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THE PREPARATION AND REACTIONS OF STABLE PHOSPHORUS YLIDES DERIVED FROM MALEIC ANHYDRIDES, MALEIMIDES OR ISOMALEIMIDES

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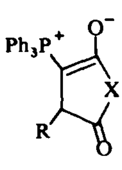
Abstract—A number of stable triphenylphosphoranylidenesuccinimide derivatives have been prepared from maleimides or isomaleimides and triphenylphosphine. Also a stable ylide has been obtained from citraconic anhydride and triphenylphosphine. The succinimide ylides were found to react with a wide variety of aldehydes giving the corresponding ylidene derivatives in high yields. Although these triphenylphosphoranylidenes did not react with ketones, a tri-n-butylphosphoranylidene derivative did react with cyclohexanone to give a cyclohexylidenesuccinimide.

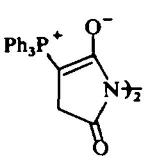
In contrast, the recently discussed triphenylphosphoranylidenesuccinic anhydride reacts with cinnamaldehyde or phenylpropopargyl aldehyde to give the corresponding diylidene succinic anhydrides (fulgides). Intractable mixtures were obtained with the other aldehydes investigated. Furthermore, the stable ylide derived from triphenylphosphine and N-phenylmaleimide gives a ketenimine with phenyl or methyl isocyanate or phenyl isothiocyanate. The resulting ketenimines react with amines or benzenethiol to give diaminoethylene derivatives (ketenaminals) or a phenylthioaminoethylene derivative, respectively. Also, this phosphorus ylide reacts with nitrosobenzene to give 3-anilino-N-phenylmaleimide. The synthetic utility of these stable phosphorus ylides is discussed as well as other features of their reactions.

INTRODUCTION

IN THE course of an investigation[1] concerned with the chemistry of isomaleimides and maleimides we found that triphenylphosphine reacts with both of these isomers to give ylide adducts (**1** and **2**) having structures analogous to the recently discussed maleic anhydride adduct **1a**.[2] Subsequently, we discovered that, except for **1a**, these readily obtained, stable adducts undergo the Wittig reaction with CO compounds to give derivatives which correspond to those which, in part, one would otherwise obtain from the Stobbe condensation.[3] Because of the ease of preparation of these ylides and the high yields of Wittig reaction products obtained in our initial experiments with aldehydes, we embarked on an investigation to define their synthetic utility.



1a: R = H, X = O
b: R = H, X = NH
c: R = H, X = NPh
d: R = H, X = N—NC$_4$H$_8$O
e: R = Me, X = O
f: R = Me, X = NPh



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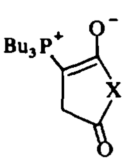


3a: X = NPh
b: X = NH

RESULTS AND DISCUSSION

Preparation of ylides **1**, **2**, and **3**. The ylides **1** and **2** were prepared by combining an excess of triphenylphosphine and the maleic anhydride or maleimide in glacial acetic acid. In some cases the reaction mixture was warmed on the steam bath for periods of about ½ hr. The ylide was precipitated by addition of excess ether and recrystallized in most cases from acetone. The yields were generally 50% or better. Some spectral properties of these ylides are summarized in Table 1.

TABLE 1. SPECTRAL PROPERTIES OF YLIDES **1** AND **2**

Anhydride or Imide	Ylide	δ(ppm)[a]				Area Ratio[b]	λ(μ)[c]	
Maleic[d]	**1a**			3·25sb	7·6m	2:15	5·60	5·93[e]
Malemide	**1b**			—	—	—	5·81	6·09
N-Phenylmalemide	**1c**			3·20d	7·6m	2:20	5·85	6·09
N,N'-Morpholine maleimide	**1d**	2·88d	3·40m	3·75m	7·5m	2:8:15	5·82	6·12
Citraconic	**1e**		0·82d	3·4q	7·5m	1:3:15	5·59	5·90
N-Phenylcitraconimide	**1f**		0·90d	3·3m	7·6m	3:1:20	5·83	6·08
N,N'-Bimaleimide	**2**		—	—	—	—	5·75	6·00

[a] NMR obtained in deuterochloroform with tetramethylsilane as internal standard; s, singlet; sb, broad singlet; etc.

[b] Nearest integral area ratios are listed in order of high field resonance to low field resonance as in column 3.

[c] Infrared spectra were obtained in Nujol mulls.

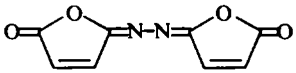
[d] lit.[2b] δ 3·25s, 7·6m in deuterochloroform.

[e] lit.[2c,d] λ C=O 5·63, 5·94 μ in Nujol mull.

The structure proof for the previously prepared triphenylphosphoranylidenesuccinic anhydride (**1a**) was based on the IR[2d] and NMR spectra,[2a,b] synthesis from chlorosuccinic anhydride,[2a,b] and methanolysis to a half acid which when treated with diazomethane gave authentic dimethyl triphenylphosphoranylidenesuccinate.[2c] The correspondence of the IR CO bands between the adducts derived from maleimides and **1a** along with NMR data (Table 1) indicate an analogous ylide structure for the former. Also, in our case chemical proof of structure for the triphenylphosphine adducts can be obtained from their characteristic Wittig reaction products (see below).

Previous workers[2] either used benzene or acetone as a reaction solvent for preparation of triphenylphosphoranylidenesuccinic anhydride (**1a**). In our work we generally found that use of acetic acid as a reaction solvent led to more easily isolated, cleaner products. For example, Osuch *et al.*[2c] were unable to prepare the citraconic anhydride-triphenylphosphine adduct (**1e**) in ether, while in acetic acid we found that **1e** was readily obtained as a stable crystalline solid. In contrast, the tri-n-butylphosphine adducts **3**, which were similarly prepared in acetic acid, were found to be oils which were best characterized by the reaction with aldehydes (see below).

