A Carbon-13 and Proton Magnetic Resonance Study of Syn–Anti Isomerism in Maleisoimides and Succinisoimides

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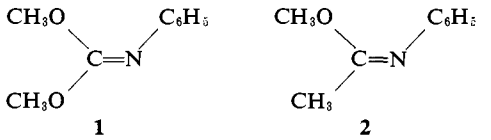
Abstract: Syn and anti isomers of five *N*-arylmaleisoimides and two *N*-aryl-2,2-dimethylsuccinisoimides have been observed using carbon-13 and proton magnetic resonance spectral measurements. Assignments of the syn and anti structures have been made on the basis of chemical shift values. Solvents and substituents have little effect on the position of the equilibria in the maleisoimide systems. The isomerization rates of *N*-phenyl-2,2-dimethylsuccinisoimide and *N*-*p*-anisyl-2,2-dimethylsuccinisoimide in CD_3CN have been estimated and the substituent effect (*p*-H > *p*-OCH_3) is in the direction and of the order of magnitude expected for the inversion mechanism which has been proposed for the isomerization of other >C=NR systems.

Syn–anti isomerism about the carbon–nitrogen double bond has been studied in a variety of chemical systems.[2] A remarkable variation in the equilibrium composition and the rates of interconversion of syn–anti isomers has been observed for compounds with varying substituents attached to nitrogen.[3] Considerable variation in configurational stability with variation in substituents attached to the carbon of the C=N group has also been noted.[2] Of particular interest to the present work is the fact that iminocarbonates such as **1** interconvert rapidly[4,5] at room temperature, while methyl *N*-alkyl- and *N*-arylacetimidates such as **2** have a high barrier to interconversion and are apparently stable up to 120° in the anti form shown.[6] Intermediate between these two extremes is the behavior of phenyl *N*-methylacetimidate (**3**), which exists in a 2:1 mixture



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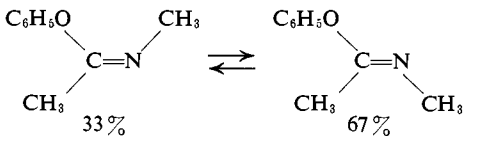

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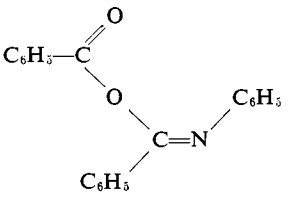
of the isomers and begins to interconvert rapidly on the nmr time scale at 70°.[7]

Although phthalisoimides and maleisoimides have received a considerable amount of recent attention and the ^1H nmr spectra of the latter compounds have been reported,[8] spectral evidence for syn–anti isomerism has not been previously found and the 60-MHz nmr spectra of a variety of maleisoimides appeared to be temperature-invariant.[9] Furthermore, only the anti isomer of the acyclic isoimide **4** was observed, although the syn



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isomer was postulated as an intermediate in the thermal rearrangement of the isoimide to the imide.[10]

In this paper we wish to report carbon-13 magnetic resonance data which demonstrate that syn–anti isomers do exist for *N*-arylmaleisoimides as well as for *N*-arylsuccinisoimides.

Results and Discussion

Carbon-13 magnetic resonance spectra of a series of *N*-arylmaleisoimides indicated the presence of a minor isomer which varied in amount from 8 to 20% depending on the substituents attached to the aromatic ring. The possibility that the peaks attributed to these isomers were instead representative of the corresponding maleamic acids, products of the hydrolysis of isoimides,[11] was ruled out by an examination of the ^{13}C spectra of the amic acids. Similarly, the possibility that the minor isomers were the structurally isomeric *N*-arylmaleimides was eliminated.

Evidence for the fact that the spectra derive from two slowly equilibrating geometric isomers was obtained from variable temperature experiments. When *N*-phenylmaleisoimide in *sym*-perdeuteriotetrachloroethane was heated to 80° the signals of the separate isomers merged to single resonances for each carbon; chemical shift values of these single resonance lines were only slightly shifted from those of the major isomer at 38°. When the solution was recooled to 38°, the original pattern of the spectrum reappeared.

