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Reaction of Vinylphosphonium Salts with Sulfoxonium Ylides. Synthesis of Cyclopropylphosphonium Salts

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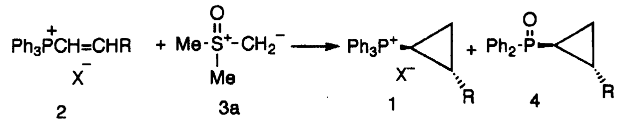
Reactions of (dimethylamino)phenylsulfoxonium methylide with triphenylvinylphosphonium salts gave the corresponding cyclopropyltriphenylphosphonium salts (*E*-form) in high yields, when 1,8-diazabicyclo-[5.4.0]undec-7-ene was used as a base. Reactions of cyclopropyltriphenylphosphonium salts with sodium hydride in the presence of tris[2-(2-methoxyethoxy)ethyl]amine afforded the corresponding ylides, which further reacted with aldehydes to give alkylidenecyclopropanes in high yields.

The formation and reactions of cyclopropyl compounds are of current interest.[1—5] Cyclopropylphosphonium salts (**1**) belong to an important class of compounds for the synthesis of alkylidenecyclopropanes and cyclobutanones.[6—10] Several methods for the preparation of cyclopropylphosphonim salts have been reported. Typical methods include the base-induced cyclization of 3-halopropylphosphonium salts.[8] Recently, we have reported the synthesis of vinylphosphonium salts (**2**) from 2-hydroxyalkylphosphonium salts and the one-pot synthesis of (diamino)cyclopropylsulfoxonium salts from (diamino)methylsulfoxonium salts.[11—13] These results prompted us to investigate the synthesis of **1** from several kinds of sulfoxonium ylides (**3**) and vinylphosphonium salts, **2**. We report herein the stereoselective synthesis and reaction of **1**.

Results and Discussion

Reaction of *E*-Vinylphosphonium Salts with Sulfoxonium Ylides. We first tried the reaction of **2** (*E*-form) with commercially available trimethylsulfoxonium iodide in the presence of sodium hydride in dimethyl sulfoxide (DMSO). Treatment of dimethylsulfoxonium methylide (**3a**) with in DMSO resulted in the formation of the corresponding cyclopropyldiphenylphosphine oxides (**4**) in high yield. Under these conditions, cyclopropyltriphenylphosphonium salts (**1**) were not obtained (Scheme 1). Table 1 lists the experimental results obtained. The obtained (2-methylcyclopropyl)diphenylphosphine oxide (**4b**) is found to have *E*-form by use of ^{1}H NMR decoupling technique ($J_{\mathrm{trans}}=4$ Hz). Only one isomer was found in the ^{1}H NMR spectrum of the reaction mixture. Since trimethylsulfoxonium iodide, a precursor of **3a**, is practically insoluble in THF or dichloromethane, the reaction did not proceed smoothly in these solvents. Trimethylsulfoxonium iodide was recovered in 35 and 55% amounts, respectively. Under these conditions, the yields of salts **1** are low. Thus, another kind of sulfoxonium ylides for the preparation of **1** is desirable.



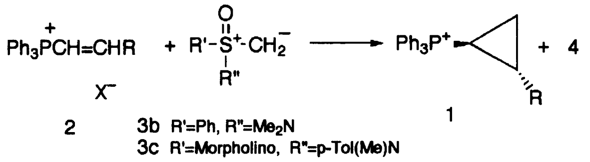
Scheme 1.

Recently, we have reported a one-step synthesis of cyclopropyl(dimethylamino)phenylsulfoxonium tetrafluoroborates from (dimethylamino)phenylsulfoxonium methylide (**3b**) with aldehydes.[12] This result prompted us to apply the synthesis of **1** by using **3b** instead of ylide **3a**. Treatment of **3b** derived from (dimethylamino)methylphenylsulfoxonium tetrafluoroborate and DBU with **2** in refluxing dichloromethane resulted in the formation of corresponding salts **1** in high yields. We have also found that the reaction of (*N*-methyl-*N*-*p*-tolylamino)morpholinosulfoxonium methylide (**3c**) with vinylphosphonium salts afforded **1** in high yields (Scheme 2). It is also noteworthy that this reaction has high stereoselectivity and forms *E*-type of **1** salts. Only one stereoisomer of **1** was obtained in the reaction mixture according to the ^{1}H NMR spectroscopic analyses. Salt **1b** was converted into **4b** (*E*) in quantitative yield by the reaction with aqueous sodium