Interestingly, when the isomaleimides **4**[1a] and **5**[4] were combined with triphenylphosphine in acetic acid, the adducts **2** and **1c** were also isolated in high yields. It is not known whether prior rearrangement of the isoimide occurs, induced by triphenylphosphine, or if an initially formed triphenylphosphine-isoimide adduct rearranges to the imide isomer under the reaction conditions. Many examples of catalyzed and non-catalyzed 1,3 acyl O to N rearrangements of isoimides to imides have been observed in both cyclic and acyclic systems.[1b,5] Actually, the triphenylphosphine adduct **1d** was obtained from the readily prepared isoimide **6** rather than the imide and the use of the biisoimide **4** for preparation of **2** is similarly more convenient than the use of N,N'-bimaleimide since the former is more readily obtained than the latter.[1a]



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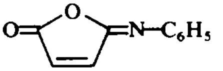

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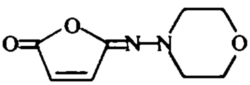

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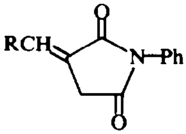
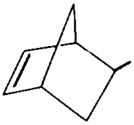
Reaction of ylides **1**, **2**, *and* **3** *with aldehydes and ketones.* It was previously reported that the vigorous reaction of benzaldehyde, p-nitrobenzaldehyde, or butyraldehyde[2b] with triphenylphosphoranylidenesuccinic anhydride (**1a**) gives an intractable product from which only traces of the Wittig product could be isolated. A better yield of dichlorovinylmaleic anhydride (25%) was obtained from the reaction of chloral and **1a** and this was interpreted as involving initial formation of the expected Wittig product.[2b] We have confirmed the result with benzaldehyde and **1a**. In contrast, the reaction of a wide variety of aldehydes with our triphenylphosphoranylidenesuccinimide derivatives proceeds smoothly giving high yields of the crystalline

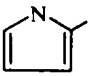


7a: R = Ph
b: R = CH:CHPh
c: R = p-C_5H_4N

d: R =

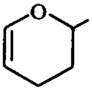


e: R =

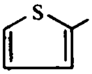


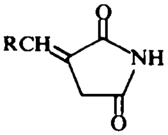
f: R =

g: R =

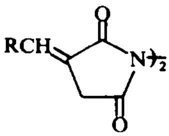


h: R =

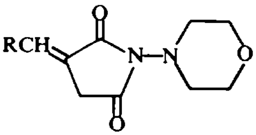




8a: R = Ph
b: R = p-C_5H_4N
c: R = Et



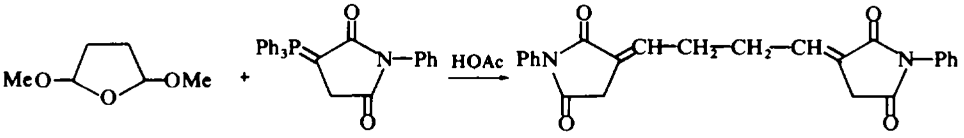
9a: R = Ph
b: R = CH:CHPh



10: R = p-C_5H_4N

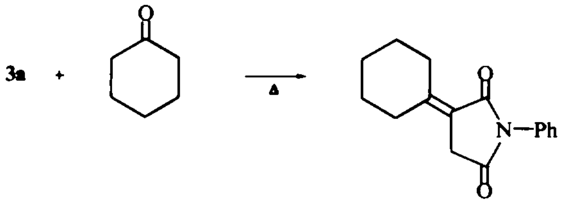
Wittig products. For example, **1c** when combined with a variety of aldehydes gives the anticipated Wittig products **7** in 70% yields or better. Similar results were obtained with **1b**, **1d**, and **2** giving the Wittig products **8**, **10**, and **9** respectively although a much more limited range of aldehydes were investigated. Generally, these reactions were carried out simply by mixing the aldehyde and ylide, warming the mixtures for a few minutes, and then letting them stand at room temperature for periods of 1–5 hr. In some cases, such as **7c**, **7g**, **7h** and **8b** it was advantageous to use methanol or dimethylsulfoxide as a solvent. Purification was readily achieved by washing the crude reaction products with methanol or ether to remove triphenylphosphine oxide and recrystallization from a suitable solvent.

An interesting example of reaction of a disguised dialdehyde is that between 2,5-dimethoxytetrahydrofuran and the triphenylphosphoranylidene derivative **1c** in acetic acid which gives the biimide derivative **11** in 50% yield.



1c **11**

Preliminary attempts to obtain Wittig reaction products from benzaldehyde and the methyl substituted ylides **1e** and **1f** were unsuccessful. These ylides appear to be somewhat more stable than the unsubstituted examples. Furthermore, we found that all of the triphenylphosphine ylides synthesized here did not react with ketones such as cyclohexanone, benzophenone, or acetone, which is consistent with the lack of reactivity of other resonance stabilized ylides with ketones.[6] In fact, acetone was often used as the recrystallizing solvent. Attempts to catalyze the reaction with ketones with benzoic acid[7] or other organic acids were unsuccessful. However, the tri-n-butylphosphine derivative **3a** did react with cyclohexanone giving the cyclohexylidene derivative **12** in 20% yield. Also, the ylide **3b** was most conveniently used to prepare the propylidine derivative **8c**.



