Aromatic Systems with 10π Electrons Derived from 3a-Azapentalene. XXXV (1). Quaternary Salts of 3-Methyl-*s*-triazolo[4,3-*a*]benzimidazole

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Quaternary salts with general structures **3** and **4** are obtained by reaction of 3-methyl-*s*-triazolo[4,3-*a*]benzimidazole and its alkyl derivatives **1** and **2** (R ≠ H) with alkyl halides. Compound **1** quaternizes at N_1 and N_2, whereas **2** quaternizes only at N_9. Compounds **3** and **4** are useful models for the study of the sites of protonation in this series. Structures are unequivocally assigned by hydrolysis and dealkylation.

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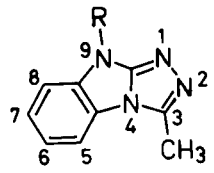
In a recent paper of this series (2) we studied the annular tautomerism and the site of protonation of 3-methyl-*s*-triazolo[4,3-*a*]benzimidazole (**1a** ⇌ **2a**) by means of ^{13}C nmr spectroscopy. Previous work, based on uv (3) and ^{1}H nmr (4) spectral data, and on dipolemetric measurements (5), showed the equilibrium between both tautomers **1a** and **2a** to be very sensitive to the nature of the solvent.

The determination of the site (or sites) of protonation of the compound **1a** ⇌ **2a** was accomplished with the aid of its quaternary salts, likewise the methylated models **1b** and **2b** with known structures were used for tautomeric studies (3). In this note we report the preparation and the unequivocal structural assignment of such salts.



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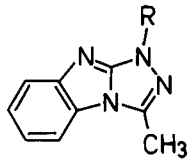

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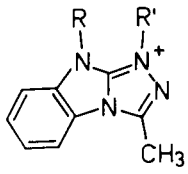

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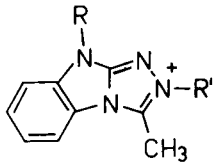

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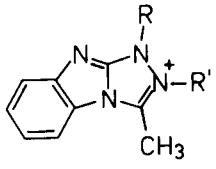

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a, R = H
b, R = CH_3
c, R = C_2H_5
d, R = $(CH_2)_3OH$
e, R = $(CH_2)_3Cl$
f, R = R' = CH_3
g, R = CH_3, R' = C_2H_5
h, R = C_2H_5, R' = CH_3

or

a, R = H
b, R = CH_3
c, R = C_2H_5
d, R = $(CH_2)_3OH$
e, R = $(CH_2)_3Cl$
f, R = R' = CH_3
g, R = CH_3, R' = C_2H_5
h, R = C_2H_5, R' = CH_3

Only three different types of monocations, **3-5**, can be obtained by protonation (R and/or R′ being H) or quaternization of **1a** ⇌ **2a** and its alkylated derivatives, depending on what of the pyridinoid nitrogen atom of the system will remain with its free electron pair (6). The pyrrole nitrogen and a ring carbon atom can be excluded as sites of protonation or quaternization, since this would represent a loss of π conjugation. In fact, a C-protonation or a protonation on a pyrrole nitrogen has never been observed for any monocation derived from aromatic 3a-azapentalenes with at least one pyridinoid nitrogen (7).

The reaction of pure 1,3-dimethyl-*s*-triazolo[4,3-*a*]-benzimidazole (**2b**) with an excess of iodomethane yielded a quaternary salt of m.p. 239° and starting material, as the sole products, whereas the same reaction with the 3,9-dimethyl isomer **1b** yielded a mixture of two salts, together with starting material and a small amount of compound **2b**. The nmr analysis of the mixture showed the minor component (*ca.* 25%) to be identical with the compound of m.p. 239° obtained in the first reaction by methylation of **2b**.

