3-diphenylpropene) is S'2.

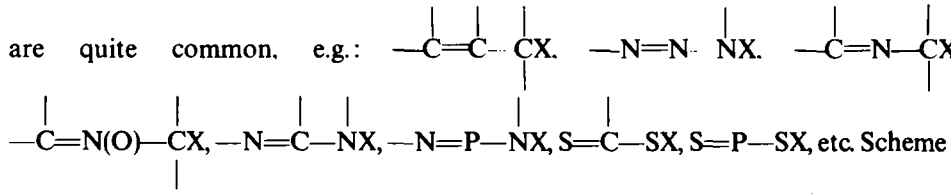
THE determination of substitution mechanisms in potentially tautomeric systems (such as allylic, methyleneazomethine, triazene, etc) is difficult, on the one hand, on account of the diversity of possible reaction mechanisms leading to identical products[1] and on the other hand, by the inadequacy and ambiguity of present-day (mainly kinetic) analytical methods.

Bordwell and Schexnayder[2] came to the conclusion that in only a few cases can the S'_N2 mechanism be considered to have been proved unequivocally. This conclusion appears to hold also for other potentially tautomeric systems, and for other types of substitution reactions. The same authors noted that for allylhalogenides it is practically impossible to differentiate between the S'_N2 reaction and the consecutive reactions S'_Ni and S_N2 and listed a number of difficult conditions which they considered necessary to fulfil for the unambiguous determination of reaction mechanisms in systems of this kind.

In this paper we propose a new isotopic method for the elucidation of substitution mechanisms in potentially tautomeric systems. Since this method depends on neither kinetic measurements nor the isolation of a pure tautomeric form of the starting material it circumvents many of the difficulties while permitting unambiguous discrimination between the S1, S2 or S'2 mechanisms. In the interplay of several reaction types usually their relative importance leads itself to quantitative estimation. In its initial form the proposed method was used more than 10 years ago for the study of diazoaminobenzene reactions,[3] and it was subsequently used for the study of tautomeric equilibria.[4–7]

* Died 26 June 1970

† To whom correspondence should be addressed

In the meantime we have shown[8] that this method is applicable not only to the study of tautomeric equilibria as such or to differentiate it from dual reactivity due to other causes, but it also permits elucidation of substitution mechanisms in symmetrical potentially tautomeric systems of the type A=B—AX, where B may or may not equal A and X is either hydrogen or a substituent group. Systems of this type are quite common, e.g.:  shows the reaction of a compound CY with a potentially tautomeric compound A=B—AX (**5**). The double bonded atom A of the initial compound and of the products is designated as $A_{(1)}$ and is isotopically labelled. If the interaction between the compounds proceeds by the S_N2 or S_E2 mechanisms (regardless of whether a cyclic 4-membered active complex **4** is formed or CY first dissociates into ions and the atom $A_{(2)}$ is then attacked by the ion Y with simultaneous heterolytic cleavage of the $A_{(2)}$—X bond), the end product **1** will have the same isotopic composition of atoms $A_{(1)}$ and $A_{(2)}$ as the starting material (**5**), i.e. the label is 100% at atom $A_{(1)}$ and 0% at atom $A_{(2)}$. In the case of S'_N2 or S'_E2 mechanisms (i.e. reaction via the 6-membered cyclic active complex **6** or by concurrent attack of atoms $A_{(1)}$ and X by the dissociated ions Y and C) it is the single bonded atom A, i.e. atom $A_{(2)}$ of the reaction product **3** which is labelled, while atom $A_{(1)}$ contains no label. In the case of intermediate formation of the anion **7** (reaction S_E1) or its corresponding cation (reaction S_N1) or of free radical **8** (reaction S_R) from the compound **4** these entities are ambident, and their atoms $A_{(1)}$ and $A_{(2)}$ as a result of the symmetrical structure of the initial compound are indistinguishable.* Consequently, there is equal probability of attack of such ions (or radicals) by the ion Y (or radical Y') at $A_{(1)}$ and $A_{(2)}$ so that an equimolecular mixture of isotopic isomers **1** and **3** is formed (i.e. the atoms $A_{(1)}$ and $A_{(2)}$ are equalized in label). Lastly, if tautomeric equilibrium **1** $\rightleftarrows$ **5** precedes the reaction then similar levelling of the isotopic composition of the two A atoms in both the initial compound and reaction products occurs regardless of the mechanisms by which the tautomeric forms **2** and **5** react with CY.

All these regularities are summarized in Table 1, from which is apparent that every type of substitution reaction, or every type of dual reactivity, leads to its own characteristic label distribution between atoms $A_{(1)}$ and $A_{(2)}$ in both products and unreacted initial compound.†

The only exceptions are the S1 and S_R mechanisms; however, as a rule, it is possible to distinguish between ionic and free radical reactions by means of a number of their characteristic features.

The above method is of course applicable only to symmetrical systems, but it is the only approach to such cryptotautomeric systems, which are especially suitable for

* Of course, there is no difference in the S_E1 and S'_E1, S_N1 and S'_N1, and S_R and S'_R mechanisms for symmetrical molecules.

