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Regioselective alkylation of 1*H*-7-ethoxycarbonyl-6-methyl-3-phenyl-pyrazolo[5,1-*c*][1,2,4]triazole and 1*H*-6-methyl-3-phenyl-pyrazolo[5,1-*c*][1,2,4]triazole

Valentin Badea,[a,*] Maria D. Şofei,[a] Monica M. Venter[b] and Vasile N. Bercean[a]

[a] *'Politehnica' University Timişoara, Faculty of Industrial Chemistry and Environment Engineering, Carol Telbisz 6, RO-300006 Timişoara, Romania*
[b] *'Babeş-Bolyai' University Cluj-Napoca, Faculty of Chemistry and Chemical Engineering, Arany Janos 11, RO-400028 Cluj-Napoca, Romania*

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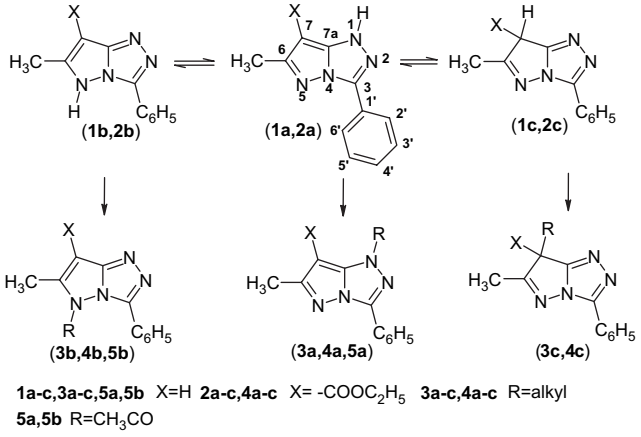
Abstract—Alkylation of 1*H*-6-methyl-3-phenyl-pyrazolo[5,1-*c*][1,2,4]triazole and 1*H*-7-ethoxycarbonyl-6-methyl-3-phenyl-pyrazolo-[5,1-*c*][1,2,4]triazole using different alkylating agents leads regioselectively to 1-*N*-alkylated products. The hydrolysis–decarboxylation of 1,6-dimethyl-7-ethoxycarbonyl-pyrazolo[5,1-*c*][1,2,4]triazole yields a compound identical with that obtained by the direct methylation of 1*H*-6-methyl-3-phenyl-pyrazolo[5,1-*c*][1,2,4]triazole. The 1-N-alkylation is confirmed by NMR spectroscopy and mass spectrometry.

1. Introduction

The interest for pyrazolo[5,1-*c*][1,2,4]triazole derivatives relies on their industrial applications, such as precursors for photosensitive materials (i.e., inks and toners)[1–5] and ingredients in cosmetics.[6,7] To the best of our knowledge, the properties of the title class of compounds have been poorly investigated so far. There are very few scientific papers dealing with this topic and none of them reports on the alkylation reactions of such derivatives. As a result, we became interested in the preparation[9,12,14] and properties[8,9–11,13–15] of the heterocyclic pyrazolo[5,1-*c*][1,2,4]triazole systems. For example, one of our previous reports established that the acetylation of 1*H*-6-methyl-3-phenyl-pyrazolo[5,1-*c*][1,2,4]-triazole **1** leads mainly to the monoacetylated product **5a** mixed with very small amount of the **5b** isomer (Scheme 1).[10]

The aim of this work is to study the alkylation reaction of 3,6-disubstituted and 3,6,7-trisubstituted pyrazolo[5,1-*c*]-[1,2,4]triazole systems as well as 1*H*-6-methyl-3-phenyl-pyrazolo[5,1-*c*][1,2,4]triazole **1** and 1*H*-7-ethoxycarbonyl-6-methyl-3-phenyl-pyrazolo[5,1-*c*][1,2,4]triazole **2**.



Scheme 1. Possible alkylation and acylation pathways of the heterocyclic pyrazolo[5,1-*c*][1,2,4]triazole system.

2. Results and discussion

In a similar fashion to the acetylation process, the monoalkylation of 1*H*-6-methyl-3-phenyl-pyrazolo[5,1-*c*][1,2,4]triazole **1**, which can exist in three tautomeric forms **1a–c**, might lead theoretically to the corresponding isomeric products **3a–c** (Scheme 1). Furthermore, the monoalkylation of 1*H*-7-ethoxycarbonyl-6-methyl-3-phenyl-pyrazolo[5,1-*c*]-[1,2,4]triazole **2**, which may also exist in three tautomeric forms **2a–c**, could lead theoretically to the corresponding isomers **4a–c** (Scheme 1).

Keywords: Pyrazolo[5,1-*c*][1,2,4]triazoles; N-Alkylation; Hydrolysis–decarboxylation.
* Corresponding author. Tel.: +40 742 044969; e-mail: valentin.badea@chim.upt.ro

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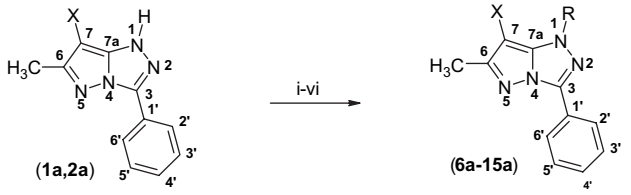
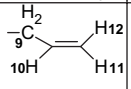
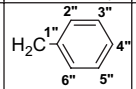


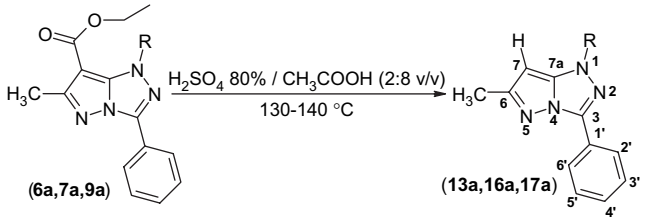
i=R_2SO_4 / NaOH / DMF (**6a,7a**); ii=RBr / NaOH / DMF (**6a-8a**);
iii=RBr / K_2CO_3 / KI / MEK (**8a-12a**); iv=$(CH_3)_2SO_4$ / NaOH 5% or CH_3I / K_2CO_3 / MEK (**13a**);
v=RBr / C_2H_5ONa / C_2H_5OH (**14a**); vi=$ClCH_2COOH$ / NaOH 5% (**15a**)

	6a	7a	8a	9a	10a	11a
X	$COOC_2H_5$	$COOC_2H_5$	$COOC_2H_5$	$COOC_2H_5$	$COOC_2H_5$	$COOC_2H_5$
R	C_2H_5	CH_3			$CH_2COOC_2H_5$	$CH(CH_3)COOCH_3$
Yield (%)	75	92	86.5	91	31	45

	12a	13a	14a	15a	16a	17a
X	$COOC_2H_5$	H	H	H	H	H
R	$CH(C_2H_5)CHCOOCH_3$	CH_3	$CH_2COOC_2H_5$	CH_2COOH	C_2H_5	$CH_2C_6H_5$
Yield (%)	30	68	40	48	76	90

Scheme 2. Alkylation of 1*H*-6-methyl-3-phenyl-pyrazolo[5,1-*c*][1,2,4]triazole **1** and 1*H*-7-ethoxycarbonyl-6-methyl-3-phenyl-pyrazolo[5,1-*c*][1,2,4]triazole **2**.

