Tetrahedron. Vol. 30, pp. 3997 to 4012. Pergamon Press 1974. Printed in Great Britain

1,2,4-TRIAZINES AND CONDENSED DERIVATIVES—XIV[a]

THERMAL AND ACID CATALYSED DEGRADATIONS OF 3-ALKYLTHIO-6,7-DIHYDRO-[1.2.4]TRIAZINO[1.6-*c*]QUINAZOLIN-5-IUM-1-OLATES

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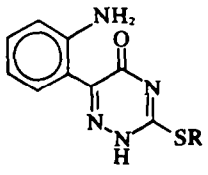
(*Received in UK* 8 *March* 1974; *Accepted for publication* 24 *June* 1974)

Abstract—3 - Alkylthio - 6,7 - dihydro - [1.2.4]triazino - [1.6-*c*]quinazolin - 5 - ium - 1 - olates (3), prepared by condensation of 3 - alkylthio - 6 - (2 - aminophenyl) - 1,2,4 - triazin - 5(2*H*) - ones (1) with aldehydes, ketones or their equivalents are transformed by thermolysis and/or acid treatment into 3 - alkylthio - [1.2.4]triazino[5.6-*b*]indoles (4) and/or 4 - (5 - alkylthio - *s* - triazol - 3 - yl) - quinolines (5). Alkylation and acylation reactions of the compounds 5 are discussed, as well as their NMR and UV spectra and those of their alkylation and acylation products.

In part XII[1] of the present series the condensation of 3 - alkylthio - 6 - (2 - aminophenyl) - 1,2,4 - triazin - 5(2*H*) - ones (1) with aldehydes, ketones or their equivalents to yield what has originally been assumed to be the corresponding tricyclic 3 - alkylthio - 6,7 - dihydro - [1.2.4]triazino[5.6-*d*] - [3,1]benzoxazepines (2) was described. Doubt was cast on this structure assignment by the result of the methylation studies,[2] and the X-ray molecular structure determination of the acetone condensation product of 1 (R = Me)[3] confirmed the dipolar structures 3 based on the methylation studies.



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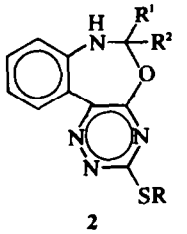

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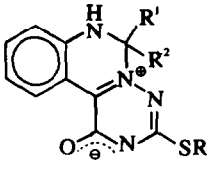

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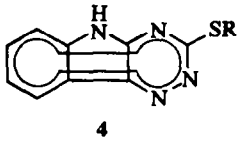

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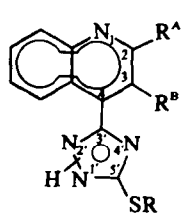
In the present paper we wish to describe the results of the thermal and acid catalysed degradations of compounds 3. While the aldehyde condensation products 3 (R^1 = H) proved thermally stable up to 150°, most of the condensation products 3 (R^2 = R″–CH_2, $R^1 \neq H$) obtained with ketones were transformed into ring contraction products of type 4[4] (under elimination of the ketone component) and/or dehydration products of type 5 ($R^A = R^1$, R^B = R″) when refluxed with DMF. (For the proof of structure of the dehydration products, see below.)



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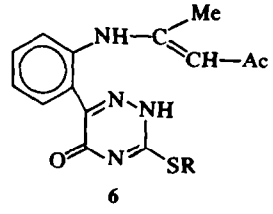

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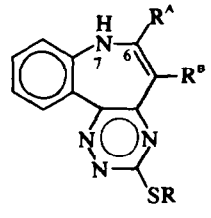

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If, in the ketone condensation products, R^1 is also of the type R′–CH_2, and R′ ≠ R″, formation of two isomeric (*s*-triazolyl)quinolines 5—with $R^A = R^1$, R^B = R″ and $R^A = R^2$, R^B = R′, respectively—could be expected. In one case, where the substituents R^1 and R^2, of the starting compound (3, R = R^1 = Me, R^2 = Et) did not differ greatly in their electronic nature, the two expected (*s*-triazolyl)quinolines were indeed formed (experiment No. 4, Table 1). In the other case studied, where the substituents R^1 and R^2 greatly differed in their electronic nature (3,

*For Part XIII see Ref 2.

Table 1. Thermolysis and acidolysis of 3-alkylthio-6,7-dihydro[1,2,4]triazino[1,6-c]quinazolin-5-ium-1-olates 3

	Starting compound, 3				Isolated products										
					4[a],	5									
No.	R^1	R^2	R	Conditions	yield %	R^A	R^B	yield %	M.p. °C	Solvent of recrystallization	Formula	M.wt	Calc'd/Found C%	H%	N%	S%
1[a]				10 min at 190° with 5 parts of $AcNH_2$	35[c] 13[d]			56[c] 32[d]								
2[a]	Me	Me	Me	90 min in 3 ml/g of refluxing anhydrous DMF	42[c,e]	Me	H	50[c] 29[d]	213–214	i-PrOH	$C_{13}H_{12}N_2S$	256·3	60·91 60·51	4·72 4·86	21·86 21·47	12·51 12·44
3[a]				15 min in a refluxing mixture of 2 ml/g of anhydrous DMF and 0·2 ml/g of $BF_3 . Et_2O$	26[d]			59[c] 24[d]								
4[a]	Me	Et	Me	1 h in 3 ml/g of refluxing anhydrous DMF	21[c]	Me	Me	5·3[d,f]	207–208 (sintering from 180)	$MeNO_2$	$C_{14}H_{14}N_2S$	270·35	62·19 61·99	5·22 5·65	20·73 20·95	11·86 11·68
						Et	H	18[d]	203–204	EtOAc			62·19 62·29	5·22 5·72	20·73 20·68	11·86 11·76
5[a]	$-(CH_2)_4-$	Me		15 min in 5 ml/g of refluxing anhydrous DMF	—	$-(CH_2)_3-$		97[c] 27[d]	225	i-PrOH	$C_{15}H_{14}N_4S$	282·36	63·80 63·60	5·00 5·48	19·84 19·43	11·36 11·72
6[b]	$-(CH_2)_4-$	$-C_2H_4OH$		10 min in 4 ml/g of refluxing anhydrous DMF	—	$-(CH_2)_3-$		25[d]	185–186 (dec.)	$MeNO_2$	$C_{16}H_{16}N_4OS$	312·34			17·94 17·69	10·26 10·03
7[a]				30 min in 5 ml/g of refluxing anhydrous DMF	29[c]			34[c]								
8[a]	$-(CH_2)_5-$	Me		Same but purification of the product according to[f]	10[d] —	$-(CH_2)_4-$		48[c] 35[d,f]	213–214	$MeNO_2$	$C_{16}H_{16}N_4S$	296·39	64·83 64·90	5·44 5·27	18·91 19·46	10·82 11·01
9[b]				5 min in a refluxing mixture of 5 ml/g of anhydrous DMF and 1 ml/g of $BF_3 . Et_2O$	57[c,g]	Me	Ph	—								
10[b]	Me	$PhCH_2$	Me			$PhCH_2$	H	—								
				15 min in a refluxing mixture of 12 ml/g ethanol under introduction of gaseous HCl	26[c]	Me	Ph	64[c]	199–200[h]	BuOH	$C_{19}H_{16}N_4S$	332·42				9·64 9·57
11[a]				2 min in 12 ml/g of refluxing 10% aqueous HCl	—	Me	Ac	75[c]	235–236	EtOH	$C_{15}H_{14}N_4OS$	298·36	60·38 60·96	4·73 5·20	18·78 18·73	10·75 10·77
12[a]	Me	$AcCH_2$	Me	5 min at 170–175°	—	Me	Ac	46[c]								
13[a]				5 min in 12 ml/g of refluxing anhydrous EtOH under introduction of gaseous HCl	—	Me	COOEt	97[c] 80[d]								
14[a]	Me	CH_2COOEt	Me	2 min in 10 ml/g of refluxing 15% aqueous ethanolic (1:1) hydrochloric acid	—	Me	COOEt	58[c,i]	187–188	$MeNO_2$	$C_{16}H_{16}N_4O_2S$	328·39	58·52 58·61	4·91 5·36	17·06 17·71	9·76 9·92
15[b]	Me	CH_2COOEt	$PhCH_2$	10 min in 6 ml/g of refluxing anhydrous EtOH under introduction of dry gaseous HCl	—	Me	COOEt	77[c] 52[d,i]	134 (sintering from 100)	$MeNO_2$	$C_{22}H_{20}N_4O_2S$	404·48			13·86 14·28	7·93 8·40

16[e]	COOMe	Me	Me	20 min in a refluxing mixture of 8 ml/g of anhydrous DMF and 1 ml/g of $BF_3 . Et_2O$	—	COOMe	H	74[c] 47[d,j]	226–228	DMF	$C_{14}H_{12}N_4O_2S$	300·34	55·98 55·95	4·03 4·92		10·68 10·83
17[a]	Me	H	Me	1 hr in a refluxing mixture of 10 ml/g of anhydrous DMF and 1 ml/g of $BF_3 . Et_2O$	48[e,j]	H	H	—								
18[a]	Ph	H	Me	No reaction occurred on refluxing for 1 h in DMF, not even in the presence of $BF_3 . Et_2O$	—											
19[a]	H	CH_2COOMe	Me	90 min in refluxing anhydrous MeOH under introduction of dry gaseous HCl	—	H	COOMe	45[c] 30[d,j]	100–105 (dec.)	$MeNO_2$	$C_{14}H_{12}N_4O_2S . H_2O$	318·35	52·82 52·73	4·43 4·77	17·60 17·50	10·07 10.34

[a] The preparation of the starting compound has been described in Ref. 1.
[b] The starting compound is new. For the method of its preparation, see Experimental.
[c] Almost pure (IR spectrum!) crude product.
[d] Chemically pure product.
[e] The acetone formed as a by-product has been detected in the form of its condensation product with **1** (R = Me), *c.f.* Ref. 4.
[f] Purified through the N-acetyl derivative.
[g] On refluxing of the starting compound for 15 min in 5 ml/g of anhydruous DMF, profound decomposition took place and neither of the corresponding compounds **4** and **5** could be isolated.
[h] Dried at 130°C *in vacuo* in order to remove one molecule of water of crystallization. The monohydrate melts at 110–112°C and, after resolidification, at 199–200°C. Calc'd N, 15·99; S, 9·15. (Found: N, 15·75; S, 9·39%.)
[i] On simple thermal treatment profound decomposition took place and neither of the corresponding compounds **4** and **5** could be isolated.
[j] No reaction occurred on refluxing in DMF.