† It must be mentioned that some substitution reactions of allylic compounds have been previously studied by isotopic techniques (*cf.* for example, 9, 10), but only here has the method for the first time been presented in a most general form and together with a very convenient experimental technique (*vide infra*).

the study of general relationships in various substitution reactions. The symmetrical structure itself eliminates the necessity of accounting for the effect of substituents. which is especially pronounced if the substitution reaction can proceed by two (or more) competitive mechanisms.

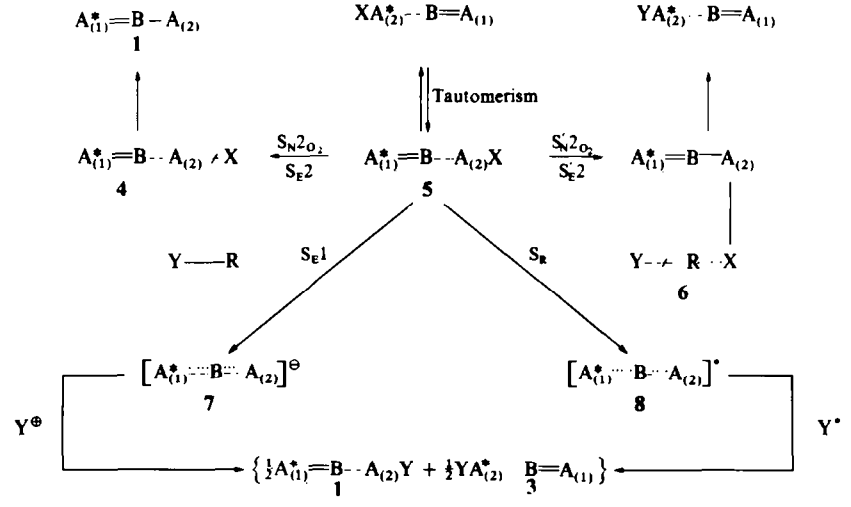
TABLE 1

Reaction type	Label content in % of the original*			
	Unreacted initial compound form the reaction mixture		Reaction products	
	A(1)	A(2)	A(1)	A(2)
Tautomerism	50	50	50	50
S_N2 or S_E2	100	0	100	0
S'_N2 or S'_E2	100	0	0	100
S_N1. S_E1 or S_R	100	0	50	50

* The initial compound is labelled at A(1)

In the practical application of this method both radioactive and stable isotopes can be used. However. the latter. and especially ^{13}C and ^{15}N have in the case of adequate enrichment the very significant advantage that both ^{13}C or ^{15}N NMR spectrometry*

SCHEME 1



and by use of appropriate procedure mass spectrometry can be used for the determination of isotope distribution. Thus, the time-consuming and often difficult degradation of the compounds under study for the determination of atomic isotope contents is no longer necessary. This circumstance is quite significant since it simplifies

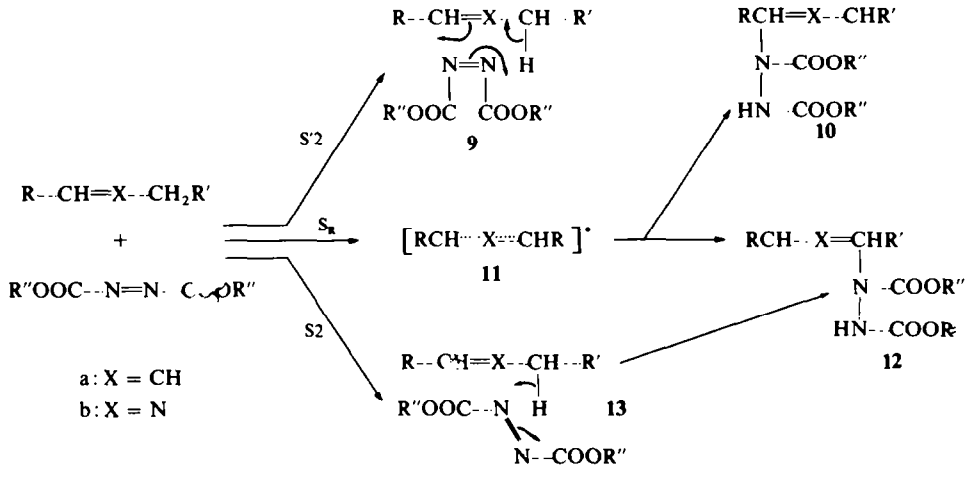
* In the case of groups like —C=C—CH—, —C=N—CH—, —N=C—NH, etc. determination of the ^{13}C and ^{15}N contents can be carried out using the respective satellite lines in the proton spectra.

the application of the proposed method. For a molecule of the general type $A_{(1)}$=B--$A_{(2)}$X (**5**) the label may be introduced into either position $A_{(1)}$ or $A_{(2)}$, or even into the adjacent substituent groups, if their migration during the reaction is completely excluded.