The alkylation process of the pyrazolo-triazole systems was studied following the transformation of **1** into **3a**–**c** by methylation, transformation of **2** into **4a**–**c** by methylation, ethylation, allylation and benzylation (Scheme 2), as well as by the hydrolysis–decarboxylation of the 1-*N*-alkylated products (**6a**, **7a** and **9a**) (Scheme 3). In addition, the alkylation of **1** and **2** with esters of α-halogeno-alkanoic acids was performed (Scheme 2).



Scheme 3. Preparation of 1-alkyl-6-methyl-3-phenyl-pyrazolo[5,1-*c*]-[1,2,4]triazoles (**13a**, **16a** and **17a**) by the hydrolysis–decarboxylation of 1-alkyl-7-ethoxycarbonyl-6-methyl-3-phenyl-pyrazolo[5,1-*c*][1,2,4]triazoles (**6a**, **7a** and **9a**).

The ethylation and methylation of **2** were performed by reacting the title compound with diethylsulfate and dimethylsulfate, respectively, in dimethylformamide (DMF) and excess NaOH. In both cases, the syntheses yielded a single isomer, the 1-*N*-ethylated **6a** and 1-*N*-methylated **7a**, respectively, in very good yields (Scheme 2).

The monoethylation and monomethylation were confirmed by mass spectrometry. The mass spectra of **6a** and **7a** show the molecular peaks at 298.06 and 284.17 amu, respectively. These peaks also show the highest amplitude suggesting that the molecular ions are easily generated and/or are very stable. Moreover, the molecular fragmentation of the title products is characteristic of the aromatic esters $M^+-{\bullet}OC_2H_5$ and the McLafferty type transposition $M–CH_2{=}CH_2$.

In order to elucidate the position where the alkylation takes place, the products **6a** and **7a** were investigated by 2-D NMR spectroscopy: $^1H–^1H$ COSY, $^1H–^{13}C$ COSY, HETCOR (HMQC) and $^1H–^{13}C$ HMBC. The $^1H–^{13}C$ HMBC spectrum of the *N*-methylated product **7a** shows the $^3J_{7a\text{-}C,\ 1\text{-}N–CH_3}$ coupling between the 7a-C carbon atom and the protons of the $N–CH_3$ unit. Such a coupling is possible only if the alkylation takes place at the 1-N nitrogen atom.

Alternatively, if the alkylation took place at the 5-N nitrogen atom, the coupling distance would be much larger and the coupling would not be noticeable in the $^1H–^{13}C$ HMBC spectrum. Moreover, the $^3J_{6\text{-}C,\ 5\text{-}N–CH_3}$ coupling, which could support the 5-N-alkylation is absent. Other proton–carbon couplings noticed in the $^1H–^{13}C$ HMBC spectrum of **7a** can be mentioned as follows: $^2J_{–OCH_2CH_3,\ –OCH_2CH_3}$, $^2J_{–OCH_2CH_3,\ –OCH_2CH_3}$, $^2J_{6\text{-}C,\ 6\text{-}C–CH_3}$, $^3J_{C=O,\ OCH_2CH_3}$, $^3J_{7\text{-}C,\ 6\text{-}C–CH_3}$, $^3J_{3\text{-}C,\ 2',6'\text{-}H}$, $^3J_{4'\text{-}C,\ 2',6'\text{-}H}$, $^3J_{2'(6')\text{-}C,\ 6'(2')\text{-}H}$, $^3J_{2',6'\text{-}C,\ 4'\text{-}H}$, $^3J_{1'\text{-}C,\ 3',5'\text{-}H}$, and $^3J_{3'(5')\text{-}C,\ 5'(3')\text{-}H}$.

The ethylation reaction also yields the 1-*N*-alkyl isomer **6a**, which is supported by the assignment of the $^3J_{7a\text{-}C,\ 1\text{-}N–CH_2–CH_3}$ coupling, as well as by the absence of the $^3J_{6\text{-}C,\ 5\text{-}N–CH_2–CH_3}$ coupling in the $^1H–^{13}C$ HMBC spectrum. In addition, the spectrum shows couplings similar to compound **7a**, except $^2J_{–NCH_2CH_3,\ –NCH_2CH_3}$, and $^2J_{–NCH_2CH_3,\ –NCH_2CH_3}$ assigned to the ethyl group.

The ethylation and methylation of **2** with alkyl halides (ethyl bromide and methyl iodide, respectively) in DMF and excess NaOH led to the same 1-*N*-ethylated **6a** and 1-*N*-methylated **7a** products (Scheme 2). The N-allylation and N-benzylation of **2** were performed following similar procedures.

The alkylation of **2** with allyl bromide in DMF and excess NaOH occurred with very low yield (~2%). On the other hand, 1-allyl-7-ethoxycarbonyl-6-methyl-3-phenyl-pyrazolo[5,1-*c*][1,2,4]triazole **8a** was obtained successfully

by reacting the same starting materials in methyl ethyl ketone (butanone, MEK) in the presence of K_2CO_3 and KI. The alkylation of the 1-N atom is supported by the presence of the $^3J_{7a\text{-}C,\ 1\text{-}N-CH_2-CH=CH_2}$ coupling and the absence of the $^3J_{6\text{-}C,\ 5\text{-}N-CH_2-CH=CH_2}$ coupling in the $^1H-^{13}C$ HMBC spectrum of **8a**. In addition, the spectrum shows couplings similar to the previous derivatives, except $^2J_{9\text{-}C,\ 1\text{-}N-CH_2-CH=CH_2}$, $^2J_{10\text{-}C,\ 9\text{-}H}$ and $^2J_{11,12\text{-}C,\ 9\text{-}H}$ characteristic to the allyl group (Scheme 2). The $^1H-^1H$ COSY spectrum reveals the $J_{10\text{-}H,\ 9,11,12\text{-}H}$ couplings of the allyl protons.

1-Benzyl-7-ethoxycarbonyl-6-methyl-3-phenyl-pyrazolo-[5,1-*c*][1,2,4]triazole **9a** was prepared by the reaction of **2** with benzyl bromide, in good yields (Scheme 2). The mass spectrum of **9a** reveals the fragmentation of the molecular ion by the release of the benzyl radical, $M^+-{\bullet}CH_2C_6H_5$, and the formation of the tropylium ion ($C_7H_7^+$, 91 amu). The latter ion was also assigned as the base peak, as expected for benzyl derivatives.

