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Synthesis of Stable N-Substituted Phosphorous Ylides of Triazene and Triazole and Chemoselective Investigation

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ABSTRACT

Triazene and trizole derivatives have biological and industrial activities. For instance N-substituted phosphorous benzotriazole derivatives are used for peptide synthesis. This study describes a simple, efficient and metal free method for synthesis of N-substituted derivatives of benzotriazoles and diphenyltriazenes containing phosphorous atom through a chemoselective process. The chemical structures of the new compounds were confirmed by elemental and spectral (^{1}H NMR, ^{13}C NMR and IR) analysis.

Keyword: Triazole, triazene, Chemoselective reaction, phosphorous ylide

INTRODUCTION

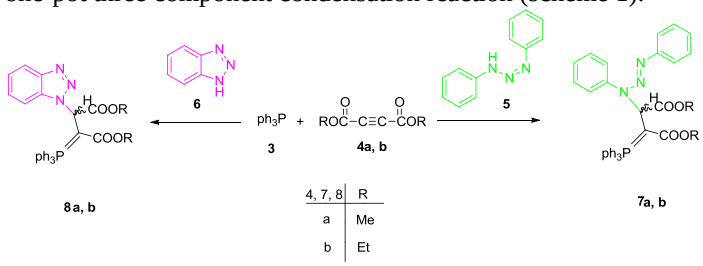
Doubtless, organic compounds containing nitrogen heteroatoms play an important role in industrial additives as well as pharmaceutical compounds and related intermediate, specifically in drug discovery process. Among These compounds triazenes and triazoles captured our attention for many reasons; mainly due to their biological activities. Aryl triazene and benzotrizole derivatives are interesting structures considering their biological and industrial activities. Aryl triazene derivatives have antiviral and cytotoxic activities [1]. Some derivatives of them are also possessing antitumor characterization [2]. On the other hand, organic compounds containing triazene moiety are well-known compounds in the pharmaceutical and medicinal fields [3-5].

N-substituted benzotriazoles also are widely used in synthetic organic chemistry [6] and materials science [7]. Furthermore, benzotriazole derivatives have also pharmaceutical importance possessing several remarkable biological activities[8**]**, such as antibacterial[9,10] antifungal[11], antiadrenergic and DNA cleavage[12] antitubercular[13], anticancer and antiemetic[14], antitumor[15**],** anti-inflammatory[16], anticonvulsant as protein kinase inhibitors[17,18] and respiratory syndrome protease inactivators[19] analgesic[20] and antiviral[21]. Besides, macro chemical companies have lunched diverse and expensive new N-substituted phosphorous benzotriazole derivatives for peptide synthesis recently [22]. The biological activities of derivatives of both aryl triazenes and benzotriazoles aroused our interest in seeking an innovative, uncomplicated and efficient method for synthesis of N-substituted derivatives of benzotriazoles and aryl triazenes containing phosphorous atom.

Phosphorous ylides are reactive systems which take part in many reactions of value in organic synthesis [23, 24]. Organo phosphorous compounds bearing a carbon atom directly bond to a phosphorous atom are synthetic targets of interest, because widely used as reagents for linking synthetic building blocks through the formation of carbon-carbon double bonds [25, 26]. Over the last few years, several methods have been developed for preparation of phosphorous ylides [27-29]. Recently, these ylides are prepared by treatment of phosphonium salts which is produced by Micheal addition of phosphorus nucleophiles to active olefins followed by nucleophiles attack.