$R = R^1 = Me$, $R^2 = AcCH_2$),* a single dehydration product (**5**, $R = R^A = Me$, $R^B = Ac$) was formed. The orientation is governed by the tendency of the more activated methylene group of the starting compound to be incorporated into the newly formed quinoline ring. No ring contraction product **4** was obtained in this case (experiment No 12, Table 1). No ring contraction products **4** were formed on thermolysis of the cyclopentane spiro compounds **3**, $R^1 + R^2 = -(CH_2)_4-$, either (experiments No's 5 and 6, Table 1).

No definite products were obtained from the condensation products **3** obtained with benzyl methyl ketone ($R^1 = PhCH_2$, $R = R^2 = Me$) and ethyl acetoacetate ($R^1 = CH_2COOEt$, $R^2 = Me$, $R = Me$ or $PhCH_2$). These compounds underwent profound decomposition on heating. The methyl pyruvate condensation product ($R^1 = COOMe$, $R^2 = Me$), on the other hand, proved stable when heated under reflux in DMF, as did also the condensation products obtained with acetaldehyde, benzaldehyde and methyl propiolate ($R^1 = H$, $R^2 = Me$, Ph, CH_2COOMe respectively).

Both the ring contraction and dehydration of compounds **3** are accelerated in the presence of hydrogen chloride or boron trifluoride etherate. The product ratio, however, was only slightly affected (compare experiments No's 2 and 3, and 11 and 12, respectively). In the presence of these catalysts, certain compounds **3** whether they are stable or suffer decomposition when heated under reflux in DMF, may be transformed into the corresponding dehydration and/or ring contraction products (experiments No's 9, 10, 13–17, 19, Table 1). The benzaldehyde condensation product **3** ($R^1 = H$, $R^2 = Ph$), however, proved stable even when heated under reflux in DMF in the presence of boron trifluoride etherate.

The acetylacetone, ethyl acetoacetate, methyl propiolate and methyl pyruvate condensation products furnished no ring contraction products **4** on degradation in the presence of hydrogen chloride or boron trifluoride etherate (experiments No's 11, 13–16, 19, Table 1). In the case of the two isomeric dehydration products which could theoretically be formed in experiments No's 11, 13–15, the only one isolated was the one in which the active methylene group of the starting compound had been incorporated into the quinoline ring of the product.

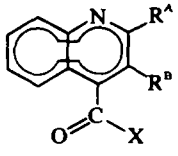
The benzyl methyl ketone condensation product **3** ($R = R^1 = Me$, $R^2 = PhCH_2$) furnished **4** ($R = Me$) as a single product in the presence of boron trifluoride etherate while, in the presence of ethanolic hydrogen chloride the dehydration product **5** ($R = R^A = Me$, $R^B = Ph$) was formed in addition (experiments No's 9, 10). The orientation in the latter was again governed by the tendency of the active methylene group of the starting compound to be incorporated into the quinoline ring of the product.

Proof of structure of compounds **5**. Two alternative structures, *viz* **5** and **7** (with $R^A = R^1$, $R^B = R''$ or $R^A = R^2$, $R^B = R^1$), were tentatively derived for the dehydration products. This was based on the stoichiometry of their formation (elimination of 1 molecule of water) and their NMR spectra, which demonstrated that the methylene group either of R^1 or of R^2 had been incorporated into a newly formed ring. Proof of structure **7** was attempted by introducing suitable substituents into the NH group of the dehydration product and subsequent ring closure towards position 8 or under participation of a suitable substituent R^A. Since all attempts to achieve such ring closures were unsuccessful, structure **7** had to be rejected. Structure **5**, on the other hand, has been proved by synthesis.

Since **1** is the condensation product of isatinic acid and thiosemicarbazide (or, more correctly, of the *S*-methyl derivative of the latter), both **3** and **5** may ultimately be considered as the condensation products of isatinic acid, an oxo compound and thiosemicarbazide. The first two components may be easily condensed to yield a 4-quinolinecarboxylic acid—actually this is an example of the well-known Pfitzinger synthesis[5] of quinolines—, and the carboxyl or modified carboxyl group of the latter may be used with the aid of thiosemicarbazide for the construction of the attached *s*-triazole ring.

The following two syntheses corresponding to the above general pattern were performed.

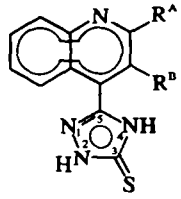
(1): 2 - Methyl - 4 - quinolinecarbohydrazide (**8**), prepared by reacting the corresponding methyl ester[6] with hydrazine hydrate, was reacted with ammonium thiocyanate to yield the *s*-triazolinethione **13**;



8–12

8–14

	R^A	R^B	X
8, 13	Me	H	$NHNH_2$
9	Me	Me	OMe
10, 14	Et	H	OMe
11	Et	H	$NHNH_2$
12	Me	H	NHNHCSNHMe



13†,14†

*This compound has earlier[1] been shown to exist, depending on the conditions, either as a mixture of the tricyclic and the open chain forms **6**, or as the pure compound **6**.

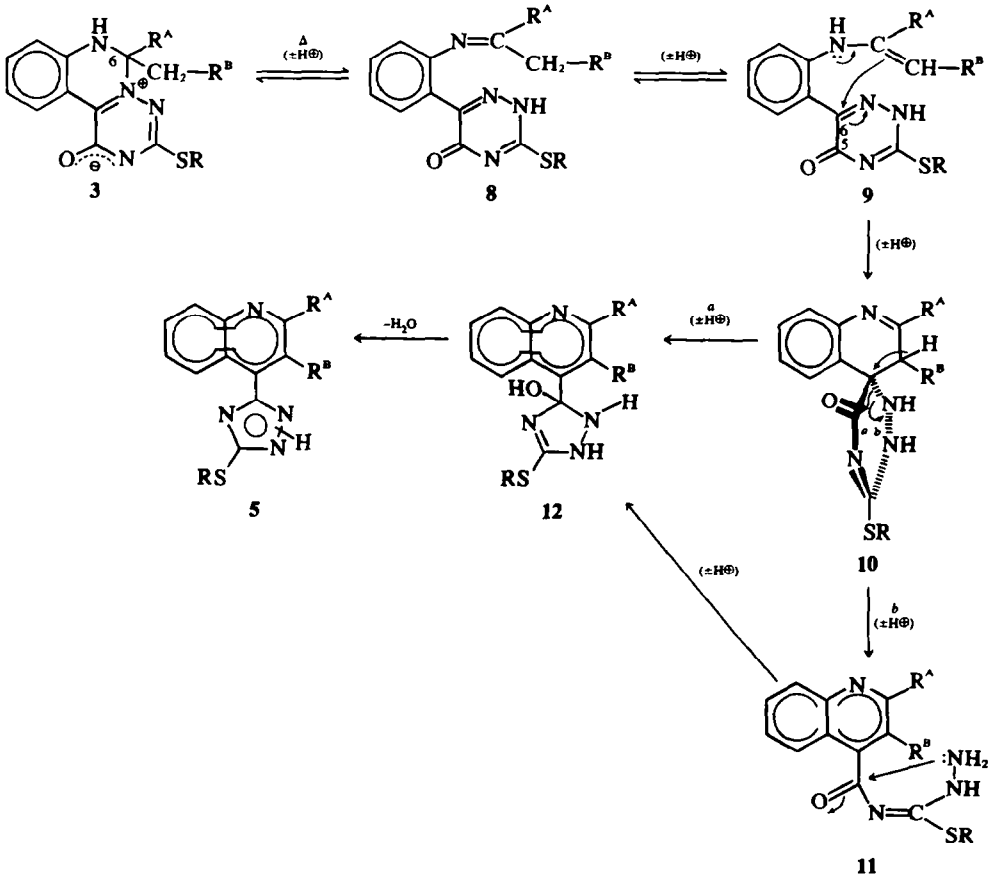
†Tautomeric structure arbitrarily assigned to the triazoline cycle.

The S-methyl derivative **5** of the latter was identical in every respect with the product obtained by thermolysis of **3** ($R^1 = R^2 = R = Me$).

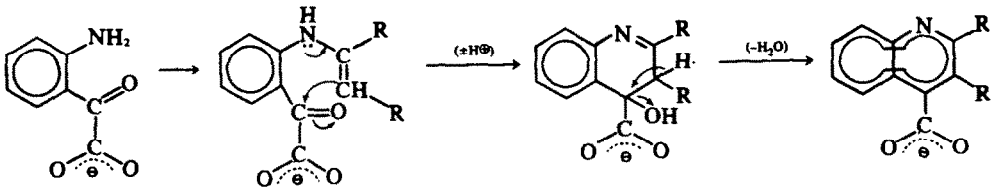
(2): A mixture of 2,3-dimethyl- and 2-ethyl-4-quinolinecarboxylic acids, obtained according to v. Braun *et al.*,[7] was reacted with diazomethane and the resulting mixture of the corresponding methyl esters **9** and **10** was treated with hydrazine hydrate. The ester **10** was thereby smoothly transformed into the hydrazide **11** whereas the isomeric ester **9**[7] did not react. After separation of **11** from unchanged **9*** the former was reacted with ammonium thiocyanate and the resulting *s*-triazolinethione (**14**) was methylated to yield a *S*-methyl derivative **5**, identical in every respect with one of the products obtained by thermolysis of **3** ($R^1 = Et$, $R^2 = R = Me$).