Compounds **10a**–**12a** were prepared by the alkylation of **2** with alkyl α-halogeno-alkanoic esters in MEK, in the presence of K_2CO_3 and KI (Scheme 2). In the case of compound **10a**, the alkylation was performed with ethyl 2-bromoacetate and it is supported by the assignment of $^3J_{7a\text{-}C,\ 1\text{-}N-CH_2-COOC_2H_5}$ and the absence of $^3J_{6\text{-}C,\ 5\text{-}N-CH_2-COOC_2H_5}$ couplings in the $^1H-^{13}C$ HMBC spectrum. In addition, the spectrum reveals the $^2J_{1\text{-}N-CH_2-COOC_2H_5,\ 1\text{-}N-CH_2-COOC_2H_5}$ and $^3J_{1\text{-}N-CH_2-COOCH_2H_3,\ 1\text{-}N-CH_2-COOCH_2CH_3}$ couplings, along with those common for the entire range of derivatives.

The alkylation of 1*H*-6-methyl-3-phenyl-pyrazolo[5,1-*c*][1,2,4]triazole (**1**) with dimethylsulfate in 5% NaOH solution or with methyl iodide in MEK, in the presence of K_2CO_3 and KI, yielded the *N*-alkylated homologue 1,6-dimethyl-3-phenyl-pyrazolo[5,1-*c*][1,2,4]triazole (**13a**) (Scheme 2). The fact that the 7-C atom was not alkylated is supported by the assignment of δ(7-C–H) at 5.72 ppm in the ^1H NMR spectrum.

The alkylation of **1** with ethyl 2-bromoacetate in C_2H_5ONa/C_2H_5OH yielded the *N*-alkylated product 1-(ethoxycarbonyl-methyl)-6-methyl-3-phenyl-pyrazolo[5,1-*c*][1,2,4]-triazole (**14a**) (Scheme 2). Similar to the previous case, the ^1H NMR spectrum of **14a** shows δ(7-C–H) at 5.75 ppm. In addition, the mass spectrum of the title compound shows the molecular peak at M=284 amu.

The alkylation of **1** with chloroacetic acid in 5% NaOH solution, at pH=8–9, yielded the *N*-alkylated product 1-(carboxy-methyl)-6-methyl-3-phenyl-pyrazolo[5,1-*c*][1,2,4]triazole (**15a**) (Scheme 2). The N-alkylation is supported by the assignment of δ(7-C–H) at 5.75 ppm in the ^1H NMR spectrum, as well as by the presence of $^3J_{7a\text{-}C,\ 1\text{-}N-CH_2-COOH}$ coupling and the absence of $^3J_{6\text{-}C,\ 5\text{-}N-CH_2-COOH}$ coupling in the $^1H-^{13}C$ HMBC spectrum of **15a**. The mass spectrum of the product reveals the molecular fragmentation typical to carboxylic acids, M^+-45 (M^+-COOH).

1-Alkyl-7-ethoxycarbonyl-6-methyl-3-phenyl-pyrazolo[5,1-*c*]-[1,2,4]triazole derivatives were subjected to single-step hydrolysis–decarboxylation processes by heating them to 130–140 °C in an 80% H_2SO_4/CH_3COOH (2:8 v/v) mixture. The reaction yielded 1-alkyl-3-phenyl-6-methyl-pyrazolo-[5,1-*c*][1,2,4]triazoles (Scheme 3). Compound **13a** prepared by this route is identical with that obtained by the N-alkylation of **1** with dimethylsulfate or methyl iodide. 1-Ethyl-6-methyl-3-phenyl-pyrazolo[5,1-*c*][1,2,4]triazole (**16a**) and 1-benzyl-6-methyl-3-phenyl-pyrazolo[5,1-*c*][1,2,4]triazole (**17a**) were prepared in a similar manner. The mass spectrum of **17a** shows the base peak at 91 amu assigned to the tropylium cation ($C_7H_7^+$), as expected for benzyl derivatives.

3. Conclusions

The monoalkylation of 1*H*-7-ethoxycarbonyl-6-methyl-3-phenyl-pyrazolo[5,1-*c*][1,2,4]triazole **2** with dimethyl- and diethylsulfate, and methyl, ethyl, allyl and benzyl halides, or esters of α-halogeno-alkanoic acids in alkaline media leads to the 1-*N*-alkylated derivative in each case.

The monoalkylation of 1*H*-6-methyl-3-phenyl-pyrazolo[5,1-*c*]-[1,2,4]triazole **1** with methyl iodide or dimethylsulfate in alkaline media leads to the same 1-*N*-methyl homologue.

The hydrolysis–decarboxylation of 1-alkyl-7-ethoxycarbonyl-6-methyl-3-phenyl-pyrazolo[5,1-*c*][1,2,4]triazole derivatives (alkyl=methyl, ethyl or benzyl) yields 1-alkyl-6-methyl-3-phenyl-pyrazolo[5,1-*c*][1,2,4]triazoles. In the case of R=methyl, the product is identical with that obtained by direct methylation of **1**.

4. Experimental

4.1. General

The chemical reagents were purchased from commercial sources (Merck, Fluka) and used in syntheses with no further purification. 1*H*-6-Methyl-3-phenyl-pyrazolo[5,1-*c*][1,2,4]-triazole **1** and 1*H*-7-ethoxycarbonyl-6-methyl-3-phenyl-pyrazolo[5,1-*c*][1,2,4]triazole **2** were prepared by literature methods.[1] The preparation methods used for the N-alkylation of pyrazolo-triazoles are the modifications of the N-alkylation of 1,2,4-triazole[16] and benzimidazole.[17]

The melting points were determined on a Böetius PHMK apparatus (Veb Analytik Dresden). TLC was performed on 60 F_{254} Merck silica gel plates using benzene/ethyl acetate=1:1 (v/v) as eluent. The IR spectra were recorded as KBr pellets, using a Jasco FT/IR-410 spectrometer. The ^1H and ^{13}C NMR spectra were recorded on Bruker DRX 400 (400 MHz for ^1H and 100 MHz for ^{13}C), Varian Gemini 300 (300 MHz for ^1H and 75 MHz for ^{13}C) or Bruker AC 200 (200 MHz for ^1H and 50 MHz for ^{13}C) spectrometer, using TMS as an internal reference. The mass spectra were recorded on a Varian FINNIGAN MAT 212 instrument at 54 eV.

4.2. Alkylation of 1*H*-7-ethoxycarbonyl-6-methyl-3-phenyl-pyrazolo[5,1-*c*][1,2,4] triazole (2)

4.2.1. 7-Ethoxycarbonyl-1-ethyl-6-methyl-3-phenyl-pyrazolo[5,1-*c*][1,2,4]triazole (6a). *Alkylation with diethylsulfate in NaOH/DMF*: 0.675 g (2.5 mmol) of **2** and 0.36 mL

(2.75 mmol) of Et_2SO_4 were added to a solution of 0.4 g (10 mmol) of NaOH in 10 mL DMF under continuous stirring. After stirring for 1 h, the product was precipitated in 20–30 mL distilled water and filtered.

