4-AMINOETHYLENE DERIVATIVES OF 2-METHYLBENZOTRIAZOLE

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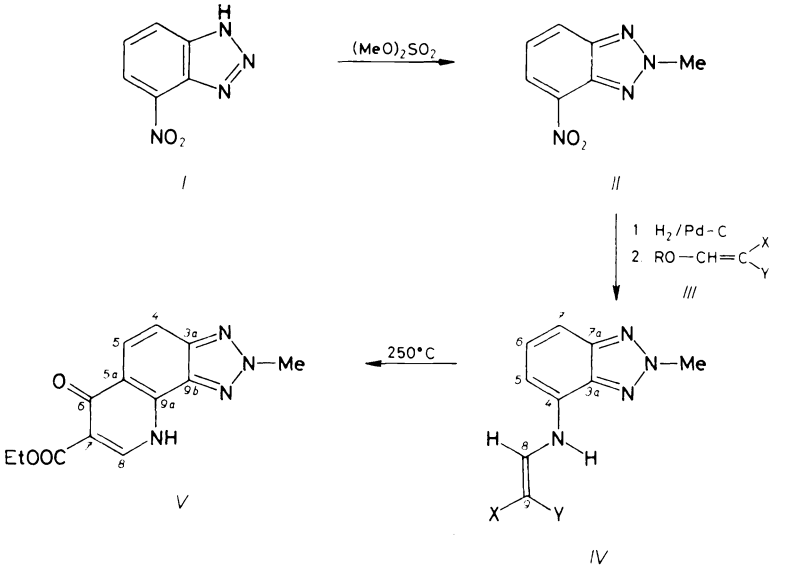
N-Methylation of 4(7)-nitrobenzotriazole (*I*) afforded a mixture of three isomers; one of them, 4-nitro-2-methylbenzotriazole (*II*) could easily be isolated. Catalytical hydrogenation of *II* led to the corresponding amine which in turn, afforded products of nucleophilic substitution *IVa*—*IVi* on reaction with alkoxymethylene derivatives *IIIa*—*IIIi*. Thermal cyclocondensation of *IVi* yielded 7-ethoxycarbonyl-6,9-dihydro-6-oxo-2-methyl-2*H*-triazolo[4,5-*h*]quinoline (*V*). The structure of all products was deduced from the IR, UV, ^{1}H and ^{13}C NMR spectral data.

An alkoxy group in alkoxymethylene derivatives of diesters or dinitriles of malonic acid[1,2], of 2,4-pentanedione[1], alkyl cyanoacetate[2] or acetoacetate[1] can easily be replaced by a suitable nucleophile such as e.g. aniline[2-4], or heterocyclic amines[5]. These products of substitution cyclized to form a 4-pyridone ring fused to the starting aromatic or heteroaromatic skeleton[6]. The 4- and 5-substituted aminobenzazoles either with[6] or without[7] tautomerism in the azole ring furnished under condition of the Gould–Jacobs reaction, similarly as 5-substituted 2-methylbenzotriazole derivatives[8] angularly annelated substituted azoloquinolones.

This paper presents the preparation of 2-methylbenzotriazole derivatives having an aminoethylene substituent in position 4, and two electron-accepting groups (nitrile, acetyl, alkoxycarbonyl or their combination); the condition for thermal cyclization of *IVi* (Scheme 1) was examined, too.

The starting material for the synthesis of 4-substituted derivatives *IV* (Table I) was 4-nitro-2-methylbenzotriazole (*II*), obtained by methylation of the tautomeric 4(7)-nitrobenzotriazole[9] with dimethylsulfate in sodium hydroxide solution. In accord with the literature, origination of only two products was observed, namely the 1- and 2-methyl-4-nitrobenzotriazoles, whereas the formation of 1-methyl-7--nitrobenzotriazole[10] was not mentioned. The ^{1}H NMR spectrum of the reaction mixture after methylation showed unequivocally the existence of all three isomers

in approximately equal proportion differing in position of the methyl group at the triazole ring. 2-Methyl-4-nitrobenzotriazole (*II*) differs from the other two isomers in its insolubility in concentrated hydrochloric acid; it was, therefore, possible to separate it similarly as 2-methyl-5-nitrobenzotriazole after methylation of tautomeric 5(6)-nitrobenzotriazole[11]. Purity of these products was verified by gas chromatography.