The isotopic technique was used to elucidate the mechanism of additive substitution in allylic and methyleneazomethine systems in the reactions of azodicarboxylic ester with 1.3-diphenylpropene and N-benzylidenebenzylamine. Both reactions belong to additive substitution reactions, including although the reactions of active hydrogen containing compounds with maleic anhydride, formaldehyde (hydroxymethylation), acrylonitrile (cyanoethylation), acetylenedicarboxylic ester, dehydrobenzene, etc.

The mechanism of allylic substitution in the reaction of olefins with azodicarboxylic ester has been investigated.[11-18] Some authors considered it to be a onestep concerted process that proceeds via a 6-membered transition state **9a** (Scheme 2) and leads to migration of the double bond in the resulting product **10a** (this mechanism we designate in the following as S'2)*, other authors proposed a two-step free radical

SCHEME 2



mechanism, involving the formation of an ambident allylic radical **11a** from the initial olefine (this mechanism is further designated as S^R).

Assignment of the reaction of azodicarboxylic ester with olefin to S'2 or S_R was based largely on the structure of the products (elucidation of whether migration of the double bond occurs in the course of the reaction) and on the effect of initiators and inhibitors of radical reactions on the yield of the reaction products and on the reaction kinetics. Both criteria are insufficient even as a first approximation. Migration of the bouble bond in itself cannot be considered as unambiguous evidence of the S'2 mechanism, inasmuch as an S_R reaction (general case) owing to formation of the ambident radical **11a** should result in two products--compound **12a** (without double bond migration) and compound **10a** (with double bond migration), of which

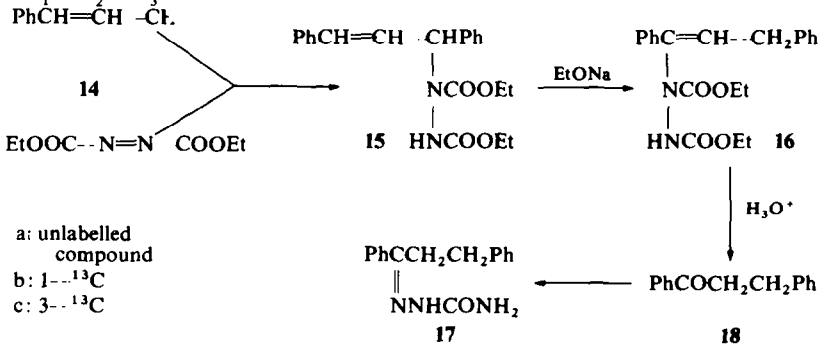
* In the quoted scheme of cyclic transfer of electrons each of the reagents the olefin as well as the azo ester possess both nucleophilic and electrophilic properties. Consequently, strictly speaking, such a mechanism can be considered to be neither S'_N2, nor S'_E2.

one could be predominant or even the only compound depending upon the substituents R and R'. Moreover, for a number of olefins like isobutylene, 1,3-diphenylpropene, cyclopentene and other cycloolefins, migration of the double bond in the reaction with azodicarboxylic ester cannot be detected by the usual methods because of the symmetrical structure of these molecules. It must also be pointed out that strictly speaking the possibility of tautomeric conversion of the three-carbon (allylic) system before or during the main reaction (especially in the presence of basic substance) cannot be completely ruled out, and this can also lead to the migration of the double bond.

Concerning the influence of initiators and inhibitors of free radical reactions on the rate and product yield, in some cases (such as for example, cyclopentene and cyclohexene[12]) the experimental results are not sufficiently definite to allow on unequivocal assignment of an S_R mechanism to the reaction of these olefins. This criterion is especially unreliable if the olefin reacts with the azo ester simultaneously by both the S_R and S'2 mechanisms, because then the initiators and inhibitors would only affect the relative contribution of each mechanism without affecting the overall yield. The isotopic method discussed here is, therefore especially promising for the study of additive substitution reaction mechanisms in allylic systems. The reaction between azodicarboxylic ester and 1,3-diphenylpropene was selected since the mechanism was studied for the 1,3-diarylpropenes. Huisgen and Pohl[12] have shown that with azodicarboxylicester, each of the isomeric phenyl-*p*-tolypropenes (1-phenyl-3-*p*-tolylpropene-1 and 1-*p*-tolyl-3-phenylpropene-1) forms only one product, differing from the initial compound by the location of the double bond, and that initiators and inhibitors of free radical reactions do not affect the yield of this product. From this it was concluded that a one-stage cyclic S'2 is the sole mechanism of the reaction.

The previously uninvestigated reaction between 1,3-diphenylpropene **14a** and ethyl azodicarboxylate (Scheme 3) was run under practically the same conditions as for tolylphenylpropenes.[12] the only difference being the use of benzene in place of cyclohexane as solvent. The reaction product **15a** was characterized both chemically and by IR, NMR and mass spectra. With sodium ethoxide in ethanol it changed to a tautomeric mixture of **15a** and **16a** with the latter predominant. The NMR spectrum of **16a** shows the presence of two benzylic protons (instead of one in the case of **15a**) and absence of benzylidene protons, while hydrolysis of **16a** with mineral acids led to phenyl phenethyl ketone **18a** evidently via the intermediate enehydrazine.