Yield: 0.566 g of white powder, 75%; mp: 112–114 °C (*n*-hexane); IR (KBr) ν_{max}: 3060, 2978, 2933, 2910, 1679, 1598, 1489, 761, 688 cm^{-1}; δ_H ($CDCl_3$, 400 MHz): 8.38–8.36 (m, 2H, 2′-H, 6′-H), 7.53–7.43 (m, 3H, 3′-H, 5′-H, 4′-H), 4.66 (q, 2H, J=7.1 Hz, –N–CH_2CH_3), 4.33 (q, 2H, J=7.1 Hz, –O–CH_2CH_3), 2.61 (s, 3H, 6-C–CH_3), 1.50 (t, 3H, J=7.1 Hz, 1-N–CH_2CH_3), 1.39 (t, 3H, J=7.1 Hz, –O–CH_2CH_3); δ_C ($CDCl_3$, 100 MHz): 163.2 (C=O), 160.9 (6-C), 147.1 (7a-C), 138.8 (3-C), 130.2 (4′-C), 128.8 (3′-C, 5′-C), 126.5 (2′-C, 6′-C), 125.4 (1′-C), 88.1 (7-C), 59.7 (–O–CH_2CH_3), 46.0 (1-N–CH_2CH_3), 15.7 (6-C–CH_3), 15.5 (–N–CH_2CH_3), 14.4 (–O–CH_2CH_3); MS (54 eV) *m/z*: 298 (M^+, 100%), 283 ($M^+-{\bullet}CH_3$, 6%), 270 ($M^+-H_2C{=}CH_2$, 9%), 253 ($M^+-{\bullet}OC_2H_5$, 25%). Anal. Calcd (%) for $C_{16}H_{18}N_4O_2$: C, 64.41; H, 6.08; N, 18.78. Found (%): C, 64.02; H, 5.94; N, 18.03.

Alkylation with ethyl bromide in NaOH/DMF: 0.1 g (0.37 mmol) of **2** and 0.058 mL (0.77 mmol) of CH_3CH_2Br were added to a solution of 0.1 g (2.5 mmol) of NaOH in 5 mL DMF under continuous stirring. After stirring for 1 h, the product was precipitated in 20 mL distilled water and filtered. Yield: 0.07 g of white powder, 62%; mp: 112–116 °C (*n*-hexane); identical with the product prepared by the previous method (TLC, IR, NMR and MS).

4.2.2. 1,6-Dimethyl-7-ethoxycarbonyl-3-phenyl-6-pyrazolo[5,1-*c*][1,2,4]triazole (7a). *Alkylation with dimethylsulfate in NaOH/DMF*: 0.675 g (2.5 mmol) of **2** and 0.26 mL (2.75 mmol) of Me_2SO_4 were added to a solution of 0.4 g (10 mmol) of NaOH in 10 mL dimethylformamide (DMF) under continuous stirring. After stirring for 1 h at room temperature, the product was precipitated in 20–30 mL distilled water and filtered.

Yield: 0.67 g of white powder, 92%; mp: 138–139 °C (*n*-hexane); IR (KBr) ν_{max}: 3065, 2980, 2937, 2909, 1677, 1609, 1492, 775, 688 cm^{-1}; δ_H ($CDCl_3$, 400 MHz): 8.36–8.34 (m, 2H, 2′-H, 6′-H), 7.53–7.43 (m, 3H, 3′-H, 4′-H, 5′-H), 4.32 (q, 2H, J=7.1 Hz, –O–CH_2CH_3), 4.23 (s, 3H, 1-N–CH_3), 2.60 (s, 3H, 6-C–CH_3), 1.39 (t, 3H, J=7.1 Hz, –O–CH_2CH_3); δ_C ($CDCl_3$, 100 MHz): 163.2 (C=O), 160.9 (6-C), 147.8 (7a-C), 138.8 (3-C), 130.2 (4′-C), 128.8 (3′-C, 5′-C), 126.4 (2′-C, 6′-C), 125.2 (1′-C), 88.1 (7-C), 59.7 (–O–CH_2CH_3), 37.9 (1-N–CH_3), 15.6 (6-C–CH_3), 14.5 (–O–CH_2CH_3); MS (54 eV) *m/z*: 284 (M^+, 100%), 269 ($M^+-{\bullet}CH_3{\bullet}$, 2%), 256 ($M^+-CH_2{=}CH_2$, 21%), 239 ($M^+-{\bullet}OC_2H_5{\bullet}$, 37%). Anal. Calcd (%) for $C_{15}H_{16}N_4O_2$: C, 63.37; H, 5.67; N, 19.71. Found (%): C, 63.17; H, 5.34; N, 19.55.

Alkylation with methyl iodide in NaOH/DMF: 0.1 g (0.37 mmol) of **2** and 0.023 mL (0.37 mmol) of CH_3I were added to a solution of 0.1 g (2.5 mmol) of NaOH in 5 mL DMF under continuous stirring. After stirring for 1 h at room temperature, the product was precipitated in 10–15 mL distilled water and filtered. Yield: 0.08 g of white powder, 76.5%; mp: 138–139 °C (*n*-hexane); identical with the product prepared by the previous method (TLC, IR, NMR and MS).

4.2.3. 1-Allyl-7-ethoxycarbonyl-6-methyl-3-phenyl-pyrazolo[5,1-*c*][1,2,4]triazole (8a). *Alkylation with allyl bromide in NaOH/DMF*: 0.1 g (0.37 mmol) of **2** and 0.058 mL (0.67 mmol) of allyl bromide were added to a solution of 0.1 g (2.5 mmol) of NaOH in 5 mL DMF under continuous stirring. After stirring for 1 h, the product was precipitated in 20 mL distilled water and filtered. Yield: 0.002 g of white powder (2%).

Alkylation with allyl bromide in the presence of anhydrous K_2CO_3 and KI: 0.364 g (2.6 mmol) of finely ground K_2CO_3 and 0.5 g (1.85 mmol) of **2** were added to a solution of 0.24 mL (2.77 mmol) allyl bromide and 0.34 g (2.0 mmol) of finely ground KI in 15 mL MEK. After heating the reaction mixture to 70 °C for 4 h, the solid residue was filtered off and the filtrate was evaporated to dryness on a rotavapor. The resulting solid mass was dissolved in 20 mL ethyl acetate and the solution was washed twice with 10 mL distilled water and dried with anhydrous Na_2SO_4. After evaporating the ethyl acetate, the product was obtained as a white powder.