Table 1. The Reaction of Vinylphosphonium Salts **2** with Dimethylsulfoxonium Methylide **3a**

Vinyl salts		Conditions				Products (Yield/%)			
2		Base	Solvent	Temp/°C	Time/h	**1**		**4**	
2a	R=H X=Br	NaH	DMSO	60	5	**1a**	0	**4a**	90
2a		BuLi	THF	0	6	**1a**	15	**4a**	0
2a		DBU[a)]	THF	Reflux	8	**1a**	12	**4a**	0
2a		DBU	CH_2Cl_2	Reflux	5	**1a**	6	**4a**	0
2b	R=Me X=BF_4	NaH	DMSO	60	5	**1b**	0	**4b**	91
2b		BuLi	THF	0	6	**1b**	0	**4b**	43
2b		DBU	THF	Room temp	8	**1b**	0	**4b**	26
2c	R=Et X=BF_4	NaH	DMSO	60	5	**1c**	0	**4c**	71

a) DBU=1,8-diazabicyclo[5.4.0]undec-7-ene.



Scheme 2.

hydroxide. Table 2 lists the experimental results obtained.

The difference in the reactivity might be due to the content of water in the solvents and the bases used. Dichloromethane is insoluble in water and was used in the present reaction as a solvent for azeotropic separation. In refluxing dichloromethane, amino- or diamino sulfoxonium ylide reacted with vinyl salts to give cyclopropylphosphonium salts **1**. In the case of DMSO–NaH system, the small amount of water in the solvent gave hydroxide ions, which further reacted with salts **1** to afford cyclopropylphosphine oxides **4**. Hydrolysis of salts, **1** in basic condition might result in the formation of **4**.[7)] Actually, the reaction of cyclopropyltriphenylphosphonium bromide, **1a**, with refluxing alcoholic sodium hydroxide afforded the corresponding phosphine oxide, **4a** in almost quantitative yield. As for the base, DBU is a good reagent for proton abstraction reaction but not so strong a base as dimsyl sodium. Even if water exists in the medium, the system is not sufficiently basic for the conversion of **1** to **4**. To confirm this assumption, the reactions of **3b** with **2a** in dichloromethane–water (9 : 1) or THF–water (9 : 1) were carried out. The corresponding salt **1a** was isolated in 85 and 75% yields, respectively. These results suggest that solvents and bases are very important in the present reaction.

Manske and Gosselck reported that the reaction of phosphonium ylides with vinylsulfonium salts gave a mixture of **1**, alkylphosphonium salts, and vinyl sulfides.[14)] Isolation of **1** was practically difficult. Hammerschmidt and Zbiral reported that the vinylphosphonium salts with an electron-attracting substituent (COR, CN, or COOMe) were transformed into the corresponding cyclopropylphosphonium salts by the reaction with stabilized sulfonium ylides ($Me_2S^+{-}^-CHX$).[15)] These electron-deficient salts **1** reacted with sodium hydroxide to afford only a mixture of *cis* and *trans* cyclopropanes and triphenylphosphine oxide. Nevertheless, the reaction of alkyl-substituted vinylphosphonium salts with sulfoxonium methylides **3** has not been reported.

Previously, alkyl-substituted cyclopropylphosphonium salts, **1** were prepared by 3-haloalkylphosphonium salts with bases. The present method gives another process for the synthesis of cyclopropylphosphonium salts **1**. Vinylphosphonium salts were used for the formation of heterocycles or dienophiles.[16)] The present method offers another reaction of vinylphosphonium salts.