In recent years, Ren has reported a regioselective synthesis of N- substituted benzotriazoles from aryltriazenes via a novel 1, 7-palladium migration and intermolecular amination-dealkylation sequence [30]. Due to potentially toxic contamination of pharmaceutical products, effective removal of Pd or Cu in active pharmaceutical ingredients (API) poses critical health problems [31]. On the basis of API For large scale synthesis, it is better to avoid the use of Pd during the last three steps and place Pd-coupling reactions early in the process in order to reducing the amount of metal throughout the synthesis. Practically, when a synthetic scheme requires the use of a metal such as Pd at the end of a synthesis and the standards of metal content permitted in the API are exceeded, it is necessary to find a disposal method such as Nano-filtration or use scavenging agents, which is costly in time and money [31]. Considering the above reports, it is not surprising that many synthetic routes have been developed for these compounds [32-37]. However, to the best of our knowledge there is no report of a reaction product formed from benotriazole or aryltriazene, triphenylphosphine and acetylenedicarboxilates. So, as a part of our ongoing program to develop new, efficient and environmentally friendly methods for the preparation of biological active compounds from readily available building blocks [38-42], we undertook a study to achieve a green synthesis of novel benzotriazole and diphenyltriazene intermediate derivatives (precursor for other N-substituted

triazens) via a facile, metal free, environmentally benign and one-pot three component condensation reaction (scheme 1).

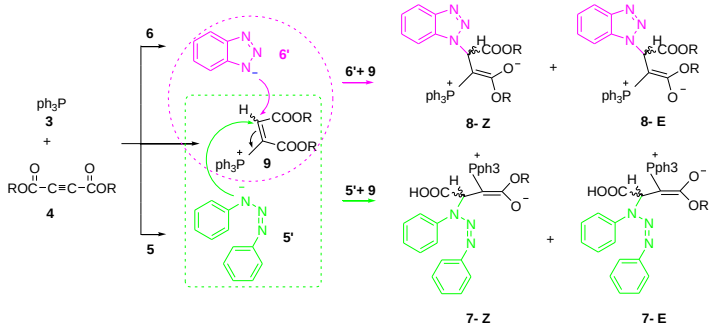


Scheme 1 synthesis of benzotriazole and triazene phosphorous ylides via metal free reaction medium

Capability of the reaction toward the interamolecular chemoselectivity was investigated. The results of our investigation showed that benzotriazole **6** reacts with triphenylphosphine and dialkyl acetylene dicarboxilate **4** in the presence of diphenyltriazene **5**, to produce stable N- substituted phosphorus ylide **8** in a chemoselective manner and at the end of the reaction, diphenyltriazene **5** was recovered. It is pertinent that this reaction is an interamolecular chemoselective reaction. Moreover, phosphorus stable intermediate **7** was not observed.

RESULTS AND DISCUSSION

We have not established a mechanism for the formation **7, 8** experimentaly, but on the basis of the well-established chemistry of trivalent phosphorus nucleophiles,[43, 44] phosphorus ylides **7, 8** was produced in the nucleophilic reaction between triphenylphosphine and dialkyl acetylene dicarboxilate **4**. Subsequently, protonation of the high reactive 1:1 adduct by diphenyltriazene **5** or benzotriazole **6** leads to the vinyltriphenylphosphonium salt **9**, follow by the attack of the triazene anion on the vinyltriphenylphosphonium cation to form the corresponding phosphorans (Scheme 2).

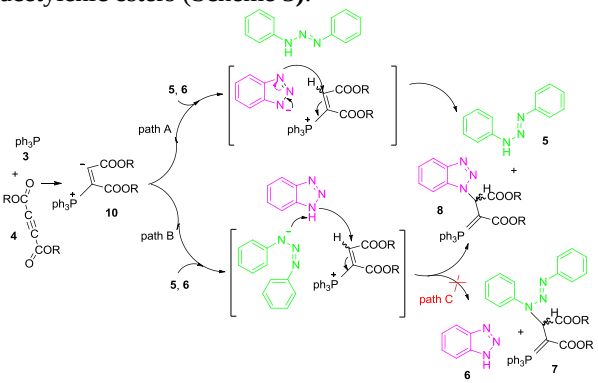


Scheme 2 proposed mechanism for synthesis of stable intermediates 7, 8

All the compounds **7a, b** and **8a, b** are stable solid powders whose structures are fully supported by elemental analysis, ^{1}H, ^{13}C NMR and IR spectral data. The NMR spectra of phosphoranes **7a, b** and **8a, b** exhibited them to be a mixture of two conformational stereo isomers. The ylide moiety of these compounds is strongly conjugated with the adjacent ester group and the rotation about the partial double bond in **7**-Z, **7**-E and also **8**-Z, **8**-E diastereoisomer pairs is slow on the NMR timescale at ambient temperature (Scheme 2). Rotamer forms in phosphoranes have been previously established and reported in the literature [45-47].

