Reaction of 1-*tert*-butyl-3,4-diphenyl-1,2,4-triazol-5-ylidenes with a malonic ester†

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Four stable carbenes, 1-*tert*-butyl-3,4-diaryl-1,2,4-triazol-5-ylidenes **1a–d**, including new fluorine-containing compounds **1c,d**, react with a malonic ester to afford heterocyclic zwitterionic compounds **5a–d**. The reactions with more acidic compounds (ethyl acetoacetate, malononitrile and 1,3-dimethylbarbituric acid) proceed with substrate deprotonation to form the respective azolium salts **6a–c**. The X-ray crystal structure of **5a** was also determined.

Introduction

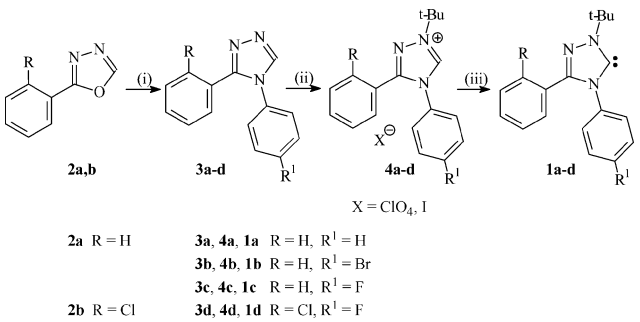
The reactions of *in situ*-generated carbenes with C–H acidic compounds are well known. For example, Pazdro and Polaczkova[1] showed that dithiol-2-ylidene dimers will insert into the C–H bonds of malononitrile, acetylacetone, ethyl acetoacetate and cyclopentanone to afford the corresponding dihydrodithiol derivatives. However, it is not clear whether such reactions really proceed *via* the intermediacy of a free carbene. Similar transformations with acetonitrile, dimethyl sulfone and acetylene (pK_a = 20–25) have been studied with stable carbenes[2–5] and resulted in the isolation of the respective C–H insertion products, *i.e.* cyanomethylazolines.

To the best of our knowledge,[6] the reactions of isolable carbenes with an ester functional group have not been studied thus far. However, it is known that *in situ*-generated 1,3-diphenylcyclopropene-2-ylidene reacts with the C=C bond of dimethyl fumarate to form a spirocyclic adduct.[7] Likewise, the stable (phosphanyl)(silyl)carbenes react with the double bond of dimethyl fumarate and other electron-poor alkenes to give the corresponding *trans*-cyclopropanes.[8] In the case of the reaction of 1,3,4-triphenyl-1,2,4-triazol-5-ylidene, the initially formed [2 + 1] cycloaddition product undergoes ring opening and a 1,2-hydrogen shift to afford methylenetriazoline derivatives.[9]

In the present contribution we describe (i) the synthesis of new stable fluorine-containing carbenes of the 1,2,4-triazole series, namely 1-*tert*-butyl-3-aryl-4-fluoroaryl-1,2,4-triazol-5-ylidenes; (ii) the first Claisen reaction of stable carbenes with an ester functional group of malonic esters to form new heterocyclic zwitterionic compounds; and (iii) the deprotonations of 1,3-dimethylbarbituric acid, malononitrile and ethyl acetoacetate by the carbene.

Results and discussion

The stable carbenes **1a–d**, including the new stable fluorine-containing carbenes **1c,d**, were synthesized by the ring transformations of 2-phenyl-1,3,4-oxadiazole **2a,b** with anilines in the presence of trifluoroacetic acid according to the literature method,[10] followed by quaternization of the resulting triazoles **3a–d** with *t*-BuI to form the triazolium salts **4a–d** (Scheme 1). Deprotonation of the latter salts with potassium *tert*-butoxide in tetrahydrofuran solution afforded the desired carbenes **1a–d**. It is noteworthy that the quaternization of triazoles **3a–d** takes place exclusively at the 1-position, hence only one isomer of salt **4a–d** is formed. The generation of *tert*-butyl iodide was carried out *in situ* by treatment of *tert*-butyl chloride with sodium iodide in acetic acid solution.