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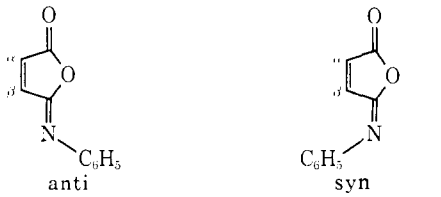
Table I. Carbon-13 Chemical Shift Assignments for *N*-Arylmaleisoimides and *N*-Arylsuccinisoimides[a]

Solvent	^{13}C chemical shifts C=O	α	β	$(CH_3)_2$	C=N	N–C	Ortho	Meta	Para	% major[b] / % minor
					N-Phenylmaleisoimide					
Acetone-d_6	167.8	129.2	143.9		151.7	145.0	125.0	129.6	127.3	87 anti
		131.3	134.1				122.2	129.9	126.2	13 syn
CD_2Cl_2	167.5	128.4	143.4		150.8	144.3	124.9	129.3	127.3	89 anti
	167.2	130.8	133.3			145.3	121.8	129.6	126.1	11 syn
DMSO-d_6	167.5	129.2	143.3		151.2	144.1	123.8	128.9	126.4	87 anti
		131.1	133.9				121.6		125.6	13 syn
$CDCl_2$–$CDCl_2$	167.2	127.9	143.1		150.0	143.5	124.8	128.9	127.2	89 anti
		130.4	132.9				121.4	129.3	126.0	11 syn
$CDCl_2$–$CDCl_2$ (80°)	167.0	127.8	143.1		150.0	143.7	124.9	129.0	127.2	
					N-*p*-Anisylmaleisoimide[c]					
Acetone-d_6	168.3	127.8	144.3		149.9	137.7	128.5	114.9	159.9	92 anti
		130.9	134.0				123.9	115.3		8 syn
					N-*p*-Chlorophenylmaleisoimide					
Acetone-d_6	167.7	129.7	143.9		152.5		126.7	129.7	133.4	85 anti
		132.3	133.8				124.0	130.0		15 syn
					N-*p*-Acetylphenylmaleisoimide[d]					
DMSO-d_6	167.1	130.1	143.0		152.6	148.6	123.0	129.3	134.3	84 anti
		131.7	132.2				121.7			16 syn
					N-*o*-Anisylmaleisoimide					
DMSO-d_6	167.3	129.5	142.8		151.7	130.3		*f*		80[e] anti
	166.9	131.6	133.7		158.2	134.4				20 syn
					N-Phenyl-2,2-dimethylsuccinisoimide[g]					
DMSO-d_6	{178.6}	{40.1}	38.2	{24.4}	160.6	146.1	120.5	{128.7}	{124.2}	58 syn
	{178.7}	{40.4}	41.2	{24.5}	152.5	145.3	122.0	{129.2}	{124.4}	42 anti
$CDCl_3$	{178.0}	40.3	42.3	{24.8}	151.5	144.7	122.5	{129.3}	{124.9}	54 anti
	{178.1}	40.7	38.7	{24.9}	159.8	146.0	120.4	{128.7}	{124.5}	46 syn
					N-*p*-Anisyl-2,2-dimethylsuccinisoimide[g,h]					
DMSO-d_6	{178.3}				150.3	137.6	124.4	{114.1}	{157.0}	55 anti
	{178.2}				159.9	138.9	121.8	{114.5}	{156.7}	45 syn

[a] For each compound in a given solvent, the first horizontal row contains the assignments for the major isomer, the second row contains assignments for the minor isomer. The lack of an entry means that the peak was too weak to be observed or it was masked by a larger one. The former was generally true of the unprotonated carbons of the minor isomers—small N.O.E., long spin-lattice relaxation times.[19a] [b] Calculated from the peak height of ortho-carbons. This method will not ordinarily give accurate results; however, because paired peaks in similar isomers are involved, peak heights can be used in this case. See Discussion. [c] Major isomer, OCH_3: 55.7. [d] Major isomer, acetyl group: CH_3, 25.7; C=O, 196.9. [e] Calculated from peak heights of C-3 and C-5 carbons of each isomer (see footnote *f*). [f] Numbering the N–C carbon as 1 and the CH_3O–C carbon as 2, etc., the shifts are as follows. Major isomers: C-2, 151.2; C-3, 112.1; C-4, 127.0; C-5, 120.3; C-6, 122.6; OCH_3, 55.3. Minor isomer: C-2, 150.0; C-3, 111.3; C-4, 125.4; C-5, 120.7; C-6, masked; OCH_3 masked. [g] Brackets are placed on pairs of chemical shifts to signify that definitive assignments of these shifts to the major and minor isomers could not be made. [h] Contaminated with amic acid and imide; aliphatic chemical shift assignments could not be made.