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The structure proof for all these Wittig reaction products is based on the elemental composition, the mode of synthesis, and the NMR and IR spectral data. Actually, our structural problem involves the distinction between the alkylidene or arylidene succinimide structure (**13** or **14**) and the alkyl or aryl maleimide structure (**15**) as well as the problem of geometrical isomerism exemplified by structures **13** or **14**. With respect to the former the NMR spectra (Table 2) of the alkylidene derivatives **7d**,

TABLE 2. SPECTRAL PROPERTIES OF WITTIG REACTION PRODUCTS

Product	δ(ppm)[a]					Area Ratio[b]	λ(μ)[c]				
7a			3·95d	7·52m	9·1t(T)	2:10:1		5·64	5·88	6·10	
7b				3·78d	7·5m(T)	2:13		5·68	5·88	6·10	
7c	4·18d	7·5m	8·02s	8·30d	8·98d(T)	2:5:1:2:2		5·59	5·86	6·05	
7d			0·8–3·1m	3·41d	6·0–7·6m(C)	7:2:8		5·65	5·89	6·00	
7e			—	—	—	—	3·00	5·68	5·89	5·95	6·10
7f		3·88d	7·5m	7·80d	8·12s(C + T)	2:7:1:1		5·68	5·90br	6·06	
7g	1·8–2·2m	3·59m	4·6–4·9m	6·3–6·6dt	6·9m–7·45m(C)	4:2:2:1:1:5		5·65	5·85	5·95	6·09
7h				3·50d	7·2–7·5m(C)	—[d]		5·69	5·90	6·06	
8a			3·92d	7·52s	7·83t(T)	2:5:1	3·2–3·8br	5·70	5·8br	6·05br	
8b		4·08s	7·95s	8·30d	8·95d(T)	2:1:2:2		4·0br	5·70	5·89	6·05
8c		1·15t	2·0–3·1m	3·32sb	6·8tt(C)	3:2:2:1		3·3br	6·0br		
9a			4·15d	7·68s	8·10t(T)	2:5:1		5·62	5·75	6·02	
9b				3·92sb	7·0–8·0m(T)	4:1			5·68	5·80br	
10	3·33sb	3·75sb	7·65s	8·0d	8·90d(C + T)	4:6:1:2:2			5·61	5·85	6·02
11			2·70m	3·80sb	7·2–7·7m(T)	2:2:6		5·68	5·89	5·99	6·30
12	1·62sb	2·20m	3·08m	3·33s	7·4m(C)	6:2:2:2:5			5·68	5·90b	6·05

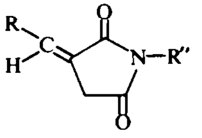
[a] NMR obtained in solvents indicated with tetramethylsilane as internal standard; C, deuterochloroform; T, trifluoroacetic acid; s, singlet; sb, broad singlet; etc.

[b] (footnote *b*—Table 1).

[c] (footnote *c*—Table 1).

[d] Too insoluble to obtain precise integral; approximate area ratios were consistent with structure.

7g, **8c**, **11**, and **12** clearly rule out the maleimide structure **15** for these derivatives. In particular the resonance at 3·3–4·2 ppm for the succinimide ring methylene protons generally appear as an approximate doublet ($J \approx 1$–2 c/s), a broad singlet, or for the case of **12** as a sharp singlet. Also, the vinyl proton resonance for **8c** appears as a complex multiplet (approximately a triplet of triplets) which further rules out the maleimide isomer for this product. Since the tendency of the double bond to rearrange into the imide ring under the reaction conditions should decrease for the arylidene derivatives compared to the alkylidene derivatives and also since the succinimide methylene proton resonances in the former closely parallel those of the latter, all of these Wittig reaction products must have the general structure **13** or **14**.[*]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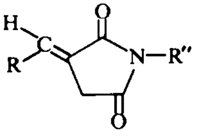
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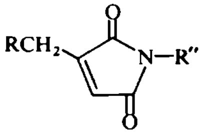
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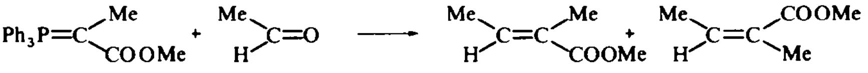
With respect to the problem of geometrical isomerism, we have only limited experimental information at present. In all cases, crystalline, rather sharp melting products were obtained which suggests the predominance of one isomer. Also, the NMR spectra generally lacked any feature clearly suggesting the presence of geometrical isomers. Thus, it is probable that our reaction product consists predominantly of one isomer. It is generally accepted that resonance stabilized phosphoranes (e.g. carbomethoxymethylenetriphenylphosphorane) give predominantly one olefinic isomer in the Wittig reaction with aldehydes, which is the one with the alkyl or aryl group derived from the aldehyde being *trans* to the carbomethoxy group.[9] The most pertinent example involves the reaction of methyl carbomethoxymethylenetriphenylphosphorane with acetaldehyde which gives a 96:4 ratio of **16** and **17** in 90% overall yield.[10] This result was interpreted in terms of the relative stability of the two most probable betaine conformations. Analogously, the major product in our reactions is probably the isomer with the alkyl or aryl group derived from the aldehyde being *trans* to the imide carbonyl (**14**).



$$Ph_3P{=}C(Me)(COOMe) + MeCH{=}O \longrightarrow (Me)(H)C{=}C(Me)(COOMe) + (Me)(H)C{=}C(COOMe)(Me)$$

16 (96%) **17**(4%)

Although the reaction of **1a** with most aldehydes generally gives intractable mixtures, we have discovered that **1a** does react cleanly with cinnamaldehyde to give a good yield of a red, relatively insoluble crystalline product which on the basis of the elemental analysis and IR spectrum has the fulgide structure **18**. This was confirmed by synthesis of **18** by the Stobbe condensation of cinnamaldehyde with sodium succinate,[11] although in very low yields (0·5%). Consequently, the Wittig route is clearly a superior method for the synthesis of **18**. We also found that phenylpropargyl aldehyde reacts with **1a** to give the corresponding fulgide **19** in 55% yield.

