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Direct Dichlorovinylation of Some Carbonyl Compounds by Trichloroethylene Under Conditions of Phase-Transfer Catalysis

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Abstract—Reaction of ketones **1** and **3** with trichloroethylene (TRI) carried out in the presence of 50% aq. NaOH and TBAHS as a catalyst, in ethyl ether (phase-transfer catalysis, PTC) afford 1,2-dichlorovinylated ketones **2** and **4**, respectively in good yields, usually as mixtures of *Z* and *E* isomers. PTC reaction of aldehydes **5** with TRI, carried out with DMSO instead of TBAHS, yields O-dichlorovinylated products **6**, as mixtures of isomers in the case of **6a**. These products are formed via C- or O-addition of ambident enolate anions to dichloroacetylene (generated from TRI by a base) and fast protonation of highly basic dichlorovinyl anions thus formed.

Introduction

Treatment of trichloroethylene (TRI) with a base generates dichloroacetylene (DCA), which is prone to add carbanions with the formation of 1,2-dichlorovinyl substituted derivatives, and occasionally other products.[1] Thus, tertiary enolates formed from esters, chain and cyclic ketones by means of LDA in HMPA,[1,2] and carbanions generated from 2-substituted phenylacetonitriles[3] under conditions of phase-transfer catalysis (PTC),[4] both give with TRI products of dichlorovinylation. The latter reaction is carried out under particularly convenient conditions, and affords the products in good yields.

To determine the scope of this simple PTC dichlorovinylation procedure, some ketones and aldehydes were allowed to react with TRI.

Results and Discussion

We found that stirring of ketones **1** with TRI in the presence of 50% aq. sodium hydroxide and tetra-*n*-butylammonium hydrogen sulfate (TBAHS) as a catalyst (phase-transfer catalysis, PTC), at temperature 5–25°C, produces 1,2-dichlorovinyl substituted derivatives **2**, usually as mixtures of *Z* and *E* isomers, in 54–83% yield (Scheme 1, Table 1).

The crude reaction mixtures were purified by Kugelrohr distillation (products **2a**–**f**) or crystallization (products **2g**,**h**) to afford ketones **2** of purity at least 95%, except **2d** and **2f** (Table 1). In the case of **2e** pure samples of both isomers were isolated by careful fractional crystallization. Comparison of measured and calculated chemical shifts of vinylic protons in ^{1}H NMR spectra[5] allowed us to ascribe tentatively *Z* and *E* stereochemistry to both isolated samples of ketone **2e**[6] (Fig. 1).

Taking into account that the vinylic proton in the *Z* isomer absorbs at higher field than *E*-isomer of **2e**, we determined *Z* and *E* stereochemistry of other products **2** (Table 1). In all cases *E* isomers prevail (**2a**–**e**) or are the only products isolated (**2f**–**h**).

Phenylacetone derivatives, namely 3-phenylheptan-2-one and 3,4-diphenylbutan-2-one,[7] formed rather complex products mixtures when allowed to react with TRI under different PTC conditions (above described liquid–liquid system with TBAHS or DMSO and solid–liquid system with powdered sodium hydroxide and TBAHS, at −20–35°C). It seems that in the case of these two ketones isomeric methyl enolate anions participate in reactions with TRI. However, attempted reaction of isobutyrophenone, which possesses only one acidic site, with TRI under PTC conditions revealed that it remains intact, probably because of relatively low acidity. On the other hand, 3-cyano-3-phenylpropan-2-one (**3**) does react with TRI to give one, (presumably *E*) isomer of the expected product of dichlorovinylation **4**. Due to formation of large amounts of tarry material in this reaction, the ketone **4** was isolated in moderate yield (Scheme 2). The high acidity of the methine hydrogen in **3** (and the activity of enolate anion thus formed), totally prevents competitive generation of the methyl enolate.