The chemical shift assignments for the major and minor isomers are summarized in Table I. In each case the major isomer was assigned the anti configuration; spectra for the minor isomer were attributed to the syn configuration as illustrated for *N*-phenylmaleisoimide (**5**).



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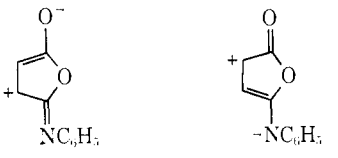
The assignments are based on the following rationale. A carbonyl group adjacent to a double bond is known to shift the resonance of a proton attached to the β position downfield compared to the resonance for the proton attached to the α position. The spectra for the first five model compounds in Table II illustrate this phenomenon, which is believed to stem from the existence of resonance contributions of the type >C=C—C=O ↔ >C⁺—C=C—O⁻, which deshields the β position. An analogous effect has been noted for carbon-13 chemical shifts and is also illustrated by data in Table II. The carbon-13 and proton chemical shifts for the major isomers of the maleisoimides present a similar pattern, although the separation between the resonances for the α and β protons and the α- and β-carbons is smaller for the maleisoimides than for the model compounds. This must be the result of contributions from resonance structures such as **5b** as well as **5a**. The carbonyl group would be expected to be more



5a **5b**

Table II. Proton and Carbon-13 Chemical Shifts for Unsaturated Carbonyl Compounds

Compound	^{1}H chemical shift, ppm			^{13}C chemical shift, ppm		
	α	β	Ref	α	β	Ref
Cyclohexen-3-one	5.93	6.88	12	129.3	150.7	13
Cyclopenten-3-one	6.10	7.71	12b, 14	133.8	165.1	13
Coumarin	6.42	7.72	15			
Δ^2-Butyrolactone	6.15	7.63	15			
α-Pyridone				120.1	134.8	16
N-p-Anisylmaleisoimide (major isomer)	6.75	7.47	8	127.8	144.3	*a*
N-p-Tolylmaleisoimide (major isomer)	6.79	7.50	8			
N-p-Phenylmaleisoimide (major isomer)	6.84	7.54	8	129.2	143.9	*a*
N-p-Chlorophenylmaleisoimide (major isomer)	6.86	7.53	8	129.7	143.9	*a*
N-p-Acetylphenylmaleisoimide (major isomer)	6.92	7.58	8			
N-n-Butylmaleisoimide (major isomer)				129.6	143.3	*b*

[a] This work; acetone-d_6. [b] This work; neat.

polarized than the imino group, since oxygen is more electronegative than nitrogen. Chemical evidence confirms this; the site of nucleophilic attack on neutral isoimides is the carbonyl carbon.[17]

Further confirmation that the carbonyl group is more effective in electron withdrawal than the *N*-phenylimino group and that such withdrawal has an effect on carbon-13 chemical shifts is shown by the chemical shifts for aromatic carbons para to substituents containing carbonyl or *N*-phenylimino groups. These data are summarized in Table III. Substituent constants (σ^+) for various carbonyl and *N*-phenylimino compounds were calculated according to the method of Nelson, *et al.*[18] Values for σ^+ are found to be substantially higher for the carbonyl-containing substituents than for the *N*-phenylimino ones. Therefore, the greater contribution of **5a** to the structure of maleisoimides is implied; however, the σ^+ values support some contribution from **5b** also.

Further indications that **5b** has some importance result from an examination of the effect of substitution of the ring attached to nitrogen on the chemical shifts of the carbon and hydrogen at the position α to the carbonyl group. Both the carbon and hydrogen chemical shifts change somewhat more at the α position than they do at the β position as the substituent on the phenyl ring changes.

Table III. Carbon-13 Chemical Shifts of Para Carbons in Substituted Benzenes and Calculated Values for σ^+ at 38°[a]

Substituent, X	^{13}C chemical shift, ppm for C para to X	σ^+[b]
–CHO	134.5	0.75[c]
–CH=NC$_6$H$_5$[d]	131.4	0.38
–COOC$_6$H$_5$	133.9	0.68
C$_6$H$_5$OC(=NC$_6$H$_5$)[d]	130.9	0.32
C$_6$H$_5$N=COC$_6$H$_4$-Br-*p*[d]	131.1	0.34

[a] All spectra were measured in DMSO-d_6. [b] Calculated according to the method of Nelson, *et al.*[18] [c] Previously reported value from ^{13}C chemical shift data is 0.73 in CCl_4.[18] [d] Only a single isomer was observed at 38°.