SCHEME 3

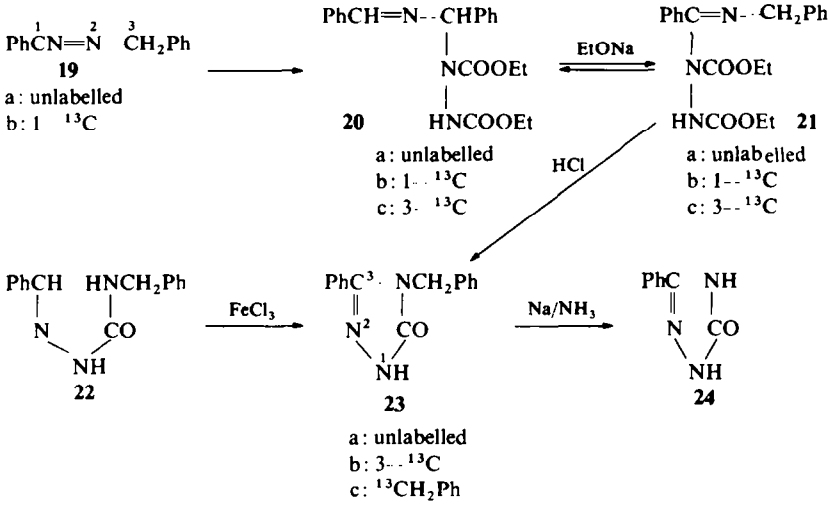


For reasons given above the stable isotope ^{13}C is most convenient for the tracer study of substitution reactions in the allylic system. The necessary initial compound 1,3-diphenylpropene-(1-^{13}C) **14b** was prepared from $Ba^{13}CO_3$ (*ca* 50 at % ^{13}C) via $Ph^{13}COOH$, $Ph^{13}CHO$ and 1,3-diphenylpropanol-1-(1-^{13}C).[19] The position of the label in olefin **14** was confirmed by the ^{13}C NMR spectrum, while the compound prepared from this olefin and azodicarboxylic ester, namely 1,3-diphenyl-3-(N,N'-dicarbethoxyhydrazino)-propene-^{13}C contained 85–88% of the original ^{13}C in position 3 and 12–15% in position 1 by both ^{13}C NMR spectroscopy and mass spectrometry (the methods are described in more detail later), and so presented a 15: 85 mixture of the isotopic isomers (**15b** and **15c**). At the same time in the unreacted olefin **14b** from the reaction mixture NMR showed only the methine group to be labelled, the methylene group containing no ^{13}C; this excludes any possibility of tautomeric conversion or hydrogen migration in the initial compound. The good agreement of NMR and mass spectrometric data is indicative of the reliability of these methods and the results led to the following conclusions. On the basis of our method and from Scheme 2 it can be seen that S'2 substitution associated with the double bond migration should lead exclusively to the isotopic isomer **15c**, or, in other words, to complete redistribution of the label between the position 1 and 3 in the course of the reaction, resulting in incorporation of all 100% of the initial ^{13}C into the $C_{(3)}$ position of the product. In case of any other substitution mechanism the ^{13}C content (per cent of the initial) in this position could not exceed 50% (Table 1). Since 85% of ^{13}C content was found in position $C_{(3)}$ of the product, it means that it is the S'2 mechanism which predominantly underlies but the substitution mechanism is not the only one. The other mechanisms for this substitution are still unresolved since our results alone give no firm basis for choosing between the S2 and S_R mechanisms. By the former, S2 (Scheme 2) involving the 4-membered transition state **13a** the only product **12a** is formed without double bond migration, and in the case of the labelled olefin **14b** this mechanism should lead exclusively to the isotopic isomers **15b**. As shown by our data, the contribution of mechanism S2 (if it occurs) in the reaction of 1,3-diphenylpropene with azodicarboxylic ester should be about 15%. As to the S_R mechanism, in general it should lead to the formation of two products (**10a** and **12a**), and therefore the labelled olefin **14b** would give an equimolecular mixture (without accounting for the isotope effect) of isotopic isomers (**15b** and **15c**), i.e. the S_R mechanism would tend to equalize the label content at $C_{(1)}$ and $C_{(3)}$ of the product. Since actually the ^{13}C content at $C_{(1)}$ amounts to only 15% of the total amount of ^{13}C in the molecule, the contribution by the free radical mechanism which according to the literature[11–18] is the most probable other mechanism for the reaction under study, cannot exceed 30%. It must be stressed again, however, that no matter which is the true mechanism of the side reaction, the present isotopic method gave unequivocal proof of the predominance (over 70%) of the S'2 mechanism in the reaction of 1,3-diphenylpropene with azodicarboxylic ester and showed also that this was not the only mechanism. The reason why this conclusion differs from the one by Huisgen and Pohl[12] (see above) may possibly be due to the inadequate sensitivity of their methods but it is also possible that even minute differences in the structure of the olefins may have a strong effect on the relative contribution of the substitution mechanisms, which could result in significant decrease or even total disappearance of the S_R mechanism.