Keywords: phase-transfer; enolates; dichloroacetylene; addition reactions.
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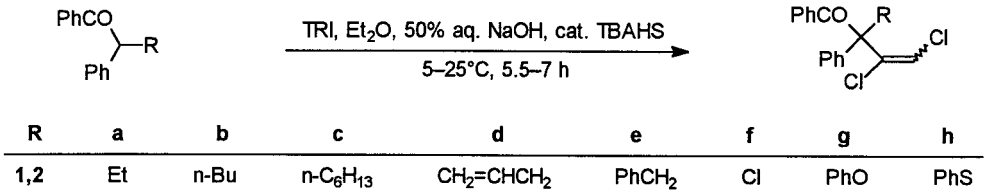


Scheme 1.

Finally, aldehydes **5** when allowed to react with TRI under PTC conditions with DMSO, afforded O-alkylated products, the corresponding enol ethers **6**, in good yields (Scheme 3). Under these conditions, less intractable material is formed than in reactions catalyzed by TBAHS.

Calculated and measured chemical shifts of vinylic protons in **6a** are consistent, and indicate that possibly *Z*-**6a** is the main product (Fig. 2).

Apart from correct analytical data (e.g. lack of strong band of carbonyl group in IR spectra at $\nu \sim 1700\ cm^{-1}$) the enol ether structure of **6** was confirmed by acid catalyzed hydrolysis, which gave starting aldehydes **5** and other products.

To collect more information on the above described processes we carried out reaction of ketone **1b** with independently synthesized dichloroacetylene (DCA).[8b] It led to formation of ketone **2b** as mixture of *Z* and *E* isomers of similar ratio like in reaction of **1b** with TRI, but produced rather complex product mixtures which contained some unreacted **1b**. This result is not unexpected since DCA, apart from the desired reaction with enolate anion (the concentration of which in PTC processes is low not exceeding that of the catalyst[4]), can react with water and/or hydroxy anions with formation of side products. On the other hand, concentration of DCA generated from TRI in the presence of C–H acid is much lower, therefore it is able to react more selectively with enolate anions from **1**. The experiment described above indicates that DCA is indeed involved in PTC reactions of carbonyl compounds with TRI (Scheme 4).

Carbanions usually add *trans* to acetylenes to generate a highly basic vinylic anion.[9] In the case of symmetrically disubstituted acetylenes, protonation of this anion gives *E* alkenes. The simultaneous formation of *Z* and *E* isomers of products **2** is probably result of competitive *cis* (minor pathway) and *trans* (major pathway) addition of **1** to DCA. Due to more sterically crowded carbon center in enolate anions, in comparison with nitrile ones, some products **2** are formed in a non-stereoselective fashion. On the other hand, formation of **6a**,**b** with possibly *E*-geometry of dichlorovinyl group, indicates *trans*-addition of enolate anion to DCA. The O-center of the enolate anion is less sterically crowded than the C-centered anion and this explains why in the case of aldehydes **5** only one, possibly *E*-isomer of **6**, is isolated.

As a result of our investigations, PTC dichlorovinylation is extended to relatively acidic ketones **1**, cyanoketone **3** and phenylacetaldehyde derivatives **5**, to afford respectively, C-**2**,**4** or O-substituted derivatives **6**. The process is very simple, performed on easily available substrates (ketones **1a**–**e** can be prepared by PTC alkylation of desoxybenzoine[10]), and affords the products in good yields. Chloroacetylenes are strong lachrymators and react violently with oxygen from air.[11] However, the described reactions are safe since they are carried out in ethyl ether which forms a stable complex with DCA.[12]

Experimental

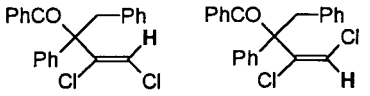
General

Boiling points and melting points (determined in open capillary tube apparatus) are uncorrected. ^{1}H NMR spectra were measured in $CDCl_3$ on a Varian Gemini 200 or Varian Gemini 500 (at 200 or 500 MHz, respectively), ^{13}C NMR spectra on a Varian Gemini 200 (at 50 MHz). Chemical shifts (δ) are given in ppm relative to TMS and coupling constants (J) are given in Hz. Gas chromatography (GC)