Since structure **3f** can be derived from methylation of either **1b** or **2b**, one could in principle assign this structure to the compound of m.p. 239°, the structure of the other salt being thus **4f**. In summary:

4f ⇌ **1b** → **3f** (m.p. 239°) ⇌ **2b**

However, the formation of small amounts of the 1,3-dimethyl derivative **2b** during the quaternization of **1b**, which must take place through the loss of a molecule of iodomethane from **3f**, cast some doubt on the above assumption. As a matter of fact, the salt of m.p. 239° could likewise have structure **5f**, arising from methylation of **2b**, which is present in both reactions. In this hypothesis, the major quaternary salt of the second reaction should now be represented either by structure **3f**, or by structure **4f**. Schematically:

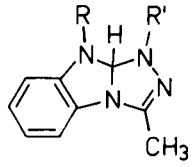
4f ⇌ **1b** → **3f** → **2b** → **5f** (m.p. 239°)

In order to distinguish between both possibilities, the following experiments were carried out:

When the quaternary salt of m.p. 239° was refluxed in *o*-dichlorobenzene with continuous removal of the formed

iodomethane from the reaction vessel (8), a mixture of **1b** and **2b** was produced in an approximate ratio of 1:3 (nmr). The same treatment of the mixture of salts obtained by methylating **1b**, yielded again both compounds, **1b** and **2b**, but now in a relative ratio of 4:1. These results strongly favor structures **3f** (m.p. 239°) and **4f** for the quaternary compounds, because **4f** can only yield **1b** by demethylation, whereas **3f** will decompose yielding both isomers. The ratio 1:3 would indicate a higher energy barrier for the loss of the methyl group at N_1. According to this ratio, the relative amounts (4:1) obtained after heating the mixture of salts, correspond to the theoretical ratio that would be anticipated by considering the amount of **3f** present in the initial mixture (25%).

On the other hand, none of the salts were catalytically hydrogenated under mild conditions. When treated with lithium aluminium hydride, the only products isolated after hydrolysis had open-chain structures with identical nmr spectra as the products derived from the direct treatment of the salts with a dilute solution of sodium hydroxide. We never detected structures such as **6-8**, expected from the respective reduction of structures **3-5**, the presence of which would provide a simple method for differenciate the salts.



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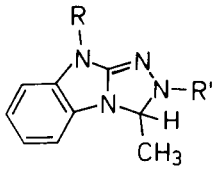

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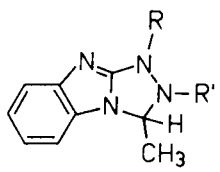

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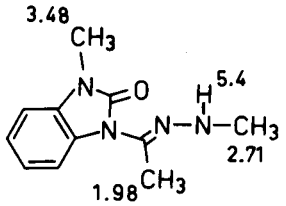
However, the structures proposed for the hydrolysis products are entirely consistent with formulae **3f** and **4f** for the quaternary salts. As a matter of fact, the hydrolysis of the salt of m.p. 239° afforded the hydrazone **9**, as deduced from the nmr spectrum of the compound in deuteriochloroform (the assignment of the signals is indicated on the figure), and from the carbonyl absorption at 1722 cm^{-1}. The shielded methyl at 1.98 ppm eliminates the alternative formulation **10** for the compound. At the same time, the coupling of the methyl signal at 2.71 ppm with the adjacent proton (9) discards formula **11**, which should derive from the hydrolysis of a compound of structure **5f**. This result definitively confirms structure **3f** for the compound of m.p. 239°.