The ^{1}H NMR data of compounds 7 and 8 showed the 7-E and 7-Z rotamers in about 10-15% to 85-90% mole ratio while the percentage for rotamers 8-E and 8-Z were showed 25-30% and 70-75% respectively. The ^{1}H NMR spectrum of compounds **8a** exhibited two sharp lines at δ 3.19 and 3.72 arising from methoxy protons which correspond to the *Z*-isomer, and two singlets at 3.70 and 3.71 ppm for *E*-isomer. The shift at 3.19 of the methyl group of the *Z*-isomer is shielded due to the anisotropic effect of phenyl groups of triphenylphosphine. This effect confirms that the **8**-*E* and **8**-*Z* isomers appear as the minor and major rotamers, respectively. The signals for methine protons appeared at δ 5.86 and δ 5.76 as two doublets with coupling constant 16.1 and 17.8 Hz, respectively for the *Z*- and *E*- diastereoisomers. The ^{1}H NMR spectrum of **8b** is similar to that of **8a** except its ester group, which showed characteristic signals with appropriate chemical shafts. The ^{1}H NMR spectrum of **7a-c** shows a different pattern from those of **8a** and **8b**. They also show two doublets and four sharp singlet signals for methine and methyl protons respectively which is in accord to the single rotamers Z and E. The ^{13}C NMR spectrum of **8a** displayed 32 distinct resonances in agreement with the mixture of two phosphorane rotamers. Partial assignments of the ^{13}C NMR resonance for compound **8a-b** and **7a-b** are given in experimental section. Although, existence of two conformational stereo isomers E and Z for **7a-b** and **8a-b** were proved by ^{1}H and ^{13}C NMR data, further evidence was obtained from ^{31}P NMR spectra. In each spectrum of both **7a-b** and **8a-b** compounds two singlets ^{31}P signals were observed at about δ 24 ppm (downfield from 85% H_3PO_4) for *E* and *Z* rotamers, respectively. These shifts are similar to those observed for stable phosphorus ylides ($ph_3P{=}C$) [48]. The structural assignments made on the basis of the ^{1}H and ^{13}C NMR spectra of compounds **7a–b** and **8a–b** were supported by their IR spectra. The carbonyl region of the spectrum exhibited absorption bands at 1727-1741 cm^{-1} and carbon-carbon double bonds shown absorption bands at 1641-1649 cm^{-1}.

For chemoselectivity assessment of the reaction toward benzotriazole and diphenyltriazene we examined that in the equimolar **5** and **6** in the presence of triphenylphosphine and acetylenic esters (Scheme 3**)**.



Scheme 3 plausible mechanism for chemoselective formation of **8** in the present of equimolar **5** and **6** as reactant

Adduct **10** can be protonated in two paths A and B. Both of these two paths were terminated to the stable N- substituted phosphorus ylide **8** in a chemoselective manner and path C did not occur. At the end of the reaction, diphenyltriazene **5** was recovered and phosphorus intermediate **7** was not observed.

The results of our investigation exhibited that in this reaction benzotriazole **6** is more reactive than diphenyltriazene **5** and it is pertinented that this is an interamolecular chemoselective reaction.