Table 1. 1,2-Dichlorovinylated ketones **2a**–**h**

Entry	**2**	Reaction conditions		Yield (%)	Bp (°C/Torr)[a] or mp (°C)	*E*/*Z*[b]	Purity (%)[b]
		Temp. (°C)	Time (h)				
1	**a**	20–25	6	63	155–160/0.2	2.3	95
2	**b**	20–25	6.5	71	155–160/0.15	2.3[c]	99
3	**c**	20–25	6	62	160–165/0.1	2.0[d]	98
4	**d**	5–10	6.5	54	150–155/0.3	2.0	82
5	**e**	5–10	7	79	170–175/0.1	1.8[e]	98.5
6	**f**	5–10	6	62	155–160/0.2	[f]	89
7	**g**	20–25	6	76	116–117 (MeOH)	[f]	ca 100
8	**h**	20–25	5.5	83	114–115 (MeOH)	[f]	ca 100

[a] Kugelrohr distillation (bath temperature).
[b] Determined in distilled or crystallized products by GC and/or ^{1}H NMR.
[c] *E*-**2b**, mp 92–93°C (EtOH).
[d] *E*-**2c**, mp 68–69°C (EtOH).
[e] *Z*-**2e**, mp 94–95°C (MeOH), *E*-**2e**, mp 100–101.5°C (MeOH).
[f] One, possibly *E* isomer (by GC and/or ^{1}H NMR).



	Z-2e	E-2e
measured	δ_H = 5.34 ppm	δ_H = 5.55 ppm
calcd	δ_H = 6.02 ppm	δ_H = 6.18 ppm

Figure 1.

analyses were performed with a Hewlett–Packard 5890 Series II chromatograph, equipped with HP50+ capillary column (30 m). IR spectra were recorded on Perkin–Elmer 577 spectrometer, liquids as films and solids as potassium bromide pellets. Elemental analyses were performed with a Perkin–Elmer CHNO/S Series II, 2400 microanalyzer. Column chromatography was carried out on Merck Kieselgel 60 (230–400 mesh) with hexane–ethyl acetate as eluent. Ketones **1a**–**e**,[10] **1f**,[13] **1g**,[14] **1h**,[15] and **3**[16] were prepared according to literature procedures. Commercially available aldehydes **5a**,**b** were vacuum distilled before use.

Caution: We have never encountered the explosive nature of dichloroacetylene but its fumes may explode on contact with air.

Preparation of dichlorovinyl substituted derivatives 2a–h and 4

A mixture of ketone **1a**–**h** or **3** (20 mmol), 50% aq. NaOH (6.6 g, 4.3 mL, 80 mmol), ethyl ether (5 mL; 10 mL in the case of **3**) and TBAHS (0.07 g, 0.2 mmol) was stirred, while a solution of TRI (3.4 g, 2.3 mL, 26 mmol) in ethyl ether (3 mL) was slowly added (ca 0.5 h) at the temperature indicated in Table 1, in the case of **3** at 20–25°C (small exothermal effect was observed). The mixture was stirred at the temperature and for the time given in Table 1 (in the case of **3** at 20–25°C for 6 h), diluted with water (25 mL), the phases were separated, the water phase was extracted with ethyl ether (2×15 mL), combined organic extracts were washed with water (2×20 mL), dried ($MgSO_4$), the solvent was evaporated, the residue was distilled on Kugelrohr apparatus or crystallized, and analyzed by GC and/or ^1H NMR to determine ratio of *Z*/*E* isomers as well as their purity (Table 1). Pure *E* isomers of **2b**,**c** and pure *Z* and *E* isomers of **2e** were isolated from distillates respectively by crystallization or by fractional crystallization (Table 1). Analytical samples of **2a**,**d**,**f** were prepared by column chromatography.