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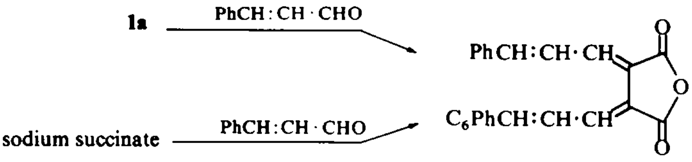
[*] In a recent note the reaction of ethylmaleic anhydride with ammonia was shown to give both the ethyl maleimide and ethylidene isomers.[8]



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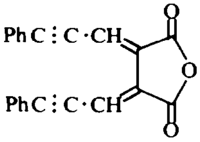

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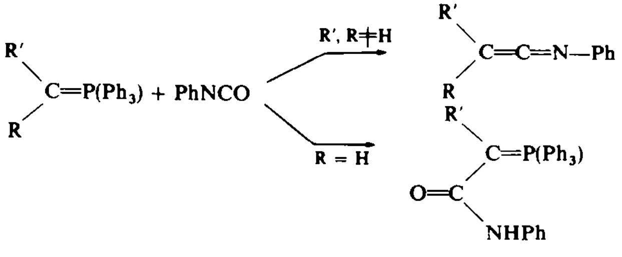
The above results suggest that one problem with the Wittig reaction of **1a** may involve polymerization or telomerization of the initially formed ylidene derivative via secondary active methylene condensation reactions. Since the fulgides **18** or **19** are quite insoluble in the reaction mixture they are diverted from further reactions by precipitation. On the other hand, our success with ylides derived from maleimides may result from the reduced acidity of the succinimide ring methylene proton compared to corresponding protons of the succinic anhydride derivatives.

Reaction of ylide **1c** *with isocyanates, isothiocyanates, and nitrosobenzene.* The reaction of benhydrylidenetriphenylphosphorane with phenyl isocyanate, which gives triphenylketenimine,[12] was one of the first Wittig reactions. This reaction has been more recently explored by Trippett and Walker.[13] They found that depending on the extent of substitution on the triphenylphosphinemethylene either acylation or ketenimine formation occurred as shown below.



Consistently, we found that when the ylide **1c** was combined with either phenyl or methyl isocyanate or phenyl isothiocyanate, the corresponding ketenimines **20** were obtained as crystalline solids in high yields. These derivatives had characteristic IR absorption at $4\cdot90\,\mu$ and consistent NMR spectra. However, they are best characterized by their reaction products with amines. In contrast to triaryl ketenimines such as diphenylketene N-*p*-tolylimine where amidine derivates are obtained,[14] the ketenimines **20** gave excellent yields of the diaminoethylene derivatives (keteneaminals) **21**. In most cases the crude ketenimine was used directly in these reactions. The proof of structure for **21** primarily involves the NMR spectral data along with the IR spectra and the elemental composition. The NMR data (Table 3) in particular

TABLE 3. SPECTRAL PROPERTIES OF **21**, **23**, AND **24**

Structure	δ(ppm)[a]						Area ratio	λ(μ)[c]						
21a			1·58sb	3·12sb	3·50s	6·8–7·5m	6:4:2:7				5·80	6·05	6·21	6·35
21b			1·14t	3·20q	3·42s	6·9–7·5m	6:4:2:10			5·81	6·10	6·20	6·25sh	6·40
21c				2·15s	3·51s	7·0–7·6m	4:2:10			5·79	6·10	6·21	6·31sh	6·40
21d	2·25sb	2·82d	3·39s	3·75sb	5·80sb	7·4m	2:3:4:2:2:5				5·84	6·15	6·30	6·45sh
23				3·55s	7·50m	7·80s	2:10:5					5·75	6·01	6·35br
24					5·82s	7·4m[d]	1:10	3·10	3·20	3·29	5·69	5·91	6·20	6·30sh

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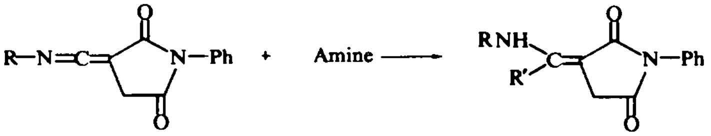
[a] NMR obtained in deuterochloroform with tetramethylsilane as internal standard unless noted; s, singlet; sb, broad singlet; etc.

[b] Ref. *b* from Table 1.

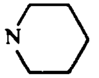
[c] Ref. *c* from Table 1.

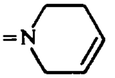
[d] NMR solvent was dimethylsulfoxide—d_6.

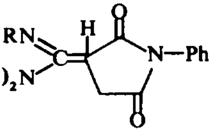
unequivocally rule out the amidine structure **22** since a singlet was generally observed at 3·4–3·5 ppm corresponding to 2 succinimide methylene protons. A similar product (**23**) was obtained from **20a** and thiophenol in 57% yield.