In formulae *III* and *IV*: *a*, R = Et ; X = CN ; Y = CN
b, R = Et ; X = COMe ; Y = CN
c, R = Me ; X = COOMe ; Y = CN
d, R = Et ; X = COOEt ; Y = CN
e, R = Et ; X = COMe ; Y = COMe
f, R = Me ; X = COOMe ; Y = COMe
g, R = Et ; X = COOEt ; Y = COMe
h, R = Me ; X = COOMe ; Y = COOMe
i, R = Et ; X = COOEt ; Y = COOEt

SCHEME 1

Catalytic hydrogenation of the nitro group over palladium on charcoal in ethanol yielded the respective amine, which was then subjected to the reaction with alkoxymethylene derivatives *III* obtained by the condensation of alkyl orthoformate with esters *IIIf*, *IIIg*, *IIIh*, *IIIi* (ref.[1]), *IIIc*, *IIId* (ref.[3]), dinitrile *IIIa*, or 2,4-pentanedione (*IIIe*, ref.[1]). 2-Ethoxymethylene-3-oxobutanonitrile (*IIIb*) was prepared by hydrolysis

of 3-amino-2-butenonitrile[12] to 3-oxobutanonitrile followed by a direct condensation with ethyl orthoformate. Compound *IIIb* has not been synthesized as yet (cf. Experimental). Thermal cyclocondensation at 250°C of ethyl 2-ethoxycarbonyl-3-(4-(2-methylbenzotriazolyl)amino)-2-propenoate (*IVi*) in an inert solvent gave the angularly fused 7-ethoxycarbonyl-6,9-dihydro-9-oxo-2-methyl-2*H*-triazolo[4,5-*h*]quinoline (*V*). Formation of another product was not observed.

The IR spectra of compounds *IV* (Table II) revealed stretching vibrations of the cyano group at 2 200 cm^{-1}, CH and NH bonds at 2 950–3 160 and 3 445 cm^{-1}, respectively. The out-of-plane vibrations of protons in aromatic ring, γ(CH), appeared at 800 cm^{-1}. Vibrations of carbonyl groups were often overlapped by those of C=C and HN—C=C groupings (ref.[14]); other bands occured at 1 630 to 1 730 cm^{-1}. The higher energy of intramolecular hydrogen bonding between the imine hydrogen and carbonyl of the acetyl group was manifested by lower frequency of the latter when compared with an ester carbonyl group[15].

TABLE I

2-Methyl-4-benzotriazolylaminoethylenes *IV*

Compound	Formula (M.w.)	M.p., °C Yield, %	Calculated/Found		
			% C	% H	% N
IVa	$C_{11}H_8N_6$	239–242	58·93	3·60	37·48
	(224·2)	32	58·48	3·68	37·18
IVb	$C_{12}H_{11}N_5O$	190–193	59·78	4·60	29·05
	(241·1)	64	59·58	4·48	29·14
IVc	$C_{12}H_{11}N_5O_2$	218–220	56·02	4·31	27·22
	(257·3)	58	55·99	4·26	27·20
IVd	$C_{13}H_{13}N_5O_2$	195–197	57·58	4·83	25·82
	(271·2)	53	57·52	4·76	25·64
IVe	$C_{13}H_{14}N_4O_2$	167–169	60·47	5·47	21·70
	(258·2)	51	60·26	5·39	21·75
IVf	$C_{13}H_{14}N_4O_3$	143–145	56·95	5·15	20·43
	(274·2)	72	56·70	5·38	19·98
IVg	$C_{14}H_{16}N_4O_3$	123–125	58·19	5·58	19·39
	(288·2)	75	58·12	5·61	19·28
IVh	$C_{13}H_{14}N_4O_4$	137–138	53·81	4·86	19·31
	(290·2)	44	53·61	4·72	19·31
IVi	$C_{15}H_{18}N_4O_4$	72–74	56·60	5·70	17·60
	(318·3)	53	56·58	5·60	17·48