A reasonable pathway for the transformations **3**→**5** is shown in Scheme 1. The enamines **9** are thought to be the key intermediates of the reaction sequence. (At least one equilibrium of the type **3** ⇄ **9** actually exists as has been shown for the acetylacetone condensation product, see footnote on p. 4000). Nucleophilic attack of the β-carbon atom of the enamine moiety against C-6 of the triazine ring should then lead to **10** which subsequently rearranges to **12** either directly or through **11**. **12** should readily lose one molecule of water, the driving force of the last two processes being the aromatization of the quinoline and *s*-triazole rings, respectively. The transformations leading from **9** to **5** are, of course, analogous to the individual steps of the Pfitzinger synthesis (Scheme 2). In addition, Scheme 1 explains the catalytic effect of acids and boron trifluoride on the reactions **3**→**5**, as well as the observation that the benzaldehyde condensation product **3** ($R = Me$, $R^1 = Ph$, $R^2 = H$), which is incapable of furnishing an enamine form, is thermally stable even in the presence of boron trifluoride.

*The methyl ester **9** did not react with hydrazine hydrate even under more vigorous conditions than necessary for achieving transformation **10**→**11**. Steric hindrance caused by the Me group in position 3 of the quinoline nucleus may explain the observation that 2,3-dimethyl-4-quinolinecarboxylic acid did not condense with 2-methylthiosemicarbazide under conditions required for the reaction with the 2-monomethyl analogue (see below).



SCHEME 1



SCHEME 2

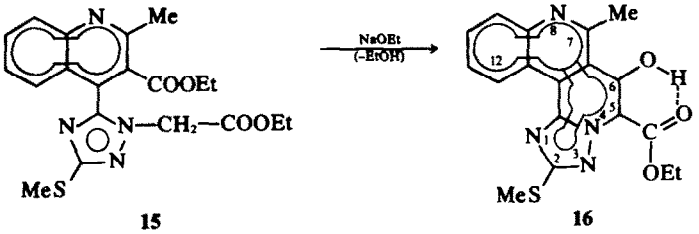
Compounds of types **8** and/or **9** may be considered as the intermediates of the ring contractions **3**→**4**. Under non-anhydrous conditions (which may be simply the result of the concomitant dehydration reactions **3**→**5**) these could, possibly, be hydrolysed to yield the corresponding compounds **1** which are known[4] to be converted both thermally or in the presence of acids into compounds **4**. This hydrolysis pathway is not the only one leading to the ring contraction since both the acetaldehyde and the benzyl methyl ketone condensation products (**3**, $R = R^1 = Me$, $R^2 = H$ and $PhCH_2$, respectively) when thermolysed in the presence of boron trifluoride etherate under *anhydrous* conditions, are transformed into **4** (R = Me) without concomitant formation of any dehydration products. If an alternative, non-hydrolytic pathway really exists for the transformations **3**→**4**, it must involve some kind of bond formation between the anionic O atom and C–6 of **3** since, in this case, the O atom of the resulting oxo compound must necessarily originate from the O atom of **3**.

Alkylation of the (s-triazolyl)quinolines **5**. The *s*-triazolylquinolines can be smoothly N-alkylated with diazomethane or, in the presence of base, with methyl iodide, chloroacetone and ethyl or methyl bromoacetate. Mixtures of isomeric products (containing the newly introduced N-alkyl group attached to different positions of the triazole ring) were always obtained, and from these only one of the isomers could be isolated easily. The presence and the ratio of the isomers in the alkylating reaction mixtures (Table 2) was detected and determined by NMR spectroscopy (see the section discussing the NMR spectra of the compounds **5** below).

Two of the three possible N-Me derivatives of **5** ($R^A = R = Me$, $R^B = H$) were prepared by structure proving syntheses and used as reference substances. Thus, 2 - methyl - 4 - quinolinecarboxylic acid was reacted with 2 - methylthiosemicarbazide[8] to yield, in two consecutive steps, the 1'–Me derivative of **13**. Methylation of the product furnished the 1'–Me derivative of **5** ($R^A = R = Me$, $R^B = H$).

The hydrazide **8**, on the other hand, reacted with methyl isothiocyanate to yield the aroyl thiosemicarbazide **12** which was cyclised by sodium ethoxide to the 4'-Me derivative of **13**, and the latter, when methylated with methyl iodide, furnished the 4'–Me derivative of **5** ($R^A = R = Me$, $R^B = H$).

Support for the position of the "alkyl" group in the case of compound **15** came from its Dieckmann type reaction induced by sodium ethoxide.



15 **16**

Acylation of the (s-triazolyl)quinolines **5**. Acetylation of all (s-triazolyl)quinolines **5** studied (see Table 3) resulted in only one N-acetyl derivative. For the acetyl derivatives of compounds **5** (R^A = Me, Et, COOMe, $R^B = H$, R = Me and $R^A + R^B = -(CH_2)_3-$, R = Me) the point of attachment of the acetyl group could be located by NMR at position 1' (see below). In the remaining cases the position of the acetyl group could not be established unequivocally.

An intramolecular acylation was achieved by treating **5** ($R^A = R = Me$, R^B = COOH), prepared by alkaline saponification of the corresponding ethyl ester, with acetic anhydride. The only possible sites of acylation of the triazole cycle in this case are, for steric reasons, positions 2' and 4'. Since simple *s*-triazoles are always acylated at N–1 or N–2,[9,10] we feel that the first of the two alternative structures (**17**, **18**) is the more likely.

NMR spectra. A low-field one-proton signal of the dd pattern ($J_o \approx 8$, $J_m \approx 2$ Hz) at about δ9 ppm which we attribute to the C–5 proton and should be

Table 2. Alkylation of 4-(5′-methylthio-*s*-triazol-3′-yl)quinolines **5**

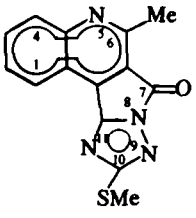
Starting compound: **5**			Alkylating agent and conditions	Isolated product: Position of entering group[a] and yield	M.p.	Recryst'd from	Formula (Mol. wt.)	Calc'd/found C	H	N	S	Ratio of 1′-, 2′- and 4′-alkylated products formed[a]
R^A	R^B	R										
			Diazomethane, 0°C									58:38:4
Me	H	Me	Diazomethane, r.t.	1′; 39%	101°	ligroine	$C_{16}H_{14}N_4S$	62·19	5·22		11·86	63:27:10
			MeI + NaOMe/MeOH, 0°C				(270·35)	62·13	5·01		11·91	59:33:8
			MeI + NaOMe/MeOH, refl.	1′; 39%	101°	ligroine						63:28:9
			$BrCH_2COOMe$ + NaOMe/MeOH	1′; 53%	132–133°	ligroine	$C_{16}H_{16}N_4O_2S$	58·52	4·91	17·07		65:35:0
							(328·30)	58·65	5·54	16·91		
Et	H	Me	Diazomethane, r.t.									60:40:0
			MeI + NaOMe/MeOH, 0°C	1′; 52%	184°	2-propanol	$C_{15}H_{14}N_4O_2S$			17·82	10·20	
							(314·36)			17·92	10·32	
COOMe	H	Me	$ClCH_2Ac$ + KI + NaOMe/MeOH, refl.	1′; 51%	168–170°	2-propanol	$C_{17}H_{16}N_4O_3S$	57·29	4·53	15·72	8·90	
							(356·4)	57·32	3·92	15·83	9·31	
			$BrCH_2COOMe$ + NaOMe/MeOH, refl.									main product: 1′-alkyl derivative
Me	Me	Me	Diazomethane, r.t.	2′; 65%	160–161°	ligroine	$C_{13}H_{16}N_4S$	63·15	5·67	19·30	11·28	
							(284·38)	63·70	5·73	19·61	11·41	
			Diazomethane, r.t.	2′; 65%	119°	ligroine	$C_{17}H_{18}N_4O_2S$	59·63	5·30	16·37	9·36	
Me	COOEt	Me	MeI + NaOEt/EtOH, refl.				(342·41)	60·06	5·26	16·99	9·62	46:46:8
			$BrCH_2COOEt$ + NaOEt/EtOH, refl.	2′; 28%[b]	126°	2-propanol or ligroine	$C_{20}H_{22}N_4O_4S$	57·95	5·35	13·52	7·74	
							(414·48)	58·20	5·36	13·35	8·18	65:35:0

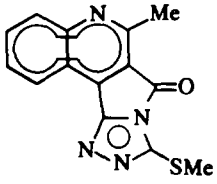
[a] As determined by NMR spectrometry.
[b] 10% of compound **16** were obtained as a by-product in addition to compound **15**.

Table 3. Acetylation of 4-(5′-methylthio-*s*-triazol-3′-yl)quinolines **5** with acetic anhydride/pyridine

Starting compound, **5**			Isolated product							
			Position of entering group and yield	M.p., °C	Recryst'd. from	Formula (Mol. wt.)	Calc'd/found			
R^A	R^B	R					C	H	N	S
Me	H	Me	1′;[a] 79%	159–160	CCl_4/petroleum ether or acetic anhydride	$C_{15}H_{14}N_4OS$ (298·36)	60·38 60·31	4·73 4·98	18·78 18·50	10·75 10·85
Et	H	Me	1′;[a] 70%	102	ligroine	$C_{16}H_{16}N_4OS$ (312·39)	61·51 61·90	5·16 5·34		
COOMe	H	Me	1′;[a] 96%	197[d]	chloroform/ether	$C_{16}H_{14}N_4O_3S$ (342·37)	56·13 56·06	4·12 4·25	16·37 15·80	9·36 9·40
—$(CH_2)_3$—		Me	1′;[a] 46%	144–145	aqueous EtOH	$C_{17}H_{16}N_4OS$ (324·40)	62·94 62·77	4·97 5·30	17·27 17·07	9·88 10·13
—$(CH_2)_4$—		Me	2′(?);[b] 58%[c]	173	ligroine	$C_{18}H_{18}N_4OS$ (338·42)	63·88 63·91	5·36 5·27	16·56 16·50	9·47 9·87
Me	Ph	Me	2′(?);[b] 53%	182	ligroine	$C_{21}H_{18}N_4OS$ (374·45)	67·35 67·54	4·85 4·98	14·96 14·96	
Me	COOEt	Me	2′(?);[b] 70%	149–150	CCl_4/petroleum ether	$C_{18}H_{18}N_4O_3S$ (370·42)	58·36 58·43	4·89 5·20	15·13 15·77	8·65 9·04

[a] As deduced from the NMR spectrum, see text.
[b] As deduced from the UV spectrum, see text.
[c] The crude **5** ($R^A + R^B$ = —$(CH_2)_4$—, R = Me), obtained by thermolysis of the corresponding **3** in boiling DMF, was directly acetylated. The yield stated is the combined yield of the processes.
[d] At 179–180° an allotropic change (from small cubes to needles) takes place.