In order to investigate the influence of reagent structure on the additive substitu-

tion mechanism we studied the reaction of azodicarboxylic ester with the nitrogen analogue of 1,3-diphenylpropene, namely, N-benzylidenebenzylamine **19a**. This only known example of additive substitution in a methyleneazomethine system had been accomplished some years ago[20] and in comparison with similar reactions in the allylic series has remained almost unexplored. The information on this reaction was confined to the preparation of the substitution product **20a** and proof of its structure by spectral methods. Some additional reactions of this compound are presented in Scheme 4: alkaline tautomerization leads to an equilibrium mixture of **20a** and **21a** which without separation was subjected to acid hydrolysis giving 3-phenyl-4-benzyl-1,2,4-triazolone-5 **23a**. The structure of the latter compound was confirmed by spectral data and through cleavage to toluene and 3-phenyl-1,2,4-trizzolone-5 **24**[21] and finally established by its synthesis from benzaldehyde benzylsemicarbazone **22** through oxidation with $FeCl_3$.[22]

SCHEME 4



The mechanism of the benzylidenebenzylamine reaction with azodicarboxylic ester was studied by the isotopic technique under the conditions used in the case of 1,3-diphenylpropene. The methine-labelled benzylidenebenzylamine **19b** was prepared by condensation of $Ph^{13}CHO$ with benzylamine and the position of the ^{13}C label confirmed by its ^{13}C NMR spectrum. The interaction of this labelled azomethine with azodicarboxylic ester (under conditions, identical to those used for the reaction of 1,3-diphenylpropene with azo ester) led to the labelled 1,3-diphenyl-3-(N,N'-dicarbethoxyhydrazino)-2-azapropene-1, in which the ^{13}C label was distributed between the 1 and 3 positions in the ratio $(30 \pm 10):(70 \pm 10)$ (according to the ^{13}C NMR data)* or 40:60 (from mass spectral data), that is to say the ratio between the isotopic isomers (**20b** and **20c**) is *ca* 40:60. In unreacted azomethine **19** the distribution of ^{13}C was not changed during the reaction. As in the case of olefins this means that under our conditions the initial benzylidenebenzylamine did not undergo any tautomeric interconversion or hydrogen migration.

* The limited precision of the ^{13}C NMR data was due to inadequate size of sample at out disposal.

All three additive substitution mechanisms – S2, S'2 and S_R (Scheme 2, X=N)* are possible for methyleneazomethines. The presence of more than 50% of the initial ^{13}C content in possition 3 of the product shows that the S'2 mechanism is one of the competing mechanisms in the reaction of benzylidenebenzylamine with azodicarboxylic ester. The relative contributions by this and other mechanisms is still to be determined. If it is the S2 mechanism that competes with the S'2 mechanism then their ratio is 40:60 and the S'2 mechanism is still predominant, if, however, S_R is the second mechanism, then the relative importance of S'2 is diminished to *ca* 20% and the free radical mechanism is the predominant one (up to 80%), although there is as yet no direct evidence of its being present. Lastly, all three mechanisms may operate simultaneously and then the contribution by the S'2 mechanism can vary from 20 to 60%. Thus no matter which mechanisms are competing with the S'2 mechanism, its importance is significantly less in the reaction of azodicarboxylic ester with benzylidenebenzylamine than with 1,3-diphenylpropene.

Two methods were used for determining the isotope content and distribution in the ^{13}C-labelled compounds, namely, NMR of ^{13}C and mass spectrometry. The ^{13}C NMR spectra were obtained on a special spectrometer[23] with the use of frequency sweep, total decoupling of hydrogen nuclei and time sharing (a pulse method that practically eliminates all zero drift and instability). The ^{13}C content at all positions in the molecule was measured as the mean value of the ratios of the corresponding peak heights in the spectra of equiconcentrational solutions of enriched and unenriched (1.1 at % of ^{13}C) compounds[24,25]. In some cases rapid adiabatic passage dispersion spectra were used instead of absorption spectra for enhanced sensitivity, even though this led to distorted line shapes and some difficulties in the measurement of peak height ratios. The ^{13}C chemical shifts of the atoms $C_{(1)}$, $C_{(2)}$ and $C_{(3)}$ in the compounds under study are given in Table 2, the error of measurement being 1 ppm for the compounds **15** and **20** and 0·5 ppm for the others.

TABLE 2

No.	Compound	^{13}C chemical shift in ppm from CS_2		
		C(1)	C(2)	C(3)
1.	1,3-Diphenylpropanol	122	162	154
2.	1,3-Diphenylpropene (**14**)	61·6	67·6	154·2
3.	1,3-Diphenyl-3-(N,N'-dicarbethoxyhydrazino)-propene-1 (**15**)	60	57–64*	128
4.	1,3-Diphenyl-2-azapropene (**19**)	31·7		128·5
5.	1,3-Diphenyl-3-(N,N'-dicarbethoxyhydrazino)-2-azapropene-1 (**20**)	35		112

* Coincides with the peaks of aromatic C atoms.