Yield: 0.5 g, 86.5%; mp: 94–97 °C (*n*-hexane); IR (KBr) ν_{max}: 3084, 3061, 2981, 2935, 1678, 1643, 1599, 1490, 763, 685 cm^{-1}; δ_H ($CDCl_3$, 400 MHz): 8.39–8.36 (m, 2H, 2′-H, 6′-H), 7.53–7.44 (m, 3H, 3′-H, 5′-H, 4′-H), 6.12–6.02 (qt, 1H, $J_{10\text{-H},\ 9\text{-H}}$=5.6 Hz, $J_{10\text{-H},\ 11\text{-H}}$=12.2 Hz, 10-H), 5.26–5.21 (m, 4H, 2×9-H, 11-H, 12-H), 4.33 (q, 2H, J=7.1 Hz, –O–CH_2CH_3), 2.61 (s, 3H, 6-C–CH_3), 1.39 (t, 3H, J=7.1 Hz, –O–CH_2CH_3); δ_C ($CDCl_3$, 100 MHz): 163.2 (C=O), 160.9 (6-C), 147.5 (7a-C), 139.2 (3-C), 132.6 (10-C), 130.3 (4′-C), 128.8 (3′-C, 5′-C), 126.6 (2′-C, 6′-C), 125.3 (1′-C), 118.2 (11,12-C), 88.3 (7-C), 59.8 (–O–CH_2CH_3), 52.7 (9-C), 15.7 (6-C–CH_3), 14.5 (–O–CH_2CH_3); MS (54 eV) *m/z*: 310 (M^+, 100%), 283 ($M^+-CH_2{=}CH{\bullet}$, 8%), 281 ($M^+-{\bullet}C_2H_5{\bullet}$, 13%), 265 ($M^+-{\bullet}OC_2H_5{\bullet}$, 23%). Anal. Calcd (%) for $C_{17}H_{18}N_4O_2$: C, 65.79; H, 5.85; N, 18.05. Found (%): C, 65.54; H, 5.43; N, 17.53.

4.2.4. 1-Benzyl-7-ethoxycarbonyl-6-methyl-3-phenyl-pyrazolo[5,1-*c*][1,2,4]triazole (9a). *Alkylation with benzyl bromide in MEK, in the presence of K_2CO_3 and KI*: 0.27 g (1.9 mmol) of finely ground K_2CO_3 and 0.4 g (1.48 mmol) of **2** were added to a solution of 0.23 mL (1.93 mmol) of benzyl bromide and 0.27 g (1.63 mmol) of finely ground KI in 12 mL MEK. After heating the reaction mixture to 70 °C for 4 h, the solid residue was filtered off and the filtrate was evaporated to dryness on a rotavapor. The resulting solid mass was dissolved in 20 mL ethyl acetate and the solution was washed twice with 10 mL distilled water and dried with anhydrous Na_2SO_4. After evaporating the solvent, the product was obtained as a white powder.

Yield: 0.53 g, 91%; mp: 145–147 °C (*n*-hexane); IR (KBr) ν_{max}: 3064, 2981, 2936, 2910, 1682, 1601, 1489, 1543, 767, 712, 692 cm^{-1}; δ_H (DMSO-d_6, 300 MHz): 8.32–8.29 (m, 2H, 2′-H, 6′-H), 7.62–7.53 (m, 3H, 3′-H, 5′-H, 4′-H), 7.39–7.28 (m, 5H, 2″-H, 6″-H, 3″-H, 5″-H, 4″-H), 5.81 (s, 2H, –CH_2–Ph), 4.23 (q, 2H, J=7.1 Hz, –O–CH_2CH_3), 2.53

(s, 3H, 6-C–CH_3), 1.21 (t, 3H, J=7.1 Hz, –O–CH_2CH_3); δ_C (DMSO-d_6, 75 MHz): 162.2 (C=O), 160.1 (6-C), 150.1 (7a-C), 138.4 (3-C), 136.7 (1″-C), 130.8 (4′-C), 129.2 (3′-C, 5′-C), 128.7 (2″-C, 6″-C), 127.8 (4″-C), 127.2 (3″-C, 5″-C), 126.1 (2′-C, 6′-C), 124.5 (1′-C), 96.7 (7-C), 59.6 (–O–CH_2CH_3), 53.2 (–CH_2–Ph), 15.4 (6-C–CH_3), 14.2 (–O–CH_2CH_3); MS (54 eV) m/z: 360 (M^+, 64%), 331 ($M^+-\bullet C_2H_5\bullet$, 5%), 315 ($M^+-\bullet OC_2H_5\bullet$, 9%), 269 ($M^+-C_6H_5CH_2\bullet$, 7%), 91 ($C_7H_7^+$, 100%). Anal. Calcd (%) for $C_{21}H_{20}N_4O_2$: C, 69.98; H, 5.59; N, 15.54. Found (%): C, 69.71; H, 5.19; N, 15.37.

4.2.5. 7-Ethoxycarbonyl-1-(ethoxycarbonyl-methyl)-6-methyl-3-phenyl-pyrazolo[5,1-*c*][1,2,4]triazole (10a). *Alkylation with ethyl 2-bromoacetate*: 0.4 mL (3.525 mmol) of $BrCH_2COOC_2H_5$ was added dropwise over 1 min to a suspension of 0.685 g (2.5 mmol) of **2** and 0.38 g (2.75 mmol) of K_2CO_3 in 5 mL MEK. The reaction mixture was heated to 40 °C and stirred for 4 h (TLC monitoring). The resulting solution was poured into 50 mL distilled water and the precipitate was filtered and dried.

Yield: 0.28 g of white powder, 31%; mp: 103–105 °C (methanol); IR (KBr) ν_{max}: 3063, 2992, 2972, 2934, 1751, 1701, 1605, 1543, 1494, 1453, 1227, 1125, 1094, 768, 690 cm^{-1}; δ_H ($CDCl_3$, 400 MHz): 8.38–8.36 (m, 2H, 2′-H, 6′-H), 7.53–7.45 (m, 3H, 3′-H, 5′-H, 4′-H), 5.36 (s, 2H, 1-N–CH_2), 4.29 [q, 2H, J=7.1 Hz, (7-C)–O–CH_2CH_3], 4.24 [q, 2H, J=7.1 Hz, (1-N)–O–CH_2CH_3], 2.61 (s, 3H, 6-C–CH_3), 1.36 [t, 3H, J=7.1 Hz, (7-C)–O–CH_2CH_3], 1.27 [t, 3H, J=7.1 Hz, (1-N)–O–CH_2CH_3]; δ_C ($CDCl_3$, 100 MHz): 167.6 (–CH_2–C=O), 163.1 (7-C–C=O), 160.9 (6-C), 148.2 (7a-C), 139.7 (3-C), 130.5 (4′-C), 128.8 (3′-C, 5′-C), 126.7 (2′-C, 6′-C), 124.5 (1′-C), 88.8 (7-C), 61.9 [(1-N)–O–CH_2CH_3], 59.8 [(6-C)–O–CH_2CH_3], 51.9 (1-N–CH_2–), 15.5 (6-C–CH_3), 14.4 [(1-N)–O–CH_2CH_3], 14.1 [(7-C)–O–CH_2CH_3]; MS (54 eV) m/z: 356 (M^+, 49%), 328 ($M^+-CH_2{=}CH_2$, 1%), 311 ($M^+-\bullet OC_2H_5$, 9%), 283 ($M^+-\bullet COOC_2H_5\bullet$, 100%). Anal. Calcd (%) for $C_{18}H_{20}N_4O_4$: C, 60.67; H, 5.66; N, 15.72. Found (%): C, 60.39; H, 5.39; N, 15.57.