(*Z*+*E*)-**2a**, yellow oil [Found C, 64.91; H, 5.44; Cl, 24.24. $C_{16}H_{16}Cl_2O$ requires C, 65.09; H, 5.46; Cl, 24.02]; ν_{max} (film) 3108, 3060, 2972, 2932, 1624, 1492, 1444, 1096, 760, 700 cm^{-1}; δ_H (500 MHz, $CDCl_3$, in parentheses data for *E* isomer) 0.93 (1.02) [3H, t, *J*=18.5 Hz (19.0 Hz), CH_3], 2.42 (2.68) [2H, q, *J*=18.5 Hz (19.0 Hz), CH_2], 5.26 (5.46) [1H, s, HC=], 7.04–7.56 (10H, m, ArH of both isomers).

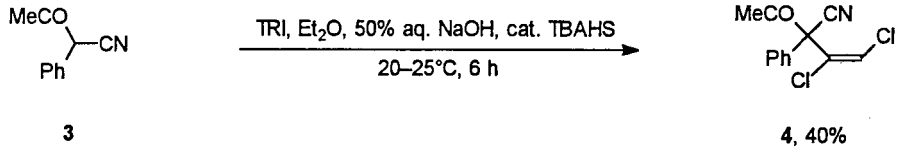
Z-**2b**, colorless oil; ν_{max} (film) 3104, 3060, 2960, 2928, 1624, 1464, 1444, 1100, 760, 700 cm^{-1}; δ_H [200 MHz, $CDCl_3$, read from the spectrum of (*Z*+*E*)-**2b**] 0.77 (3H, t, *J*=7.1 Hz, CH_3), 1.20–1.31 (4H, m, CH_2), 2.40 (2H, t, *J*=7.4 Hz, CH_2), 5.28 (1H, s, HC=), 7.28–7.35 (1H, m, ArH), 7.38–7.45 (7H, m, ArH), 7.50–7.55 (2H, m, ArH).

E-**2b**, colorless crystals [Found C, 68.96; H, 5.79; Cl, 20.19. $C_{20}H_{20}Cl_2O$ requires C, 69.17; H, 5.80; Cl, 20.42]; ν_{max} (KBr) 3104, 3060, 2956, 2928, 1620, 1496, 1444, 1100, 768, 704 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 0.88 (3H, t, *J*=7.0 Hz, CH_3), 1.33–1.38 (4H, m, CH_2), 2.66 (2H, t, *J*=7.5 Hz, CH_2), 5.46 (1H, s, HC=), 7.07–7.18 (6H, m, ArH), 7.23–7.42 (3H, m, ArH), 7.50–7.52 (1H, m, ArH).

Z-**2c**, pale yellow oil; ν_{max} (KBr) 3100, 3062, 2954, 2928, 1622, 1494, 1444, 1104, 764, 702 cm^{-1}; δ_H [200 MHz, $CDCl_3$, read from the spectrum of (*Z*+*E*)-**2c**] 0.83 (3H, t, *J*=7.7 Hz, CH_3), 1.05–1.41 (8H, m, CH_2), 2.38 (2H, t, *J*=6.4 Hz, CH_2), 5.28 (1H, s, HC=), 7.26–7.55 (10H, m, ArH).

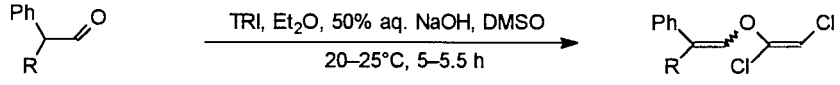
E-**2c**, colorless crystals [Found C, 70.3; H, 6.41; Cl, 18.69. $C_{22}H_{24}Cl_2O$ requires C, 70.4; H, 6.44; Cl, 18.89]; ν_{max} (KBr) 3100, 3060, 2960, 2928, 1624, 1492, 1444, 1104, 764, 700 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 0.95 (3H, t, *J*=7.7 Hz, CH_3), 1.44–1.68 (8H, m, CH_2), 2.64 (2H, t, *J*=6.7 Hz, CH_2), 5.49 (1H, s, HC=), 7.12–7.51 (10H, m, ArH).