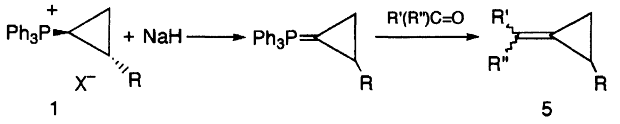
Reaction of Cyclopropylphosphonium Salts with Aldehydes. We carried out the reaction of cyclopropylphosphonium ylides with aldehydes. However, under usual conditions, alkylidenecyclopropanes (**5**) were obtained in very low yields. Initial attempts to carry out the Wittig reaction between **1** and alde-

Table 2. Reaction of Vinylphosphonium Salts with Amino- or Diaminosulfoxonium Methylides

Compounds		Conditions				Products/%			
2	**3**	Base	Solvent	Temp/°C	Time/h	**1**		**4**	
2a	**3b**	DBU	Dichloromethane	Reflux	2	**1a**	76	**4a**	0
2a	**3b**	NaH	DMSO	50	4	**1a**	0	**4a**	66
2a	**3c**	DBU	Dichloromethane	Reflux	2	**1a**	75	**4a**	0
2b	**3b**	DBU	Dichloromethane	Reflux	2	**1b**	83	**4b**	0
2b	**3c**	DBU	Dichloromethane	Reflux	2	**1b**	91	**4b**	0
2c	**3b**	DBU	Dichloromethane	Reflux	2	**1c**	73	**4c**	0
2c	**3c**	DBU	Dichloromethane	Reflux	5	**1c**	74	**4c**	0

Table 3. The Reaction of Cyclopropylphosphonium Salts with Carbonyl Compounds

Salts	Carbonyl compounds		Conditions			Products/%		E : Z
1	R′	R″	Solvent	Temp/°C	Time/h	**5**		
1a	Ph	Ph	Toluene	Reflux	8	**5a**	65	
1b	H	p-ClC_6H_4	Toluene	Reflux	8	**5b**	72	62 : 38
1b	H	p-$CH_3C_6H_4$	THF	Reflux	12	**5c**	38	71 : 29
1b	H	p-$CH_3C_6H_4$	Toluene	Reflux	8	**5c**	67	60 : 40
1b	H	p-$NO_2C_6H_4$	Toluene	Reflux	8	**5d**	74	65 : 35
1b	Ph	Ph	Toluene	Reflux	8	**5e**	79	



Scheme 3.

hydes were uniformly unsuccessful. Standard methods led either to the recovery of unreacted **1** or to its hydrolyzed products, **4**. Stafford and McMurry have reported that the reaction of unsubstituted cyclopropylphosphonium salts **1a** with sodium hydride in the presence of tris[2-(2-methoxyethoxy)ethyl]amine (TDA-1), followed by the addition of aldehydes, afforded the corresponding alkylidenecyclopropanes (**5**) in good yields (Scheme 3).$^{17)}$ We then applied this reaction for substituted cyclopropylphosphonium salts. As Table 3 shows, the yields of olefins were improved to 65—79%.

In summary, we have described the general synthesis of alkyl-substituted cyclopropylphosphonium salts. The reaction of these salts with sodium hydride in the presence of TDA-1, followed by the addition of carbonyl compounds, afforded the corresponding alkylidenecyclopropanes in high yields.

Experimental

General. Melting points are uncorrected. ^{1}H and ^{13}C NMR spectra were obtained with a JEOL FX-90Q or a JEOL GSX-400 spectrometer. Chemical shifts are given in ppm units downfield from tetramethylsilane. TLC analyses were performed using Merck Silica gel 60 F_{254} aluminium plates.

Material. Vinylphosphonium salts (E form) were prepared by the method described previously.$^{11,18)}$ Sulfoxonium salts **3b** and **3c** were prepared by the methods described by Johnson et al.$^{19)}$ and by us.$^{20)}$

Reaction of Vinylphosphonium Salts with Dimethylsulfoxonium Methylide 3a. A solution of NaH (60% mineral oil dispersion, 0.12 g, 3.0 mmol) in DMSO (5 ml) was warmed up to 60 °C and stirred for 1 h. To this solution was added trimethylsulfoxonium iodide (0.66 g, 3.0 mmol) at room temperature. After stirring for 2 h, vinylphosphonium salt **2a** (0.78 g, 2.0 mmol) was added into the solution. The reaction mixture was stirred for 5 h, then it was poured into water (20 ml), and extracted with dichloromethane (15 ml×3). The combined extract was dried over anhydrous magnesium sulfate and evaporated to give pale yellow oily crystals, which were recrystallized from methanol to give the corresponding cyclopropyldiphenylphosphine oxide (**4a**) (0.46 g, 1.8 mmol) in 90% yield. Other reactions were carried out in a similar manner.