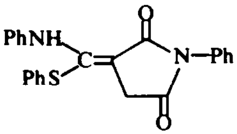
20a: R = Ph
b: R = Me

21a: R = Ph, R' =

b: R = Ph, R' = NEt_2
c: R = Ph, R' =

d: R = Me, R' =




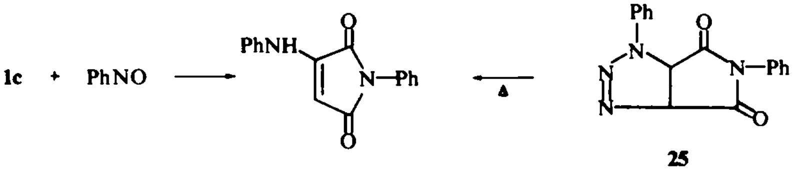
22



23

These results are consistent with the inference that **21** has more stability than **22** because of the increased opportunity for conjugation in **21** compared to **22**. On this basis, even if **22** were the initial reaction product, rearrangement to **21** would occur in the basic reaction medium. Similar considerations would apply to **23**.

We also found that **1c** reacts with nitrosobenzene, as does fluorenylidenetriphenylphosphorane,[15] to give the maleimide **24**. The proof of structure is based on the NMR which reveals no resonance from succinimide methylene protons and one singlet resonance corresponding to a maleimide olefinic proton. The same product was recently reported[16] by Awad *et al.* to result from the thermal decomposition of the triazoline. **25**. Our IR spectra corresponds exactly with that given by these workers[16] for **24**.



25

24

This result suggests that the imine tautomer of **24**, which presumably is the initial reaction product, is less stable than **24**. In contrast, the isoelectronic benzylmaleimide would appear to be less stable than N-phenyl benzylidenesuccinimide (**7a**) to the extent that the observed Wittig reaction result reflects thermodynamic stability. The question of the stability of **24** compared to its tautomer clearly involves a number of factors such as the relative C=N and C=C bond strengths, the relative strengths of NH and CH bonds in the two tautomers and of course the relative conjugation energies associated with the respective π systems of the two tautomers.

Conclusion. The most significant features of these reactions are their simplicity and high yields. The preparation of the ylides as well as the Wittig reactions in all cases was most conveniently carried out in open Erlenmeyer flasks or even test-tubes and the products were all readily purified crystalline materials. The inertness of these ylides to ketones suggest the possibility of using them as a specific reagents for characterization of aldehydes. Alternatively, if reactions with ketones are desired, it is conceivable that this may be promoted by using ylides derived from trialkylphosphines.

The alternate synthetic method for many of the compounds reported here would involve the Stobbe condensation as a key step. However, the Stobbe condensation with aldehydes generally gives relatively low yields of ylidene derivatives and a number of by-products because of the highly basic reaction medium.[3] The use of potassium t-butoxide eliminates these complications to a large extent.[3, 17] However, the synthetic procedures involved in carrying out reactions with potassium butoxide are clearly less convenient than the Wittig reactions described here. Consequently, it is conceivable that the latter synthetic methods may find applications which formerly would involve the Stobbe condensation.[3]

Although an exhaustive survey was not carried out, it is shown that the ylides derived from maleimides will undergo reactions characteristic of resonance stabilized ylides other than reactions with aldehydes. These ylides should also react with imines, ketenes,[18] azides,[19] and epoxides.[20]

EXPERIMENTAL

Triphenylphosphoranylidenesuccinic anhydride (**Ia**). Maleic anhydride (2·0 g, 0·02 mole) and 6·0 g triphenylphosphine were stirred in 30 ml glacial AcOH for 3 hr. Ether was added and the crystalline ppt was recrystallized from acetone giving 3·3 g (46%), m.p. 157–159° dec (lit.[2] m.p. 162·5–163·5° dec).

Triphenylphosphoranylidenesuccinimide (**Ib**). Maleimide (1·0 g) and 2·6 g triphenylphosphine were stirred in 20 ml glacial AcOH for 30 min on the steam bath. Work-up as above gave 3·6 g (~100%), m.p. 220°. (Found: C, 73·32; H, 5·27; N, 4·14. Calc. for $C_{22}H_{18}NO_2P$: C, 73·52; H, 5·04; N, 3·89%.)

N-*Phenyltriphenylphosphoranylidenesuccinimide* (**Ic**). N-phenylmaleimide (0·9 g) and 1·5 g triphenylphosphine were stirred in 20 ml glacial AcOH on the steam bath for 1 hr. The reaction mixture was cooled and worked up as above giving 1·5 g (66%), m.p. 176·5–178·5°. (Found: C, 77·88; H, 5·12; N, 3·40. Calc. for $C_{28}H_{22}NO_2P$: C, 77·22; H, 5·09; N, 3·21%.)

The same product was obtained in 44% yield when N-phenylisomaleimide[4] was substituted for N-phenylmaleimide in the above reaction.

Methyltriphenylphosphoranylidenesuccinic anhydride (**Ie**). Citraconic anhydride (3·4 g, 0·03 mole) and 6·6 g triphenylphosphine in 30 ml glacial AcOH were stirred on the steam bath until a homogeneous soln was obtained (ca. 10 min) and then stirred 1 hr at room temp. Work-up as above gave 5·9 g (52%), m.p. 179–181°. (Found: C, 73·68; H, 5·29. Calc. for $C_{23}H_{19}O_3P$: C, 73·78; H, 5·11%.)

Methyl-N-*phenyltriphenylphosphoranylidenesuccinimide* (**If**). N-phenylcitraconimide (1·87 g, 0·01 mole) and 2·7 g triphenylphosphine in 3·0 ml glacial AcOH were stirred on a steam bath for 2 hr. Work-up as above gave 2·1 g (47%), m.p. 184–186°. (Found: C, 77·23; H, 5·33; N, 2·92. Calc. for $C_{27}H_{24}NO_2P$: C, 77·49; H, 5·38; N, 3·11%.)

