Reaction of diaryltriazenes with dimethyl acetylenedicarboxylate and PPh_3 as a method for synthesis of polyfunctional trisubstituted triazenes

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A series of triazene derivatives with polyfunctional substituents, such as the ylide moiety and ester groups, were synthesized by the reaction of dimethyl acetylenedicarboxylate with 1,3-diaryl-1-triazenes in the presence of triphenylphosphine in ethyl acetate.

Key words: 1,3-diphenyl-1-triazene, dimethyl acetylenedicarboxylate, phosphorus compounds.

Triazenes compose a class of compounds attracting increased interest in the recent time. These compounds were studied from the viewpoint of their anticancer properties and used as protecting groups in the synthesis of natural compounds and for the synthesis of new heterocycles.[1—4]

1,3-Diphenyl-1-triazene (diazoaminobenzene) was used in the synthesis of polymers and dyes; in addition, it was found as an impurity in colorants used in food products,[5] lipsticks, and orally and externally applied drugs.[6] Exposure of humans to 1,3-diphenyl-1-triazene induces many toxic effects, including eye and skin irritation, as well as nausea and vomiting. The conversion of such compounds to systems containing polyfunctional groups, which favor their successful use in organic synthesis, has been an important goal for chemists for a long time from both the theoretical and synthetic points of view. In the present work, we studied the multicomponent conversion of 1,3-diaryltriazenes to a system containing polyfunctional groups, *viz.*, phosphorus-ylide moiety and carbonyl groups. The advantage of this system is due to the presence of several functional groups, which considerably increase the synthetic potential for the preparation of alkenes,[7] heterocyclic compounds,[8] and antibiotics.[9]

Results and Discussion

Compounds **1a—d** were synthesized by the one-pot reaction of 1,3-diaryl-1-triazenes **2a—d** with dimethyl acetylenedicarboxylate (**3**) in the presence of triphenylphosphine in ethyl acetate (Scheme 1). As shown by TLC, the reaction was completed in 30 min, and the triazene derivatives were isolated as yellow powders.

Taking into account the well studied[10—12] chemistry of trivalent phosphorus, it is reasonable to assume that triazenes **1a—d** are formed due to the primary addition of triphenylphosphine to compound **3** and protonation of the adduct (1 : 1) by compound **2**. Then the positively charged ion attacks by the conjugated base to form triazenes **1** (Scheme 2). The structure of compounds **1a—d** was proved by ^1H and ^{13}C NMR spectroscopy, IR spectroscopy, mass spectrometry, and elemental analysis. The obtained results agree with the presence of two rotamers. In these compounds the ylide moiety is strongly conjugated with the adjacent carbonyl group, and rotation about this bond in geometric isomers *E*-**1** and *Z*-**1** is hindered at room temperature. The presence of the geometric isomers in phosphoranes has been found earlier.[13—16] For instance, the ^1H NMR spectrum of compound **1a** contains four distinct lines belonging to the methoxyl protons at δ 3.06, 3.83 and 3.59, 3.80 for the *Z*- and *E*-isomers, respectively, and the signal of the methine protons at δ 5.92, appearing as a doublet ($^3J_{P,H}$ = 17.3 Hz). The aromatic protons are manifested as a multiplet at δ = 7.08—7.65. The ^{13}C NMR spectrum of compound **1a** exhibits twenty seven distinct resonance signals according to the presence of two rotamers. Although the presence of the ^{31}P nuclei impedes the ^1H and ^{13}C NMR spectra of compound **1a**, this helps to assign signals of the far-range spin-spin interaction of the ^1H and ^{13}C nuclei. Compounds **1b—d** have similar ^1H and ^{13}C NMR spectra, except for the signal of the methyl group in the spectrum of **1b**, which appears with the corresponding chemical shift.

Thus, the new method of conversion of 1,3-diaryl-1-triazenes to the system containing polyfunctional groups in an appropriate yield was developed. Advantages of this