4.2.6. 7-Ethoxycarbonyl-1-(1-methoxycarbonyl-ethyl)-6-methyl-3-phenyl-pyrazolo[5,1-*c*][1,2,4]triazole (11a). *Alkylation with methyl 2-chloropropionate*: 0.15 g (0.88 mmol) of KI was added to a mixture of 0.1 mL (0.88 mmol) of methyl 2-chloropropionate in 5 mL MEK. The mixture was heated to 50–60 °C for 10 min and another 0.22 g (0.8 mmol) of **2** and 0.11 g (0.8 mmol) of K_2CO_3 were added. After 4 h of refluxing the chromatographic test revealed the presence of unreacted starting materials. To the reaction mixture an excess of 3 mL butanone, 0.055 g (0.4 mmol) of K_2CO_3, 0.1 g (0.66 mmol) of NaI and 0.089 mL (0.78 mmol) of methyl 2-chloropropionate were added. After stirring and refluxing for another 4 h, the solution was poured into 50 mL distilled water and the solid product was filtered and dried.

Yield: 0.13 g of white powder, 45%; mp: 153–155 °C; IR (KBr) ν_{max}: 3069, 2978, 2959, 2928, 2872, 1754, 1680, 1605, 1546, 1490, 1214, 1157, 1117, 768, 691 cm^{-1}; δ_H (DMSO-d_6, 300 MHz): 8.30–8.27 (m, 2H, 2′-H, 6′-H), 7.61–7.54 (m, 3H, 3′-H, 5′-H, 4′-H), 6.02 (q, 1H, J=7.2 Hz, 1-N–CH<), 4.19 (q, 2H, J=7.0 Hz, –O–CH_2CH_3), 3.66 (s, 3H, –O–CH_3), 2.48 (s, 3H, 6-C–CH_3), 1.83 (d, 3H, J=7.2 Hz, CH_3–CH<), 1.25 (t, 3H, J=7.0 Hz, –O–CH_2CH_3); δ_C (DMSO-d_6, 75 MHz): 170.2 (>CH–C=O), 162.1 (7-C–C=O), 159.9 (6-C), 147.2 (7a-C), 138.1 (3-C), 130.8 (4′-C), 129.1 (3′-C, 5′-C), 126.0 (2′-C, 6′-C), 124.4 (1′-C), 88.2 (7-C), 59.6 (–O–CH_2CH_3), 57.4 (–O–CH_3), 52.7 (>CH–CH_3), 15.8 (6-C–CH_3), 15.2 (>CH–CH_3), 14.1 (–O–CH_2CH_3); MS (54 eV) m/z: 356 (M^+, 46%), 311 ($M^+-\bullet OC_2H_5$, 7%), 297 ($M^+-\bullet COOCH_3$, 100%). Anal. Calcd (%) for $C_{18}H_{20}N_4O_4$: C, 60.67; H, 5.66; N, 15.72. Found (%): C, 60.49; H, 5.32; N, 15.35.

Alkylation with methyl 2-bromopropionate: 0.3 mL (2.625 mmol) of methyl 2-bromopropionate and 0.38 g (2.75 mmol) of K_2CO_3 were added to a mixture of 0.675 g (2.5 mmol) of **2** in 10 mL MEK. After stirring and refluxing the reaction mixture for 4 h, the solution was poured into 50 mL distilled water and the solid product was filtered and dried. Yield: 0.45 g of white powder, 50%; identical with the product prepared by the previous method (TLC, IR, MS and NMR).

4.2.7. 7-Ethoxycarbonyl-1-(1-methoxycarbonyl-propyl)-6-methyl-3-phenyl-pyrazolo[5,1-*c*][1,2,4]triazole (12a). *Alkylation with methyl 2-bromobutyrate*: 0.43 g (2.6 mmol) of KI was added to a solution of 0.3 mL (2.625 mmol) of methyl 2-bromobutyrate in 10 mL MEK and the resulting mixture was heated to 50 °C for 10 min. Another 0.675 g (2.5 mmol) of **2** and 0.38 g (2.75 mmol) of K_2CO_3 were then added. After stirring and refluxing for 8 h, the solution was poured into distilled water and the solid product was filtered and dried.

Yield: 0.3 g, 30%; mp: 95–97 °C; IR (KBr) ν_{max}: 3068, 2970, 2951, 2928, 2870, 1753, 1681, 1602, 1543, 1490, 1215, 1160, 1118, 765, 690 cm^{-1}; δ_H (DMSO-d_6, 200 MHz): 8.42–8.30 (m, 2H, 2′-H, 6′-H), 7.68–7.55 (m, 3H, 3′-H, 5′-H, 4′-H), 5.97 (t, 1H, J=6.3 Hz, 1-N–CH<), 4.25 (q, 2H, J=7.0 Hz, –O–CH_2CH_3), 3.69 (s, 3H, –O–CH_3), 2.54 (s, 3H, 6-C–CH_3), 2.43–2.28 (m, 2H, CH_3–CH_2–CH<), 1.32 (t, 3H, J=7.0 Hz, –O–CH_2CH_3), 0.98 (t, 3H, J=7.2 Hz, CH_3–CH_2–CH<); δ_C (DMSO-d_6, 50 MHz): 169.4 (>CH–C=O), 162.1 (7-C–C=O), 159.9 (6-C), 147.0 (7a-C), 138.6 (3-C), 130.8 (4′-C), 129.0 (3′-C, 5′-C), 126.2 (2′-C, 6′-C), 124.5 (1′-C), 88.1 (7-C), 62.9 (–O–CH_3), 59.6 (–O–CH_2CH_3), 52.6 (CH_3–CH_2–CH<), 23.2 (CH_3–CH_2–CH<), 15.3 (6-C–CH_3), 14.2 (–O–CH_2CH_3), 10.7 (CH_3–CH_2–CH<); MS (54 eV) m/z: 370 (M^+, 45%), 325 ($M^+-\bullet OC_2H_5$, 5%), 311 ($M^+-\bullet COOCH_3$, 100%). Anal. Calcd (%) for $C_{19}H_{22}N_4O_4$: C, 61.61; H, 5.99; N, 15.13. Found (%): C, 61.37; H, 5.58; N, 14.89.

4.3. Alkylation of 1*H*-6-methyl-3-phenyl-pyrazolo [5,1-c][1,2,4]triazole (1)

4.3.1. 1,6-Dimethyl-3-phenyl-pyrazolo[5,1-*c*][1,2,4]triazole (13a). *Alkylation with dimethylsulfate in 5% NaOH solution*: 5.8 mL 5% NaOH solution (7.7 mmol NaOH) was added dropwise to a mixture of 0.1 g (0.5 mmol) of **1** and 0.2 mL (2.15 mmol) of $(CH_3)_2SO_4$ at room temperature and under continuous stirring. After refluxing the reaction

mixture for 4 h, the product was extracted with ethyl acetate. The organic layer was washed successively with 10 mL distilled water, 10 mL 5% NaOH solution and finally with another 10 mL of water. The resulting organic layer was dried with anhydrous Na_2SO_4 and the solvent was removed using a rotavapor.