The UV spectra of *IV* (Table III) displayed an absorption band with two inflections at 280 and 290 nm, resembling that of 2-methylbenzotriazole[16], but of lower intensities. Introduction of a polar aminoethylene substituent to the 2-methylbenzotriazole skeleton resulted in appearance of the most intense maximum at 350 nm. The stronger intramolecular hydrogen bonding of the acetyl group in comparison with an ester carbonyl was also seen in the UV spectra. Thus, compounds *IVb*, *IVe*–*IVg* had, in contrast to *IVc*, *IVd*, *IVh*, *IVi*, the longest wave band bathochromic-

TABLE II

IR spectra of compounds *IV*

Compound	ν_{max}, cm^{-1}							
	(C≡N)	(C=O)				(CH)	(NH)	(CH)
IVa	2 215[a]	—	—	—	—	3 215	3 450	805
IVb	2 206	—	—	1 653	1 634	3 165	3 446	794
IVc	2 212	1 730	1 693	1 650	1 632	3 156	3 420	797
IVd	2 218	1 710	1 694	1 647	1 637	2 990	3 450	796
IVe	—	—	—	1 647	1 637	3 015	3 445	800
IVf	—	1 705	—	—	1 640	2 955	3 450	800
IVg	—	1 710	—	—	1 637	2 980	3 440	793
IVh	—	1 726	1 694	—	1 634	2 956	3 448	799
IVi	—	1 730	1 693	1 650	1 632	2 986	3 446	802

[a] The wavenumber 2 222 cm^{-1} was ascribed to the second C≡N group.

TABLE III

UV spectra of compounds *IV*

Compound	λ_{max}, nm (log ε, m^2 mol^{-1})									
IVa	221·0	(3·43)	—		281·8	(3·02)	289·9	(3·00)	345·8	(3·52)
IVb	218·7	(3·40)	—		284·1	(2·81)	292·4	(2·74)	361·8	(3·41)
IVc	218·7	(3·37)	—		281·8	(2·92)	290·7	(2·86)	348·7	(3·46)
IVd	218·3	(3·43)	—		281·8	(2·96)	290·7	(2·90)	349·7	(3·51)
IVe	219·9	(3·32)	264·6	(2·94)	282·5	(2·88)	291·5	(2·75)	360·8	(3·44)
IVf	219·3	(3·40)	242·7	(2·92)	283·3	(2·80)	292·4	(2·70)	360·2	(3·44)
IVg	219·9	(3·39)	242·7	(2·93)	283·8	(2·81)	291·3	(2·74)	359·7	(3·45)
IVh	221·4	(3·34)			279·6	(2·77)	290·7	(2·68)	349·2	(3·37)
IVi	222·0	(3·48)	—		279·3	(2·92)	290·1	(2·84)	349·7	(3·49)

ally shifted by 10 nm (ref.[15]). Compounds *IVe*–*IVg* disclosed also inflections at 242 or 265 nm. Spectra of *IVa*, *IVc* and *IVi*, unlike those of derivatives having a tautomeric imino hydrogen[5] instead of a methyl group at the triazole ring, showed all bands bathochromically shifted by up to 20 nm. Analogous substances possessing a 2-methylbenzotriazole ring and the same substituents, but in positions 5 (ref.[17]) did not absorb at 290 nm; the longest wave bands of *IVa*, *IVc* and *IVi* were shifted by 15–18 nm, thus indicating, like in the preceding case, greater conjugation between the substituent and the ring.

Derivatives *IVb*–*IVd*, *IVf* and *IVg* can exist as two isomers with respect to their asymmetric substitution (X ≠ Y, Scheme 1) at the aminoethylene residue. The relative ratio of the individual geometric isomers could be estimated from their NMR spectral data (Tables IV and V) considering the integral intensities of signals and coupling constants ^3J(C, H) between the olefinic proton and the carbonyl or cyano groups carbon. For instance the *E* : *Z* ratio for *IVb* was found to be 1 : 1, whereas with other compounds the energetically more favoured *E* isomers prevailed. The *E* : *Z* ratio of derivatives with a cyano group (*IVc*, *IVd*) was 65 : 35, that of derivatives with bulkier acetyl group (*IVf*, *IVg*) was 85 : 15 and 88 : 12, respectively. This finding can most probably be explained by the existence of an intramolecular hydrogen bonding between the acetyl group and the imino-group hydrogen; this bond, however, does not exist in *E*-isomers of cyano derivatives *IVc*, *IVd*. For acetoacetate derivatives *IVf*, *IVg*, this intramolecular bond is stronger with carbonyl of the acetyl group than with that of the ester group this being evidenced by a remarkable NH signal shift towards lower field (up to 1·70, ref.[15]).