Scheme 1 *Reagents and conditions*: (i) *p*-H_2N-C_6H_4-R^1 (− H_2O); (ii) 1. *t*-BuI; 2. $NaClO_4$; (iii) *t*-BuOK (− *t*-BuOH).

A two-stage isolation of carbenes **1a–d** by solvent evaporation in the presence of an inorganic salt permitted complete decomposition of the intermediate triazolium alkoxides. In the method described earlier,[5] the carbenes were isolated by filtration of the inorganic salt, concentration of the filtrate and recrystallisation of the crystalline residues in order to remove the remaining azolium alkoxide impurities.

The reactions of carbenes **1a–d** with diethyl malonate (pK_a = 13) were carried out in refluxing toluene for 2–4 h under conditions such that evolved ethanol was removed by a controlled stream of nitrogen. If this procedure is not followed, the reaction times

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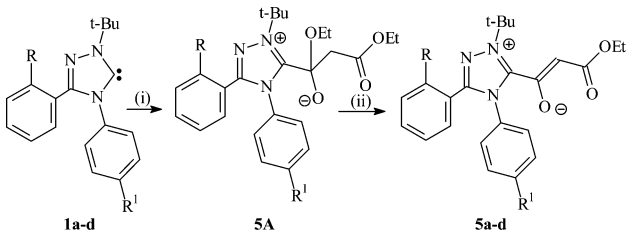
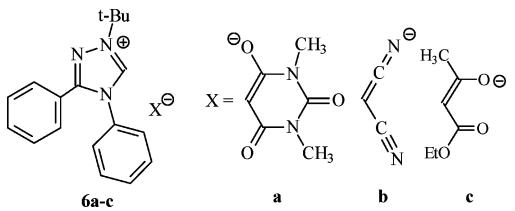
increase to ~40 h and the transformations are incomplete. Following work-up of the reaction mixtures, the zwitterionic compounds **5a–d** were obtained in isolated yields of 51–81%. The outcomes of the reactions can be rationalized on the basis of initial nucleophilic attack of the carbene on the ester functional group to form intermediate **5A** (Scheme 2), followed by loss of EtOH to produce the zwitterionic compounds **5a–d**. It is noteworthy that C–H insertion products are not observed in these processes. Moreover, this new transformation can be considered to be a carbene analogue of the Claisen reaction of esters.



1a, **5a** R = H, R^1 = H
1b, **5b** R = H, R^1 = Br
1c, **5c** R = H, R^1 = F
1d, **5d** R = Cl, R^1 = F

Scheme 2 *Reagents and conditions*: (i) $CH_2(COOEt)_2$, Δ; (ii) Δ (– EtOH).

The reaction of **1a** with 1,3-dimethylbarbituric acid (pK_a = 4.68) results in protonation of the substrate and affords salt **6a**. Compound **6a** is a stable compound that does not undergo further reaction. Less acidic malononitrile (pK_a = 9) and ethyl acetoacetate (pK_a = 11) also undergo reaction with carbene **1b** to afford salts **6b** and **6c**, respectively. Compound **6b** was isolated as a toluene solvate. Carbon–hydrogen insertion was not observed in any of these reactions.



Compounds **1** and **3–6** are colorless crystalline solids that were characterized by elemental analysis, ^{1}H, ^{13}C NMR, IR and mass spectroscopy. The molecular structure of compound **5a** was established by single-crystal X-ray diffraction.