In conclusion, we have described an efficient chemoselective one-pot procedure for phosphorus derivatives of 1,2,3-triazenes and triazoles. Excellent yields, easy work-up, being eco-friendly, one-pot and atom economy are the main aspects of presented method. Furthermore, to the best of our knowledge this procedure provides the first example of three-component method for the synthesis of dialkyl-2-(1,2,3-triazene or triazole)-3-(triphenylphosphosphoranylidene)-butanedioate derivatives. Besides, we were able to divert the route of the reaction of 1,2,3-diphenyltriazene, dialkyl acetylenedicarboxilate and triphenylphosphine derivatives in the presence of benzotriazole from phosphoran **7** to compound **8**. It is evident that this reaction is an interamolecular chemoselective reaction. Moreover, we determined the free enthalpy of activation for exchange between Z and E conformers might be useful in pharmacological studies. So, phosphoran ylides **7a-b** and **8a-b** may be considered potentially useful synthetic intermediates and we expect to find numerous applications for this protocol in the pharmaceutical fields.

EXPERIMENTAL

The chemical used in this work were obtained from Fluka and Merck and were used without purification. Melting points were measured on an Elecrtothermal 9100 apparatus and uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a BRUKER DRX-250 AVANCE spectrometer at 250 and 62.5 MHz, respectively. ^{1}H, ^{13}C and ^{31}P NMR spectra were obtained on solutions in $CDCl_3$ using tetramethylsilane (TMS) as internal standard. Chemical shifts have been given as δ values against TMS and *J* values in Hz. IR spectra were recorded using an FTIR apparatus. Elemental analyses were performed on a Heraeus CHN-O rapid analyzer.

General procedure for preparation of dimethyl-2-(N1-benzotriazole)-3-(triphenylphosphosphoranylidene)-butanedioate **(8a)**

At -5°C a mixture of dimethyl acetylenedicarboxylate (60 µL, 0.5 mmol) in 1 ml ethyl acetate was added dropwise to a magnetically stirred solution of triphenylphosphine (0.13 g, 0.5 mmol), benzotriazol (0.06 g, 0.5 mmol) in ethyl acetate (3 mL) over 10 min. After the addition was completed the reaction solution was allowed to warm up to room temperature and stirred for 3 h and the product was subsequently filtered. The solid collected in the filter was washed thoroughly with cold diethylether (2-3 ml) to afford the pure product **8a** as white powder, yield (96%). Mp 172-173°C (decomp.). IR (KBr) (υ_{max}, cm^{-1}): 1729 (C=O), 1629 (C=C). Anal. Calcd. for $C_{30}H_{26}N_3O_4P$: C, 68.83; H, 5.01; N, 8.03. Found: C, 68.89; H, 4.96; N, 7.98.

Major rotamer (8a; Z). (75%) ^{1}H NMR (250.1 MHz, $CDCl_3$, Me_4Si) δ_H (ppm)
3.19 and 3.72 (6H, 2s, 2OCH_3), 5.86 (1H, d, $^{3}J_{HP}$ 16.1 Hz, P-C-*CH*), 7.38-8.10 (19H, m, $3C_6H_5$ and C_6H_4); ^{13}C NMR ($CDCl_3$, Me_4Si) δ_c (ppm) 42.19 (d, $^{1}J_{CP}$ 125.8 Hz, P=*C*), 49.47 and 52.81 (2s, 2O*Me*), 64.01 (d, $^{2}J_{pc}$ 15.9 Hz, P-C-*C*H), 113.15, 119.12, 123.36 and 126.83 (4CH, C_6H_4), 125.80 (d, $1J_{CP}$ 91.8 Hz, C_{ipso}), 128.88 (d, $^{3}J_{CP}$ 12.3 Hz, C_{meta}), 132.40 (d, $^{4}J_{CP}$ 2.6 Hz, C_{para}), 133.60 (d, $^{2}J_{CP}$ 9.8 Hz, C_{orto}), 146.40 (s, 2C, C_6H_4), 169.49 (d, $^{3}J_{CP}$ 12.8 Hz, C=O ester), 170.59 (d, $^{3}J_{CP}$ 13.3 Hz, C=O ester). ^{31}P NMR ($CDCl_3$, H_3PO_4) δ_P (ppm) 23.59 (s, ph_3P=C).