Similarly, we propose structure **12** for the compound resulting from the hydrolysis of the other quaternary salt,



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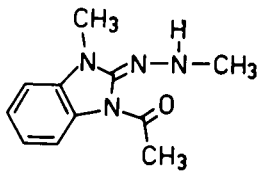

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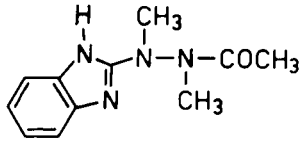

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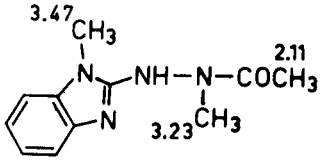

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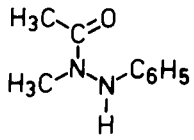


13 (Z+Z conformation shown)

on the basis of the low value of the carbonyl absorption (1665 cm^{-1}) and the comparison of its methyl resonances in deuteriochloroform (13) with those of methyl groups in the related compounds 2-hydrazino-1-methylbenzimidazole (14) and 1-acetyl-1-methyl-2-phenylhydrazine (**13**) (15), in the same solvent. As for compound **13**, we believe **12** to be preferently in a Z-*s*Z conformation.

Once structures **3f** and **4f** had been established, we obtained the series **g** and **h**, with different alkyl groups, through similar procedures; either by reacting the methylated compounds **1b** and **2b** with bromoethane, or the ethylated analogs **1c** and **2c** with iodomethane, the only difference being the anion, bromide or iodide, associated with the salt. Thus, salt **3g** was obtained as the iodide by reacting compound **2c** with iodomethane, and as the bromide, together with salt **4g**, by the action of bromoethane on compound **1b**. Similarly, the reaction of **2b** with bromoethane afforded the bromide of the salt **3h**, and **1c** with iodomethane yielded a mixture of the iodides **3h** and **4h**. Series **g** and **h** are useful models for the correct assignation of the *N*-methyl signals in the ^1H and ^{13}C nmr spectra of the quaternary salts (2).

Table I summarizes the alkyl resonances in trifluoroacetic acid of the compounds described. In this solvent, the spectra of compounds **1** and **2** (**a-c**) are actually those of their conjugate acids. In quaternary salts of type **4**, the methyl group at C_3 is shielded by 0.23 ppm (0.29 ppm in series **g**), with respect to isomeric salts of type **3**.

This fact accounts for a better delocalization of the positive charge over the triazole moiety in these structures **4**, as can be seen by considering canonical structures for both classes of compounds. Reciprocally, the N_9-methyl group in **3f** (**3g**) appears at a 0.22 ppm (0.20 ppm) lower field than the same group in **4f** (**4g**), reflecting again the different charge distribution in structures **3** and **4**. No such effect is observed on the other *N*-methyl group (N_1 in **3f** and **3h**, N_2 in **4f** and **4h**), which always is located on a positively charged nitrogen.

The chemical shift of *C*-methyl and *N*-alkyl groups in compounds **1** and **2** (**a-c**) reveals that protonation closely parallels quaternization, *i.e.*, structures **2** are protonated mainly at N_9, whereas structures **1** are protonated both at N_1 and N_2 (16).

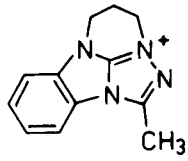
Table I

^{1}H Nmr Spectra in Trifluoroacetic Acid

Compound	R	R′	Methyl at C_3
1a⇌2a	---	---	3.13
1b	4.04	---	3.11
1c	1.67 and 4.50 (a)	---	3.11
2b	4.14	---	2.97
2c	1.67 and 4.50 (a)	---	2.97
3f	4.13	4.30	2.97
3g	4.11	1.67 and 4.60 (a)	2.91
3h	1.70 and 4.62 (a)	4.27	2.97
4f (b)	3.91	4.25	3.20
4g (b)	3.91	1.70 and 4.59 (a)	3.20
4h (b)	1.70 and 4.57 (a)	4.25	3.20

(a) J = 7 Hz. (b) Not isolated from the mixture with the corresponding salt of type **3**.