Strong polarization of the aminoethylene residue was reflected by the C-9 signal shift. When the ethylene residue was substituted by two equal substituents (X = Y), the most electron-accepting groups were nitriles (*IVa*, δ 52·5), worse acceptors were alkoxycarbonyls (*IVh*, *IVi*, δ 93·7 and 94·1, respectively) and the least accepting were acetyls (*IVe*, δ 113·2).The substituent with unequal groups (X ≠ Y) the most polarized were cyanoacetates (*IVc*, *IVd*), followed by 3-oxobutanenitrile (*IVb*) and 3-oxobutanoic acid esters (*IVf*, *IVg*). This effect is also less observable on the C-8 signal shift. Protons H-5, H-6 and H-7 form a strongly coupled ABC system with H-7 signals at the lowest field (HETCOR technique). The ^3J(5, 6) and ^3J(6, 7) coupling constants for *IVe* were 7·8 and 8·4 Hz, respectively; in the spectra of other compounds they were unresolved.

The ^{13}C NMR spectra reflect the influence of asymmetrically substituted aminoethylene residue at C-4 (X ≠ Y) on carbon atoms of the benzene ring; the greatest influence was seen at C-5, the smallest at C-6. Signals of quaternary carbons were assigned according to their various relaxation times and by comparison with the ^{13}C NMR spectrum of 2-methylbenzotriazole[18].

The electron impact mass spectra of compounds *IV* (Table VI) showed intense peaks of molecular ions. Origination of more intense species could be explained by

TABLE IV

^{1}H NMR spectra of compounds *IV*

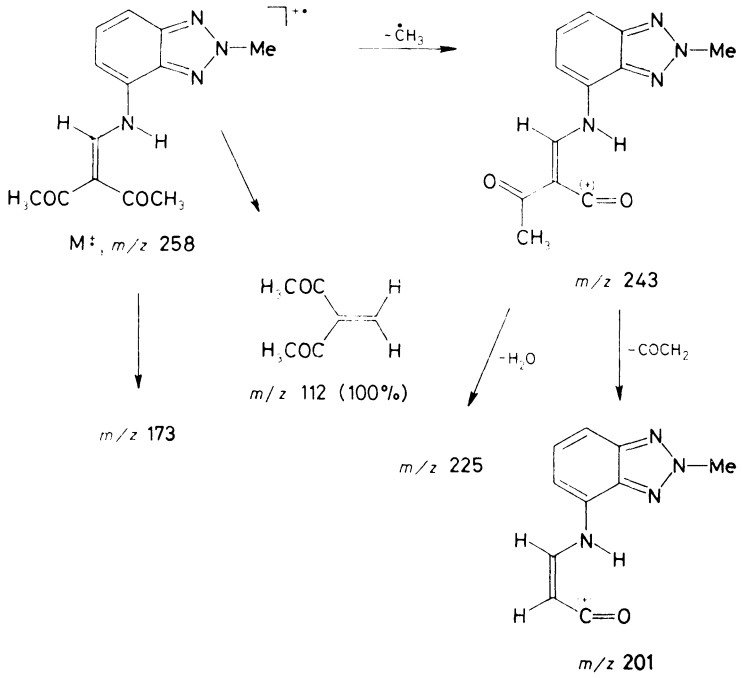
Compound		H-5, H-6	H-7	H-8	NH	^3J(H-8, NH)	NMe	X, Y
IVa		7·36 m (2 H)	7·66 m	8·93 s	11·62 s	—	4·53 s	—
IVb		7·40—7·60 m (2 H)	7·70 m	8·85 d 9·50 s	12·59 d 11·20 s	12·9	4·44 s	2·21 s (CH_3) 2·24 s (CH_3)
IVc	*E*	7·38—7·60 m (2 H)	7·68 m	9·54 d	—	—	4·55 s	3·75 s (OCH_3)
	Z			8·94 d	11·23 d	13·5		3·82 s (OCH_3)
IVd	*E*	7·20—7·44 m (2 H)	7·56 m	9·47 s	—	—	4·44 s	4·11 q (OCH_2); 1·18 t (CH_3)
	Z			8·83 d	11·13 d	13·5		4·18 q (OCH_2); 1·20 t (CH_3)
IVe		7·57 d 7·44 m	7·70 d	9·04 d	12·91 d	12·7	4·55 s	2·39 s (CH_3); 2·41 s (CH_3)
IVf	*E*	7·30—7·40 m (2 H)	7·62 m	9·07 d	12·96 d	13·5	4·52 s	3·72 s (OCH_3); 2·43 s ($COCH_3$)
	Z							3·82 s (OCH_3); 2·37 s ($COCH_3$)
IVg	*E*	7·30—7·43 m (2 H)	7·68 m	9·23 d	12·90 d	13·2	4·53 s	4·18 q (OCH_3); 1·32 t (CH_3); 2·45 s ($COCH_3$)
	Z							4·29 q (OCH_3); 1·34 t (CH_3); 2·39 s ($COCH_3$)
IVh		7·34 m (2 H)	7·59 d	9·11 d	11·23 d	13·5	4·52 s	3·76 s (OCH_3); 3·69 s (OCH_3)
IVi		7·34 m (2 H)	7·60 d	9·16 d	11·15 d	13·6	4·51 s	4·25 q (OCH_2); 4·15 q (OCH_2); 1·28 t (CH_3)