(*Z*+*E*)-**2d**, yellow oil [Found C, 68.75; H, 4.60; Cl, 21.12. $C_{19}H_{16}Cl_2O$ requires C, 68.89; H, 4.68; Cl, 21.41]; ν_{max} (film) 3104, 3060, 3028, 2960, 2928, 2864, 1688, 1624, 1448, 1268, 1104, 828, 760, 700 cm^{-1}; δ_H (200 MHz,



3 **4, 40%**

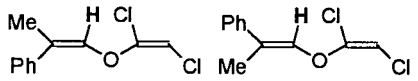
Scheme 2.



5a, R = Me
5b, R = Ph

6a, 70%
6b, 75%

Scheme 3.



	Z-**6a**	*E*-**6a**
measured	δ_H = 6.76 ppm	δ_H = 6.48 ppm
calcd	δ_H = 6.76 ppm	δ_H = 6.50 ppm

Figure 2.

$CDCl_3$) 1.82–1.88 (2.22–2.31) [2H, m, CH_2], 4.93–5.14 (2H, m, H_2C= for both isomers), 5.68–5.95 (1H, m, HC= for both isomers), 6.45 (6.95) [1H, s, HCCl=], 7.06–8.11 (10H, m, ArH of both isomers).

Z-**2e**, colorless crystals [Found C, 72.60; H, 4.60; Cl, 18.48. $C_{23}H_{18}Cl_2O$ requires C, 72.68; H, 4.77; Cl, 18.65]; ν_{max} (KBr) 3084, 3060, 2920, 2852, 1620, 1496, 1444, 1100, 1056, 700 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 3.80 (2H, s, CH_2), 5.34 (1H, s, HC=), 7.10–7.14 (3H, m, ArH), 7.19–7.23 (3H, m, ArH), 7.26–7.30 (2H, m, ArH), 7.38–7.40 (5H, m, ArH), 7.57–7.59 (2H, m, ArH); δ_C (50 MHz, $CDCl_3$) 39.17, 99.35, 126.04, 126.73, 127.04, 127.78, 127.93, 128.22, 128.28, 128.53, 128.93, 129.05, 129.21, 129.45, 218.46.

E-**2e**, colorless crystals [Found C, 72.55; H, 4.62; Cl, 18.42. $C_{23}H_{18}Cl_2O$ requires C, 72.68; H, 4.77; Cl, 18.65]; ν_{max} (KBr) 3096, 3060, 2920, 2852, 1620, 1496, 1444, 1100, 1054, 700 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 3.92 (2H, s, CH_2), 5.55 (1H, s, HC=), 7.08–7.19 (6H, m, ArH), 7.25–7.31 (2H, m, ArH), 7.37–7.41 (5H, m, ArH), 7.52–7.61 (2H, m, ArH); δ_C (50 MHz, $CDCl_3$) 38.42, 99.12, 125.96, 126.09, 126.78, 127.66, 127.93, 128.16, 128.33, 129.01, 129.76, 129.92, 212.03.

E-**2f**, pale yellow oil [Found C, 58.91; H, 3.35; Cl, 32.34. $C_{16}H_{11}Cl_3O$ requires C, 59.02; H, 3.40; Cl, 32.66]; ν_{max} (KBr) 3104, 3072, 1612, 1440, 1248, 1096, 824, 696 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 5.29 (1H, s, HC=), 7.10–7.55 (7H, m, ArH), 7.56–7.96 (3H, m, ArH).

E-**2g**, colorless crystals [Found C, 68.83; H, 4.36; Cl, 18.21. $C_{22}H_{16}Cl_2O_2$ requires C, 68.94; H, 4.20; Cl, 18.49]; ν_{max} (KBr) 3108, 3020, 1612, 1476, 1444, 1096, 828, 700 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 5.52 (1H, s, HC=), 6.88–7.00 (3H, m, ArH), 7.15–7.37 (9H, m, ArH), 7.55–7.71 (3H, m, ArH).