Yield: 0.072 g of white powder, 68%; mp: 62–63 °C; IR (KBr) ν_{max}: 3127, 3059, 2926, 1606, 1467, 1080, 765, 690 cm^{-1}; δ_H (DMSO-d_6, 300 MHz): 8.35–8.32 (m, 2H, 2′-H, 6′-H), 7.60–7.47 (m, 3H, 3′-H, 4′-H, 5′-H), 5.72 (7-C–H), 3.85 (s, 3H, 1-N–CH_3), 2.32 (s, 3H, 6-C–CH_3); δ_C (DMSO-d_6, 75 MHz): 157.4 (6-C), 148.6 (7a-C), 136.6 (3-C), 129.8 (4′-C), 128.9 (3′-C, 5′-C), 125.7 (1′-C), 125.4 (2′-C, 6′-C), 77.2 (7-C), 36.51 (1-N–CH$_3$), 14.8 (6-C–CH$_3$); MS (54 eV) *m/z*: 212 (M^+, 100%). Anal. Calcd (%) for $C_{12}H_{12}N_4$: C, 67.91; H, 5.70; N, 26.40. Found (%): C, 67.75; H, 5.57; N, 26.23.

Alkylation with methyl iodide in MEK, in the presence of K_2CO_3: 0.125 mL (2.0 mmol) of CH_3I was added to a mixture of 0.1 g (0.5 mmol) of **1** and 0.14 g (1.0 mmol) of K_2CO_3 in 8 mL butanone, under continuous stirring, at a maximum temperature of 40 °C. After heating to 40 °C and stirring for 5 h, the reaction mixture was discharged into 20 mL distilled water and the product was extracted with 20 mL ethyl acetate. The organic layer was washed successively with 10 mL distilled water, 10 mL 5% NaOH solution and finally with another 10 mL of water. The resulting organic layer was dried with anhydrous Na_2SO_4 and the solvent was removed using a rotavapor. Yield: 0.053 g, 50%; mp: 62–63 °C; identical with the product prepared by the previous method (TLC, IR, NMR and MS).

4.3.2. 1-(Ethoxycarbonyl-methyl)-6-methyl-3-phenyl-pyrazolo[5,1-*c*][1,2,4]triazole (14a). *Alkylation with ethyl 2-bromoacetate*: a solution of 0.3 mL (2.52 mmol) of ethyl 2-bromoacetate in 3 mL absolute ethanol was added dropwise to a solution of 0.42 g (2.52 mmol) of **1** in 3 mL EtONa/EtOH solution (2.52 mmol EtONa), under continuous stirring, at the water bath temperature. After completing the reaction at room temperature for 2 h, the reaction mixture was diluted with 10 mL distilled water and the product was extracted with 3×10 mL ethyl acetate. The ethyl acetate layer was washed successively with 3×5 mL 5% NaOH solution, followed by 2×5 mL water. The resulting solution was dried over anhydrous Na_2SO_4 and the solvent was removed using a rotavapor.

Yield: 0.26 g, 40%; mp: 80–82 °C; IR (KBr) ν_{max}: 3059, 2982, 2935, 1739, 1617, 1537, 1472, 1219, 1107, 1024, 765, 692 cm^{-1}; δ_H (DMSO-d_6, 300 MHz): 8.38–8.35 (m, 2H, 2′-H, 6′-H), 7.61–7.52 (m, 3H, 3′-H, 5′-H, 4′-H), 5.75 (s, 1H, 7-C–H) 5.19 (s, 2H, 1-N–CH_2–), 4.17 (q, 2H, J=7.1 Hz, –O–CH_2CH$_3$), 2.34 (s, 3H, 6-C–CH$_3$), 1.20 (t, 3H, J=7.1 Hz, –O–CH$_2$$CH_3$); δ_C (DMSO-d_6, 75 MHz): 167.7 (–CH$_2$–C═O), 157.6 (6-C), 148.8 (7a-C), 137.5 (3-C), 130.15 (4′-C), 129.0 (3′-C, 5′-C), 125.7 (2′-C, 6′-C), 125.4 (1′-C), 78.4 (7-C), 61.3 (–O–CH$_2$CH$_3$), 50.6 (1-N–CH$_2$–), 14.8 (6-C–CH$_3$), 14.0 (–O–CH$_2$$CH_3$); MS (54 eV) *m/z*: 284 (M^+, 100%), 211 (M^+−•$COOC_2H_5$, 93%). Anal. Calcd (%) for $C_{15}H_{16}N_4O_2$: C, 63.37; H, 5.67; N, 19.71. Found (%): C, 63.12; H, 5.38; N, 19.51.

4.3.3. 1-(Carboxy-methyl)-6-methyl-3-phenyl-pyrazolo[5,1-*c*][1,2,4]triazole (15a). *Alkylation with chloroacetic acid*: 2 mL 5% NaOH solution was added dropwise and under continuous stirring to a mixture of 0.24 g (2.5 mmol) of $ClCH_2COOH$ in 1 mL distilled water and 2 g ice. To the previous solution a solution of 0.5 g (2.5 mmol) of **1** in 1 mL 10% NaOH was added. The resulting reaction mixture was heated to 80–90 °C and the pH was maintained at 8–9 by adding 5% NaOH until the reaction was completed (TLC monitoring). By the end of the process, the pH increased slightly and the heating was left on for another 30 min. The reaction mixture was filtered. The filtrate was acidified with 15% aq HCl until the pH decreased to 2–3 and it was filtered again.

Yield: 0.37 g of white powder, 48%; mp: 190–192 °C; IR (KBr) ν_{max}: 3065, 2992, 2953, 1712, 1608, 1475, 1214, 1108, 765, 716, 690 cm^{-1}; δ_H (DMSO-d_6, 400 MHz): 13.17 (br s, 1H, –COOH), 8.38–8.35 (m, 2H, 2′-H, 6′-H), 7.60–7.47 (m, 3H, 3′-H, 4′-H, 5′-H), 5.75 (7-C–H), 5.06 (s, 2H, 1-N–CH_2–), 2.35 (s, 3H, 6-C–CH_3); δ_C (DMSO-d_6, 100 MHz): 169.0 (C═O), 157.5 (6-C), 148.8 (7a-C), 137.2 (3-C), 129.9 (4′-C), 128.9 (3′-C, 5′-C), 125.6 (2′-C, 6′-C), 125.4 (1′-C), 78.2 (7-C), 50.6 (1-N–CH$_2$–), 14.7 (6-C–CH$_3$); MS (54 eV) *m/z*: 256 (M^+, 100%), 211 (M^+−45, 69%). Anal. Calcd (%) for $C_{13}H_{12}N_4O_2$: C, 60.93; H, 4.72; N, 21.86. Found (%): C, 60.76; H, 4.49; N, 21.47.

4.4. General procedure for the hydrolysis–decarboxylation of 1-alkyl-7-ethoxycarbonyl-6-methyl-3-phenyl-pyrazolo[5,1-*c*][1,2,4]triazole derivatives

A mixture of 1.54 mmol 1-alkyl-7-ethoxycarbonyl-3-phenyl-6-methyl-pyrazolo[5,1-*c*][1,2,4]triazole in 10 mL 80% H_2SO_4/AcOH 2:8 (v/v) mixture was refluxed for 17–20 h (TLC monitoring). The resulting solution was poured into 100 mL distilled water and the pH was brought to neutral by adding Na_2CO_3. The product was extracted with 3×15 mL ethyl acetate. The organic layer was dried over anhydrous Na_2SO_4 and then the solvent was removed using a rotavapor.