TABLE V
^{13}C NMR spectra of compounds *IV*

Compound		C-3a	C-4	C-5	C-6	C-7	C-7a	C-8	C-9	NMe	Y-*trans*[a]			X-*cis*[a]		
IVa		135·9	128·6	114·1[b]	126·5	114·3[b]	145·3	156·8	52·5	43·5	116·4			113·6		
IVb		136·6[b]	128·4[b]	114·3[b]	127·4	115·0	146·2[b]	154·8[b]	85·6[b]	44·2	117·4			191·8		27·2
		136·9[b]	130·1[b]	112·3[b]	127·4	115·0	145·5[b]	153·4[b]	87·2[b]		197·2		29·0	120·4		
IVc	*E*	136·2	128·3	114·0[b]	127·0	113·8[b]	145·8	155·0	75·1	43·8	115·9			165·2	52·2	
	Z	136·5	129·6	111·4	127·1	114·4	145·2	153·8	75·1		167·1	52·3		119·1		
IVd	*E*	136·5	130·1	114·1	127·4	114·6	146·2	155·3	75·8	44·2	116·3			165·2	61·2	14·9
	Z	136·8	130·7	111·6	127·5	114·3	145·5	154·1	75·7		167·1	61·6	14·8	118·3		
IVe		136·4	128·7	111·8	126·9	113·6	145·0	152·8	113·2	43·5	200·0		31·6	195·2		27·4
IVf	*E*	136·2	128·4	111·9	126·8	113·8	145·1	152·2	102·6	43·5	166·4	51·1		199·0		30·8
	Z	136·2	128·4	111·9	126·8	113·3	145·1	151·9	102·6		[c]		30·2	[c]	51·3	
IVg	*E*	136·1	128·5	112·3	126·9	113·8	145·2	152·5	102·8	43·5	166·0	59·6	14·2	199·0		30·8
	Z	136·1	128·5	111·4	126·9	113·3	145·2	152·3	104·2		[c]		30·5	163·1	60·1	14·2
IVh		136·0	128·7	111·0	126·8	113·0	145·1	152·1	93·7	43·4	168·0	51·3[b]		165·0	51·2[b]	
IVi		135·8	128·7	110·6	126·6	112·7	145·1	151·7	94·1	43·3	167·5	59·8[b]	14·1[b]	164·4	59·5[b]	14·0[b]

[a] Relative to H-8; [b] unresolved; [c] signal unobserved.

bond fissions, mainly in the aminoethylene chain. Molecular ions of derivatives with an ester group (*IVc, IVd, IVf–IVi*) lose molecules of the corresponding alcohol and carbon oxide. Formation of the fragment ions was verified by detection of the metastable transition. Formation of various fragment ions resulting from rupture of the N—C bond in β-position with respect to the ring depends on the localization of charge on the molecular ion. Thus, whilst the fragment ion at *m/z* 148 from the diacetyl derivative *IVe* (Scheme 2) was formed via a hydrogen transfer to nitrogen,



SCHEME 2

the base peak in the spectrum was created from the precursor with the charge localized in the other part of the molecule. The rearrangement process is associated with formation of the ion at *m/z* 159 with a $CHN^{(+)}$ group at the nucleus, as well. The greatest relative representation of this fragment showed the dicyano derivative.