4a: Mp 128—130 °C, (lit,$^{7)}$ mp 132—133 °C); ^{1}H NMR ($CDCl_3$) δ=0.94—1.02 (m, 2H, CH_2), 1.03—1.11 (m, 2H, CH_2), 1.25—1.36 (m, 1H, PCH), 7.49—7.55 (m, 6H, Ar), 7.73—7.79 (m, 4H, Ar).

4b: Mp 146—147 °C; ^{1}H NMR ($CDCl_3$) δ=0.72—0.79 (m, 1 H, C$\underline{\mathrm{H}}$H, J_{PH}=8 Hz, J_{gem}=9 Hz, J_{cis}=9 Hz, J_{trans}=4 Hz), 0.97—1.06 (m, 1H, PCH, J_{PH}=14 Hz, J_{cis}=9 Hz, J_{trans}=4 Hz, J_{trans}=6 Hz), 1.18—1.27 (m, 1H, CH$\underline{\mathrm{H}}$), 1.21—1.23 (d, 3H, CH_3, J=5.5 Hz), 1.27—1.51 (m, 1H, CH, J_{PH}=12 Hz, J_{cis}=8 Hz, J_{trans}=4 Hz, J_{trans}=4 Hz, J_{MeH}=5.5 Hz), 7.43—7.54 (m, 6H, Ar), 7.65—7.76 (m, 4H, Ar); ^{13}C NMR ($CDCl_3$) δ=11.14 (d, CH_2, J_{PC}=5.5 Hz), 11.62 (d, CH, J_{PC}=3.7 Hz), 15.49 (d, PCH, J_{PC}=104.8 Hz), 18.37 (CH_3), 117.98—135.14 (Ph). Found: C, 74.94; H, 6.84%. Calcd for $C_{16}H_{17}OP$: C, 74.99; H, 6.69%.

4c: Mp 152—153 °C; ^{1}H NMR ($CDCl_3$) δ=0.78—0.82 (m, 1H, CH_2), 0.88—0.91 (t, 3H, CH_3, J=6.7 Hz), 1.03—1.08 (m, 1H, PCH), 1.23—1.30 (m, 1H, CH_2), 1.35—1.52 (m, 3H, CH, CH_2), 7.45—7.51 (m, 6H, Ar), 7.65—7.77 (m, 4H, Ar); ^{13}C NMR ($CDCl_3$) δ=9.91 (d, CH_2, J_{PC}=5.5 Hz), 13.21 (CH_3), 14.30 (d, PCH, J_{PC}=104.8 Hz), 18.68 (d, CH, J_{PC}=3.7 Hz), 26.60 (d, CH_2, J_{PC}=3.6 Hz), 128.26—134.30 (Ph). Found: C, 75.64; H, 6.86%. Calcd for $C_{17}H_{19}OP$: C, 75.55; H, 7.03%. By using butyllithium as a base: To a suspension of trimethylsulfoxonium iodide (0.44 g, 2.0 mmol) in THF (20 ml) was added a solution of butyllithium (1.6 M in hexane (1 M=1 mol dm^{-3}), 1.3 ml, 2.1 mmol) via syringe at 0 °C. After stirring for 2 h, salts **2a** (0.78 g, 2.0 mmol) was added to this suspension and the reaction mixture was stirred for 6 h at this temperature. The resulting suspension was washed with water (50 ml) and extracted with dichloromethane (20 ml×3). The combined extract was dried over anhydrous magnesium sulfate, filtered, and evaporated to give pale brown oily crystals, which were recrystallized from methanol to give salts **1a** (0.12 g, 0.30 mmol) in 15% yield.