17


18

strongly deshielded by the adjacent *s*-triazole ring, is the most striking peculiarity of the NMR spectra of those compounds (**5**) which do not bear a substituent attached to position 3 ($R^B = H$, compounds No's 1 and 11 of Table 4), as well as of the 1′-Me derivative of the former (compound No. 2 of Table 4), obtained by synthesis (see above). This assignment comprises the assumption (born out also by inspection of molecular models) that the above compounds possess comparatively stable planar or quasi-planar conformers. The signal of H–3, too, appears, in agreement with this assumption, at rather low field in the NMR spectra of the above compounds.

The 5–H signal of those compounds (**5**) which have a substituent at C–3 (compounds No's 16, 21, 24 and 26 of Table 4), as well as of the 4′-Me derivative (compound No. 4) obtained by synthesis (see above) is, on the other hand, not separated from the multiplet of the other aromatic protons. The reason of this behaviour is, of course, that the C–3 and N–4′ substituents, respectively, prevent the molecules by steric interference from adopting planar or quasi-planar conformations. As a consequence, the signal of H–3 in the spectrum of compound No. 4, too, is considerably (by about 0·5 ppm) diamagnetically shifted with respect to the signal of the same proton in the spectra of the parent substance and of the 1′-Me analogue (compounds No's 1 and 2, Table 4). The spectrum of the 2′-Me derivative (compound No. 3 of Table 4), although similar to that of the 4′-Me isomer, displays some important differences (see below).

The behaviour of the 2,3-trimethylene derivatives (compounds No's 18 and 20 of Table 4) as well as of the 3-acetyl derivative (compound No. 23) is intermediate between that of the above two groups: the H–5 signal is separated from the signals of the remaining aromatic protons but it is diamagnetically shifted by about 0·5 ppm with respect to the signal of the same proton in the spectra of group 1 compounds. Evidently, the steric interference exerted by the fused cyclopentene ring and the 3-acetyl group, respectively, is not able to completely prevent the adoption of quasi-planar conformations.

Thus, the NMR spectra provide a means for distinguishing between compounds **5** (and their derivatives substituted in the triazole cycle) possessing or not possessing low-energy planar or quasi-planar conformations and hence, in many instances, for distinguishing between the isomeric derivatives of compounds **5** carrying a substituent attached to N–1′ or to another N atom of the triazole cycle.

In the case of compound **5** ($R^A = R = Me$, $R^B = H$) the spectra of all three isomeric N–Me derivatives (compounds No's 2–4 of Table 4) have been obtained. In addition to the differences between these spectra, a useful correlation concerning the positions of the N–Me signals was obtained: δ(N–Me): 1′-methyl >2′-methyl > 4′-methyl isomer.

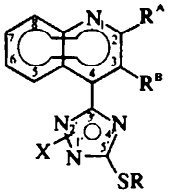
It was found that the 1′- and 2′-methyl isomers are the main products of methylation of compound **5** ($R^A = R = Me$, $R^B = H$), under all conditions tested, while the 4′-methyl isomer was always obtained as a minor product. (This agrees with the orientation observed during alkylation of simple *s*-triazoles where the 4-alkyl derivatives could only be isolated as minor by-products.[11,12])

By applying one or the other of the above correlations, the structures of the alkylation and of some acetylation products of the compounds **4** could be established with a high degree of reliability. A few examples follow.

The main methoxycarbonylmethylation product of **5** ($R^A = R = Me$, $R^B = H$), which was also obtained in pure form (compound No. 5 of Table 4), must be the 1′-substituted product, the two diagnostic signals being those of 3–H and 5–H. The only other isomer formed in appreciable amounts (compound No. 6 of Table 4) must be the 2′-substituted derivative since the 4′-substituted compound would be only a minor product. The situation is analogous in the methoxycarbonylmethylation of **5** (R^A = COOMe, $R^B = H$, R = Me) although in this case the two products (compounds No's 13 and 14, Table 4) have not been separated. The acetyl derivatives of compounds **4** (R^A = Me, Et, COOMe, $R^B = H$, R = Me) are the 1′-isomers (compounds No's 7, 10 and 15 of Table 4), the two diagnostic signals being again those of 3–H and 5–H. The same is true for the acetylation product (compound No. 19 of Table 4) of the trimethylene derivative as well but, in this instance, only the signal of 5–H may be used for establishing the structure. In the case of compounds 22, 32 and 35, on the other hand, the positions of the acetyl groups could not be deduced from the NMR spectra.

The ratio of the three isomers (compounds No's 27–29 of Table 4), formed on methylation of **5** ($R^A = R = Me$, R^B = COOEt), could be determined by comparing the intensities of the three N–Me signals of the crude methylation mixture; the N–Me signals, in turn, were assigned to the individual isomers, among others, by using the correlation pertaining to the relative chemical shifts of these groups (see above).

Table 4. NMR spectra[a] of compounds **5** and of their alkylation and acetylation products



No.[b]	R^	R^B	R	X	Solvent	Assignment of signals[c] R^	R^B	5-H	6-H–8-H	R	X
1	Me	H	Me	H	DMSO-d_6	2·8, s	8·0, s	9·15, dd[d]	490–450	2·8, s	—
					TFA	3·2 or 3·0, s	8·4, s	8·9, dd[d]	510–490	3·2 or 3·0, s	—
2[e]	Me	H	Me	1'-Me	CCl_4	2·76 or 2·69, s	7·95, s	9·15, dd[d]	495–440	2·76 or 2·69, s	3·7, s
					$CDCl_3$	2·80 or 2·75, s	8·0, s	9·1, dd[d]	495–440	2·80 or 2·75, s	3·8, s
3[f]	Me	H	Me	2'-Me	$CDCl_3$		7·34, s				3·65, s
4[g]	Me	H	Me	4'-Me	$CDCl_3$	2·86 or 2·82, s	7·5, s	[i]	495–460	2·86 or 2·82, s	3·43, s
5	Me	H	Me	1'-CH_2COOMe	$CDCl_3$	2·8, s	8·02, s[h]	9·1, dd[d,h]	495–450	2·8, s	5·0, s, 2H + 3·82, s, 3H,
6[j]	Me	H	Me	2'-CH_2COOMe	$CDCl_3$	2·8 or 2·7, s	7·4, s	[i]		2·8 or 2·7, s	4·75, s, + 3·75, s[j]
7	Me	H	Me	1'-Ac	$CDCl_3$	2·79 or 2·72, s	8·05, s[h]	9·08, dd[d,h]	475–440	2·79 or 2·72, s	2·79 or 2·72, s
8[k]	Et	H	Me	1'-Me	$CDCl_3$	3·1, q + 2·98, q +	[i]	9·00, dd[d,h]	495–440	2·75, s	3·9, s
9[k]	Et	H	Me	2'-Me	$CDCl_3$	1·42, t + 1·38, t[l]	[i]	[i]		2·82, s	3·72, s
10	Et	H	Me	1'-Ac	$CDCl_3$	3·1, q + 1·45, t[l]	8·05, s[h]	9·02, dd[d,h]	500–440	2·78, s	2·78, s
11	COOMe	H	Me	H	DMSO-d_6	4·1, s	8·8, s	9·35, dd[d]	505–470	2·83, s	—
12	COOMe	H	Me	1'-AcCH$_2$	$CDCl_3$	4·1, s	8·92, s[h]	9·2, dd[d,h]	505–460	2·8, s	5·0, s, 2H + 2·28, s, 3H
13[m]	COOMe	H	Me	1'-CH_2COOMe	$CDCl_3$	4·1, s	8·9, s[h]	9·2, dd[d,h]	505–460	2·8, s	5·0, s + 3·82, s[j]
14[m]	COOMe	H	Me	2'-CH_2COOMe	$CDCl_3$		[i]	[i]		2·7, s	4·85, s + 3·7, s[j]
15	COOMe	H	Me	1'-Ac	$CDCl_3$	4·1, s	8·8, s[h]	9·05, dd[d,h]	505–445	2·78 or 2·77, s	2·78 or 2·77, s
16	Me	Me	Me	H	DMSO-d_6	2·75 or 2·74, s	2·35, s	[i]	495–450	2·75 or 2·74, s	—
17	Me	Me	Me	2'-Me	$CDCl_3$	2·75 or 2·65, s	2·25, s	[i]	490–425	2·75 or 2·65, s	3·55, s
18	–$(CH_2)_3$–		Me	H	DMSO-d_6	3·2, m, 4H + 2·15, m, 2H		8·4, dd[d]	490–450	2·75, s	—
					TFA	3·6, m, 4H + 2·6, m, 2H		[i]	505–485	3·0, s	—
19	–$(CH_2)_3$–		Me	1'-Ac	$CDCl_3$	210–185, 4H + 150–125, 2H		8·6, dd[d,h]	495–440	2·80 or 2·75, s	2·80 or 2·75, s
20	–$(CH_2)_3$–		–C_2H_4OH	H	DMSO-d_6	210–175, m, 4H[n] + 2·15, t[o], 2H		8·35, dd[d]	485–445	3·74, t[p], 2H, OCH_2 + 210–175, m, 2H[r]	
21	–$(CH_2)_4$–		Me	H	DMSO-d_6	3·15, m, 4H + 1·85, m, 4H		[i]	490–445	2·7, s	—
					TFA	3·6, m, 4H + 2·15, m, 4H		[i]	505–465	3·0, s	—
22	–$(CH_2)_4$–		Me	x'-Ac[s]	$CDCl_3$	200–170, 4H + 130–105, 4H		[i]	490–435	2·74 or 2·70, s	2·74 or 2·70, s
					DMSO-d_6	195–170, 4H + 130–105, 4H		[i]	490–435	2·71 or 2·68, s	2·71 or 2·68. s