EXPERIMENTAL

The melting points were measured on Kofler micro hot-stage. The IR spectra (0·5 mg of the substance per 300 mg KBr) and the UV spectra ($1 \cdot 10^{-4}$ mol dm^{-3} in methanol, cell width 2 mm) were recorded with Specord M 80 (Zeiss, Jena) and Specord (Zeiss, Jena) spectrophoto-

meters, respectively. The ^1H and ^{13}C NMR spectra of hexadeuterodimethylsulfoxide solutions (*IIIb* in deuterochloroform) run with Varian VXR-300 instrument at 298 K are relative to hexamethyldisiloxane (internal reference for ^1H NMR) and hexadeuterodimethylsulfoxide (δ 39·5) or chloroform (δ 77·27) for ^{13}C NMR spectra. Saturated solutions were measured in a 5 mm multinuclear probe. The ^1H NMR spectra were recorded at the spectral width 4 kHz, number of points 16 000. The ^{13}C NMR spectra were measured at 75 kHz operating frequency, spectral width 16 kHz and 64 k words of datapoints per spectrum. Number of accumulations of proton decoupled ^{13}C NMR spectra varied within 250 and 1 000. The pulse repetition time 3 s, flip angle 45°. The electron impact mass spectra were taken with an MS 902S (AEI-Kratos) instrument at 70 eV electron energy and 100 μA trap current.

2-Ethoxymethylene-3-oxobutanonitrile (*IIIb*)

3-Amino-2-butenenitrile (82 g, 1 mol) dissolved in eter (1 000 ml) was added to a well stirred hydrochloric acid (15%, 230 ml) at 0°C. The aqueous layer was extracted with ether (2 × 150 ml), the combined ethereal extract was washed with water (2 × 250 ml) and dried with sodium sulfate. The obtained solution of 3-oxobutanenitrile was added with stirring to ethyl orthoformate (148 g, 1 mol) at 40—60°C bath temperature at a rate ensuring a fluent removal of ether. Further ethyl orthoformate (148 g, 1 mol) was added to the mixture after addition of one half of the 3-oxobutanenitrile solution. Finally, the solvent being removed at up to 90°C, the

TABLE VI
The most important ions in the mass spectra of compounds *IV*

Compound	*m/z* (relative intensity, %)
IVa	225 $(M + 1)^{+\cdot}$ (16), 224 $(M^{+\cdot})$ (100), 160 (11), 159 (96), 154 (21), 148 (18), 105 (13), 78 (14), 77 (18), 51 (15)
IVb	242 $(M + 1)^{+\cdot}$ (17), 241 $(M^{+\cdot})$ (100), 226 (34), 199 (17), 198 (29), 183 (13), 173 (79), 159 (23), 148 (14), 43 (47)
IVc	258 $(M + 1)^{+\cdot}$ (14), 257 $(M^{+\cdot})$ (90), 26 (20), 225 (100), 197 (47), 182 (15), 159 (25), 155 (16), 154 (94), 77 (16)
IVd	272 $(M + 1)^{+\cdot}$ (17), 271 $(M^{+\cdot})$ (100), 226 (23), 225 (99), 198 (21), 197 (45), 182 (16), 159 (19), 155 (16), 154 (79)
IVe	258 $(M^{+\cdot})$ (65), 243 (19), 225 (50), 201 (23), 173 (86), 159 (24), 148 (15), 112 (100), 70 (26), 43 (60)
IVf	274 $(M^{+\cdot})$ (64), 242 (34), 227 (13), 214 (62), 199 (100), 173 (40), 172 (34), 129 (24), 128 (23), 43 (36)
IVg	288 $(M^{+\cdot})$ (60), 243 (13), 242 (34), 214 (71), 199 (100), 173 (53), 172 (32), 142 (27), 129 (19), 43 (34)
IVi	318 $(M^{+\cdot})$ (51), 272 (100), 199 (25), 198 (24), 172 (26), 148 (21), 133 (14), 129 (19), 115 (17), 29 (41)