Although mass spectrometry is the best micro method for determining both the total content and distribution of the heavy isotope in the molecule, it is not directly applicable to study of triad systems of the type A=B=AX which under electron impact are converted into ambident cations $[A\cdots B\cdots A]^+$ with both A atoms equivalent and

* Ionic mechanism (S_N1 and S_E1) can be practically excluded under our conditions (non-polar solvent with no ionizing additives).

equal probability of cleavage of both A···B bonds (for a more detailed analysis see[26]). For the mass spectrometric determination of the isotope contents in the positions $C_{(1)}$ and $C_{(3)}$ of ^{13}C-labelled compounds (**14**, **15**, **19** and **20**) they must first be converted into non A=B···AX derivatives. Such conversions of 1,3-diphenyl-3-(N,N'-dicarbethoxyhydrazino)-propene-^{13}C (**15b** and **c**) and 1,3-diphenyl-3-(N,N'-dicarbethoxyhydrazino)-2-azapropene-^{13}C (**20b** and **c**) are shown in Schemes 3 and 4. In both cases tautomerisation by EtONa in EtOH followed by acid hydrolysis was used. In contrast to the initial 1,3-diphenylpropene **14** and N-benzylidenebenzylamine **19** prototropy cannot equalize the $C_{(1)}$ and $C_{(3)}$ positions in compounds (**15** and **20**) since both tautomeric forms (**15** and **16**) and (**20** and **21**) are chemically not identical and the intermediate ambident anion is not symmetrical. The resulting hydrolysis products—phenyl phenethyl ketone-^{13}C (**18b** and **c**) and phenylbenzyltriazolone-^{13}C (**23b** and **c**) were analysed by mass spectrometry. The content of the isotopic isomer **18c** and thereby the ratio of the isotopic isomers **18b**:**18c** was determined from the percentage of ^{13}C in the benzyl fragment (m/e 91). This ratio is equal to the ratios (**16b**:**16c** and **15c**:**15b**). As a check the ketone-^{13}C was converted to the corresponding semicarbazone, where the content of the isotopic isomer **17b** was determined by mass spectrometry from the ^{13}C content in the fragment $[PhC{=}N{-}NH_2]^+$ (*m/e* 104) specific for semicarbazones. In both cases the ^{13}C distribution between the positions $C_{(1)}$ and $C_{(3)}$ in the compounds (**15b** and **c**) was the same (12:88). Likewise, the ratio of isotopic isomers (**23c** and **23b**) and thereby the distribution of ^{13}C between the positions $C_{(1)}$ and $C_{(3)}$ (40:60) of the compounds (**20b** and **c**) was determined from the ^{13}C content in the benzyl fragment (*m/e* 91) of phenylbenzyltriazolone-^{13}C.

EXPERIMENTAL

All m.ps are uncorrected. IR spectra were measured in paraffin oil on a UR-10 spectrometer. The proton NMR spectra were recorded with TMS as internal standard in $CDCl_3$ using a JNM C-60 spectrometer. The ^{13}C NMR measurements were made on a special spectrometer[23] at room temperature with CS_2 as external standard; saturated sols in $CHCl_3$ were used (from 0·1 to 1 g samples in 2 ml of the solvent). Mass spectra were registered on a MX-1303 spectrometer.

Benzaldehyde ^{13}C was prepared from $Ba^{13}CO_3$ (^{13}C content *ca* 50 at %) though $Ph^{13}COOH$ $Ph^{13}COCl$, $Ph^{13}CONH_2$ and $Ph^{13}CN$ as described for benzaldehyde ^{14}C,[22] only for the conversion of $Ph^{13}CONH_2$ into $Ph^{13}CN$ by dehydration $SOCl_2$ (refluxing in benzene for 6 hr) was used instead of $AlCl_3 \cdot NaCl$.

Benzylidenebenzylamine-^{13}C (**19b**) was prepared by condensation of $Ph^{13}CHO$ with $PhCH_2NH_2$ (azeotropic distillation of water from a boiling benzene soln).

1,3-*Diphenylpropanol*-(1-^{13}C). A soln of 2·64 g benzaldehyde ^{13}C in 5 ml dry ether was added to a stirred soln of $PhCH_2CH_2MgBr$ (prepared from 0·65 g of Mg and 5·5 g phenethyl bromide in 150 ml dry ether), boiled 2 hr with stirring and decomposed with a conc NH_4Cl aq. The water layer was extracted with ether, the combined ether soln dried over Na_2SO_4, and 1,3-diphenylpropanol-(1-^{13}C), remaining after evaporation of the solvent distilled to yield 3·67 g (about 70%) of product, b.p. 150° (1 mm).[28] n_D^{20} 1·5711.