N,N′-*Bitriphenylphosphoranylidenemaleimide* (**2**). N,N′-Biisomaleimide[1] (1·0 g, 0·005 mole) and excess triphenylphosphine in 20 ml Ac_2O were stirred on the steam bath for 1 hr. Work-up as above gave the adduct in quantitative yield, m.p. >350°. Purification was achieved by trituration with ether. (Found: C, 73·26; H, 5·02; N, 4·02. Calc. for $C_{22}H_{17}NO_2P$: C, 73·73; H, 4·78; N, 3·90%.)

The same product was obtained when N,N'-bimaleimide[1] was substituted for the isomaleimide in the above reaction.

N,N'-Morpholinotriphenylphosphoranylidenemaleimide (**1d**). N,N'-morpholinoisomaleimide (1·82 g, 0·01 mole), which was prepared from maleic anhydride and N-aminomorpholine as shown below, and 2·7 g (0·01 mole) triphenylphosphine in 20 ml glacial AcOH was stirred for 30 min on the steam bath. The soln was then let stand for 30 min at room temp. Work-up as above 2·1 g (50%), m.p. 132–134°. This compound was further characterized by its reaction with pyridine-4-carboxaldehyde (see below).

N-Morpholinoisomaleimide. N-aminomorpholine (5·1 g) and maleic anhydride (6·0 g) were stirred in glacial AcOH for 1 hr. After filtration a nearly quantititive yield of the maleamic acid was obtained, m.p. 177–179°. This was cyclized to the isoimide in excess trifluoroacetic anhydride.[1b] After removal of excess trifluoroacetic anhydride the residue was crystallized from ether to give 1·6 g of product, m.p. 121–123°. The IR had characteristic isoimide bands and the NMR was consistent with the structure. (Found: C, 52·76; H, 5·56; N, 15·47. Calc. for $C_8H_{10}N_2O_3$: C, 52·73; H, 5·53; N, 15·38%.)

Benzylidene-N-phenylsuccinimide (**7a**). The ylide **1c** (1·0 g, 0·0023 mole) was mixed with excess benzaldehyde in a test-tube. An exotherm was observed. After 15 min the mixture was triturated with MeOH and filtered. The product (0·48 g, 79%) was recrystallized from benzene, m.p. 193–195°. (Found: C, 77·60; H, 5·15; N, 5·56. Calc. for $C_{17}H_{13}NO_2$: C, 77·57; H, 4·97; N, 5·32%.)

Cinnamalidene-N-phenylsuccinimide (**7b**). The ylide **1c** (1·0 g, 2·3 mmoles) and excess cinnamaldehyde were heated on the steam bath until the mixture became homogeneous. Work-up as above gave the product as pale yellow crystals (0·55 g, 83%), m.p. 213–215°. (Found: C, 78·80; H, 5·29; N, 4·99. Calc. for $C_{19}H_{15}NO_2$: C, 78·87; H, 5·22; N, 4·84%.)

N-Phenyl(4-pyridylidene)succinimide (**7c**). A slight excess of pyridine-4-carboxaldehyde was slowly added to a solution of 2·18 g (5 mmole) of **1c** in 20 ml MeOH. A rapid reaction occurred. Upon cooling, the product crystallized. This was filtered and washed with MeOH giving 1·1 g (83%), m.p. 210–212°. (Found: C, 72·46; H, 4·58; N, 10·38. Calc. for $C_{16}H_{12}N_2O_2$: C, 72·71; H, 4·57; N, 10·60%.)

2-(2,2,1-Bicyclohept-5-ene)methylene-N-phenylsuccinimide (**7d**). A mixture consisting of a slight excess of norbornene-2-carboxaldehyde and 2·18 g (5 mmole) of **1c** was heated on the steam bath for 1 hr. Upon addition of MeOH 1·0 g (72%) of the crystalline product was obtained, m.p. 175–177°. (Found: C, 77·12; H, 6·16; N, 4·99. Calc. for $C_{18}H_{17}NO_2$: C, 77·39; H, 6·13; N, 5·01%.)

N-Phenyl(2-pyrrylmethylene)succinimide (**7e**). A slight excess of pyrrole-2-carboxaldehyde and 2·18 g (5 mmole) of **1c** were mixed and heated on the steam bath for 5 min. The mixture was cooled and triturated with cold MeOH. After filtration, the ppt was recrystallized from MeOH giving 1·1 g (87%), m.p. 246–248°. (Found: C, 71·41; H, 4·76; N, 11·05. Calc. for $C_{15}H_{12}N_2O_2$: C, 71·45; H, 4·79; N, 11·10%.)

Furfurylidene-N-phenylsuccinimide (**1f**). The reaction between furfural and **1c** was carried out and worked-up as above. A 76% yield was obtained and after recrystallization from MeOH had m.p. 197–199°. (Found: C, 71·76; H, 4·35; N, 5·62. Calc. for $C_{15}H_{11}NO_3$: C, 71·13; H, 4·37; N, 5·53%.)

(2-3,4-Dihydro-2H-pyranyl)methylene-N-phenylsuccinimide (**7g**). The reaction between 3,4-dihydro-2H-pyran-2-carboxaldehyde and **1c** was carried out as above giving a 67% yield, m.p. 156–158°. (Found: C, 71·22; H, 5·67; N· 5·41. Calc. for $C_{16}H_{15}NO_3$: C, 71·35; H, 5·61; N, 5·20%.)

(2-Thiophenyl)methylene-N-phenylsuccinimide (**7h**). The reaction between **1c** and thiophene-2-carboxaldehyde was carried out as above giving an 83% yield, m.p. 249–250°. (Found: C, 67·13; H, 4·17; N, 4·86. Calc. for $C_{15}H_{11}NO_2S$: C, 66·89; H, 4·11; N, 5·19%.)