E-**2h**, yellow crystals [Found C, 66.07; H, 4.19; Cl, 16.85. $C_{22}H_{16}Cl_2OS$ requires C, 66.17; H, 4.04; Cl, 17.05]; ν_{max} (KBr) 3100, 3028, 1624, 1488, 1444, 1132, 760, 692 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 5.58 (1H, s, HC=), 7.03–7.31 (8H, m, ArH), 7.36–7.39 (3H, m, ArH), 7.61–7.68 (4H, m, ArH).

4, pale yellow oil [Found C, 56.66; H, 3.54; N, 5.45; Cl, 27.66. $C_{12}H_9NOCl_2$ requires C, 56.72; H, 3.56; N, 5.51; Cl, 27.80]; ν_{max} (film) 2956, 2864, 2244, 1616, 1460, 1036, 760, 700 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 2.48 (3H, s, CH_3), 6.02 (1H, s, HC=), 7.36–7.57 (5H, m, ArH).

Preparation of enol ethers 6a,b

Aldehyde **5** (50 mmol), TRI (8.5 g, 6.0 mL, 65 mmol), ethyl ether (7.3 mL) and DMSO (10 mL) were stirred, while 50% aq. NaOH (16.0 g, 10.0 mL, 200 mmol) was added slowly dropwise at 20°C, and the mixture was stirred at 20–25°C for 5–5.5 h, worked-up as above and distilled on Kugelrohr apparatus. Fresh analytical samples of **6a**,**b** were isolated by column chromatography.

(*Z*+*E*)-**6a**, colorless oil (8.0 g, 70%), purity 98%, bp 125–130°C/0.3 Torr; [Found C, 57.62, H, 4.38, Cl, 30.81. $C_{11}H_{10}Cl_2O$ requires C, 57.67, H, 4.4, Cl, 30.94]; ν_{max} (film) 3100, 2920, 1620, 1115, 760, 700 cm^{-1}; δ_H (200 MHz, $CDCl_3$, in parentheses data for *Z* isomer) 2.08 (2.21) [3H, d, *J*=1.4 Hz (1.4 Hz), CH_3], 5.64 (5.68) [1H, s, HCCl=], 6.48 (6.76) [1H, q, *J*=1.4 Hz (1.4 Hz), HC=), 7.22–7.40 (3H, m, ArH of both isomers), 7.60–7.65 (2H, m, ArH of both isomers).

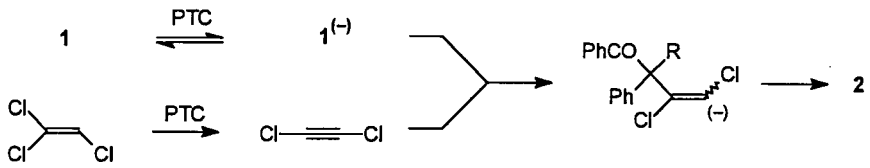
6b, colorless oil (10.9 g, 75%), purity 98%, bp 165–170°C/0.3 Torr; [Found C, 65.89; H, 4.08, Cl, 24.15. $C_{16}H_{12}Cl_2O$ requires C, 65.99, H, 4.15, Cl, 24.35]; ν_{max} (film) 3050, 1615, 1100, 770, 700 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 5.71 (1H, s, HC=), 6.84 (1H, s, HC=), 7.25–7.68 (10H, m, ArH).

Acidic cleavage of enol ethers 6

Divinyl ether **6** (0.4 mmol), dioxane (5 mL), water (5 mL) and conc. hydrochloric acid (0.1 mL) were refluxed for 2 h, diluted with water (15 mL), extracted with ethyl ether (3×10 mL), the organic extracts were washed with water (2×15 mL), dried ($MgSO_4$) and evaporated. The residue was analyzed by GC to show aldehydes **5** (main component) and other products.