The ^{1}H NMR spectra of salts **4c,d** feature the signals for the *tert*-butyl group (δ 1.72–1.76 ppm), aromatic protons (δ 7.3–7.7 ppm) and the C5-H proton of the triazolium nucleus (δ 10.65–10.73 ppm). The ^{1}H NMR spectra of carbenes **1c,d** exhibit similar signals for the *tert*-butyl (δ 1.78–1.79 ppm) and aromatic protons (δ 6.5–7.3 ppm). However, the chemical shift for the latter is notably upfield relative to that of the salt. The ^{13}C NMR spectra of **1c,d** exhibit resonances for the *tert*-butyl carbon atoms (δ 30.2–30.4 and *ipso*-C 59.2–59.4 ppm), aromatic nuclei (δ 115.0–164.0 ppm), C3 (δ 148.7–150.7 ppm) and the C5 atoms (δ 206.6–208.6 ppm) of the triazole nucleus. The ^{1}H NMR spectra of zwitterionic compounds **5a–d** are characterized by the presence of resonances for the *tert*-butyl protons (δ 1.80–1.87 ppm), aromatic protons (δ 7.0–7.5 ppm), the ethyl group of an ester fragment (δ 1.12–1.16 and 3.91–3.96 ppm), and the CHC group of an aliphatic fragment (δ 4.78–4.84 ppm). The ^{13}C NMR spectrum (see Fig. 1 for the atom numbering scheme) is distinguished by the presence of resonances for the *tert*-butyl carbon atoms (δ 28.6–28.8 and 65.8–66.1 ppm), the carbon atoms of the ethyl group (δ 14.5–14.7 and 58.0–58.1 ppm) and benzene nuclei (δ 115.8–134.0 ppm), the triazole atoms C1 and C2 (δ 149.0–150.5; 153.9–154.6 ppm), C21 of the aliphatic fragment (δ 90.3–90.6 ppm), and two signals for the carbonyl group (δ 163.7–164.4 and 170.9–171.2 ppm). The former signal was assigned to the C19=O group, and the latter to the C21=O moiety. The IR spectrum of **5a** shows the absence of typical carbonyl stretching vibrations. The detection of a vibration at 1653 cm^{-1} is consistent with the proposed delocalized structure for **5a**. The mass spectra of compounds **5a,c** show molecular ions $[MH]^+$ corresponding to the monomers (*m*/*z* 392.5 for **5a**; 410.0 for **5c**). The molecular ions of compounds **5b–d** undergo further decomposition by elimination of isobutene and malonyl fragments (see the Experimental section).

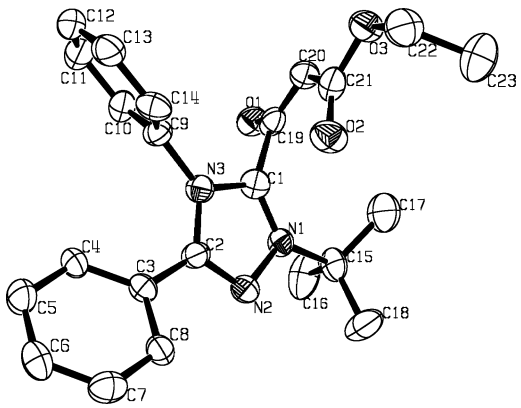


Fig. 1 X-Ray crystal structure of zwitterionic compound **5a**.†

Crystals of compound **5a** suitable for X-ray diffraction study were grown from diethyl ether solution. The X-ray data† confirm the ionic character of the triazole ring. Significant structural features are the somewhat elongated bonds of both C=O groups (123.6 and 126.6 pm), a shortened C19–C20 bond (137.3 pm) and, to a lesser extent, a shortened C20–C21 aliphatic linkage (141.9 pm) (see Fig. 1 and Fig. 2). The C1–C19 bond distance of 152.6 pm corresponds to that of a typical C–C single bond, and the C19=O1 carbonyl group is twisted with respect to the plane of the triazolium nucleus. The benzene rings attached to C2 and N3

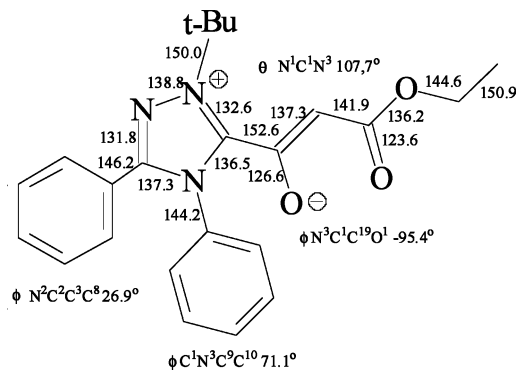


Fig. 2 Selected bond lengths (pm) and angles (°) for compound **5a**.

subtend dihedral angles of 26.9 and 71.1°, respectively, in relation to the plane of the triazolium ring. All the foregoing structural data are consistent with the proposed zwitterionic structure for **5a**.