1a (Br^-): Mp 186—187 °C; (lit, $^{7)}$ mp 189—190 °C).

Reaction of Vinylphosphonium Salts with (Dimethylamino)phenylsulfoxonium Methylide 3b. To a solution of vinylphosphonium salt **2b** (0.78 g 2.0 mmol) and (dimethylamino)methylphenylsulfoxonium tetrafluoroborate (0.81 g, 3.0 mmol) in dichloromethane (10 ml) was added a solution of DBU (0.46 g, 3.0 mmol) in dichloromethane (3 ml). After refluxing for 2 h, the reaction mixture was washed with water, then dried over anhydrous magnesium sulfate. The resulting filtrate was evaporated to give pale yellow oily crystals, which were recrystallized from methanol to afford (2-methylcyclopropyl)triphenylphosphonium tetrafluoroborate (**1b**) in 83% yields.

Other reactions were carried out in a similar manner.

1a ($\mathbf{Br^-}$): Mp 186—187 °C; (lit,[7] Mp 189—190 °C).

1b ($\mathbf{BF_4{}^-}$): Mp 145—146 °C; ^{1}H NMR ($\mathrm{CDCl_3}$) δ=0.61—0.89 (m, 1H, $\mathrm{CH_2}$), 1.01—1.12 (m, 1H, CH), 1.43—1.45 (d, 3H, $\mathrm{CH_3}$, J=6.1 Hz), 1.50—1.58 (m, 1H, $\mathrm{CH_2}$), 2.24—2.31 (m, 1H, PCH), 7.69—7.80 (m, 15H, Ar); ^{13}C NMR ($\mathrm{CDCl_3}$) δ=6.60 (d, PCH, J_{PC}=86.4 Hz), 12.36 (d, $\mathrm{CH_2}$, J_{PC}=5.6 Hz), 14.16 (d, CH, J_{PC}=3.7 Hz), 17.07 ($\mathrm{CH_3}$), 117.89—135.16 (Ph). Found: C, 65.40; H, 5.45%. Calcd for $\mathrm{C_{22}H_{22}BF_4P}$: C, 65.38; H, 5.49%.

1c ($\mathbf{BF_4{}^-}$): Mp 138—139 °C ^{1}H NMR ($\mathrm{CDCl_3}$) δ= 0.79—0.86 (m, 1H, $\mathrm{CH_2}$), 0.98—1.02 (t, 3H, $\mathrm{CH_3}$, J=7.6 Hz), 1.53—1.61 (m, 2H, $\mathrm{CH_2}$), 1.79—1.83 (m, 1H, CH), 1.83—1.89 (m, 2H, $\mathrm{CH_2}$), 2.23—2.33 (m, 1H, PCH), 7.68—7.82 (m, 15H, Ar); ^{13}C NMR ($\mathrm{CDCl_3}$) δ=5.78 (d, PCH, J_{PC}=86.4 Hz), 11.30 (d, $\mathrm{CH_2}$, J_{PC}=5.5 Hz), 13.18 ($\mathrm{CH_3}$), 21.06 (d, CH, J_{PC}=5.5 Hz), 25.45 ($\mathrm{CH_2}$), 118.00—135.17 (Ph). Found: C, 66.04; H, 6.11%. Calcd for $\mathrm{C_{23}H_{24}BF_4P}$: C, 66.05; H, 5.78%.

Reaction of Vinylphosphonium Salts with Diaminosulfoxonium Methylide. To a solution of vinylphosphonium salt **2b** (0.78 g, 2.0 mmol) and methyl(N-methyl-N-p-tolylamino)morpholinosulfoxonium tetrafluoroborate (1.1 g, 3.0 mmol) in dichloromethane (10 ml) was added a solution of DBU (0.46 g, 3.0 mmol) in dichloromethane (3 ml). After being refluxed for 2 h, the reaction mixture was washed with water (15 ml×3) and dried over anhydrous magnesium sulfate. The resulting filtrate was evaporated to afford the corresponding cyclopropylphosphonium salts in 91% yield. Recrystallization from methanol gave (2-methylcyclopropyl)triphenylphosphonium tetrafluoroborate (E-form) (**1b**).