In an attempt to obtain a structure of type **5**, we performed the reaction between 3-methyl-*s*-triazolo[4,3-*a*]benzimidazole (**1a ⇌ 2a**) and 1,3-dibromopropane, in the hope that, from the two isomeric cyclic salts **14** and **15**, the latter, being less strained than the former (17), should be formed in a higher proportion. However, the



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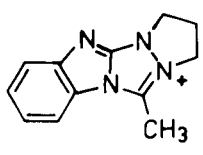

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only product isolated from the reaction was the salt **14** (18). We proceeded also in a stepwise manner, following the method already employed for a similar reaction in benzotriazole (19,20). The starting compound **1a ⇌ 2a** was alkylated with 3-bromo-1-propanol, yielding the isomeric alcohols **1d** and **2d**, which were separated by column chromatography and identified by comparison of their uv and nmr spectra with those of the other compounds **1** and **2** listed above (see also references 2-5). The substitution of the hydroxylic function of each alcohol by a chlorine atom was performed with thionyl chloride (21). The chloride **1e** was not isolated, since it cyclized directly to the salt **14**, whereas the chloride **2e** was easily obtained in pure form, and fully identified by spectroscopic methods. When refluxed in 1-butanol, **2e** was quantitatively transformed into the same salt **14**, without any significant amount of the isomeric salt **15**.

EXPERIMENTAL

Melting points are uncorrected. ^{1}H nmr spectra were obtained on a Perkin-Elmer R-12A (TMS as internal standard). The ir spectra were recorded with a Pye-Unicam SP 1100 instrument. Uv spectra were obtained with a Perkin-Elmer 124 spectrophotometer. Absorbances are expressed as log ϵ. Most of the uv spectra of the compounds are listed in references 2 and 3. For the preparation of 3-methyl-*s*-triazolo[4,3-*a*]benzimidazole (**1a ⇌ 2a**) and its methyl derivatives **1b** and **2b**, see also reference 3.

Ethylation of 3-Methyl-*s*-triazolo[4,3-*a*]benzimidazole (**1a ⇌ 2a**).

The reaction was carried out with bromoethane in sodium ethoxide or with diethyl sulfate in aqueous sodium hydroxide. Procedures were identical as those described for the methylation of the same compound (3). Total yield was 75% (ratio **1c**:**2c** = 35:65) with bromoethane and 65% (50% of each isomer) with ethyl sulfate. The separation of the products was accomplished by column chromatography (silica gel). Chloroform eluted **2c**, whereas ethyl acetate-methanol (9:1) was needed to elute **1c**.

9-Ethyl-3-methyl-*s*-triazolo[4,3-*a*]benzimidazole (**1c**).

This compound had m.p. 95°; ir (potassium bromide): 3060, 2990, 1630, 1610, 1500, 1470 and 745 cm^{-1}; uv (ethanol): 297 (3.71), 291 (3.70), 245 shoulder (3.73) and 232 (3.95) nm; ^{1}H nmr (deuteriochloroform): δ 2.76 (methyl at C_3), 1.50 and 4.15 (J = 7 Hz, ethyl at N_9), 7.0-8.0 (aromatic protons) ppm.

Anal. Calcd. for $C_{11}H_{12}N_4$: C, 65.98; H, 6.04; N, 27.98. Found: C, 65.79; H, 6.07; N, 27.89.

1-Ethyl-3-methyl-*s*-triazolo[4,3-*a*]benzimidazole (**2c**).

This compound had m.p. 57°; ir (potassium bromide): 3060, 2990, 1650, 1595, 1575, 1555, 1470, 1445, 1430, 1225, 750 and 740 cm^{-1}; uv (ethanol): 299 (3.45), 291 (3.48), 259 (3.87), 253 (3.88) and 233 (4.03) nm; ^{1}H nmr (deuteriochloroform): δ 2.68 (methyl at C_3), 1.51 and 4.22 (J = 7 Hz, ethyl at N_1), 7.0-8.0 (aromatic protons) ppm.

Anal. Calcd. for $C_{11}H_{12}N_4$: C, 65.98; H, 6.04; N, 27.98. Found: C, 65.87; H, 6.11; N, 27.91.

Quaternization of 3-Methyl-*s*-triazolo[4,3-*a*]benzimidazoles.