23	Me	Ac	Me	H	DMSO-d_6	2·75 or 2·70, s	2·35, s	8·5, dd[d]	495–450	2·75 or 2·70, s	
24	H	COOMe	Me	H	DMSO-d_6	9·15, s	3·65, s	"	495–450	2·57, s	—
26	Me	COOEt	Me	H	DMSO-d_6	2·75 or 2·73, s	4·2, q, 2H + 1, 17, t, 3H[j]	"	510–450	2·75 or 2·73, s	
					TFA	3·3 or 3·0, s	4·55, q, 2H + 1·4, t, 3H[j]	"	510–480	3·3 or 3·0, s	—
27[l]	Me	COOEt	Me	1'-Me	$CDCl_3$	R^ + R:	4·35, q + 4·25, q	9·1, dd[d,h]		R^ + R:	3·85, s
28a[l]	Me	COOEt	Me	2'-Me	$CDCl_3$	2·9 + 2·83 + 2·75 +	+ 1·28, t + 1·16, t[j,k]	"	500–440	2·9 + 2·83 + 2·75 +	3·62, s
29[l]	Me	COOEt	Me	4'-Me	$CDCl_3$	2·65, s		"		2·65, s	3·3, s
28	Me	COOEt	Me	2'-Me	CCl_4	2·82 or 2–56, s	4·15, q, 2H + 1·15, t, 3H[l]		490–435	2·82 or 2·56, s	3·55, s
30[m]	Me	COOEt	Me	1'-CH_2COOEt	$CDCl_3$			8·45, dd[d,h]			4·95, s
31	Me	COOEt	Me	2'-CH_2COOEt	$CDCl_3$	2·85 or 2·65, s	4·25 or 4·05, q + 1·2 or 1·13, t[j,l]	"	495–450	2·85 or 2·65, s	4·65, s + 4·25 or 4·05, q + 1·2 or 1·13, t[j,v]
32	Me	COOEt	Me	x'-Ac[e]	CCl_4	2·8, 2·72 or 2·68, s	4·22, q, 2H + 1·22, t, 3H[l]	"	510–440	2·8, 2·72 or 2·68, s	2·8, 2·72 or 2·68, s
35	Me	Ph	Me	x'-Ac[e]	$CDCl_3$	2·58 or 2·5, s	7·28, s	"	500–450	2·58 or 2·5, s	2·58 or 2·5, s

[a] NMR spectra were obtained at 60 MHz with the aid of Varian (Type A60D) and Perkin-Elmer (Type R-12) NMR spectrometers.

[b] The serial numbers are identical in Tables 4 and 5.

[c] The positions of the signals have, wherever possible, been given in δ values. In the case of complex multiplets the limits of the intervals in which the signals appear are stated in Hz downfield from TMS.

[d] $J_o \approx 8$, $J_m \approx 2$ Hz.

[e] Authentic product, prepared by structure proving synthesis, see text.

[f] This compound has not been obtained in pure form. The chemical shift values of its most prominent signals have been obtained by subtraction of the spectra of its 1'- and 4'-methyl analogues from the spectrum of the crude methylation mixture of **5** (R_A = R = Me, R^B = H).

[g] Merged with the signals of 6-H–8-H.

[h] Diagnostic for the structure.

[i] This compound has not been obtained in pure form. The chemical shift values of its most prominent signals have been obtained by subtraction of the spectrum of the 1'-methoxycarbonylmethyl analogue from that of the crude methoxycarbonylmethylation mixture of **5** (R^A = R = Me, R^B = H).

[j] Intensity ratio 2:3.

[k] The NMR spectrum of the crude methylation product of **5** (R^A = Et, R^B = H, R = Me), i.e. of the mixture of compounds 8 and 9 of the present table, has only been obtained. The more important signals have been assigned by analogy with the methylation products of **5** (R^A = R = Me, R^B = H).

[l] $J \approx 7{\cdot}5$ Hz.

[m] The NMR spectrum of the crude methoxycarbonylmethylation product of **5** (R^A = COOMe, R^B = H, R = Me), i.e. of the mixture of compounds 13 and 14, has only been obtained. The more important signals have been assigned by analogy.

[n] Merged with the signal of the S–CH_2 group.

[o] Distorted triplet, $J \approx 7{\cdot}5$ Hz.

[p] Distorted triplet, $J \approx 6$ Hz.

[q] Merged with the signals of the terminal protons of the –$(CH_2)_3$– group.

[r] Point of attachment of the acetyl group uncertain.

[s] The NMR spectrum of the crude methylation product of **5** (R^A = R = Me, R^B = COOEt) has only been obtained. The more important signals have been assigned by analogy.

[t] The NMR spectrum of a mixture of the 1'- and 2'-ethoxycarbonylmethyl isomers has only been obtained. The more important signals of the former have been assigned by subtraction of the signals of the latter from the spectrum of the mixture.

[u] Intensity ratio 2:2:3.

UV and IR spectra. The 4 - (5 - methylthio - *s* - triazol - 3 - yl)quinolines (**5**), as well as their alkylated and acylated derivatives are, with the exception of compound **17**, colourless crystalline substances. The UV spectra of the non-acylated compounds have three absorption bands at about 210, 240 and 310 mm, respectively, the first and/or third band showing, in some cases, a fine structure. Alkylation causes no significant changes in the UV spectra and, particularly, there was no significant difference between the spectra of the isomeric N-alkyl derivatives in the few cases where such a comparison could be made. Thus, the UV spectra do not seem suitable for establishing the tautomeric structures of compounds **5**. The UV spectra of the compounds **5** and their N-alkyl derivatives have been compiled in Table 5.*

The case of the acyl derivatives is less simple. The tetracyclic acyl derivative **17** (formed by intramolecular acylation at position 2' of **5** (R^A = R = Me, R^B = COOH) is yellow, yet its UV spectrum, taken in ethanol, is practically identical with that of compound **5** (R^A = R = Me, R^B = COOEt; compound No. 26 of Table 5). Evidently the γ-lactam ring of **17** has been cleaved by the solvent.† Support for this assumption comes from the observation that the UV spectrum of **17** obtained in cyclohexane is different (*Experimental*).

Consequently, the UV spectra of the acetyl derivatives of compounds **5** were run in cyclohexane and/or anhydrous dioxane. The resulting spectra were found to belong to two distinct classes: compounds No's 7, 15 and 19 of Table 5, which have, according to the NMR spectra, the acetyl group attached to N-1', exhibit UV spectra which are completely analogous to those of the non-acetylated compounds. The UV spectra of compounds No's 22, 32 and 35, on the other hand, have a new absorption band at about 280 nm in addition to the three bands characteristic for the non-acetylated analogues. This may be due either to the attachment of the acetyl groups to a different position than in compounds 7, 15 and 19 or to conformational differences (distortions from planarity).

The IR spectra (in KBr pellets) of most of the compounds **5** have a very broad NH band which is characteristic for azoles having a free NH group and which is the result of strong N–H ... N association.

*The UV spectra will be published in full in Ref 13.

†The high degree of reactivity of the $\left\{CO—N\right\diagup$ bond of **17** is reflected also in the high value (1775 cm^{-1}) of the corresponding Amide I band.

‡The present method is a considerably improved variation of the original method described in Ref 1 for the preparation of this compound.

EXPERIMENTAL

NMR spectra have been obtained at 60 MHz with the aid of Perkin Elmer (Type R 12) and Varian (Type A-60D) NMR spectrometers. UV spectra were obtained with the aid of a MOM (Hungarian Optical Works, Budapest) Type Spectromom 201 UV spectrometer.

Preparation of new 3 - *alkylthio* - 6,7 - *dihydro*[1.2.4] - *triazino*[1.6-*c*]*quinazolin* - 5 - *ium* - 1 - *olates* (**3**)

(1) Isatine (20 g; 136 mmoles) was dissolved in a warm soln of NaOH (16 g; 400 mmoles) in water (150 ml). Thiosemicarbazide (12·4 g; 136 mmoles) was added and the soln was refluxed for 30 min. The mixture was cooled to r.t., 2-chloroethanol (10 ml; 150 mmoles) was added and the soln was allowed to stand for 2 hr at r.t. The insoluble impurities were filtered off, and to the soln of **1** (R = CH_2CH_2OH) thus obtained a mixture of EtOH (150 ml), cyclopentanone (30 ml; 340 mmoles) and AcOH (25 ml) was added. The soln was heated to boiling and allowed to cool. A brown oil which slowly solidified separated. The latter was filtered by suction and washed with two portions of MeOH (30 ml, each) to yield 27 g (60%) of a crude product which was recrystallized from EtOH (250 ml) to yield 8 g (18%) of pure **3**, $R^1 + R^2 = -(CH_2)_4-$, R = $-C_2H_4OH$, m.p. about 140°C (dec) (Found: S, 9·98. $C_{16}H_{18}N_4O_2S$ (330·40) requires: S, 9·70%).

(2) A mixture of **1**[4] (R = Me; 6·0 g; 26 mmoles), methyl propiolate (6·0 g; 72 mmoles), MeOH (50 ml) and water (25 ml) heated to boiling and, subsequently, allowed to stand in a refrigerator at 0° yielded 5·4 g (66%) of **3** (R^1 = H, R^2 = CH_2COOMe, R = Me),‡ m.p. 189–192° (dec), lit.[1] m.p. 198–199°C (dec). The product was pure enough for further transformation, see below.