Reaction of 1a with Aqueous Sodium Hydroxide. To a solution of sodium hydroxide (0.40 g, 10 mmol) in water (10 ml) was added **1a** (0.76 g, 2.0 mmol) in one portion. After refluxing for 3 h, the reaction mixture was extracted with dichloromethane (10 ml) three times. The combined extract was dried over anhydrous magnesium sulfate, filtered, and evaporated to afford colorless crystals of **4a** (0.48 g, 1.98 mmol) in 98%. Mp 128—129 °C.

Reaction of Cyclopropyltriphenylphosphonium Salts with Bases, Followed by the Addition of Aldehydes. By Using Butyllithium as a Base. To a solution of salt **1b** (0.20 g, 0.50 mmol) in THF (3 ml) was added a solution of butyllithium (1.6 M in hexane, 0.31 ml, 0.50 mmol) at 0 °C. After being stirred for 1 h, the reaction mixture was cooled to −50 °C and solution of p-chlorobenzaldehyde (0.070 g, 0.50 mmol) in THF (2 ml) was added to this solution. The reaction mixture was stirred for 2 h at the temperature and warmed up to room temperature. The resulting mixture was washed with water (15 ml×3), extracted with dichloromethane (15 ml×3), and dried over anhydrous magnesium sulfate. The filtrate was evaporated to afford a brown oil, which was chromatographed over silica gel by elution with a mixture of dichloromethane and ethyl acetate to afford p-chlorobenzyl alcohol (0.016 g, 0.12 mmol, 24%) and starting salt, **1b** (0.070 g, 0.017 mmol, 34%).

By Using NaH as a Base and TDA-1 as a Catalyst. To a solution of salt **1a** (0.25 g, 0.65 mmol) and TDA-1 (0.016 g, 0.050 mmol) in toluene (5 ml) was added NaH (60 % mineral oil dispersion, 0.039 g, 0.98 mmol). After refluxing for 2 h, a solution of benzophenone (0.091 g, 0.50 mmol) in toluene (2 ml) was added to this suspension and this mixture was refluxed for an additional 8 h. The resulting mixture was washed with water (15 ml×3) and extracted with dichloromethane (15 ml×3). The combined extract was dried over anhydrous magnesium sulfate, filtered, and evaporated to afford pale brownish oily crystals, which were chromatographed over silica gel by elution with mixture of hexane, dichloromethane, and ethyl acetate. The hexane eluant was evaporated to afford (diphenylmethylene)cyclopropane **5a** (0.070 g, 0.33 mmol, 65%). Mp 62—63 °C (lit,[8] Mp 64.5—65.5 °C). Other reactions were carried out in a similar manner.

5b: (0.056 g, 0.32 mmol, 63%); E-form: ^{1}H NMR ($\mathrm{CDCl_3}$) δ=1.00—1.02 (m, 1H, CH), 1.19—1.20 (d,3H, $\mathrm{CH_3}$, J=6.1 Hz), 1.51—1.59 (m, 2H, 2CH), 6.71 (br, s, 1H, =CH), 7.26—7.46 (m, 4H, Ar); ^{13}C NMR ($\mathrm{CDCl_3}$) δ= 7.90 ($\underline{\mathrm{C}}\mathrm{HCH_3}$), 11.72 ($\mathrm{CH_2}$), 17.83 ($\mathrm{CH_3}$), 116.52 (=CH), 127.68—136.85 (Ph), 132.33 (C=); Z-form: ^{1}H NMR ($\mathrm{CDCl_3}$) δ=0.80—0.83 (m, 1H, CH), 1.25—1.26 (d, 3H, $\mathrm{CH_3}$, J=6.1 Hz), 1.32—1.37 (m, 1H, CH), 1.71—1.80 (m, 1H, CH), 6.64 (br, s, 1H, =CH), 7.26—7.46 (m, 4H, Ar); ^{13}C NMR ($\mathrm{CDCl_3}$) δ=8.93 ($\underline{\mathrm{C}}\mathrm{HCH_3}$), 11.28 ($\mathrm{CH_2}$), 17.06 ($\mathrm{CH_3}$), 117.57 (=CH), 127.68—136.85 (Ar), 130.30 (C=). HRMS: Found: m/z 177.0461. Calcd for $\mathrm{C_{11}H_{10}^{35}Cl}$: $\mathrm{M^+}$, 177.0471.