In the above discussion, the evidence for the assignments of the olefinic carbon and hydrogen shifts in the major isomer has been put forth. We have assigned the identity of the major isomer as anti after considering the chemical shift behavior of the olefinic carbons in the minor isomer. A large steric compression shift of 9–10 ppm upfield is noted for the β positions. Steric compression shifts have been well-documented in the ^{13}C spectra of other compounds;[19] since steric compression of the β-carbon could only occur in the syn isomer, we have accordingly assigned the syn structure to the minor isomer in the *N*-arylmaleisoimide series. Calculation of the position of equilibria from ^{13}C spectra can be subject to error if the spin–lattice relaxation times, T_1, of the carbon atoms used are long relative to the pulse delay used in obtaining the spectra of if the relaxation time differs markedly from positions in one isomer to corresponding positions in the other isomer.

We used the peak heights (as an approximate measure of the peak areas) of the ortho carbons to calculate the position of the equilibrium. To test the assumption that the T_1 values for these carbons were similar in the major and minor isomers (or small relative to the pulse delay), we measured the effect of variation in the pulse delay on the relative intensities of the ortho-carbon peaks. The results of this experiment are shown in Table IV. It is apparent that the assumptions are at least approximately correct since only a 1% "change" in the equilibrium position is observed over more than

Table IV. Equilibria at 38° for *N*-Phenylmaleisoimide as a Function of Solvent and Pulse Delay

Solvent	Pulse delay, sec	% major[a]	% minor[a]
Acetone-d_6	0.8	87	13
Acetone-d_6	10.8	86	14
Dichloromethane-d_2	7.0	89	11
DMSO-d_6	3.0	87	13
sym-Tetrachloroethane-d_2	3.0	89	11
sym-Tetrachloroethane-d_2	3.8	90	10

[a] Calculated from the peak heights of the ortho carbons.

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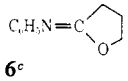
Table V. Nuclear Magnetic Resonance and Ultraviolet Spectral Data for *N*-Phenylimino Compounds

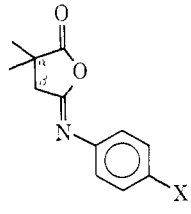
Compound	Uv data			Nmr data			
	Solvent	λ_{max}, nm	ϵ	Solvent	Chemical shift, δ syn	anti	syn/anti
$(CH_3)_2C{=}NC_6H_5$[a]				CCl_4	1.67	2.04	50/50
$C_6H_5N{=}C_6H_{10}$-c[b]	Isooctane	225.1	6500	CCl_4	2.13	2.41	50/50
		281.0	1240				
$C_6H_5N{=}C_5H_8$-c[b]	Isooctane	229.4	6000	CCl_4	2.15	2.53	50/50
		272.4	2000				
	Isooctane	238.4	3400	CCl_4	2.36	2.68	30/70
6[c]	CH_3CN	253	4180	DMSO-d_6	2.81	3.02	58/42
6				CD_3CN	2.73	2.98	56/44
6				$CDCl_3$	2.70	2.96	47/53
6				CCl_4	2.58	2.83	33/67
7[c]	CH_3CN	261	7520	$CDCl_3$	2.73	2.93	27/73
7				CD_3CN	2.76	2.91	49/51
5[d]	Dioxane	231	11,600				
		342	11,000				

[a] References 3 and 20. [b] Reference 21. [c] Reference 23. [d] Reference 8b.

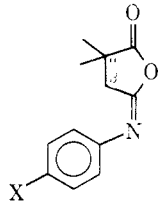
an order of magnitude change in the pulse delay. It is further apparent that the position of the equilibrium is not subject to strong solvent effects.

Syn–anti isomerism in the maleisoimide system would be expected to induce chemical shift changes in the proton resonances of the olefinic group, particularly at the position closest to the *N*-phenylimino group. These changes have not previously been observed, perhaps because the shift in the syn compound at the β position is upfield into the aromatic peaks and also because the percentage of syn isomer is small. A 100-MHz spectrum of *N*-phenylmaleisoimide in CD_2Cl_2 revealed a small doublet slightly downfield from the doublet for the hydrogen on the α position (major: δ 6.64 (J = 4.63 Hz); minor: δ 6.68 (J = 4.73 Hz)). The ratio of the peak areas was about 9:1, which tends to substantiate the hypothesis that this small doublet can be attributed to the minor isomer (compare to ^{13}C nmr observed ratios, Table IV).