1,3-*Diphenylpropene*-(1-^{13}C) (**14b**). A mixture of 3·66 g diphenylpropanol-(1-^{13}C) and 7·3 g anhyd $KHSO_4$ was heated at 140–150° for 4–5 hr under a stream of dry N_2. After cooling water was added and the mixture was extracted with ether to give after distillation 1,3-diphenylpropene-(1-^{13}C) (2·27 g, *ca* 70%), b.p. 135° (1 mm), n_D^{20} 1·5970.[29]

1,3-*Diphenyl*-3-(N,N'-*dicarbethoxyhydrazino*)-*propene*-1 (**15a**). A soln of **14b** (14·62 g) and diethyl azodicarboxylate (13·10g) in dry benzene (30 ml) was refluxed for 4 hr, the solvent distilled off and the resulting oil triturated with light petroleum (b.p. 40–60°) added portionwise. The residue in MeOH (30 ml) after some time at 0°C deposited white crystals (7·41 g). An additional 3·41 g of these were obtained from light

petroleum soln on cooling to 0°, total yield of **15a** was 10·82 g (*ca* 40%); m.p. 85–87° (from light petroleum). ν_{max} 3260, 1760, 1695, 1520, 1300, 1260, 1220, 1060 cm^{-1}. PMR spectrum showed a 6-proton quartet at 1·25 ppm (Me-groups), a 4-proton quintet at 4·14 ppm (CH_2-groups), a triplet at 6·0 ppm (H at C_2), a singlet at 6·54 ppm (H at C_3), a singlet at 6·57 ppm (NH), a multiplet at 7·20–7·35 ppm (aromatic hydrogens and H at C_1). (Found: C, 68·40; H, 6·63; N, 7·52. Calc. for $C_{21}H_{24}N_2O_4$: C, 68·47; H, 6·52; N, 7·60%).

1,3-*Diphenyl*-3-(N,N'-*dicarbethoxyhydrazino*)-*propene*-^{13}C (**15b** and **c**) was obtained analogously from 2·26 g **14b** and 2·0 g azo ester in dry benzene (10 ml), yield 1·47 g.

1,3-*Diphenyl*-3-(N,N'-*dicarbethoxyhydrazino*)-2-*azopropene* (**20a**)[20] was prepared as described from equimolar amounts of **19a** and diethyl azodicarboxylate (refluxing in benzene for 5 hr).

1,3-*Diphenyl*-3-(N,N'-*dicarbethoxyhydrazino*)-2-*azopropene*-^{13}C (**20b** and **c**) was prepared as described from **19b** and diethyl azodicarboxylate.

1,3-*Diphenyl*-1-(N,N'-*dicarbethoxyhydrazino*)-*propene* (**16a**). A soln of EtONa (from 0·5 g Na and 20 ml abs EtOH) and 2·0 g of **15a** were kept 3 days at room temp, then the alcohol was distilled off and the residue boiled for 5 hr with 30% aqueous AcOH. The resulting oil crystallized on cooling to give **16a** (1·4 g, 70%), m.p. 124–126° (from 1:4 benzene–light petroleum). ν_{max} 3260, 1755, 1700, 1520, 1245, 1050 cm^{-1}; PMR spectrum: 6-proton quartet at 1·22 ppm (Me groups), 2-proton doublet at 3·80 ppm (benzylic methylene), 4-proton quintet at 4.12 ppm (ethyl CH_2 groups), triplet at 6·0 ppm (H at C_2), singlet at 6·75 ppm (NH) and multiplet at 7·20–7·35 ppm (aromatic H). (Found: C, 68·46; H, 6·67. Calc. for $C_{21}H_{24}N_2O_4$: C, 68·47; H, 6·52%).

1,3-*Diphenyl*-1-(N,N'-*dicarbethoxyhydrazino*)-*propene*-^{13}C (**16b** and **c**) was prepared as described from labelled **15b** and **c**.

Phenyl phenethyl ketone (**18a**). 1 g of **16a** was boiled with 10% HCl (100 ml) and the resulting oil was distilled off with water. Crystalline **18a** (0·42 g) separated from the aqueous distillate in 75% yield; m.p. 70–71 (from aqueous MeOH). Semicarbazone (**17a**), m.p. 148–148·5° (from abs EtOH). (Found: N, 15·56. Calc. for $C_{16}H_{17}N_3O$: N, 15·71%).

Phenyl phenethyl ketone-^{13}C (**18b** and **c**) and the respective semicarbazones **17b** and **c** were prepared analogously from labelled compounds **16b** and **c**.

3-*Phenyl*-4-*benzyl*-1,2,4-*triazol*-5-*one* (**23a**). *A*. A soln of EtONa (from 1·4 g Na and 55 ml abs EtOH) and 7 g of **20a** were kept for 3 days at room temp; then the alcohol was distilled off and the residue boiled with 10% HCl (100 ml), the resulting benzaldehyde distilling off with water. When the initial volume was reduced to 1/3 the distillation was stopped and on cooling of the remaining acid solution **23a** separated, yield 2·4 g (*ca* 50%), m.p. 166° (from benzene). ν_{max} 3190, 1700, 1550, 1510, 940, 785, 745, 720, 700 cm^{-1}. (Found: C, 71·73; H, 5·16; N, 16·72. Calc. for $C_{15}H_{13}N_3O$: C, 71·8; H, 5·18; N, 16·72%).

B. A mixture of **22**[30] (1·96 g) and $FeCl_3$ (3·5 g) in alcohol (15 ml) was heated in a sealed tube at 130° for 3 hr, then it was poured into the cold water (200 ml), left for 12 hr at 0° and filtered to give **23a**, yield 0·65 g (35%).