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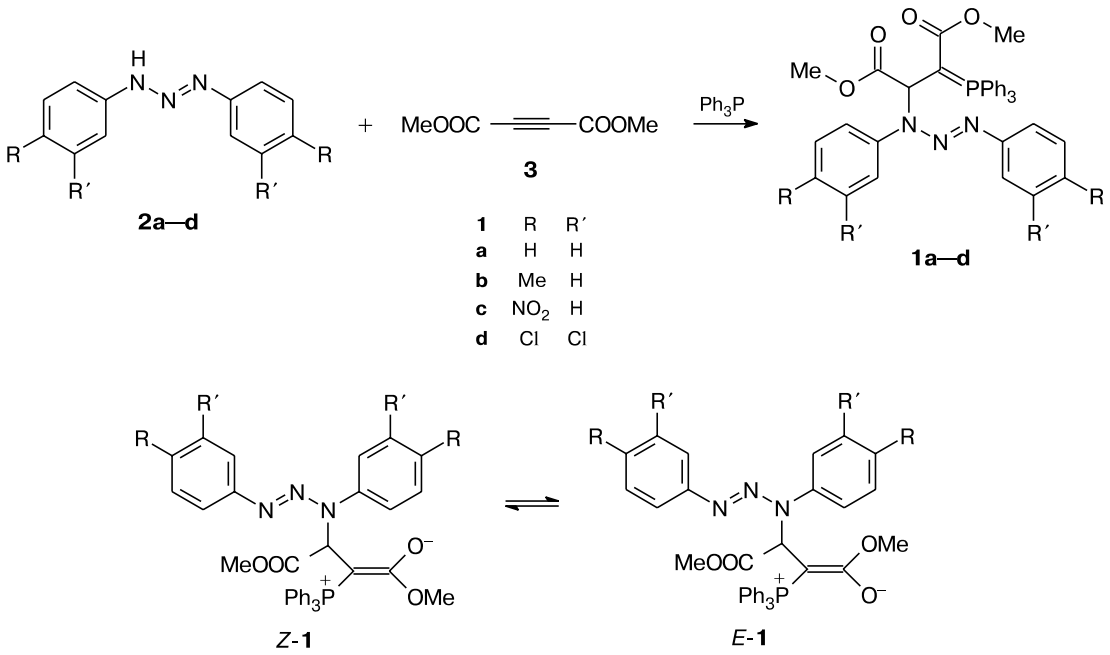
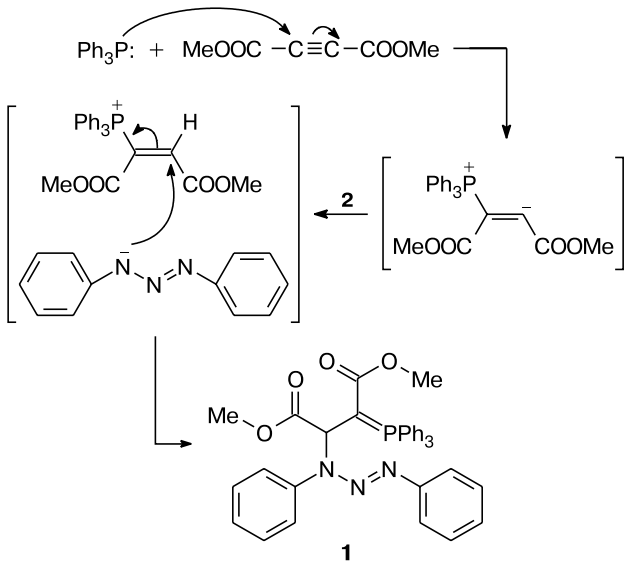
Scheme 1



Scheme 2



method are neutral conditions of the reaction and simplicity of the one-pot procedure.

Experimental

Dimethyl acetylenedicarboxylate and triphenylphosphine (Merck Chemical Co.) were used without additional purification. Melting points were determined on a Gallenkamp instrument and used uncorrected. Elemental analysis was carried out at the Tarbiat Moallem University on a Heracus CHN-O-Rapid analyzer. IR spectra were recorded on a Mattson 1000 FT-IR spectrometer (Unicam, Great Britain) (KBr pellets). ^{1}H and ^{13}C NMR spectra were measured on a Bruker DRX-500 AVANCE instrument (500 and 125.77 MHz, respectively). 1,3-Diaryl-1-triazenes were synthesized according to earlier described procedures.[17]