Minor rotamer (8a; E). (25%) ^{1}H NMR (250.1 MHz, $CDCl_3$, Me_4Si) δ_H (ppm)
3.70 and 3.71 (6H, 2s, 2OCH_3), 5.76 (1H, d, $^{3}J_{HP}$ 17.8 Hz, P-C-*CH*), 7.38-8.10 (19H, m, $3C_6H_5$ and C_6H_4); ^{13}C NMR ($CDCl_3$, Me_4Si) δ_c (ppm) 42.36 (d, $^{1}J_{CP}$ 125.8 Hz, P=*C*), 50.48 and 52.70 (2s, 2O*Me*), 63.31 (d, $^{2}J_{pc}$ 15.6 Hz, P-C-*C*H), 111.85, 119.52, 123.30 and 126.60 (4CH, C_6H_4), 125.26 (d, $1J_{CP}$ 91.8 Hz, C_{ipso}), 128.94 (d, $^{3}J_{CP}$ 12.3 Hz, C_{meta}), 132.05 (d, $^{4}J_{CP}$ 2.6 Hz, C_{para}), 133.55 (d, $^{2}J_{CP}$ 9.8 Hz, C_{orto}), 146.50 (s, 2C, C_6H_4), 169.98 (d, $^{3}J_{CP}$ 14.2 Hz, C=O ester), 170.88 (d, $^{3}J_{CP}$ 13.1 Hz, C=O ester). ^{31}P NMR ($CDCl_3$, H_3PO_4) δ_P (ppm) 23.78 (s, ph_3P=C).

diethyl-2-(N1-benzotriazole)-3-(triphenylphosphosphoranylidene)-butanedioate **(8b)**

White powder, yield (94%). Mp 149-150 °C (decomp.). IR (KBr) (υ_{max}, cm^{-1}): 1741 (C=O), 1632 (C=C). Anal. Calcd. for $C_{32}H_{30}N_3O_4P$: C, 69.68; H, 5.48; N, 7.62. Found: C, 69.73; H, 5.51; N, 7.54.

Major rotamer (8b; Z). (78%) ^{1}H NMR (250.1 MHz, $CDCl_3$, Me_4Si) δ_H (ppm)
0.47 and 1.19 (6H, 2t, $^{3}J_{HH}$ 7.30 Hz, 2O-C-CH_3), 3.74 and 4.19 (4H, 2q, $^{3}J_{HH}$ 7.3 Hz, 2O-CH_2-C), 5.87 (1H, d, $^{3}J_{HP}$ 16.7 Hz, P-C-*CH*), 7.38-8.10 (19H, m, $3C_6H_5$ and C_6H_4); ^{13}C NMR ($CDCl_3$, Me_4Si) δ_c (ppm) 13.92 and 14.10 (2s, 2O-C-*C*), 42.10 (d, $^{1}J_{CP}$ 126.3 Hz, P=*C*), 58.13 and 61.68 (2s, 2O-*C*-C), 64.12 (d, $^{2}J_{pc}$ 15.8 Hz, P-C-*CH*), 113.45, 119.04, 123.29 and 126.76 (4CH, C_6H_4), 126.10 (d, $^{1}J_{CP}$ 91.9 Hz, C_{ipso}), 128.81 (d, $^{3}J_{CP}$ 11.9 Hz, C_{meta}), 132.33 (d, $^{4}J_{CP}$ 2.9 Hz, C_{para}), 133.66 (d, $^{2}J_{CP}$ 9.8 Hz, C_{orto}), 146.34 and 146.40 (2s, 2C, C_6H_4), 169.99 (d, $^{3}J_{CP}$ 12.8 Hz, C=O ester), 177.21(d, $^{3}J_{CP}$ 12.7 Hz, C=O ester). ^{31}P NMR ($CDCl_3$, H_3PO_4) δ_P (ppm) 23.14 (s, ph_3P=C).