Two general procedures, A and B, were used. Only 1,9-dialkyl derivatives were obtained in a pure form. The 2,9-dialkyl derivatives were never isolated from their mixture with the corresponding salts of type **3**. Results are summarized in Table II.

Procedure A.

Starting material and a large excess of alkylating reagent (molar ratio 1:20) were refluxed in ethanol for 24 hours. The resulting solution was evaporated, and the residue treated with water and extracted with chloroform. The aqueous solution was evaporated *in vacuo*, yielding the corresponding quaternary salts. From the organic layer only starting material was recovered, the exception being the isolation of a small amount of **2b** in the reaction of **1b**

Table II

Quaternization of 3-Methyl-*s*-triazolo[4,3-*a*]benzimidazoles

Starting material	Reagent	Procedure	Quaternary salt obtianed	% Yield (relative ratio)
1b	Iodomethane	A	**3f, 4f**	65 (25:75)
		B	**3f, 4f**	95 (30:70)
	Bromoethane	A	**3g, 4g**	65 (30:70)
		B	**3g, 4g**	90 (40:60)
2b	Iodomethane	A	**3f**	40
		B	**3f**	100
	Bromoethane	A	**3h**	30
		B	**3h**	85
1c	Iodomethane	B	**3h, 4h**	90 (25:75)
2c	Iodomethane	B	**3g**	95

with iodomethane.

Procedure B.

The only difference with the above procedure is that the reaction was carried out heating the reagents, without solvent, in a sealed tube at 150° for 24 hours.

1,3,9-Trimethyl-*s*-triazolo[4,3-*a*]benzimidazolium Iodide (**3f**).

This compound had m.p. 239°; ir (potassium bromide): 3010, 2940, 1682, 1610, 1600, 1562, 1520, 1470, 1010, 817 and 788 cm^{-1}.

Anal. Calcd. for $C_{11}H_{13}IN_4$: C, 40.24; H, 3.96; I, 38.71; N, 17.07. Found: C, 39.97; H, 4.13; I, 38.80; N, 16.95.

1-Ethyl-3,9-dimethyl-*s*-triazolo[4,3-*a*]benzimidazolium Iodide (**3g**).

This compound had m.p. 297°; ir (potassium bromide): 3015, 2940, 1670, 1611, 1600, 1568, 1519, 1470, 1010, 817 and 770 cm^{-1}.

Anal. Calcd. for $C_{12}H_{15}IN_4$: C, 42.10; H, 4.38; I, 37.13; N, 16.37. Found: C, 42.39; H, 4.63; I, 37.35; N, 16.48.

9-Ethyl-1,3-dimethyl-*s*-triazolo[4,3-*a*]benzimidazolium Bromide (**3h**).

This compound had m.p. 237°; ir (potassium bromide): 3030, 2940, 1680, 1612, 1600, 1570, 1520, 1470, 1010, 821 and 780 cm^{-1}.

Anal. Calcd. for $C_{12}H_{15}BrN_4$: C, 48.83; H, 5.08; Br, 27.11; N, 18.98. Found: C, 48.93; H, 5.06; Br, 27.15; N, 19.21.

Reactions of 1,3,9-Trimethyl- and 2,3,9-Trimethyl-*s*-triazolo[4,3-*a*]benzimidazolium Iodides (**3f**) and (**4f**).

a) Thermal Decomposition.

Quaternary salt **3f** was refluxed in *o*-dichlorobenzene for 24 hours, with continuous removal of the formed iodomethane by distillation through a short fractionation column. The solvent was evaporated *in vacuo* and the residue dissolved in chloroform, washed with a 10% solution of sodium thiosulfate, dried and evaporated. The resulting solid consisted in a mixture (nmr) of 3,9-dimethyl- and 1,3-dimethyl-*s*-triazolo[4,3-*a*]benzimidazoles, (**1b**) and (**2b**) in a ratio 1:3.