The ^{1}H NMR spectra of the triazolium salts **6a–c** include signals that can be assigned to the protons of both the cation and the anion. Thus, the singlets at δ 9.70–10.90 ppm can be assigned to the C5-H proton of the cation, and the singlet at δ 3.50–4.05 ppm is attributable to the C2-H proton of the anion. Collectively, these data confirm the ionic structure for **6a–c**. The spectra for salts **6b,c** exhibit broad C5-H signals due to facile proton exchange.

Conclusion

In summary, we have demonstrated that the stable heteroaromatic carbenes 1-*tert*-butyl-3,4-diaryl-1,2,4-triazol-5-ylidenes **1a–d** react with the ester functional group of diethyl malonate to produce the heterocyclic zwitterionic derivatives **5a–d**. These reactions represent the first example of the carbene version of the Claisen reaction of esters. No evidence was found for C–H insertion reactions. It is known that less acidic C–H compounds either undergo insertion reactions with stable carbenes (for example, acetonitrile, ketones, sulfones, and acetylenes) or do not react (for example, dimethyl sulfoxide, alkylarenes, and saturated hydrocarbons). The reactions of **1a** with the appreciably more acidic C–H compounds, 1,3-dimethylbarbituric acid, malononitrile and ethyl acetoacetate, produce the salts **6a–c** *via* the protonation of the carbene.

Experimental

General methods

All experiments with the 1,2,4-triazol-5-ylidenes **1a–d** were carried out under an argon atmosphere. All solvents were dried by standard methods prior to use. ^{1}H and ^{13}C NMR chemical shifts are reported relative to tetramethylsilane (TMS, $\delta = 0.00$) as internal standard. Mass spectra were taken on an Agilent 1100 Series chromatomass spectrometer (APCI, 3 kV, chromatography: a column-Zorbax SB-C18, eluent acetonitrile–water 95 : 5 with 0.1% formic acid). IR spectra were measured as Nujol mulls, and thin-layer chromatography was performed on silica gel with chloroform or a 10 : 1 mixture of chloroform and methanol as eluent, followed by development with iodine. Elemental analyses were carried out at the Analytical Laboratory of the Litvinenko Institute of Physical Organic and Coal Chemistry.

General procedure for the synthesis of 1-*tert*-butyl-3,4-diphenyl-1,2,4-triazol-5-ylidenes 1a–d

Potassium *tert*-butoxide (280 mg, 2.55 mmol) was added to a dispersion of salt **4a–d** (2.65 mmol) in anhydrous tetrahydrofuran (10 mL) and stirred at room temperature for 0.5 h. The solvent was evaporated and the product was extracted with a further portion of tetrahydrofuran (10 mL). The latter solution was re-evaporated and the residue was stirred with petroleum ether (5 mL). The resulting solid was filtered off and dried to afford carbenes **1a–d**. The new fluorine-containing carbenes **1c,d** are characterized as detailed below.

1-*tert*-Butyl-3-phenyl-4-*p*-fluorophenyl-1,2,4-triazol-5-ylidene (1c). Yield 79%. Mp 180–182 °C (from toluene). Found: C, 73.1; H, 6.0; F, 6.3; N, 14.3. Calcd for $C_{18}H_{18}FN_3$: C, 73.2; H, 6.1; F, 6.4; N, 14.2%. δ_H (200 MHz, C_6D_6, Me_4Si) 1.78 (9H, s, CH_3C), 6.53 (2H, m, Ar), 7.02 (5H, m, Ar), 7.31 (2H, m, Ar). δ_C (50.3 MHz, C_6D_6, Me_4Si) 30.2 (*C*H_3C), 59.2 (CH$_3$*C*), 115.1, 115.6 (C3, ArN, *J* 22.8 Hz), 125.2 (C1, Ar-C), 128.3, 128.5, 129.39, 129.51 (Ar), 135.5 (C1, ArN), 150.7 (C3), 159.1, 164.0 (C–F, *J* 246.9 Hz), 206.6 (C5).