Minor rotamer (8b; E). (22%) ^{1}H NMR (250.1 MHz, $CDCl_3$, Me_4Si) δ_H (ppm)
1.20 and 1.26 (6H, 2t, $^{3}J_{HH}$ 7.1 Hz, 2O-C-CH_3), 3.80 and 4.18 (4H, 2q, $^{3}J_{HH}$ 7.1 Hz, 2O-CH_2-C), 5.73 (1H, d, $^{3}J_{HP}$ 18.5 Hz, P-C-*CH*), 7.38-8.10 (19H, m, $3C_6H_5$ and C_6H_4); ^{13}C NMR ($CDCl_3$, Me_4Si) δ_c (ppm) 11.18 and 11.50 (2s, 2O-C-*C*), 37.43 (d, $^{1}J_{CP}$ 131.2 Hz, P=*C*), 57.64 and 61.59 (2s, 2O-*C*-C), 64.03 (d, $^{2}J_{pc}$ 18.7 Hz, P-C-*CH*), 113.39, 119.48, 123.98 and 126.68 (4CH, C_6H_4), 125.61 (d, $^{1}J_{CP}$ 98.1 Hz, C_{ipso}), 128.89 (d, $^{3}J_{CP}$ 12.5 Hz, C_{meta}), 132.54 (d, $^{4}J_{CP}$ 2.8 Hz, C_{para}), 133.62 (d, $^{2}J_{CP}$ 9.8 Hz, C_{orto}), 145.21 and 146.49 (2s, 2C, C_6H_4), 173.28 (d, $^{3}J_{CP}$ 16.9 Hz, C=O ester), 174.49 (d, $^{3}J_{CP}$ 17.1 Hz, C=O ester). ^{31}P NMR ($CDCl_3$, H_3PO_4) δ_P (ppm) 23.84 (s, ph_3P=C).

dimethyl-2-(N1-1,3-diphenyl triazene)-3-(triphenylphosphosphoranylidene)-butanedioate **(7a)**

Yellow powder, yield (95%). Mp 194°C (decomp.). IR (KBr) (υ_{max}, cm^{-1}): 1743 (C=O), 1647 (C=C). Anal. Calcd. for $C_{36}H_{32}N_3O_4P$: C, 71.87; H, 5.36; N, 6.98. Found: C, 71.94; H, 5.35; N, 6.93.

Major rotamer (7a; Z). (80%) ^{1}H NMR (250.1 MHz, $CDCl_3$, Me_4Si) δ_H (ppm)

3.05 and 3.83 (6H, 2s, 2O*CH*$_3$), 5.89 (1H, d, $^3J_{HP}$ 17.5 Hz, P-C-*CH*), 7.10-7.63 (25H, m, 3C_6H_5-P and 2C_6H_5-N); ^{13}C NMR ($CDCl_3$, Me_4Si) δ_c (ppm) 39.43 (d, $^1J_{CP}$ 124.4 Hz, P=*C*), 49.17 and 52.61 (2s, 2O*Me*), 59.74 (d, $^2J_{pc}$ 15.8 Hz, P-C-*C*H), 121.19, 123.62, 124.81, 125.67, 128.15 and 128.31 (6s, 10CH, 2C_6H_5-N), 126.16 (d, 1J_{CP} 91.1 Hz, C_{ipso}), 128.58 (d, $^3J_{CP}$ 12.5 Hz, C_{meta}), 131.91 (d, $^4J_{CP}$ 2.5 Hz, C_{para}), 133.38 (d, $^2J_{CP}$ 10.0 Hz, C_{orto}), 142.84 and 149.89 (2s, 2C_{ipso} , 2C_6H_5-N), 169.28 (d, $^3J_{CP}$ 12.6 Hz, C=O ester), 171.89 (d, $^3J_{CP}$ 11.3 Hz, C=O ester). ^{31}P NMR ($CDCl_3$, H_3PO_4) δ_P (ppm) 23.38 (s, ph_3*P*=C).