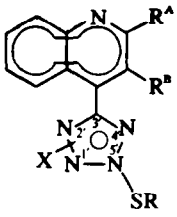
(3) A mixture of **1** (R = Me; 5·0 g; 21 mmoles), 1-phenyl-2-propanone (6·7 g; 50 mmoles) and EtOH (100 ml) was heated under reflux for 10 min. The resulting red soln was concentrated to about 20 ml *in vacuo*. Light petroleum (60 ml) was added to precipitate 5·2 g (69%) of **3** (R^1 = R = Me, R^2 = $PhCH_2$) which was isolated after the mixture had been kept overnight at 0°, m.p. 176–177° (dec) from BuOH. (Found: C, 65·14; H, 5·02; N, 15·93; S, 8·90. $C_{19}H_{18}N_4OS$ (350·43) requires: C, 65·12; H, 5·18; N, 15·99; S, 9·15%).

(4) 6 - (2 - Aminophenyl) - 3 - thioxo - 3,4 - dihydro - 1,2,4 - triazin - 5(2H) - one[4] (5·0 g; 29 mmoles) was dissolved in the soln of KOH (4·0 g; 72 mmoles) in a mixture of water (10 ml) and EtOH (50 ml). Benzyl chloride (3·44 ml; 30 mmoles) was added and the mixture was stirred for 2 hr at r.t. The insoluble impurities were filtered off, water (100 ml) and acetone (25 ml) were added and the mixture was acidified with AcOH to precipitate the orange crystals (5·2 g; 51%) of **3** (R^1 = R^2 = Me, R = $PhCH_2$), m.p. 203–205°C (dec) from DMF. (Found: C, 64·99; H, 5·40; S, 9·05. $C_{19}H_{18}N_4OS$ (350·43) requires: C, 65·12; H, 5·18; S, 9·15%).

(5) A mixture of the above product (5·0 g; 14 mmoles), water (20 ml), MeOH (30 ml) and diethylamine (7 ml; 68 mmoles) was heated to boiling, and the resulting yellow soln was evaporated to dryness *in vacuo*. The residue was dissolved in 50% aqueous MeOH and acidified under ice cooling with AcOH. The resulting yellow oil solidified on standing to yield 4·3 g (98%) of pure **1**, (R = $PhCH_2$) which, after considerable sintering from about 130°, decomposed above 230°. (Found: N, 18·14; S, 10·39. $C_{16}H_{14}N_4OS$ (310·37) requires: N, 18·05; S, 10·33%).

A mixture of this product (2·0 g; 6·5 mmoles), ethyl

Table 5. UV spectra[a] of compounds 5 and of their alkylation and acetylation products



No.[b]	R^A	R^B	R	X	Solvent	λ_{max} (log ε) I	II	III
1	Me	H	Me	H	EtOH	205 (4·54)	236 (4·49)	310 (3·94)
2	Me	H	Me	1'-Me	EtOH	~210 (~4·5)	238 (4·52)	310 (4·00)
4	Me	H	Me	4'-Me	EtOH	~202 (~4·8)	235 (4·66)	312 (4·05); 323 (4·02)
5	Me	H	Me	1'-CH_2COOMe	EtOH	216 (4·51)	238 (4·48)	308 (3·94)
7	Me	H	Me	1'-Ac	Dioxane	217 (4·54)	242 (4·48)	295 (3·98)
11	COOMe	H	Me	H	EtOH	208 (4·45); 220 (4·36), sh	244 (4·62)	320 (3·91)
15	COOMe	H	Me	1'-Ac	Dioxane	< 210	246 (4·35)	315 (3·62)
					Cyclohexane	< 210	246 (4·75)	310 (3·97)
16	Me	Me	Me	H	EtOH	210 (4·70)	235 (4·56)	294 (3·76); 308 (3·78); 322 (3·76)
17	Me	Me	Me	2'-Me	EtOH	210 (4·72)	236 (4·54)	296 (3·72); 308 (3·74); 322 (3·76)
18	$-(CH_2)_3-$		Me	H	EtOH	210 (4·64)	240 (4·54)	312 (3·94); 326 (3·94)
19	$-(CH_2)_3-$		Me	1'-Ac	Dioxane	217 (4·60)	239 (4·47)	313 (3·96)
20	$-(CH_2)_3-$		$-C_2H_4OH$	H	EtOH	212 (4·66)	240 (4·57)	312 (405); 323 (4·02)
21	$-(CH_2)_4-$		Me	H	EtOH	211 (4·68)	238 (4·56)	300 (3·80); 311 (3·85); 326 (3·85)
22	$-(CH_2)_4-$		Me	x'-Ac[c]	Dioxane	217 (4·65)	240 (4·46), sh	**280 (4·00)**; 312 (3·79); 326 (3·77)
23	Me	Ac	Me	H	EtOH	206 (4·66)	241 (4·64)	315 (3·92)
24	H	COOMe	Me	H	EtOH	208 (4·65)	240 (4·78)	302 (3·90)
25	Me	COOH	Me	H	EtOH	208 (4·62)	238 (4·52)	311 (3·81); 325 (3·76)
26	Me	COOEt	Me	H	EtOH	207 (4·58)	240 (4·60)	307 (3·78)
28	Me	COOEt	Me	2'-Me	EtOH	209 (4·58)	239 (4·60)	299 (3·68)
31	Me	COOEt	Me	2'-CH_2COOEt	EtOH	208 (4·76)	240 (4·76)	297 (3·83)
					cyclohexane		239 (4·64)	292 (3·75); 308 (3·66), sh
32	Me	COOEt	Me	x'-Ac[c]	cyclohexane	220 (4·60)	240 (4·53)	**283 (4·00)**; 310 (3·76), sh
33	Me	COOEt	$PhCH_2$	H	EtOH	< 200 (> 5·0)	240 (4·76)	305 (3·98)
34	Me	Ph	Me	H	EtOH[d]	208 (4·72)	237 (4·66)	299 (3·78); 310 (3·80); 322 (3·78)
35	Me	Ph	Me	x'-Ac[c]	cyclohexane	222 (4·73)	—	**281 (4·15)**; 305 (3·90), sh; 323 (3·84)

[a]The spectra will be published in full in *Absorption Spectra in the Ultraviolet and Visible Region* (Editor L. Láng), Vol 19, Publishing House of the Hungarian Academy of Sciences, Budapest, 1973.

[b]The serial numbers are identical in Tables 4 and 5.

[c]The point of attachment of the acetyl group to the triazole cycle is uncertain.

[d]The positions of the bands did not change on changing the solvent to cyclohexane.

acetoacetate (10 ml) and EtOH (1 ml) was stirred for 15 min on a steam bath. During this period orange crystals started to precipitate from the red soln. The separation of the product was completed by the addition of anhydrous ether (100 ml). 1·7 g (63%) of 3 (R^1 = Me, R^2 = CH_2COOEt, R = $PhCH_2$) were obtained, m.p. 124° (dec) from EtOH. (Found: N, 13·19; S, 7·94. $C_{22}H_{22}N_4O_3S$ (422·50) requires: N, 13·26; S, 7·59%).

Thermolysis of 3-alkylthio-6,7-dihydro-[1.2.4]triazino-[1.6-c]quinazolin-5-ium-1-olates 3*

Method A. A soln of 3 (R^1 = R = Me, R^2 = Et) (11 g; 38 mmoles) in anhyd DMF (30 ml) was heated under reflux for 1 hr. The intensity of the deep red colour diminished considerably during this time. When the soln was allowed to cool, 1·7 g (21%) of crude 4 (R = Me)[4] separated, m.p. 315–316° (dec). The filtrate of this product was treated with 100 ml of water to yield 6·5 g of a mixture, consisting mainly of the two isomeric compounds 5 (R^A = R^B = R = Me) and 5 (R^A = Et, R^B = H, R = Me).

The former was isolated by refluxing the mixture of the isomers for 30 min with a mixture of Ac_2O (12 ml) and anhyd pyridine (6 ml) and chilling the soln in an ice-water bath. The acetyl derivative of 5 (R^A = R^B = R = Me) which separated was filtered, washed with ice-cold Ac_2O and ether and deacetylated by refluxing with 10% NaOH aq (20 ml). Acidification of the resulting soln with AcOH gave a crude product which was recrystallized from nitromethane (250 ml) to yield 0·55 g (5·3%) of 5 (R^A = R^B = R = Me).

*For the m.ps and microanalyses of the products 5, see Table 1.

In order to isolate the second isomer, another 6·5 g of the mixture was heated to boiling with EtOAc (150 ml). The resulting soln was allowed to cool and the small amount of material which thereby separated was filtered off. The solvent was removed by distillation, and the resulting oily product, which slowly solidified on standing, was dissolved in hot MeOH (20 ml). The insoluble impurities were filtered off and a large amount of water was added to precipitate almost pure **5** (R^A = Et, R^B = H, R = Me) which was recrystallized from EtOAc to yield 1·9 g (18%) of colourless needles.

Method B. A mixture of **3** ($R^1 = R^2 = R$ = Me) (15 g; 55 mmoles) and acetamide (75 g) was kept for 10 min at 190° in an oil-bath. The mixture was allowed to cool to about 100° and poured into water (400 ml) to yield 13·5 g of a solid product. The latter was thoroughly dried and extracted by heating to boiling twice with EtOAc (200 and 100 ml, respectively). The insoluble material (4·1 g; 35%) was recrystallized from DMF (10 ml) to yield 1·5 g (13%) of pure **4** (R = Me)[4], m.p. 313° (dec).

The crude product (7·8 g; 56%), which separated when the combined hot EtOAc solns were allowed to cool, was recrystallized from 2-propanol (100 ml) to yield 4·5 g (32%) of **5** ($R^A = R$ = Me, R^B = H).