1-*tert*-Butyl-3-*o*-chlorophenyl-4-*p*-fluorophenyl-1,2,4-triazol-5-ylidene (1d). Yield 71%. Mp 103–105 °C (from toluene). Found: C, 65.8; H, 5.2; Cl, 10.7; F, 5.8; N, 12.6. Calcd for $C_{18}H_{17}ClFN_3$: C, 65.6; H, 5.2; Cl, 10.8; F, 5.8; N, 12.7%. δ_H (200 MHz, C_6D_6, Me_4Si) 1.79 (9H, s, CH_3C), 6.51 (2H, m, Ar), 6.72 (2H, m, Ar), 6.94 (1H, m, Ar), 7.13 (3H, m, Ar). δ_C (50.3 MHz, C_6D_6, Me_4Si) 30.4 (*C*H$_3$C), 59.4 (CH$_3$*C*), 115.0, 115.5 (C3, ArN, *J* 22.8 Hz), 126.7, 126.8 (C2, ArN, *J* 8.3 Hz), 126.4, 129.7, 130.9, 131.9 (Ar), 128.0 (C1, Ar-C), 134.1 (C–Cl), 135.6, 135.7 (C1, ArN, *J* 3.0 Hz) (Ar), 148.7 (C3), 159.0, 163.9 (C–F, *J* 246.5 Hz), 208.6 (C5).

Procedure for the synthesis of 3a–d

These were obtained by the ring transformations of the respective oxadiazoles **2a,b** with anilines in the presence of trifluoroacetic acid at 180 °C according to the literature method.[10,11] Isolation of the new compounds **3c,d** was carried out by washing the unpurified products with diethyl ether and then, if necessary, by recrystallization from the indicated solvent.

3-Phenyl-4-*p*-fluorophenyl-1,2,4-triazole (3c). Yield 50%. Mp 137–139 °C (from DMF). Found: C, 70.5; H, 4.2; F, 8.0; N, 17.6. Calcd for $C_{14}H_{10}FN_3$: C, 70.3; H, 4.2; F, 7.9; N, 17.6%. δ_H (200 MHz, C_6D_6, Me_4Si) 7.41 (9H, m, Ar), 8.89 (1H, s, C*H*N).

3-*o*-Chlorophenyl-4-*p*-fluorophenyl-1,2,4-triazole (3d). Yield 55%. Mp 128–130 °C (from DMF). Found: C, 61.5; H, 3.2; Cl, 13.0; F, 6.8; N, 15.4. Calcd for $C_{14}H_9ClFN_3$: C, 61.4; H, 3.3; Cl, 13.0; F, 6.9; N, 15.4%. δ_H (200 MHz, C_6D_6, Me_4Si) 7.31 (4H, m), 7.51 (3H, m), 7.69 (1H, d, *J* 6.2 Hz) (Ar), 9.05 (1H, s, C*H*N).

General procedure for the preparation of 1-*tert*-butyl-3,4-diaryl-1,2,4-triazolium perchlorates (4a–d)

A mixture of sodium iodide (20.2 g, 0.135 mol), *tert*-butyl chloride (15 mL, 0.135 mol) and the triazole **3a–d** (0.05 mol) in acetic acid (20 mL) was refluxed until the reaction was complete as monitored by TLC (typically 20 h). The reaction mixture was diluted with 0.5 L of water, heated until boiling, following which a small amount of sodium sulfite along with 1 g of activated carbon was added, and the mixture was filtered. A solution of sodium perchlorate (8.58 g, 0.07 mol) in water (20 mL) was then added and the resulting precipitate was filtered off and dried to give 67–85% of salts **4a–d**. The new compounds **4c,d** are characterized as indicated below.