Both the proton and carbon-13 spectra indicated the presence of syn and anti isomers in the two saturated isoimides **6** and **7**. The assignment of the ^1H nmr



6a, X = H
7a, X = OCH_3



6b, X = H
7b, X = OCH_3

chemical shifts for each compound was made on the basis of the following reasoning. The upfield peak of *N*-phenylacetone imine has been assigned to the methyl group syn to the phenyl ring.[3,20b] Similar assignments have been made for *N*-phenyliminocyclohexane, *N*-phenyliminocyclopentane, and 2-*N*-phenyliminotetrahydrofuran.[21] These assignments are summarized in Table V, along with ultraviolet spectroscopy data for these compounds. On the basis of the infrared stretching frequencies for the carbon–nitrogen double bond, it has been concluded that the phenyl ring is not conjugated with this double bond, but instead interacts with the lone pair of electrons on the nitrogen. The angle of twist between the plane of the C=N group and the phenyl ring has been calculated[20a] to be slightly less than 90° in a similar system; the shielding of the syn protons is attributed to the ring current of the face of the phenyl group.[21,22] Since the ultraviolet spectra of the saturated isoimides **6** and **7** are similar to that for 2-*N*-phenyliminotetrahydrofuran, a similar geometry with the phenyl ring tilted out of the plane of the five-membered ring is indicated. Accordingly, the upfield resonance signal for the methylene group has been assigned to the isomer where the tilted phenyl group is syn to the methylene group (see Table V).

With these assignments made, it is interesting to note that a steric compression shift at the methylene group (β position) is observed in the ^{13}C spectra of the saturated isoimides **6** and **7**, although the magnitude of the shift (3.0–3.6 ppm) is smaller than that observed for the β positions of *N*-arylmaleisoimides. The only other marked chemical shift difference between the syn and anti isomers is that for the carbon of the carbon–nitrogen bond. In all cases where the resonance is visible (T_1 would be expected to be long for this position) the shift for the syn isomer is 6–8 ppm downfield from the shift for the anti isomer. The origin of this effect is not known.

As a further test of the assumption that the ^{13}C nmr peak heights could be used to calculate the positions of equilibria in the succinisoimide series, the ratio of major to minor isomer was calculated for four different positions and was found to vary only by 1%. Thus for *N*-phenyl-2,2-dimethylsuccinisoimide in dimethyl-d_6 sulfoxide, calculation yields: at the ortho position, 58:42; at the β position, 59:41; at the N–C carbon, 59:41; and at the C–N carbon, 58:42. Again, similar T_1's at similar carbons or short T_1's relative to the pulse delay used (2.0 sec) are implied. Note also that this ^{13}C nmr ratio agrees very well with the observed ^1H nmr ratio in the same solvent (58:42).

Substituents on the phenyl ring attached to nitrogen

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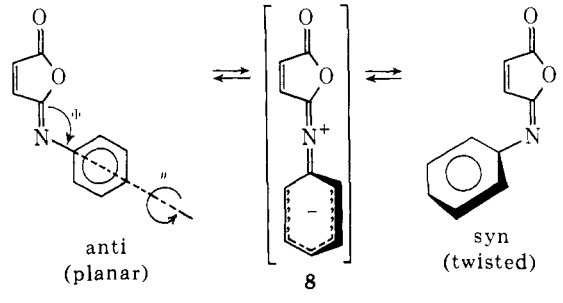
have very little effect on the position of the equilibrium. The anti isomers would be expected to be favored because of steric effects, but the fact that the syn isomer is present to the extent of 10 to 20% in the maleisoimides suggests that there is not a great deal of difference between the steric hindrance of the β-CH group and the lactone oxygen with its two sets of lone-pair electrons. The geometry of the phenyl ring is most probably different in the maleisoimides from the geometry in the succinisoimides. The uv band at 342 nm observed for *N*-phenylmaleisoimide (Table V) suggests the presence of extensive conjugation which could only exist if the molecule is planar or nearly so. Thus in the anti isomer the phenyl ring could be staggered with the oxygen lone-pair electrons. Models indicate that a planar syn compound is unlikely; the benzene ring is probably tilted out of plane in this isomer. Whatever the geometry, it is apparent that substituents have very little effect on the position of equilibrium. It has been argued that *N*-alkyl- and *N*-arylacetimidates are stable in the form illustrated in compound **2**, where the group on nitrogen and the alkyl group on carbon are trans to each other, so that the lone pair of electrons on nitrogen can be as far apart as possible from those of oxygen.[6] If the same reasoning were to be applied to the maleisoimides studied in this work, one might predict that substituents on the benzene ring would have a larger effect on the equilibrium constant for the reaction than is observed. The geometry and electron density of the ring oxygen of the isoimides would of course be changed by resonance interaction with the adjacent carbonyl group; however, 2-*N*-phenyliminotetrahydrofuran has no carbonyl group, and its equilibrium constant in carbon tetrachloride is almost identical to *N*-phenyl-2,2-dimethylsuccinisoimide in the same solvent. The importance[6] of nonbonded interactions of electron pairs on heteroatoms located 1,3 to each other is not clearly established.[24]