Dimethyl-2-(1,3-diphenyl-2-triazenyl)-3-(1,1,1-triphenyl-λ^5-phosphanylidene)succinate (1a). Dimethyl acetylenedicarboxylate (0.24 mL, 2 mmol) was added dropwise for ~10 min at ~20 °C to a stirred solution of triphenylphosphine (0.52 g, 2 mmol) and 1,3-diphenyl-1-triazene (0.28 g, 2 mmol) in ethyl acetate (10 mL). Then the mixture was additionally stirred for 20 min and filtered. The solid substance was washed with ethyl acetate, and compound **1c** (0.90 g, 75%) was obtained as a yellow powder, m.p. 178—179 °C. Found (%): C, 71.21; H, 5.42; N, 6.92. $C_{36}H_{32}N_3O_4P$ (M = 601.65). Calculated (%): C, 71.87; H, 5.36; N, 6.98. IR, ν_{max}/cm^{-1}: 3081 and 2950 (CH); 1765, 1641 (C=O); 1443 (C=C). Major conformer (*Z*)-**1a** (75%). ^{1}H NMR, δ: 3.06, 3.83 (both s, 6 H each, 2 OMe); 5.92 (d, 1 H, P=C—CH, $^3J_{P,H}$ = 17.3 Hz); 7.08—7.65 (m, 50 H, Ph). ^{13}C NMR, δ: 39.45 (d, P=C, $^1J_{P,C}$ = 125.0 Hz); 49.15, 52.57 (2 OMe); 59.82 (d, P=C—CH, $^2J_{P,C}$ = 15.1 Hz); 121.22, 124.84, 125.70 (3 CH); 126.26 (d, C_i, $^1J_{P,C}$ = 91.7 Hz); 128.16, 128.34 (2 CH); 128.61 (d, C_m, $^3J_{P,C}$ = 12.2 Hz); 131.91 (C_p); 133.41 (d, C_o, $^2J_{P,C}$ = 9.8 Hz); 149.96 (C_i); 169.28 (d, C=O, $^2J_{P,C}$ = 12.7 Hz); 171.85 (d, C=O, $^3J_{P,C}$ = 14.5 Hz). Minor conformer (*E*)-**1a** (24%). ^{1}H NMR, δ: 3.59, 3.80 (both s, 6 H each, 2 OMe). ^{13}C NMR, δ: 40.75 (d, P=C, $^1J_{P,C}$ = 138.4 Hz); 50.17, 52.31 (2 OMe); 123.69, 123.70 (2 CH); 125.76 (d, C_i, $^1J_{P,C}$ = 92.3 Hz); 128.07 (CH); 128.66 (d, C_m, $^3J_{P,C}$ = 12.2 Hz); 133.53 (d, C_o, $^2J_{P,C}$ = 10.1 Hz); 142.92 (C_i); 170.02 (d, C=O, $^2J_{P,C}$ = 17.7 Hz); 171.70 (d, C=O, $^3J_{P,C}$ = 13.2 Hz).

Dimethyl-2-[1,3-bis(4-methylphenyl)-2-triazenyl]-3-(1,1,1-triphenyl-λ^5-phosphanylidene)succinate (1b). The yield was 0.96 g

(76%), m.p. 168—169 °C. Found (%): C, 72.06; H, 5.85; N, 6.64, $C_{38}H_{36}N_3O_4P$ (M = 629.70). Calculated (%): C, 72.48; H, 5.76; N, 6.67. IR, ν_{max}/cm^{-1}: 3081, 2960 (CH); 1741 (C=O); 1666 (C=O); 1440 (C=C). Major conformer (*Z*)-**1b** (80%). ^{1}H NMR, δ: 2.29, 2.34 (both s, 6 H each, 2 Me); 3.05, 3.80 (both s, 6 H each, 2 OMe); 5.84 (d, 1 H, P=C—CH, $^3J_{P,H}$ = 17.5 Hz); 6.87—7.70 (m, 46 H, Ph). ^{13}C NMR, δ: 20.90, 21.01 (2 Me); 39.43 (d, P=C, $^1J_{P,C}$ = 125.4 Hz); 49.07, 52.24 (2 OMe); 59.68 (d, P=C—CH, $^2J_{P,C}$ = 12.6 Hz); 126.36 (d, C_i, $^1J_{P,C}$ = 91.2 Hz); 128.46 (d, C_m, $^3J_{P,C}$ = 11.8 Hz); 128.61, 128.91 (2 CH); 129.75 (C_p); 131.82, 131.87, 131.89, 132.05, 132.13, 133.38 (6 CH); 133.45 (d, C_o, $^2J_{P,C}$ = 9.8 Hz); 147.88 (C_i); 169.23 (d, C=O, $^2J_{P,C}$ = 12.7 Hz); 171.84 (d, C=O, $^3J_{P,C}$ = 14.5 Hz). Minor conformer (*E*)-**1b** (20%). ^{1}H NMR, δ: 2.45, 2.47 (both s, 6 H each, 2 Me). ^{13}C NMR, δ: 20.91, 20.98 (2 Me); 39.48 (d, P=C, $^1J_{P,C}$ = 116.5 Hz); 50.05, 52.44 (2 OMe); 123.72 (CH); 125.89 (d, C_i, $^1J_{P,C}$ = 91.1 Hz); 128.47 (d, C_m, $^3J_{P,C}$ = 10.7 Hz); 128.52, 129.14, 129.99, 131.84, 132.27, 133.09, 134.20, 135.06 (8 CH); 133.58 (d, C_o, $^2J_{P,C}$ = 9.8 Hz); 140.60 (C_i).