3-*Phenyl*-4-*benzyltriazolone*-^{13}C (**23b** and **c**) was prepared from **19b** without isolation of the intermediate (**20b** and **c**) which was directly tautomerized in the presence of EtONa and then hydrolyzed with acid under the conditions described above (method A).

3-*Phenyl*-1,2,4-*triazole*-5-*one* (**24**). To a soln of **23a** (2 g) in liquid NH_3 (100 ml) at −60°, Na (0·57 g) was added portionwise with stirring; stirring was continued for another hr and the mixture left to reach the room temp. Then 100 ml water was slowly added and the resulting toluene extracted with ether; the aqueous layer was acidified with HCl and after 1 hr at 0° **24** separated, yield 1·1 g (85%), m.p. 323–324° from EtOH.[21]

REFERENCES

1 A. N. Nesmeyanov and M. I. Kabatchnik, *Zh. Obshch. Khim.* **25**, 41 (1955)
2 F. G. Bordwell and D. A. Schexnayder, *J. Org. Chem.* **33**, 3240 (1968)
3 M. M. Shemyakin, V. I. Maimind and E. Homes, *Zh. Obshch. Khim.* **27**, 1842 (1957)
4 S. Weckerlein and W. Luttke, *Tetrahedron Letters* 1711 (1964)
5 T. Mitsuhashi and O. Simamura, *Chem. & Ind.* 578 (1964)
6 R. P. Ossorio, F. G. Herrera and R. M. Utrilla, *Nature, Lond.* **179**, 40 (1957)

[7] R. P. Ossorio, F. G. Herrera, R. M. Utrilla, A. Hidalgo and J. M. Gamboa, *An. Real. Soc. Esp. Fis. Quim.* **54B**, 481 (1958);
J. M. Gamboa, R. P. Ossorio and P. Rapun, *Ibid.* **57B**, 607 (1961);
J. M. Gamboa, R. P. Ossorio and J. M. Figuera, *Ibid.* **63B**, 241 (1967)
[8] L. A. Neiman, Dissertation, Moscow (1966)
[9] K. B. Wiberg and S. D. Nielsen, *J. Org. Chem.* **29**, 3353 (1964)
[10] R. M. Magid and J. G. Welch, *J. Am Chem. Soc.* **90**, 5211 (1968)
[11] R. Huisgen and F. Jakob, *Liebigs Ann.* **590**, 37 (1954)
[12] R. Huisgen and H. Pohl, *Chem. Ber.* **93**, 527 (1960)
[13] B. T. Gillis and P. E. Beck, *J. Org. Chem.* **27**, 1947 (1962); **28**, 3177 (1963)
[14] B. Franzus and J. H. Surridge, *J. Org. Chem.* **27**, 1951 (1962)
[15] B. Franzus, *Ibid.* **28**, 2954 (1963)
[16] W. A. Thaler and B. Franzus, *Ibid.* **29**, 2226 (1964)
[17] O. Achmatowicz and O. Achmatowicz, *Roczn. Chem.* **37**, 317 (1963)
[18] E. Koerner v. Gustorf, *Tetrahedron Letters* 4691 (1968)
[19] J. M. Gamboa, R. P. Ossorio and P. Rapun, *An. Real. Soc. Esp. Fis. Quim.* **57B**, 607 (1961)
[20] L. A. Neiman, S. I. Kirillova, V. I. Maimind and M. M. Shemyakin, *Zh. Obshch. Khim.* **35**, 1932 (1965)
[21] G. Young and E. Witham, *J. Chem. Soc.* **77**, 224 (1900)
[22] J. Boyer, *Heterocyclic Compounds* (Edited by R. C. Elderfield) vol. 7, N.Y. (1961)
[23] E. Lippmaa and T. Pehk, *Eesti NSV Tead. Akad. Toimetised. füüs.-matem.* **16**, 345 (1967)
[24] O. A. Reutov, T. N. Shatkina, E. T. Lippmaa and T. J. Pehk, *Dokl. Akad. Nauk SSSR* **181**, 1400 (1968)
[25] O. A. Reutov, T. N. Shatkina, E. Lippmaa and T. Pehk, *Tetrahedron* **25**, 5757 (1969)
[26] L. A. Neiman, S. V. Zhukova, M. M. Shemyakin, Yu. S. Nekrasov, V. A. Puchkov and N. S. Wulfson, *Zh. Obshch. Khim.* **40**, 1510 (1970)
[27] A. Murray and D. L. Williams, *Organic Synthesis with Isotopes*, part I, p. 626, Interscience, N.Y.-London (1958)
[28] W. Diekmann and H. Kammerer, *Ber Dtsch. Chem. bis.* **39**, 3046 (1906)
[29] K. T. Serijan and P. H. Wise, *J. Am. Chem. Soc.* **73**, 4766 (1951)
[30] F. J. Wilson, I. V. Hopper and A. B. Crawford, *J. Chem. Soc.* **121**, 866 (1922)