The available evidence is in agreement with a variation on the lateral shift mechanism[1] depicted in Scheme I assuming a transition state (or intermediate) resem-

Scheme I



8

bling **8**. In order for the anti isomer to begin to isomerize, there must be an increase in angle Φ and, in order to reach **8**, a simultaneous twisting of the *N*-phenyl ring (angle θ); **8** is then achieved when $\Phi \simeq 180°$ and $\theta \simeq 90°$. Now, continuing to increase only angle Φ leads to the syn isomer. (Exactly the reverse of this sequence is, of course, envisioned for the syn → anti isomerization.)

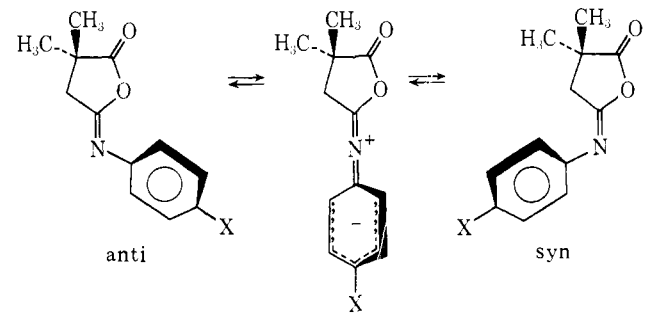
In acetonitrile the equilibrium mixture of the syn and anti isomers of **6** and **7** is close to 1:1 ratio. If the assumption is made that the rate at the coalescence temperature can be estimated from $\tau\Delta\nu/\sqrt{2}$,[25] then the isomerization rates given in Table VI may be calculated.

Table VI. Rates of Isomerization of *N*-Phenyl- and *N*-*p*-Anisyl-2,2-dimethylsuccinisoimides in CD_3CN

Substituent	Δν, Hz	T_c	k_{Tc}, sec^{-1}	$\Delta G^{\ddagger}$, kcal/mol	$k_{60°}$, sec^{-1}
H	14.4	56°	32	17	45
OCH_3	9.1	63°	20	18	16

The estimated rates of syn–anti interconversion for **6** and **7** are in the direction expected from observations made in other systems[3,5,26] and provide support for the inversion mechanism rather than the dipolar ion rotation mechanism.[1] That is, we envision the syn–anti isomerization for the succinisoimides **6** and **7** as proceeding *via* the transition state (or intermediate) **9** (Scheme II). The energy difference between the isomers appears

Scheme II



9

to be quite small and depends to some degree on the solvent shells around them. Electronic effects would be expected to be comparable and similar steric interactions should be felt by the phenyl group in each since the ether–oxygen with its directed set of unshared electron pairs should be similar in size to the CH_2 group.

Experimental Section

Nmr Analyses. All ^{13}C nmr spectra were recorded at 25.2 MHz utilizing complete ^1H decoupling at 100 MHz with a Varian Associates XL-100-15 spectrometer equipped for both CW (continuous wave-frequency sweep) and FT (pulsed Fourier transform) operations. Proton spectra were determined with either a Varian A-60-A or A-60-D spectrometer equipped for variable temperature work. Tetramethylsilane was used as an internal standard. Probe temperature for most experiments was *ca.* 38°. The probe temperatures for the variable temperature experiments were determined using ethylene glycol or methanol samples.