Minor rotamer (7a; E). (20%) ^{1}H NMR (250.1 MHz, $CDCl_3$, Me_4Si) δ_H (ppm)

3.57 and 3.79 (6H, 2s, 2O*CH*$_3$), 6.23 (1H, d, $^3J_{HP}$ 16.5 Hz, P-C-*CH*), 7.10-7.63 (25H, m, 3C_6H_5-P and 2C_6H_5-N); ^{13}C NMR ($CDCl_3$, Me_4Si) δ_c (ppm) 40.63 (d, $^1J_{CP}$ 133.4 Hz, P=*C*), 50.21 and 52.34 (2s, 2O*Me*), 59.64 (d, $^2J_{pc}$ 18.6 Hz, P-C-*C*H), 122.41, 124.08, 125.34, 125.54, 128.06 and 128.40 (6s, 10CH, 2C_6H_5-N), 125.70 (d, 1J_{CP} 91.5 Hz, C_{ipso}), 128.64 (d, $^3J_{CP}$ 12.5 Hz, C_{meta}), 132.13 (d, $^4J_{CP}$ 2.6 Hz, C_{para}), 133.51 (d, $^2J_{CP}$ 10.1 Hz, C_{orto}), 142.97 and 149.00 (2s, 2C_{ipso} , 2C_6H_5-N), 169.73 (d, $^3J_{CP}$ 12.1 Hz, C=O ester), 172.45 (d, $^3J_{CP}$ 14.1 Hz, C=O ester). ^{31}P NMR ($CDCl_3$, H_3PO_4) δ_P (ppm) 23.19 (s, ph_3*P*=C).

diethyl-2-(N1-1,3-diphenyl triazene)-3-(triphenylphosphosphoranylidene)-butanedioate **(7b)**

Yellow powder, yield (93%). Mp 137-138 °C (decomp.). IR (KBr) (υ_{max}, cm^{-1}): 1732 (C=O), 1644 (C=C). Anal. Calcd. for $C_{38}H_{36}N_3O_4P$: C, 72.48; H, 5.76; N, 6.67. Found: C, 72.41; H, 5.79; N, 6.73.

Major rotamer (7b; Z). (90%) ^{1}H NMR (250.1 MHz, $CDCl_3$, Me_4Si) δ_H (ppm)

0.37 and 1.25 (6H, 2t, $^3J_{HH}$ 7.0 Hz, 2O-C-*CH*$_3$), 3.55 and 3.73 (4H, 2q, $^3J_{HH}$ 7.1 Hz, 2O-*CH*$_2$-C), 5.87 (1H, d, $^3J_{HP}$ 17.8 Hz, P-C-*CH*), 7.11-7.69 (25H, m, 3C_6H_5-P and 2C_6H_5-N); ^{13}C NMR ($CDCl_3$, Me_4Si) δ_c (ppm) 14.12 and 14.32 (2s, 2O-C-*C*), 42.09 (d, $^1J_{CP}$ 126.3 Hz, P=*C*), 58.13 and 61.68 (2s, 2O-*C*-C), 64.14 (d, $^2J_{pc}$ 15.6 Hz, P-C-*CH*), 113.45, 119.04, 119.48, 123.29, 126.68 and 132.14 (6s, 10CH, 2C_6H_5-N), 126.10 (d, $^1J_{CP}$ 91.9 Hz, C_{ipso}), 128.80 (d, $^3J_{CP}$ 12.5 Hz, C_{meta}), 132.33 (d, $^4J_{CP}$ 3.1 Hz, C_{para}), 133.66 (d, $^2J_{CP}$ 9.3 Hz, C_{orto}), 138.00 and 146.40 (2s, 2C_{ipso} , 2C_6H_5-N), 170.10 (d, $^3J_{CP}$ 13.9 Hz, C=O ester), 177.52 (d, $^3J_{CP}$ 12.2 Hz, C=O ester). ^{31}P NMR ($CDCl_3$, H_3PO_4) δ_P (ppm) 24.29 (s, ph_3*P*=C).