1-*tert*-Butyl-3-phenyl-4-*p*-fluorophenyl-1,2,4-triazolium perchlorate (4c). Yield 85%. Mp 212–214 °C (from ethoxyethanol). Found: C, 54.5; H, 5.0; Cl, 9.1; F 4.8; N, 10.5. Calcd for $C_{18}H_{19}ClFN_3O_4$: C, 54.6; H, 4.8; Cl, 9.0; F, 4.8; N, 10.6%. δ_H (200 MHz, DMSO-d_6, Me_4Si) 1.76 (9H, s, CH_3C), 7.74 (9H, m, Ar), 10.65 (1H, s, C*H*N).

1-*tert*-Butyl-3-*o*-chlorophenyl-4-*p*-fluorophenyl-1,2,4-triazolium perchlorate (4d). Yield 79%. Mp 179–181 °C (from ethoxyethanol). Found: C, 50.5; H, 4.2; Cl, 16.5; F 4.5; N, 9.9. Calcd for $C_{18}H_{18}Cl_2FN_3O_4$: C, 50.3; H, 4.2; Cl, 16.5; F, 4.4; N, 9.8%. δ_H (200 MHz, DMSO-d_6, Me_4Si) 1.72 (9H, s, CH_3C), 7.36–7.70 (8H, m, Ar), 10.73 (1H, s, C*H*N).

1-*tert*-Butyl-3,4-diphenyl-1,2,4-triazolium 5-(2-carbethoxyvinyl-1-oxide) (5a)

Diethyl malonate (0.125 mL, 0.78 mmol) was added to a solution of triazolylidene **1a** (100 mg, 0.361 mmol) in anhydrous toluene (2 mL) and the reaction mixture was refluxed for 4 h under conditions such that the evolved ethanol was removed by a stream of dry nitrogen gas. The toluene was evaporated and the solid residue **5a** (100 mg, 71%) was washed with petroleum ether, filtered off and recrystallized from *n*-octane to afford 57.0 mg (40%) of the pure product **5a**. Mp 160–162 °C. Found: C 70.7, H 6.6, N 11.0. Calcd for $C_{23}H_{25}N_3O_3$: C 70.6, H 6.4, N 10.7%. δ_H (200 MHz, $CDCl_3$, Me_4Si) 1.14 (3H, t, *J* 7.1 Hz, CH_3CH$_2$C), 1.80 (s, 9H, CH_3C, *t*-Bu), 3.93 (2H, quart, *J* 7.1 Hz, CH$_3$CH_2C), 4.81 (1H, s, C5-*H*–N), 7.42 (10H, m, Ar). δ_C (50.3 MHz, $CDCl_3$, Me_4Si) 14.7 (*C*H$_3$CH$_2$C), 28.8 (CH_3C, *t*-Bu), 58.0 (CH$_3$CH_2C), 65.8 (CH$_3$*C*, *t*-Bu), 90.5 (C2–CO), 123.6 (C1, Ar-C), 127.2, 128.8 (enhanced int.), 129.5, 130.8, 131.4 (Ar), 132.1 (C1, ArN), 150.5 (C5), 154.6 (C3), 164.4 (C1=O), 171.1 (C3=O). *m*/*z* (APCI): 392.5 (MH$^+$), $C_{23}H_{26}N_3O_3$ requires 392.5. CCDC reference number 607811. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b712885a

1-*tert*-Butyl-3-phenyl-4-*p*-bromophenyl-1,2,4-triazolium 5-(2-carbethoxyvinyl-1-oxide) (5b)

Obtained according to the method described above for compound **5a**. Yield 50%. Mp 54–56 °C (precipitation from ether by petroleum ether). Found: C 58.8, H 5.0, Br 17.2; N 9.1. Calcd for $C_{23}H_{24}BrN_3O_3$: C 58.7, H 5.1, Br 17.0; N 8.9%. δ_H (200 MHz, $CDCl_3$, Me_4Si). 1.15 (3H, t, *J* 7.1 Hz, CH_3CH$_2$), 1.87 (9H, s, CH_3C, *t*-Bu), 3.94 (2H, quart, *J* 7.1 Hz, CH$_3$CH_2C), 4.82 (1H, s, C5-*H*–N), 7.52 (9H, m, Ar). δ_C (50.3 MHz, $CDCl_3$, Me_4Si) 14.6 (*C*H$_3$CH$_2$), 28.7 (*C*H$_3$C, *t*-Bu), 58.1 (CH$_3$*C*H$_2$), 65.9 (CH$_3$*C*, *t*-Bu), 90.6 (*C*2–CO), 123.2 (C1, Ar-C), 125.1 (C–Br), 131.5 (C1, ArN), 127.7, 128.7, 130.9, 132.7, 133.0 (Ar), 150.3 (C5), 154.4 (C3), 164.0 (C1=O), 171.1 (C3=O). *m*/*z* (APCI): 356.9 (M$^+$ − Me$_2$C=CH$_2$ + H$^+$), 299.9 (**3b** + H$^+$ or M$^+$ − Me$_2$C=CH$_2$ + H$^+$ − COCH$_2$COOEt). $C_{23}H_{24}BrN_3O_3$ requires 470.4.