5c: (0.054 g, 0.34 mmol, 67%); E-form: ^{1}H NMR ($\mathrm{CDCl_3}$) δ=0.97—1.00 (m, 1H, CH), 1.19 (d, 3H, $\mathrm{CH_3}$, J=5.5 Hz), 1.50—1.58 (m, 2H, 2CH), 2.33 (m, 3H, $\mathrm{CH_3}$–$\mathrm{C_6H_4}$), 6.72—6.74 (br, s, 1H, =CH), 7.11—7.13 (d, 2H, Ar), 7.41—7.43 (d, 2H, Ar); ^{13}C NMR ($\mathrm{CDCl_3}$), δ=7.71 ($\underline{\mathrm{C}}\mathrm{HCH_3}$), 11.68 ($\mathrm{CH_2}$), 17.93 ($\mathrm{CH_3}$), 21.15 ($\mathrm{CH_3}$–$\mathrm{C_6H_4}$), 117.18 (=CH), 126.41—136.27 (Ph), 130.18 (C=); Z-form: ^{1}H NMR ($\mathrm{CDCl_3}$) δ=0.77—0.81 (m, 1H, CH), 1.25—1.26 (d, 3H, $\mathrm{CH_3}$, J=6.1 Hz) 1.30—1.33 (m, 1H, CH), 1.69—1.79 (m, 1H, CH), 2.33 (m, 3H, $\mathrm{CH_3}$–$\mathrm{C_6H_4}$), 6.63—6.66 (br, s, 1H, =CH), 7.13—7.14 (d, 2H, Ar), 7.32—7.34 (d, 2H, Ar); ^{13}C NMR ($\mathrm{CDCl_3}$) δ=8.79 ($\underline{\mathrm{C}}\mathrm{HCH_3}$), 11.22 ($\mathrm{CH_2}$), 17.20 ($\mathrm{CH_3}$), 21.15 ($\mathrm{CH_3}$–$\mathrm{C_6H_4}$), 118.40 (=CH), 126.41—136.27 (Ar), 130.18 (C=). HRMS: Found: m/z 158.1086. Calcd for $\mathrm{C_{12}H_{14}}$: $\mathrm{M^+}$, 158.1095.

5d: (0.070 g, 0.37 mmol, 74%); E-form: ^{1}H NMR ($\mathrm{CDCl_3}$) δ=1.01—1.14 (m, 1H, CH), 1.23 (d, 3H, $\mathrm{CH_3}$, J=6.1 Hz), 1.58—1.70 (m, 2H, 2CH), 6.84—6.85 (br, s, 1H, =CH), 7.63—7.65 (d, 2H, Ar), 8.17—8.19 (d, 2H, Ar); ^{13}C NMR ($\mathrm{CDCl_3}$) δ=8.27 ($\underline{\mathrm{C}}\mathrm{HCH_3}$), 12.04 ($\mathrm{CH_2}$), 17.60 ($\mathrm{CH_3}$), 116.16 (=CH), 123.90—146.22 (Ph), 138.11 (C=); Z-form: ^{1}H NMR ($\mathrm{CDCl_3}$) δ=0.90—0.93 (m, 1H, CH), 1.28—1.30 (d, 3H, $\mathrm{CH_3}$, J=6.1 Hz), 1.41—1.46 (m, 1H, CH), 1.79—1.88 (m, 1H, CH), 6.77—6.78 (br, s, 1H, =CH), 7.53—7.55 (d, 2H, Ar), 8.18—8.20 (d, 2H, Ar); ^{13}C NMR ($\mathrm{CDCl_3}$) δ=9.23 ($\underline{\mathrm{C}}\mathrm{HCH_3}$), 11.60 ($\mathrm{CH_2}$), 16.85 ($\mathrm{CH_3}$), 117.31 (=CH), 123.90—146.22 (Ar), 138.25 (C=). HRMS: Found: m/z 189.0773. Calcd for $\mathrm{C_{11}H_{11}NO_2}$: $\mathrm{M^+}$, 189.0789.