Acid catalysed cleavage of 3 - *alkylthio* - 6,7 - *dihydro*[1.2.4]*triazino*[1.6-c]*quinazolin* - 5 - *ium* - 1 - *olates* **3***

Method A. BF_3-etherate (10 ml) was added dropwise to a mixture of **3** (R^1 = COOMe, $R^2 = R$ = Me) (8 g; 25 mmoles) and anhyd DMF (60 ml) under continuous stirring, and the resulting purple red soln was refluxed for 20 min. During this period the colour of the soln turned faint yellow. The hot mixture was poured into 300 ml ice-water to yield 5·5 g (74%) of a crude product which was recrystallized from DMF (30 ml) in the presence of decolorizing carbon to yield 3·5 g (47%) of **5** (R^A = COOMe, R^B = H, R = Me) as colourless needles.

Method B. A mixture of **3** ($R^1 = R$ = Me, R^2 = CH_2COOEt) (7·6 g; 22 mmoles), conc HCl (8 ml), EtOH and water (30 ml, each) was refluxed for 2 min. The original purple red colour of the soln faded rapidly. The almost colourless soln was diluted with water (150 ml) and neutralized by the addition of crystalline NaOAc (pH ≈ 5·5) to yield 4·2 g (58%) of almost pure **5** ($R^A = R$ = Me, R^B = COOEt) as colourless needles, m.p. 183-184°.

Method C. Crude **3** (R^1 = H, R^2 = CH_2COOMe, R = Me) (5·4 g; 17 mmoles), obtained as described was refluxed with MeOH (50 ml) for 90 min during which time a continuous stream of HCl was introduced into the soln. Ether (150 ml) was added to precipitate the crystals of the hydrochloride (4·0 g). The latter was mixed with water (20 ml) and decomposed by the addition of 30% NaOAc aq to yield 2·45 g (45%) of crude **5** (R^A = H, R^B = COOMe, R = Me) which was recrystallized from nitromethane, yielding 1·6 g (30%) of the pure product.

Some representative alkylations of the 4-(5-*methyl*-*thio*-*s*-*triazol*-3-*yl*)*quinolines* **(5)**†

(1) Compound **5** ($R^A = R$ = Me, R^B = H; 2·0 g; 7·8 mmole) was stirred with an ethereal (50 ml) diazomethane soln (containing about 1·0 g, 24 mmoles of CH_2N_2) at r.t. until the starting compound dissolved completely with evolution of N_2. The greenish soln was evaporated to dryness, the residue was dissolved in acetone (15 ml), the soln was decolorized with carbon, and warm water (40 ml) was added. A rapidly solidifying oil separated which was filtered off, dried over P_2O_5 at 80° and recrystallized from ligroine (50 ml) to yield 1·6 g (39%) of the 1'-methyl derivative of the starting compound.

(2) A mixture of **5** (R^A = COOMe, R^B = H, R = Me; 2·0 g; 6·7 mmoles), anhyd MeOH (30 ml), NaOMe (0·54 g; 10 mmoles) and MeI (0·94 ml; 15 mmoles) was refluxed for 30 min. Another portion of MeI (0·94 ml) was added and refluxing was continued for further 30 min. The resulting soln (which reacted neutral) was poured into water (150 ml) and the colourless crystalline ppt (1·8 g) was filtered off, dried and recrystallized from 2-propanol (40 ml) to yield 1·1 g (53%) of the 1'-methyl derivative of the starting compound.

(3) Metallic Na (0·39 g; 17 mmoles) was dissolved in anhyd EtOH (50 ml). **5** ($R^A = R$ = Me, R^B = COOEt; 5·0 g; 15·3 mmole) and ethyl bromoacetate (2·0 ml; 18 mmoles) were added and the mixture was refluxed for 2 hr. A small amount of a yellow ppt separated from the soln which at this point reacted neutral. Water (50 ml) was added and the insoluble by-product **16** (0·55 g; 10%), m.p. 206° (nitromethane), was filtered off.

The aqueous-ethanolic filtrate was evaporated to dryness *in vacuo*, the oily residue was triturated with water (30 ml) and the mixture was extracted 3 times with chloroform (30 ml, each). The combined chloroform solns were washed with water, dried ($MgSO_4$) and evaporated to dryness *in vacuo*. The residue was dissolved in ether (30 ml) and the product was precipitated by the addition of light petroleum (30 ml). The crude product was purified by reprecipitation from its etheral (50 ml) soln with light petroleum (50 ml). 1·8 g (29%) of the 2'-ethoxycarbonylmethyl derivative (**15**) of the starting compound was obtained.

Acetylation of compound **5** ($R^A = R$ = Me, R^B = H)

A mixture of the title compound (2·3 g; 9 mmoles), Ac_2O and pyridine (3 ml, each) was refluxed for 1 hr and allowed to stand overnight at 0°C to yield 2·1 g (79%) of the 1'-acetyl derivative. (For the m.p. and microanalyses, see Table 3.)

The other acetylations were performed similarly.

2-*Methyl*-4-*quinolinecarbohydrazide* **(8)**

A mixture of methyl 2-methyl-4-quinolinecarboxylate[6] (14·1 g; 70 mmoles), MeOH (50 ml) and hydrazine hydrate (7·5 g; 150 mmoles) was refluxed for 3 hr to yield, after being allowed to cool, 8·2 g of the colourless crystals of **8**. A second crop (2·3 g) was obtained by recrystallizing the dry residue of the filtrate from 2-propanol, the total yield amounting to 74%, m.p. 183° from 2-propanol. (Found: C, 65·05; H, 5·42; N, 20·56. $C_{11}H_{11}N_3O$ (201·22) requires: C, 65·66; H, 5·51; N, 20·88%).

5 - (2 - *Methyl* - 4 - *quinolinyl*) - $\Delta^{1,5}$ - s - *triazoline* - 3 - *thione* **(13)**‡

A thoroughly ground mixture of **8** (4·0 g; 20 mmoles) and freshly dried ammonium thiocyanate (2·5 g; 35 mmoles) was kept for 1/2 hr at 170–175° in an oil bath. The melt solidified on cooling and was extracted twice with 30 ml, each, of hot water. The residue was triturated with

*For the m.ps and microanalyses of the products **5**, see Table 1.

†For the m.p.s and microanalyses of the products, see Table 2.

‡Tautomeric structure arbitrarily assigned to the triazoline cycle.

EtOH and filtered by suction to yield 4·1 g (84%) of **13**, which decomposes above 300° from DMF-ether. (Found: C, 59·10, H, 4·35. $C_{12}H_{10}N_4S$ (242·31) requires: C, 59·48; H, 4·16%).

2 - Methyl - 4 - (5 - methylthio - s - triazol - 3 - yl)quinoline (**5**, $R^A = R = Me$, $R^B = H$)

The above thione (0·6 g; 2·5 mmol) was dissolved in DMF (10 ml) under gentle heating, the soln was cooled to r.t. and MeI (0·4 ml; 6 mmoles) was added. After being allowed to stand for 1 hr, the red soln was diluted with water (30 ml) and neutralized with 10% NaOAc aq to yield 0·43 g (68%) of the desired product, m.p. 214–215° (nitromethane) which, by mixed m.p. and IR spectra, proved identical with another sample prepared by thermolysis of the corresponding compound **3**.

2-Ethyl-4-quinolinecarbohydrazide (**11**)

EtOH (200 ml) and 2-butanone (200 ml; 2·2 moles) were added to a soln of isatine (60 g; 0·41 mole) and NaOH (25 g; 0·62 mole) in water (200 ml), and the mixture was refluxed for 36 hr. The resulting dark soln was concentrated to about 50 ml. Water (500 ml) was added and the soln was decolorized with Norite. The filtrate was acidified with AcOH and allowed to stand overnight in a refrigerator to yield 64 g of a solid product which was filtered off, washed with water and dried at 120°.

An ethereal (750 ml) diazomethane soln (containing about 65 g = 0·38 mole of CH_2N_2) was added dropwise to the suspension of the above product in MeOH (100 ml) under continuous stirring at r.t. The resulting soln was evaporated to dryness and the residual oily product (65 g) which slowly solidified was refluxed for 3 hr with a mixture of MeOH (200 ml) and hydrazine hydrate (30 g; 0·6 mole). The resulting soln was evaporated to dryness *in vacuo*, and the residue was washed with two portions of water (50 ml, each), dried over P_2O_5 and extracted twice by boiling for 10 min with ether (200 ml) under continuous stirring.

The insoluble residue was recrystallized from 2-propanol (500 ml) to yield 18·6 g (21%) of **11**, m.p. 204–205° (after an allotropic change at about 180° to crystalline needles). (Found: C, 66·16; H, 6·66; N, 19·59. $C_{12}H_{13}N_3O$ (215·24) requires: C, 66·96; H, 6·09; N, 19·53%); IR (KBr): 1695 cm^{-1}.

The ethereal extract, when evaporated to dryness, gave 21·5 g (24%) of **9** as an oily residue which solidified on standing, m.p. and lit. m.p.[7] 124°; IR (KBr): 1720 cm^{-1}. NMR ($CDCl_3$): δ 8·1 ppm, s, 1H, 5-H; 480–440 Hz, m, 3H, 6-H–8-H; δ 4·0 ppm, s. 3H, COOMe; δ 2·70 and 2·35 ppm, s, 3H, each, 2- and 3-Me. (Found: C, 72·24; H, 6·04; N, 7·14 $C_{13}H_{13}NO_2$ (215, 24) requires: C, 72·54; H, 6·09; N, 6·51%).