Benzylidenesuccinimide (**8a**). Triphenylphosphoranylidenesuccinimide (1·0 g, 2·8 mmoles) and a slight excess of benzaldehyde were mixed. An exothermic reaction occurred. After the initial reaction the mixture was warmed on the steam bath for 3 min and let stand at room temp for 1 hr. Ether was added and crude product filtered off. After recrystallization from MeOH, 0·4 g (77%) was obtained, m.p. 198–200°. (Found: C, 70·78; H, 4·87; N, 7·31. Calc. for $C_{11}H_9NO_2$: C, 70·57; H, 4·84; N, 7·48%.)

(4-Pyridinylidene)succinimide (**8b**). Triphenylphosphoranylidenesuccinimide (3·6 g, 0·01 mole) and a slight excess of pyridine-4-carboxaldehyde in 30 ml DMSO were stirred for 2 hr at 50–60°. The mixture was then heated at the b.p for a few min until homogeneous soln was obtained After cooling, crystallization occurred giving 1·75 g (92%) of a white crystalline product, m.p. 195–197°. (Found: C, 63·31; H, 4·26; N, 14·70. Calc. for $C_{10}H_8N_2O_2$: C, 63·82; H, 4·28; N, 14·88%.)

Propylidenesuccinimide (**8c**). Maleimide (1·0 g, 0·01 mole) and tri-n-butylphosphine (2·0 g, 0·01 mole) in 15 ml glacial AcOH were warmed on the steam bath for a few min and then let stand for 30 min. The solvent was evaporated at 50° (1 mm) leaving a pinkish oil residue. Distilled propionaldehyde (3 g) was added to the oil and the mixture was warmed on the steam bath and then let stand for 3 hr. Excess aldehyde was removed *in vacuo* giving an oil. This was chromatographed on Fluorisil packed in hexane. Elution with ether gave a white crystalline material, m.p. 65–70°, in 40% yield. This was purified by sublimation. (Found: C, 60·08; H, 6·52; N, 10·06. Calc. for $C_7H_9NO_2$: C, 60·42; H, 6·52; N, 10·06%.)

N,N-*Bibenzylidenesuccinimide* (**9a**). Compound **2** (1·4 g, 1·7 mmoles) and excess benzaldehyde were heated on the steam bath for 10 min. The mixture was then let stand at room temp for 3–4 hr. The reaction mixture was then triturated with boiling MeOH, cooled, and filtered. The ppt was recrystallized from benzene giving 0·6 g (82%), m.p. 270–272°. (Found: C, 71·07; H, 4·13; N, 7·50. Calc. for $C_{11}H_8NO_2$: C, 70·95; H, 4·33; N, 7·52%.)

N,N′-*Bicinnamalidenesuccinimide* (**9b**). N,N′-Bitriphenylphosphoranylidenesuccinimide (0·25 g, 0·34 mmole) and excess cinnamaldehyde were heated on the steam bath for a few min until the mixture became homogeneous. After cooling, ether was added. The ppt was washed thoroughly with more ether giving 0·14 g (ca. 100%), m.p. 280–282°. (Found: C, 73·42; H, 4·71; N, 6·51. Calc. for $C_{13}H_{10}NO_2$: C, 73·57; H, 4·74; N, 6·59%.)

N,N′-*Morpholino(4-pyridylidene)succinimide* (**10**). Compound **1d** (2·2 g) and a slight excess of pyridine-4-carboxaldehyde were combined. After an initial exothermic reaction, the mixture was warmed to 40–50° for 50 min. The reaction mixture was then chromatographed on Fluorisil packed in hexane. A 50/50 mixture of acetone–ether eluted 0·8 g (59%) of product which was recrystallized from MeOH, m.p. 227–229°. (Found: C, 61·05; H, 5·54; N, 15·08. Calc. for $C_{14}H_{15}N_3O_3$: C, 61·52; H, 5·53; N, 15·37%.)

1,4-*Bis(*N-*phenylsuccinimidylidene)butane* (**11**). To a soln of **1c** (2·17 g, 5 mmole) in 20 ml AcOH, 3 ml 2,5-dimethoxytetrahydrofuran was added. The soln was stirred overnight at 50–60°. After cooling and filtration a ppt was obtained (0·5 g, 50%) which after thorough washing with acetone had m.p. 315–317°. (Found: C, 71·30; H, 5·08; N, 6·85. Calc. for $C_{12}H_{10}NO_2$: C, 71·98; H, 5·08; N, 6·99%.)

Cyclohexylidene-N-*phenylsuccinimide* (**12**). N-phenylmaleimide (1·75 g, 0·01 mole) and 2·20 g (0·01 mole) tri-n-butylphosphine in 20 ml glacial AcOH were heated on the steam bath for 30 min. The solvent was removed *in vacuo*. The residue was washed with hexane and then combined with excess cyclohexanone. The mixture was heated on the steam bath for 4 hr and the excess cyclohexanone was removed *in vacuo*. The residue crystallized upon addition of MeOH–water. Recrystallization from MeOH gave 0·5 g (20%), m.p. 104–106°. (Found: C, 74·87; H, 6·64; N, 5·62. Calc. for $C_{16}H_{17}NO_2$: C, 75·26; H, 6·71; N, 5·48%.)

Dicinnamalidenesuccinic anhydride (**18**). A mixture of **1a** (1·0 g, 2·8 mmole), excess cinnamaldehyde, and 30 drops of glacial AcOH were heated at 60°. Within a few min the reaction mixture became homogeneous and then a red ppt formed. The ppt was washed thoroughly with MeOH giving 0·5 g (55%) of red product, m.p. 236–238° (lit.[11] m.p. 215°). This material could be recrystallized from acetonitrile. In some cases small amounts of a more soluble isomeric product having m.p. 180–200° could be obtained in this way. The IR of this material differed in the fingerprint region from that of the higher melting product. (Found: C, 80·27; H, 4·88. Calc. for $C_{22}H_{16}O_3$: C, 80·48; H, 4·87%.)