mixture was refluxed for 5 h, and distilled. The title product was collected at 150–155°C/2.4 kPa; m.p. 66–67°C. IR spectrum, cm^{-1}: 2 235 (CN), 1 680 (CO), 1 630 and 1 620 (C=C), 1 273 (=C—O—C). UV spectrum λ_{max}, nm (log ε): 256·7 (3·19). ^{1}H NMR spectrum: 1·46 t, 3 H (CCH_3); 2·37 s, 3 H ($OCCH_3$); 4·40 q, 2 H (OCH_2); 8·05 s, 1 H (—CH=). ^{13}C NMR spectrum: 15·3 (CCH_3), 28·0 ($OCCH_3$), 74·2 (OCH_2), 94·8 (=C<), 114·5 (CN), 172·3 (—CH=), 191·7 (CO).

4-Nitro-2-methylbenzotriazole (*II*)

Hydrochloric acid (36%, 600 ml) was added to the mixture (20 g) obtained by methylation of 4(7)-nitrobenzotriazole (*I*) (ref.[10]) with dimethyl sulfate in aqueous sodium hydroxide. After shaking for 1 h the insoluble 4-nitro-2-methylbenzotriazole was filtered off, washed with water (2 × 600 ml), dried and crystallized from acetone (charcoal). Yield 6·5 g (32%), m.p. 183–184°C (ref.[10], 184°C).

4-Substituted Aminoethylene Deriatives of 2-Methylbenzotriazole (*IV*)

4-Nitro-2-methylbenzotriazole (*II*, 10 mmol) in ethanol (100 ml) was hydrogenated at 120 kPa on Pd/C (10%, 200 mg) till 660 ml of hydrogen was consumed. The catalyst was filtered off, the respective alkoxymethylene derivative (*III*, 10 mmol) was added and the mixture was refluxed for 30 min. The mixture was shortly boiled with charcoal, filtered, the most part of the solvent was evaporated, the separated product was filtered off and washed with cold ethanol. Crystallization from ethanol afforded analytically pure products.

Compound *IVi* was obtained by evaporation of the solvent under reduced pressure and a two-fold crystallization from chloroform–heptane; *IVh* was purified by chromatography of the crude product on silica gel (100–150 μm) with chloroform–toluene (1 : 1). Yields and other data are presented in Table I.

Ethyl-6-oxo-6,9-dihydro-2-methyl-2*H*-triazolo[4,5-*h*]quinoline-7-carboxylate (*V*)

Compound *IVi* (1 g) and Dowtherm (20 ml) were heated at 280°C for 4 h. The mixture was cooled, heptane (100 ml) was added, the separated precipitate was filtered off, washed with heptane and ether and recrystallized with addition of charcoal from dimethyl sulfoxide and water. Yield 0·54 g (64%), m.p. 220–223°C. For $C_{13}H_{12}N_4O_3$ calculated: 60·46% C, 4·68% H, 21·69% N; found: 60·23% C, 4·50% H, 21·52% N. IR spectrum, cm^{-1}: 1 718 and 1 627 (ν(C=O). UV. spectrum, λ_{max}, (log ε): 248·0 nm (3·59), 3·08 nm inflex (2·98), 323·8 nm inflex (3·07), 336·0 nm inflex (3·03). ^{1}H NMR spectrum: 8·31 s, 1 H (H-8); 7·89 d, 1 H (H-6); 7·63 d, 1 H (H-4, J(4,5) = = 9 Hz); 4·51 s, 3 H (NCH_3); 4·22 q, 2 H (OCH_2); 1·25 t, 3 H (CH_3). ^{13}C NMR spectrum: 171·8 (C-6), 164·5 (C=O), 147·8 (C-9b), 145·4 (C-8), 143·1 (C-3a), 135·5 (C-9a), 130·0 (C-5), 118·6 (C-4), 113·8 (C-7), 123·2 (C-5a), 59·9 (OCH_2), 43·5 (NCH_3), 14·2 (C–CH_3).

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