Minor rotamer (7b; E). (10%) ^{1}H NMR (250.1 MHz, $CDCl_3$, Me_4Si) δ_H (ppm)

1.22 and 1.30 (6H, 2t, $^3J_{HH}$ 7.5 Hz, 2O-C-*CH*$_3$), 3.51 and 3.77 (4H, 2q, $^3J_{HH}$ 7.5 Hz, 2O-*CH*$_2$-C), 5.83 (1H, d, $^3J_{HP}$ 18.9 Hz, P-C-*CH*), 7.11-7.69 (25H, m, 3C_6H_5-P and 2C_6H_5-N); ^{13}C NMR ($CDCl_3$, Me_4Si) δ_c (ppm) 11.18 and 11.50 (2s, 2O-C-*C*), 43.50 (d, $^1J_{CP}$ 121.2 Hz, P=*C*), 57.64 and 61.58 (2s, 2O-*C*-C), 64.05 (d, $^2J_{pc}$ 16.3 Hz, P-C-*CH*), 116.25, 118.57, 122.15, 124.82, 126.6 and 133.15 (6s, 10CH, 2C_6H_5-N), 125.80 (d, $^1J_{CP}$ 90.7 Hz, C_{ipso}), 128.90 (d, $^3J_{CP}$ 12.5 Hz, C_{meta}), 132.21 (d, $^4J_{CP}$ 2.6 Hz, C_{para}), 133.62 (d, $^2J_{CP}$ 10.0 Hz, C_{orto}), 145.21 and 147.12 (2s, 2C_{ipso} , 2C_6H_5-N), 167.04 (d, $^3J_{CP}$ 11.5 Hz, C=O ester), 173.41 (d, $^3J_{CP}$ 10.6 Hz, C=O ester). ^{31}P NMR ($CDCl_3$, H_3PO_4) δ_P (ppm) 24.84 (s, ph_3*P*=C).

General procedure for chemoselectivity assessment of the reaction toward benzotriazole and 1,3-diphenyltriazene

At -5°C a mixture of dialkylyl acetylenedicarboxylate (0.5 mmol) in 1 ml ethyl acetate was added dropwise to a magnetically stirred solution of triphenylphosphine (0.13 g, 0.5 mmol), benzotriazol (0.06 g, 0.5 mmol) and 1,3-diphenyl triazene (0.1 g, 0.5 mmol) in ethyl acetate (3 mL) over 10 min. After the addition was completed the reaction solution was allowed to warm up to room temperature and stirred for 3 h and the product was subsequently filtered. The solid collected in the filter was washed thoroughly with cold diethylether (2-3 ml) to afford the pure product **8**.

Product **8a,** white powder, yields (95%). Mp 171-172°C (decomp.). Anal. Calcd. for $C_{30}H_{26}N_3O_4P$: Found: C, 68.78; H, 5.04; N, 8.08. The percentage of rotamers Z: E were determined 75: 25.

Product **8b,** white powder, yields (92%). Mp 149°C (decomp.). Anal. Calcd. for $C_{32}H_{30}N_3O_4P$: Found: C, 69.64; H, 5.53; N, 7.65. The percentage of rotamers Z: E were determined 78: 22.

CONCLUSION

In conclusion, we have described an efficient chemoselective one-pot procedure for phosphorus derivatives of 1,2,3-triazenes and triazoles. Excellent yields, easy work-up, being eco-friendly, one-pot and atom economy are the main aspects of presented method. Furthermore, to the best of our knowledge this procedure provides the first example of three-component method for the synthesis of dialkyl-2-(1,2,3-triazene or triazole)-3-(triphenylphosphosphoranylidene)-butanedioate derivatives. Besides, we were able to divert the route of the reaction of 1,2,3-diphenyltriazene, dialkyl acetylenedicarboxilate and triphenylphosphine derivatives in the presence of benzotriazole from phosphoran **7** to compound **8**. It is evident that this reaction is an interamolecular chemoselective reaction. So, phosphoran ylides **7a-b** and **8a-b** may be considered potentially useful synthetic intermediates and we expect to find numerous applications for this protocol in the pharmaceutical fields.

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