The same material could be obtained in about 0·5% yield from the Stobbe condensation of sodium succinate (0·05 mole), cinnamaldehyde (0·075 mole), and Ac_2O (0·05 mole) in DMF (30 ml). The reaction was carried out at 80° for 5 hr.

Di(phenylpropargylidene)succininc anhydride (**19**). Phenylpropargyl aldehyde (3·0 g) was added to a stirring soln of 3·6 g (0·01 mole) of **1a** in 50 ml of ice-cold MeOH. After stirring for 1 hr, the reaction mixture was filtered and the ppt (1·75 g, 55%) was washed thoroughly with cold MeOH, m.p. 133–135°. (Found: C, 81·14; H, 3·71. Calc. for $C_{22}H_{12}O_3$: C, 81·46; H, 3·73%.)

The IR had characteristic acetylene and anhydride bands at 4·5, 5·50 and 5·68 μ.

N′-*Anilino(*N″-*piperadinyl)methylene*-N‴-*phenylsuccinimide* (**2a**). Phenylisocyanate (1 ml) and 2·17 g (5 mmole) of **1c** were mixed at room temp. An exothermic reaction occurred. After 15 min the excess isocyanate and the triphenylphosphine oxide was removed by washing the ppt first with hexane and then with benzene. The crude ketenimine could be recrystallized from benzene giving a white product in 79% yield, m.p. 154–156°.

The IR of this material had characteristic bands at 4·90, 5·70, 5·85 sh, and 5·94 μ. The NMR in $CDCl_3$ consisted of bands at 3·80 s and 7·45 m ppm.

The ketenimine was stirred with excess piperadine on the steam bath for 5 min. After cooling, the product was precipitated by addition of MeOH. After filtration and washing with acetone 1·1 g (61%) was obtained, m.p. 172–174°. (Found: C, 72·71; H, 6·43; N, 11·58. Calc. for $C_{22}H_{23}N_3O_2$: C, 73·10; H, 6·41; N, 11·62%.)

N′-*Anilinodiethylaminomethylene*-N″-*phenylsuccinimide* (**21b**). The adduct **1c** (4·35 g, 10 mmole) was converted to the crude ketenimine as above. This was refluxed with excess Et_2NH for 15 min. The excess Et_2NH was removed *in vacuo* and upon addition of MeOH to the residue, a crystalline product was obtained in 96% yield, m.p. 149–151°. (Found: C, 71·97; H, 6·67; N, 11·84. Calc. for $C_{21}H_{23}NO_2$: C, 72·18; H, 6·63; N, 12·02%.)

N'-Anilino(N''-aziridinyl)methylene-N'''-phenylsuccinimide (**21c**). The adduct **1c** (4·35 g, 10 mmole) was converted to the crude ketenimine as above. This was combined with aziridine at room temp, whereupon an exothermic reaction occurred. After the reaction mixture cooled it was worked up as above giving 2·5 g (78%), m.p. 143–145°. (Found: C, 71·26; H, 5·45; N, 12·99. Calc. for $C_{19}H_{17}N_3O_2$: C, 71·45; H, 5·36; N, 13·15%.)

Methylamino(N'-1,2,5,6-tetrahydropyridinyl)methylene-N''-phenylsuccinimide (**21d**). The adduct **1c** (2·18 g, 5 mmole) was refluxed with excess methyl isocyanate for 10 min. The excess isocyanate was removed *in vacuo* and the residue was stirred with excess 1,2,5,6-tetrahydropyridine at 60° for 15 min. After cooling, the product was obtained by addition of MeOH in 70% yield, m.p. 150–152°. (Found: C, 68·52; H, 6·47; N, 14·19. Calc. for $C_{17}H_{19}N_3O_2$: C, 68·66; H, 6·44; N, 14·13%.)

N'-Anilino(S-phenylthio)methylene-N''-phenylsuccinimide (**23**). The crude **20a** was obtained from 2·18 g adduct **1c** and phenyl isocyanate as above. This was mixed with excess benzenethiol and heated for a few min at 50–60°, whereupon an exothermic reaction occurred. The reaction mixture was allowed to cool to room temp. Excess benzenethiol was removed by washing the crude mixture with hexane. The residue was chromatographed on Fluorisil packed in ether. Ether eluted an oil which after washing with hexane was recrystallized from cold ether giving 1·1 g (57%), m.p. 109–111°. (Found: C, 71·50; H, 4·78; N, 7·19. Calc. for $C_{23}H_{18}N_2O_2S$: C, 71·47; N, 4·69; N, 7·25%.)

3-(N'-Anilino)N''-phenylmaleimide (**24**). The adduct **1c** (2·18 g, 5 mmole) and 0·6 g nitrosobenzene in 45 ml MeOH were stirred at 50° for 15 min. The reaction mixture was cooled and let stand at room temp for 30 min. After filtration, washing with MeOH and recrystallization from acetone 1·32 g (ca. 99%) was obtained, m.p. 238–240° (lit.[16] m.p. 230°). (Found: C, 72·53; H, 4·56; N, 10·82. Calc. for $C_{16}H_{12}N_2O_3$: C, 72·71; H, 4·57; N, 10·60%.)

The IR corresponded exactly with that published[16] for **24**. The NMR obtained in DMSO-d_6 had resonances at 5·82 s and 7·4 m ppm in an area ratio of 1:10.

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