1-*tert*-Butyl-3-phenyl-4-*p*-fluorophenyl-1,2,4-triazolium 5-(2-carbethoxyvinyl-1-oxide) (5c)

Obtained according to the method described above for compound **5a**. Yield 73%. Mp 143–145 °C (from octane). Found: C 67.8, H 6.0, F 4.7; N 10.3. Calcd for $C_{23}H_{24}FN_3O_3$: C 67.5, H 5.9, F 4.6; N 10.3%. δ_H (200 MHz, $CDCl_3$, Me_4Si) 1.12 (3H, t, *J* 7.1 Hz, CH_3CH$_2$), 1.84 (9H, s, CH_3C, *t*-Bu), 3.91 (quart, 2H, *J* 7.1 Hz, CH$_3$CH_2C, Et), 4.78 (1H, s, C5-*H*–N), 7.11 (2H, dd, ^3J 8.0 Hz, ^3J_F 9.1 Hz, C3-*H*, ArN), 7.38 (7H, m, Ar). δ_C (50.3 MHz, $CDCl_3$, Me_4Si) 14.6 (*C*H$_3$CH$_2$, Et), 28.7 (*C*H$_3$C, *t*-Bu), 58.0 (CH$_3$*C*H$_2$), 65.8 (CH$_3$*C*, *t*-Bu), 90.3 (C5), 116.4, 116.8 (C3, ArN, *J* 18.0 Hz), 123.3 (C1, Ar-C), 127.5 (C1, ArN), 129.1 (C2, ArN, *J* 36.4 Hz), 128.6, 128.7, 131.4 (Ar), 150.4 (C5), 154.6 (C3), 160.8, 165.8 (C–F, *J* 252.4 Hz), 164.2 (C1=O), 171.2 (C3=O). *m*/*z* (APCI): (MH$^+$) 409.5, $C_{23}H_{26}N_3O_3$ requires 410.0; 354.2 (M$^+$ − Me$_2$C=CH$_2$), 296.3 (M$^+$ − COCH$_2$COOEt), 240.2 (**3c** + H$^+$ or M$^+$ − COCH$_2$COOEt − Me$_2$C=CH$_2$).

1-*tert*-Butyl-3-*o*-chlorophenyl-4-*p*-fluorophenyl-1,2,4-triazolium 5-(2-carbethoxyvinyl-1-oxide) (5d)