The same treatment of a mixture of the salts **3f** (25%) and **4f** (75%) yielded the same products in a relative ratio 4:1.

b) Catalytic Hydrogenation.

None of the salts consumed hydrogen when hydrogenated in methanol (catalyst: 10% palladium on carbon) at room temperature for a period of three days.

c) Reaction with Lithium Aluminium Hydride.

Equimolecular amounts of the salt **3f** and lithium aluminium hydride were refluxed in anhydrous ether for 9 hours, with vigorous stirring. The remaining hydride was destroyed with water, and the ethereal layer dried and evaporated, yielding 1-(3′-methylbenzimidazolin-2′-one-1′-yl)ethanone methylhydrazone (**9**) as a white solid of m.p. 128°; ir (potassium bromide): 3892, 2910, 2805, 1722, 1608, 1580, 1530, 1170, 1015, 760 and 740 cm^{-1}.

Anal. Calcd. for $C_{11}H_{14}N_4O$: C, 60.53; H, 6.47; N, 25.67. Found: C, 60.24; H, 6.57; N, 25.52.

When the reaction was performed with the mixture of salts **3f** and **4f**, 1-acetyl-1-methyl-2-(1′-methylbenzimidazolyl)hydrazine (**12**) was also obtained by extracting the remaining aqueous solution with chloroform. The compound showed a carbonyl absorption at 1665 cm^{-1} (potassium bromide), and could not be purified to give a correct analysis.

d) Hydrolysis.

A solution of 1.0 mmoles of the mixture of **3f** and **4f** in 40 ml. of a 10% sodium hydroxide solution was stirred for 20 hours at room temperature. The resulting solution was extracted with chloroform, and the extract dried and evaporated, yielding the same mixture of compounds **9** and **12** as in the reaction with lithium aluminium hydride.

9- and 1-(3′-Hydroxypropyl)-3-methyl-*s*-triazolo[4,3-*a*]benzimidazoles (**1d**) and (**2d**).

3-Bromo-1-propanol was reacted with 3-methyl-*s*-triazolo[4,3-*a*]benzimidazole (**1a** ⇌ **2a**) by a similar procedure as for the other alkylations of the compound. Total yield was 60% (ratio **1d**:**2d** = 30:70) using sodium ethoxide as a base. With sodium hydroxide, yield was only 50% (ratio **1d**:**2d** = 45:55). The mixture of isomeric alcohols was separated by column chromatography (silica gel). Chloroform-ether (1:1) eluted **2d**, whereas ethyl acetate-methanol (1:1) eluted **1d**.

9-(3′-Hydroxypropyl)-3-methyl-*s*-triazolo[4,3-*a*]benzimidazole (**1d**).

This compound had m.p. 143°; ir (potassium bromide): 3260, 2960, 2920, 2880, 2840, 1630, 1610, 1500, 1160 and 740 cm^{-1}; uv (ethanol): 298 (3.69), 291 (3.67) and 233 (3.92) nm; ^1H nmr

(deuteriochloroform): δ 2.76 (methyl at C_3), 3.69 (O-CH_2-), 4.33 (N-CH_2-), 2.12 (C-CH_2-C), 4.97 (OH) and 7.0-8.0 (aromatic protons) ppm.

Anal. Calcd. for $C_{12}H_{14}N_4O$: C, 62.59; H, 6.13; N, 24.33. Found: C, 62.31; H, 6.08; N, 23.98.

1-(3′-Hydroxypropyl)-3-methyl-*s*-triazolo[4,3-*a*]benzimidazole (**2d**).

This compound had m.p. 131°; ir (potassium bromide): 3200, 2920, 2860, 1650, 1600, 1575, 1550, 1470, 1440, 1430, 1220, 1060, 750 and 740 cm^{-1}; uv (ethanol): 299 (3.44), 291 (3.46), 270 (3.64), 261 (3.88), 255 (3.86), 236 shoulder (4.01) and 224 (4.10) nm; ^1H nmr (deuteriochloroform): δ 2.68 (methyl at C_3), 3.70 (O-CH_2-), 4.35 (N-CH_2-), 2.15 (C-CH_2-C), 4.60 (OH) and 7.0-8.0 (aromatic protons) ppm.