4.4.1. 1-Ethyl-6-methyl-3-phenyl-pyrazolo[5,1-*c*]-[1,2,4]triazole (16a). Yield: 0.26 g of pink powder, 76%; mp: 63–65 °C; IR (KBr) ν_{max}: 3134, 3058, 2981, 2934, 1598, 1469, 1191, 1081, 765, 692 cm^{-1}; δ_H (DMSO-d_6, 300 MHz): 8.36–8.33 (m, 2H, 2′-H, 6′-H), 7.59–7.46 (m, 3H, 3′-H, 4′-H, 5′-H), 5.74 (7-C–H), 4.17 (q, 2H, J=7.2 Hz, –CH_2CH$_3$), 2.32 (s, 3H, 6-C–CH$_3$), 1.40 (t, 3H, J=7.2 Hz, –CH$_2$$CH_3$); δ_C (DMSO-d_6, 75 MHz): 157.2 (6-C), 147.6 (7a-C), 136.6 (3-C), 129.7 (4′-C), 128.9 (3′-C, 5′-C), 125.8 (1′-C), 125.5 (2′-C, 6′-C), 77.5 (7-C), 44.8 (–CH$_2$–CH$_3$), 14.8 (6-C–CH$_3$), 13.6 (–CH$_2$–CH$_3$); MS (54 eV) *m/z*: 226 (M^+, 100%), 211 (M^+−•CH_3, 9%), 197 (M^+−•C_2H_5, 9%). Anal. Calcd (%) for $C_{13}H_{14}N_4$: C, 69.00; H, 6.24; N, 24.76. Found (%): C, 68.83; H, 6.11; N, 24.47.

4.4.2. 1,6-Dimethyl-3-phenyl-pyrazolo[5,1-*c*][1,2,4]triazole (13a). Yield: 0.21 g of brownish powder, 66%; mp: 61–63 °C. The product is identical with that obtained by alkylating compound **1** with dimethylsulfate (TLC, IR, NMR and MS).

4.4.3. 1-Benzyl-6-methyl-3-phenyl-pyrazolo[5,1-*c*][1,2,4]triazole (17a). Yield: 0.39 g of white powder, 90%; mp: 94–96 °C; δ_H (DMSO-d_6, 200 MHz): 8.45–8.29 (m, 2H, 2′-H, 6′-H), 7.65–7.47 (m, 3H, 3′-H, 5′-H, 4′-H), 7.45–7.30 (m, 5H, 2″-H, 6″-H, 3″-H, 5″-H, 4″-H), 5.48 (s, 1H, 7-H), 5.35 (s, 2H, –CH_2–), 2.31 (s, 3H, 6-C–CH_3); δ_C (DMSO-d_6, 50 MHz): 157.3 (6-C), 147.9 (7a-C), 137.1 (3-C), 135.5 (1″-C), 129.7 (4′-C), 128.8 (3′-C, 5′-C), 128.6 (2″-C, 6″-C), 128.0 (3″-C, 5″-C), 127.5 (4″-C), 125.7 (2′-C, 6′-C), 126.5 (1′-C), 77.8 (7-C), 53.4 (–CH$_2$–), 14.8 (6-C–CH$_3$); MS (54 eV) *m/z*: 288 (M^+, 55%), 197 ($M^+-C_6H_5CH_2^\bullet$, 10%), 91 ($C_7H_7^+$, 100%). Anal. Calcd (%) for $C_{18}H_{16}N_4$: C, 74.98; H, 5.59; N, 19.43. Found (%): C, 74.71; H, 5.33; N, 19.02.

References and notes

1. Bailey, J. *J. Chem. Soc., Perkin Trans. 1* **1977**, *18*, 2047–2051.
2. Bailey, J.; Bowes, E.; Marr, P. A. Brit. 1247493, 1967 (Eastman Kodak Co., USA).
3. Romanet, R. F.; Burns, P. A.; Fischer, S. M.; Spara, P. P.; Balasubramanian, R. P.; Lincoln, D. G.; Kapp, D. L. EP 936500, 1999 (Eastman Kodak Co., USA); Bose, J. A.; Valente, R. R.; Aimino, D.; Demejo, D. D. U.S. 5998629, 1999 (Eastman Kodak Co., USA); Diehl, D. R.; Mbiya, K.; Cowan, S. W. EP 1014185, 1999 (Eastman Kodak Co., USA); Diehl, D. R.; Kapiamba, M. C.; Stanley, W. U.S. 6197071, 2001 (Eastman Kodak Co., USA); Mura, A. J., Jr.; Eiff, S. L.; Russo, G. M. U.S. 6348306, 2002 (Eastman Kodak Co., USA).
4. Arakawa, J. EP 1136530, 2001 (Fuji Photo Film Co.).
5. Katsunori, K.; Takayuki, S.; Hiromi, I., JP 167305, 2002 (Konica Co., Japan).
6. Plos, G.; Lagrange, A. EP 1062937, 2000 (L′Oreal).
7. Andousset, M. EP 1040818, 2000 (L′Oreal).
8. Bercean, V.-N.; Costea, L. V.; Badea, V.; Merz, A. *Book of Abstract MP-22*, XXIst European Colloquium on Heterocyclic Chemistry, Sopron, Hungary, September 12–15, 2004.
9. Csunderlik, C.; Bercean, V.-N.; Peter, F.; Badea, V. *ARKIVOC* **2002**, *ii*, 133–141, http://www.arkat-usa.
10. Bercean, V.-N.; Badea, V.; Venter, M.; Medeleanu, M.; Csunderlik, C. *ARKIVOC* **2005**, *x*, 130–138, http://www.arkat-usa.
11. Bercean, V.; Badea, V.; Iorga, R.; Csunderlik, C. *Revista de Chimie* **2003**, *54*, 533–534.
12. Bercean, V. N.; Badea, V.; Csunderlik, C. *Revista de chimie* **2004**, *55*, 1018–1021.
13. Costea, L. V.; Bercean, V.-N.; Badea, V.; Chiriac, C. *Revista de Chimie* **2006**, *57*, 71–75.
14. Bercean, V.-N.; Badea, V.; Şofei, M.-D.; Mitroi, D.; Csunderlik, C. *Revista de Chimie* **2006**, *57*, 326–328.
15. Costea, L. V.; Bercean, V.-N.; Badea, V.; Gerdes, K.; Jordis, U. *Monatshefte für Chemie* **2006**, *137*, 737–744.
16. Katritzky, A. R.; Kuzmierkiewicz, W.; Greenhill, J. *Recl. Trav. Chim. Pays-Bas* **1991**, *110*, 369–375.
17. Irving, H.; Weber, O. *J. Chem. Soc.* **1959**, 2296–2298.