Reaction of ketone 1b with DCA

Complex[8b] of DCA with ethyl ether (0.9 g, ca 5 mmol of DCA) was added dropwise to a mixture of **1b** (1.0 g, 4 mmol), TBAHS (0.01 g, 0.04 mmol), 50% aq. NaOH (1.3 g, 0.85 mL, 16 mmol) and ethyl ether (5 mL), during stirring. The mixture was stirred at 20–25°C for 5 h, and worked up as described above for preparation of **2a**–**h** and



Scheme 4.

4. The residue after evaporation of the solvent was analyzed by GC to show ca 58% of *E* and *Z*-**2b** (ratio ca 1.5:1), ca 14% of unreacted **1b**, and other products.

Acknowledgements

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References

1. Hopf, H.; Witulski, B. *Modern Acetylene Chemistry*; Stang, P. J., Diederich, F., Eds.; VCH: Weinheim, 1995; pp 48–66.
2. Kende, A. S.; Fludzinski, P.; Hill, J. H.; Swenson, W.; Clardy, J. *J. Am. Chem. Soc.* **1984**, *106*, 3551–3562 (and references cited therein).
3. Jończyk, A.; Gierczak, A. H. *Synthesis* **1998**, 962–964.
4. (a) Dehmlow, E. V.; Dehmlow, S. S. *Phase Transfer Catalysis*, 3rd ed.; Verlag Chemie: Weinheim, 1993. (b) Starks, C. M.; Liotta, C. L.; Halpern, M. *Phase-transfer Catalysis*; Chapman and Hall: New York, London, 1994. (c) Mąkosza, M.; Fedoryński, M. *Pol. J. Chem.* **1996**, *70*, 1093–1110. (d) Mąkosza, M.; Fedoryński, M. In *Handbook of Phase Transfer Catalysis*; Sasson, Y.; Neumann, R., Eds.; Blackie Academic and Professional: London, 1997; pp 135–167.
5. Günther, H. *NMR Spectroscopy. An Introduction*, Wiley: Chichester, 1980 (Polish translation; PWN: Warszawa, 1983; pp 118–123).
6. The differences in calcd versus measured chemical shifts $\delta_{HC=}$ for *Z*-**2e** and *E*-**2e** are possibly due to unknown values of increments of $PhCOC(CH_2Ph)Ph$ substituent. To calculate $\delta_{Z\text{-}HC=}$ and $\delta_{E\text{-}HC=}$ of **2e** we assumed $\delta_Z=-0.26$ ppm and $\delta_E=-0.29$ ppm,[5] respectively.
7. Jończyk, A.; Serafin, B.; Mąkosza, M. *Roczniki Chem.* **1971**, *45*, 1027–1039; *Chem. Abstr.* **1971**, *75*, 109997e.
8. (a) Pielichowski, J.; Popielarz, R. *Synthesis* **1984**, 433–434. (b) Pielichowski, J.; Bogdał, D. *J. Prakt. Chem.* **1989**, *331*, 145–148.
9. (a) Deslongchamps, P. *Stereoelectronic Effects in Organic Chemistry*; Baldwin, J. E., Ed.; Organic Chemistry Series; Pergamon: Oxford, 1983; Vol. 1, pp 291–294. (b) Jończyk, A.; Pakulski, Z. *Tetrahedron Lett.* **1996**, *37*, 8909–8912 and references cited therein.
10. Mąkosza, M.; Jończyk, A.; Serafinowa, B.; Mroczek, Z. *Roczniki Chem.* **1973**, *47*, 77–88; *Chem. Abstr.* **1973**, *79*, 18305u.
11. Ref. 1, pp 49, 53.
12. Ref. 1, p 54.
13. Ward, A. M. *Org. Synth., Coll. Vol. II* **1943**, 159–160.
14. Bradsher, C.; Rosher, R. *J. Am. Chem. Soc.* **1939**, *61*, 1524–1525.
15. Schönberg, A.; Iskander, Y. *J. Chem. Soc.* **1942**, 90–95.
16. Julian, P. L.; Oliver, J. J.; Kimball, R. H.; Pike, A. B.; Jefferson, G. D. *Org. Synth., Coll. Vol. II* **1943**, 487–489.