Dimethyl-2-[1,3-bis(4-nitrophenyl)-2-triazenyl]-3-(1,1,1-triphenyl-λ^5-phosphanylidene)succinate (1c). The yield was 1.10 g (80%), m.p. 184—185 °C. Found (%): C, 62.17; H, 4.47; N, 9.44. $C_{36}H_{30}N_5O_8P$ (M = 691.63). Calculated (%): C, 62.52; H, 4.37; N, 10.13. IR, ν_{max}/cm^{-1}: 3081, 2957 (CH); 1740, 1666 (C=O); 1443 (C=C). Major conformer (*Z*)-**1c** (81.6%). ^{1}H NMR, δ: 3.10, 3.85 (both s, 6 H each, 2 OMe); 5.99 (d, 1 H, P=C—CH, $^3J_{P,H}$ = 16.8 Hz); 7.25—8.25 (m, 46 H, Ph). ^{13}C NMR, δ: 38.68 (d, P=C, $^1J_{P,C}$ = 123.4 Hz); 49.05, 52.55 (2 OMe); 60.66 (d, P=C—CH, $^2J_{P,C}$ = 17.2 Hz); 121.29, 124.34, 122.80, 123.47 (4 CH); 125.27 (d, C_i, $^1J_{P,C}$ = 91.8 Hz); 128.34 (d, C_m, $^3J_{P,C}$ = 12.3 Hz); 131.91 (d, C_p, $^4J_{P,C}$ = 2.5 Hz); 132.80 (d, C_o, $^2J_{P,C}$ = 9.8 Hz); 144.59, 144.75, 145.47, and 147.28 (4 C_i); 168.90 (d, C=O, $^2J_{P,C}$ = 12.4 Hz); 169.90 (d, C=O, $^3J_{P,C}$ = 15.0 Hz). Minor conformer (*E*)-**1c** (18.4%). ^{1}H NMR, δ: 3.66, 3.80 (both s, 6 H each, 2 OMe). ^{13}C NMR, δ: 50.11, 52.30 (2 OMe); 124.70 (d, C_i, $^1J_{P,C}$ = 91.3 Hz); 128.04 (d, C_m, $^3J_{P,C}$ = 12.2 Hz); 132.96 (d, C_o, $^2J_{P,C}$ = 9.7 Hz); 169.19 (d, C=O, $^2J_{P,C}$ = 12.5 Hz).

Dimethyl-2-[1,3-bis(3,4-dichlorophenyl)-2-triazenyl]-3-(1,1,1-triphenyl-λ^5-phosphanylidene)succinate (1d). The yield was 1.20 g (81%), m.p. 180—18 °C. Found (%): C, 57.98; H, 3.67; N, 5.68. $C_{36}H_{28}Cl_4N_3O_4P$ (M = 739.42). Calculated (%): C, 58.48; H, 3.82; N, 5.68. IR, ν_{max}/cm^{-1}: 3081, 2954 (CH); 1741, 1666 (C=O); 1442 (C=C). Major conformer (*Z*)-**1d** (73.7%). ^{1}H NMR, δ: 3.09, 3.83 (both s, 6 H, 2 OMe); 5.79 (d, 1 H, P=C—CH, $^3J_{P,H}$ = 16.8 Hz); 6.98—7.63 (m, 42 H, Ph). ^{13}C NMR, δ: 39.11 (d, P=C, $^1J_{P,C}$ = 125.3 Hz); 49.34, 52.78 (2 OMe); 60.74 (d, P=C—CH, $^2J_{P,C}$ = 13.6 Hz); 120.61, 122.78, 123.07, 125.30 (4 CH); 125.88 (d, C_i, $^1J_{P,C}$ = 91.8 Hz); 128.68 (d, C_m, $^3J_{P,C}$ = 12.2 Hz); 129.48 (C_i); 129.57, 130.15 (2 CH); 131.85, 131.93, 132.39 (C_i); 132.18 (d, C_p, $^4J_{P,C}$ = 2.6 Hz); 133.27 (d, C_o, $^2J_{P,C}$ = 9.7 Hz); 141.92, 148.85 (2 C_i); 169.24 (d, C=O, $^2J_{P,C}$ = 12.4 Hz); 170.74 (d, C=O, $^3J_{P,C}$ = 17.5 Hz). Minor conformer (*E*)-**1d** (26.3%). ^{1}H NMR, δ: 3.61, 3.81 (both s, 6 H each, 2 OMe). ^{13}C NMR, δ: 50.30, 52.52 (2 OMe); 125.40 (d, $^1J_{P,C}$ = 92.3 Hz).

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