5e: Colorless oil, (0.190 g, 0.40 mmol, 79%); ^{1}H NMR ($\mathrm{CDCl_3}$) δ=1.04—1.07 (q, 1H, CH), 1.22 (d, 3H, $\mathrm{CH_3}$, J=6.1 Hz), 1.53—1.58 (t, 1H, CH, J=9.2 Hz), 1.72—1.78 (m, 1H, CH), 7.25—7.46 (m, 10H, Ph); ^{13}C NMR ($\mathrm{CDCl_3}$) δ= 10.76 ($\underline{\mathrm{C}}\mathrm{HCH_3}$), 11.11 ($\mathrm{CH_2}$), 17.75 ($\mathrm{CH_3}$), 126.71 (=$\mathrm{CPh_2}$), 131.26 (=C), 126.76—140.95 (Ph). HRMS: Found: m/z 220.1265. Calcd for $\mathrm{C_{17}H_{16}}$: $\mathrm{M^+}$, 220.1252.

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References

1) M. Ihara, T. Taniguchi, and K. Fukumoto, *Tetrahedron Lett.*, **35**, 1901 (1994).

2) K. Burgess, K.-K. Ho, and C.-Y. Ke, *J. Org. Chem.*, **58**, 3767 (1993).

3) A. de Meijere, S. I. Kozhushkov, T. Spaeth, and N. S. Zefirov, *J. Org. Chem.*, **58**, 502, (1993).

4) A. Oku, Y. Ose, T. Kamada, and T. Yoshida, *Chem. Lett.*, **1993**, 573.

5) Y. Ukaji, K. Sada, and K. Inomata, *Chem. Lett.*, **1993**, 1227.

6) H. J. Bestmann and T. Denzel, *Tetrahedron Lett.*, **1966**, 3591.

7) E. E. Schweizer, C. J. Berninger, and J. G. Thompson, *J. Org. Chem.*, **33**, 336 (1968).

8) K. Utimoto, M. Tamura, and K. Sisido, *Tetrahedron*, **29**, 1169 (1973).

9) C. R. Johnson and E. R. Janiga, *J. Am. Chem. Soc.*, **95**, 7692 (1973).

10) H. Nemoto, H. Ishibashi, M. Nagamochi, and K. Fukumoto, *J. Org. Chem.*, **57**, 1707 (1992).

11) K. Okuma, M. Ono, and H. Ohta, *Bull. Chem. Soc. Jpn.*, **66**, 1308 (1993).

12) K. Okuma, Y. Sato, T. Ishii, and H. Ohta, *J. Org. Chem.*, **59**, 2390 (1994).

13) K. Okuma, Y. Sato, H. Ohta, and Y. Yokomori, *Bull. Chem. Soc. Jpn.*, **67**, 1855 (1994)

14) R. Manske and J. Gosselck, *Tetrahedron Lett.*, **1971**, 2097.

15) F. Hammerschmidt and E. Zbiral, *Justus Liebigs Ann. Chem.*, **1977**, 1026.

16) For a review see: E. Zbiral "Organophosphorus Reagents in Organic Synthesis," ed by J. I. G. Cadogan, Academic Press, London (1979), Chap. 5.

17) J. A. Stafford and J. E. McMurry, *Tetrahedron Lett.*, **29**, 2531 (1988).

18) H. J. Bestmann, H. Hartung, and I. Pils, *Angew. Chem., Int. Ed. Engl.*, **4**, 957 (1965).

19) C. R. Johnson, G. F. Katekar, R. F. Huxol, and E. R. Janiga, *J. Am. Chem. Soc.*, **93**, 3771 (1971).

20) K. Okuma, N. Higuchi, S. Kaji, H. Takeuchi, H. Ohta, H. Matsuyama, N. Kamigata, and M. Kobayashi, *Bull. Chem. Soc. Jpn.*, **63**, 3223 (1990).