5 - (2 - Ethyl - 4 - quinolinyl) - $\Delta^{1,5}$ - s - triazoline - 3 - thione (**14**)*

A thoroughly ground mixture of **11** (10 g; 46·6 mmoles) and freshly dried NH_4SCN (4·6 g; 60 mmoles) was kept for 20 min at 180–185° in an oil bath. After the evolution of gases ceased, the melt solidified and, after being allowed to cool, it was extracted with 60 ml boiling water, filtered by suction and washed with two portions (50 ml, each) of hot water. The product was dissolved in hot DMF (80 ml), the soln was decolorized with carbon and diluted with hot water (100 ml) to yield 7·5 g (63%) of **14**, dec above 320°C from DMF-MeOH. (Found: C, 61·24; H, 4·94; N, 21·89; S, 12·49. $C_{13}H_{12}N_4S$ (256·33) requires: C, 60·91; H, 4·72; N, 21·86; S, 12·51%).

2 - Ethyl - 4 - (5 - methylthio - s - triazol - 3 - yl)quinoline (**5**, R^A = Et, R^B = H, R = Me)

The above thione was treated with MeI as described for its 2-Me analogue (see above) to yield 91% of the desired product, m.p. 204–205° (EtOAc) which, by mixed m.p. and IR spectra, proved identical with another sample prepared by thermolysis of the appropriate compound **3**.

*2 - Methyl - 5 - (2 - methyl - 4 - quinolinyl) - $\Delta^{1,5}$ - s - triazoline - 3 - thione** (2 - Methyl - **13**)

A mixture of 2-methyl-4-quinolinecarboxylic acid (3·74 g; 20 mmoles), 2-methylthiosemicarbazide[8] (2·2 g; 21 mmoles), anhyd DMF (30 ml) and dicyclohexylcarbodiimide (5·2 g; 25 mmoles) was stirred for 2 hr. Heat was gently evolved and a ppt was rapidly formed. Water (100 ml) was added and the mixture was evaporated to dryness *in vacuo*, the latter operation being repeated twice after the addition of benzene (50 ml, each). The solid product was kept overnight over P_2O_5 *in vacuo* and subsequently refluxed for 8 hr with a soln of metallic Na (1·2 g; 50 moles) in anhyd EtOH (75 ml). The solvent was distilled off, the residue was dissolved in water (30 ml), the small amount of insoluble material was filtered off and the filtrate was acidified with AcOH to yield, after being allowed to stand at 0°, 1·1 g (22%) of the desired product, m.p. 300–303° (dec; after reddening and an allotropic change to crystalline needles at about 250°). (Found: C, 60·99; H, 4·83; N, 21·92; S, 12·97. $C_{13}H_{12}N_4S$ (256·33) requires: C, 60·91; H, 4·72; N, 21·86; S, 12·51%).

2 - Methyl - 4 - (1 - methyl - 5 - methylthio - s - triazol - 3 - yl) - quinoline (1'-Methyl - **5**, $R^A = R = Me$, $R^B = H$)

The above thione (0·2 g; 0·8 mmole) was dissolved under gentle heating in DMF (3 ml), and MeI (0·125 ml; 2 mmoles) was added at r.t. Yellow crystalline needles soon started to separate and were filtered off and dissolved in water (5 ml). The aqueous soln was neutralized with 10% NaOAc aq to yield 0·18 g (84%) of the colourless product, m.p. 101° (ligroine) which, according to mixed m.p. and IR spectra, proved identical with another sample prepared by methylation of the appropriate compound **5**.

4 - Methyl - 1 - (2 - methyl - 4 - quinolinecarbonyl)thiosemicarbazide (**12**)

A soln of **8** (5 g; 25 mmoles) and methyl isothiocyanate (1·9 g; 26 mmoles) in dioxane (50 ml) was refluxed for 1 hr to yield, on being allowed to cool, 6·7 g (92%) of **12**, m.p. 147–148° (dec; sintering from 100°) from MeOH. (Found: C, 53·45; H, 5·54; N, 19·24; S, 10·82. $C_{13}H_{14}N_4OS + H_2O$ (292·36) requires: C, 53·40; H, 5·52; N, 19·16; S, 10·97%).

*4 - Methyl - 5 - (2 - methyl - 4 - quinolinyl) - $\Delta^{1,5}$ - s - triazoline - 3 - thione** (4 - Methyl - **13**)

Compound **12** (3·5 g; 12 mmoles) was refluxed for 4 hr with a soln of metallic Na (0·46 g; 20 mmoles) in dry EtOH (30 ml). The resulting orange soln was diluted with an equal volume of water and acidified with AcOH to yield 2·9 g (95%) of the desired product, m.p. 274° from nitromethane. (Found: C, 61·05; H, 5·07; S, 12·45. $C_{13}H_{12}N_4S$ (256·33) requires: C, 60·91; H, 4·72; S, 12·51%).

*Tautomeric structure arbitrarily assigned to the triazoline cycle

2 - Methyl - 4 - (4 - methyl - 5 - methylthio - s - triazol - 3 - yl) - quinoline (4'-Methyl - **5**, $R^A = R = Me$, $R^B = H$)

The above thione was methylated in DMF with MeI as described for the 4'-nor analogue. The product did not precipitate on neutratization. The solution was, therefore, evaporated to dryness and the solid residue was stirred for 10 min with water (10 ml) and chloroform (70 ml). The chloroform layer was separated, washed with water, dried over $MgSO_4$ and evaporated to dryness *in vacuo*. The resulting oil, when triturated with ether (20 ml), turned into a crystalline powder which was filtered off and dissolved in hot tetrachloromethane (30 ml). The soln was decolorized, and warm light petroleum (70 ml) was added to precipitate 0·75 g (47%) of the desired product, m.p. 127° from ligroine. (Found: C, 61·78; H 5·18; N, 20·39; S, 11·86. $C_{14}H_{14}N_4S$ (270·35) requires: C, 62·19; H, 5·22; N, 20·73; S, 11·86%).

2 - Methyl - 4 - (5 - methylthio - s - triazol - 3 - yl) - 3 - quinolinecarboxylic acid

The ethyl ester (2·0 g; 6·1 mmole) of the desired product, prepared by acid catalysed cleavage of the appropriate compound **3** (Table 1), was refluxed with 10% NaOH aq (20 ml) for 30 min. The resulting soln was acidified wiht AcOH to yield 1·65 g (90%) of the acid, m.p. 278–280° (dec) from 50% aqueous EtOH. (Found: C, 56·09; H, 4·23; N, 18·60; S, 10·74. $C_{14}H_{12}O_2S$ (300·34) requires: C, 55·98; H, 4·03; N, 18·66; S, 10·66%).

6 - Methyl - 10 - methylthio - s - triazolo[1'.5'-2.3] - *pyrrolo* [4.3-c]*quinolin - 7 - one* (**17**)

The above acid (3·2 g; 10·7 mmole) was dissolved in dry pyridine (20 ml). Ac_2O (20 ml) was added dropwise under continuous stirring at r.t. Stirring was continued for another 5 min and the orange ppt of **17** (2·5 g; 83%) was filtered off and washed with ether, m.p. 223° from Ac_2O). (Found: C, 59·51; H, 4·16; N, 19·54; S, 11·36. $C_{14}H_{10}N_4OS$ (282·32) requires: C, 59·56; H, 3·56; N, 19·86; S, 11·36%); IR (KBr): 1775 cm^{-1}; NMR ($CDCl_3$): 510–450 Hz, m, 4H, ArH; δ 3·05 and 2·8, s, 3H, each, 6-Me and S-Me; UV (cyclohexane): 226, 270, 325, 336, 368, 388.*

Ethyl 6-hydroxy-7-methyl-2-methylthio-s-triazolo[5.1-a]-[2.6]*phenanthroline-5-carboxylate* (**16**)

(a) Compound **15** (0·5 g; 1·2 mmole), prepared by ethoxycarbonylmethylation of the appropriate compound **5**, was refluxed for 1 h with a soln of metallic Na (70 mg; 3 mmoles) in dry EtOH (10 ml). The resulting soln was acidified with AcOH, and water (30 ml) was added to precipitate a crude product which was filtered off, washed with water, dried *in vacuo* over P_2O_5 and recrystallized from 30 ml nitromethane to yield 0·28 g (63%) of pure **16**, m.p. 206°. (Found: C, 58·90; H, 5·00; N, 15·93; S, 9·12. $C_{18}H_{16}N_4O_3S$ (368·41) requires: C, 58·68; H, 4·38; N, 15·21; S, 8·70%); UV (EtOH): 209 (4·57); 254 (4·47), sh; 271 (4·61); 284 (4·35), sh; 336 (3·84), sh; 383 (4·00); 403 (4·02); 436 (2·90), sh; IR (KBr): 1660 cm^{-1} ($\nu C{=}O$, chelate ring); NMR ($CDCl_3$): δ 12·95 ppm, s, 1H, OH; δ 10·2 ppm, dd, $J \approx 8$, and 2 Hz, 1H, 12-H; 485–455 Hz, m, 3H, 9-H–11-H; δ 4·6 ppm, q, 2H, and 1·55 ppm, t, 3H, $J \approx 7$ Hz, OEt; δ 3·2 ppm and 2·8 ppm, s, 3H, each, 7-Me and S-Me.

(b) **5** ($R^A = R = Me$, $R^B = COOEt$) (2·5 g; 7·6 mmole) was refluxed for 1 h with a soln of ethyl bromoacetate (1·65 ml; 15 mmoles) in dry EtOH (20 ml) containing metallic Na (0·18 g; 8 mmoles). A further quantity of metallic Na (0·7 g; 30 mmoles), dissolved in dry EtOH (30 ml), was added, and refluxing was continued for another 2 h. The product (0·9 g; 32%) was isolated as described under (a) and, according to m.p. (206°), mixed m.p. and IR spectra, proved identical with the product obtained according to (a).

Acknowledgement—Thanks of the authors are due to Dr. P. Sohár and Mrs. M. Szirányi-Kiss for the NMR, to Dr. L. Láng and Mr. M. Vörös for the UV and to Mrs. I. Balogh-Batta, Miss K. Ófalvi, Mrs. S. Viszt-Simon and Mrs. I. Zauer-Csüllög for the microanalyses.

*Owing the slight solubility of **17**, in cyclohexane the log ϵ values could not be determined.

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