Obtained according to the method described above for compound **5a**. Yield 75%. Mp 50–51 °C (precipitation from ether by petroleum ether). Found: C 62.3, H 5.3, Cl 8.1, F 4.3, N 9.4. Calcd for $C_{23}H_{23}ClFN_3O_3$: C 62.2, H 5.2, Cl 8.0, F 4.3; N 9.5%. δ_H (200 MHz, $CDCl_3$, Me_4Si) 1.16 (3H, t, *J* 7.1 Hz, CH_3CH$_2$), 1.87 (9H, s, CH_3C, *t*-Bu), 3.96 (2H, quart, *J* 7.1 Hz, CH$_3$CH_2), 4.84 (1H, s, C5-*H*–N), 7.00 (2H, dd, ^3J 8.0 Hz, ^3J_F 9.1 Hz, C3-*H*, ArN), 7.39 (m, 6H, Ar). δ_C (50.3 MHz, $CDCl_3$, Me_4Si) 14.5 (*C*H$_3$CH$_2$), 28.6 (*C*H$_3$C, *t*-Bu), 58.0 (CH$_3$*C*H$_2$), 66.1 (CH$_3$*C*, *t*-Bu), 90.6 (*C*2–CO), 115.8, 116.2 (C3, ArN, *J* 23.3 Hz), 122.9 (C1, Ar-C), 127.1 (C1, ArN, *J* 12.6 Hz), 128.8 (C2, ArN, *J* 36.4 Hz), 126.9, 130.0, 132.3, 132.8 (Ar), 134.0 (*C*–C1), 149.0 (C5), 153.9 (C3), 160.6, 165.6 (C–F, *J* 254.5 Hz), 163.7 (C1=O), 170.9 (C3=O). *m*/*z* (APCI): 388.1 (M$^+$ − Me$_2$C=CH$_2$), 330.2 (M$^+$ − COCH$_2$COOEt), 274.1 (**3d** or M$^+$ − COCH$_2$COOEt − Me$_2$C=CH$_2$), $C_{23}H_{23}ClFN_3O_3$ requires 443.9 (M$^+$).

1-*tert*-Butyl-3,4-diphenyl-1,2,4-triazolium 1,3-dimethylbarbiturate (6a)

A mixture of 1,3-dimethylbarbituric acid (110 mg, 0.721 mmol) and triazolylidene **1** (200 mg, 0.72 mmol) in anhydrous toluene (3 mL) was stirred for 1.5 h. The volume of the reaction mixture was reduced by 50% and the resulting product was recrystallized from a mixture of toluene and acetonitrile (10 : 1). The solid product was filtered off and washed with petroleum ether to give 250 mg (75%) of salt **6a**. Mp 172–174 °C (from 10 : 1 toluene–acetonitrile). Found: C 66.7, H 6.5, N 16.2. Calcd for $C_{24}H_{27}N_5O_3$: C 66.5, H 6.3, N 16.2%. δ_H (200 MHz, CD_3CN, Me_4Si) 1.77 (9H, s, CH_3C), 2.99 (6H, s, CH_3N), 4.05 (4H, s, C*H*C), 7.48 (10H, m, Ar), 10.47 (1H, s, C*H*N).

1-*tert*-Butyl-3,4-diphenyl-1,2,4-triazolium dicyanomethanide (6b)

Obtained by the same procedure as that described for salt **6a** from malononitrile (173 mg, 2.70 mmol) and triazolylidene **1a** (500 mg, 1.80 mmol) in toluene (2 mL). Yield 384 mg (63%). Mp 147–149 °C (from 1 : 1 toluene–acetonitrile). Found: C 73.7, H 6.3, N 20.3. Calcd for $C_{21}H_{21}N_5$: C 73.4, H 6.2, N 20.4%. δ_H (200 MHz, CD_3CN, Me_4Si) 1.76 (s, 9H, CH_3C, *t*-Bu), 3.50 (s, 1H, CH), 7.4–7.6 (m, 10H, Ar), 9.70 (broad s, 1H, C5-H).

1-*tert*-Butyl-3,4-diphenyl-1,2,4-triazolium ethyl acetoacetate (6c)

Obtained by the same procedure as that described for salt **6a** from ethyl acetoacetate (351 mg, 2.70 mmol) and triazolylidene **1a** (500 mg, 1.80 mmol) in toluene (2 mL). Yield 420 mg (67%). Mp 131–133 °C (from toluene). Found: C 70.7, H 7.1, N 10.2. Calcd for $C_{24}H_{29}N_3O_3$: C 70.7, H 7.2, N 10.3%. δ_H (200 MHz, DMSO-d_6, Me_4Si) 1.,02 (3H, s, CH_3CH$_2$), 1.76 (9H, s, CH_3C, *t*-Bu), 1.89

(3H, s, CH_3CO), 3.74 (2H, m, CH_2CH$_3$), 4.00 (1H, broad s, CH), 7.2–7.8 (10H, m, Ar), 10.90 (1H, broad s, C5-H).

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