The ^{13}C shift assignments for the various carbons of the maleisoimides and succinisoimides (Table I) were made by comparison of the shifts in these spectra with each other, by comparison with shifts of known structures, and by comparison of observed values with those calculated using known aromatic substituent constants.[18,27]

Isoimides. The syntheses of the *N*-arylmaleisoimides and *N*-arylsuccinisoimides have been previously described.[8a,23]

Acknowledgments. We wish to acknowledge helpful

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Carbon-13 Nuclear Magnetic Resonance of Organophosphorus Compounds. VIII. Triphenylphosphoranes and Triphenylphosphonium Salts

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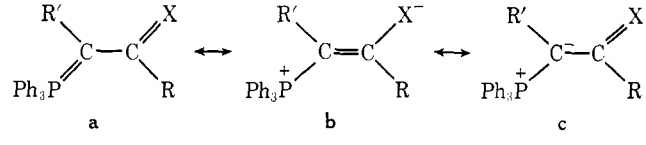
Abstract: ^{13}C chemical shifts and $^{13}C-^{31}P$ nuclear spin coupling constants have been obtained for six triphenylphosphoranes (phosphorus ylides), twelve triphenylphosphonium salts, triphenylphosphine oxide, and tetraphenylphosphonium bromide. In the salts the substituted phenyl carbon shifts vary slightly while the methylene resonance parallels analogously substituted carbon shifts in the series CH_3X, CH_3CH_2X, c-$C_6H_{11}X$, and $(C_2H_5O)_2P(O)CH_2X$. The methylene carbon $^1J_{CP}$ varies through a range of over 30%. No correlation is found with the related $^1J_{CP}$'s in the above series. The ylides show strikingly high shieldings and one-bond $^{13}C-^{31}P$ couplings for the ylide carbons. These shieldings are typical for *aliphatic* carbon and point toward high localization of negative charge on basically sp^2 carbons. Their $^1J_{CP}$ values are much larger than the one-bond couplings to the sp^2 carbons in the phenyl rings. The data indicate a delocalized cyclopentadienide phosphorane while the fluorenide phosphorane has much more localization on the ylide carbon.

Organophosphorus compounds continue to provide demanding tests of our understanding of their syntheses, equilibria, and molecular electronic structure. We have been using ^{13}C nmr as a means of probing the structures, conformation, and bonding of different kinds of these interesting compounds.[1-7] As opposed to the (now) typical use of ^{13}C spectra for chemical shifts, organophosphorus compounds also exhibit both long and short range $^{13}C-^{31}P$ nuclear spin couplings, which are especially useful in investigating stereochemistry and bonding. In part V[5] considerable attention was given to the sensitivity of the ^{13}C shifts and $^{13}C-^{31}P$ couplings in four-membered phosphorus heterocycles to the formal phosphorus oxidation state, particularly to the differences between P(IV) and P(V). In its higher oxidation "states," phosphorus has often been described as being able to form multiple bonds with adjacent atoms possessing lone-pair electrons *via* a $d\pi-p\pi$ interaction. Thus, oxides are often written as $R_3P{=}O$ (even though both lone pairs on the oxygen are usually felt to be participating in what should be viewed as a pseudotriple bond). Another class of compounds in which it is common to invoke $d\pi-p\pi$ bonding is that of phosphorus ylides, $R_3P{=}CR'R''$. These compounds are "stabilized" by using conjugating groups for R, R', and R''. A popular version of stabilized ylides is that of $Ph_3PC(R)CO_2R'$, for which ^1H nmr data are available.[8-10] It has been common to interpret their stereochemistry and bonding in terms of the general valence-bond structures **a**–**c**. The electronic differences within **a**–**c** should give rise to fundamental differences in the ^{13}C shieldings and $^{13}C-^{31}P$ couplings for atoms in the ylide bond and/or those bound to them. Structure **b** is essentially that of a phosphonium salt and **c** a carbanion which could be, in principle, either trigonal or tetrahedral with formal sp^2 or sp^3 hybridization schemes for the ylide carbon. The $d\pi-p\pi$ "back bonding" depicted by **a** presents an electronic distribution for which few ^{13}C data are available.[11]



We have now determined the ^{13}C chemical shifts and $^{13}C-^{31}P$ nuclear spin couplings in a series of phosphorus ylides of the type $Ph_3PC(R)CO_2R'$ as well as the cyclopentadienyl- and fluorenyltriphenylphosphoranes. As examples of analogous P(IV) compounds and to explore

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