Anal. Calcd. for $C_{12}H_{14}N_4O$: C, 62.59; H, 6.13; N, 24.33. Found: C, 62.23; H, 6.08; N, 24.09.

1-(3′-Chloropropyl)-3-methyl-*s*-triazolo[4,3-*a*]benzimidazole (**2e**).

A solution of 0.23 g. (1.0 mmole) of **2d** and 1.6 ml. (12 mmoles) of thionyl chloride in 100 ml. of chloroform was refluxed during 24 hours under stirring. The resulting clear solution was evaporated yielding an oil that crystallized as yellowish plates, m.p. 76-77°; ir (potassium bromide): 2940, 1655, 1600, 1570, 1555, 1470, 1450, 1430, 1215, 1120, 750 and 740 cm^{-1}; uv (ethanol): 300 (3.19), 291 (3.20), 272 (3.62), 262 (3.95), 256 (3.93) and 235 (3.98); ^1H nmr (deuteriochloroform): δ 2.68 (methyl at C_3), 3.61 (Cl-CH_2-), 4.31 (N-CH_2-), 2.39 (C-CH_2-C) and 7.0-8.0 (aromatic protons) ppm.

Anal. Calcd. for $C_{12}H_{13}ClN_4$: C, 57.95; H, 5.27; Cl, 14.25; N, 22.53. Found: C, 57.73; H, 5.27; Cl, 13.96; N, 22.29.

3-Methyl-1,9-propylene-*s*-triazolo[4,3-*a*]benzimidazolium Halides (**14**).

a) A solution of 0.32 g. (1.3 mmoles) of the chloride **2e** in 320 ml. of *n*-butanol was refluxed for 12 hours. The resulting solution was evaporated *in vacuo* and the residue dissolved in water. The aqueous solution, washed several times with chloroform, afforded on evaporation 0.12 g. of a white solid, most of which showed by nmr to be the chloride of compound **14**; ir (potassium bromide): 2990, 1755, 1600 and 770 cm^{-1}; uv (ethanol): 284 (3.72) and 278 (3.65); ^1H nmr (trifluoroacetic acid): δ 2.97 (methyl at C_3), 4.5 (N-CH_2-), 2.9 (C-CH_2-C), and 7.5-8.0 (aromatic protons) ppm. However, we could not purify the substance so as to give a correct CHN analysis.

b) 9-(3′-Hydroxypropyl)-3-methyl-*s*-triazolo[4,3-*a*]benzimidazole (**1d**) (0.23 g., 1.0 mmoles) and 1.6 ml. (12 mmoles) of thionyl chloride in 100 ml. of chloroform were refluxed for five hours, with stirring. The resulting solution was directly poured into a column of alumina, and eluted first with chloroform and then with methanol. The chloroform eluate contained a complex mixture of products (nmr), whereas the methanol eluate afforded on evaporation 0.1 g. of an oily residue. The uv, ir and ^1H nmr spectra of this material were practically identical as those of compound **14** obtained in the above reaction.

c) A solution of 2.0 mmoles of 3-methyl-*s*-triazolo[4,3-*a*]-benzimidazole (**1a** ⇌ **2a**) and 2.0 mmoles of sodium hydroxide in 200 ml. of *n*-butanol were added dropwise to a boiling solution of 1,3-dibromopropane (3.0 mmoles) in 350 ml. of the same solvent. The reaction mixture was refluxed for 48 hours, and the resulting solution treated as in reaction a), yielding a white solid composed mainly by the bromide of compound **14** (uv, ^1H nmr).

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(8) If ethanol is used as solvent, instead of *o*-dichlorobenzene, only starting material is recovered after 24 hours of reflux.

(9) The coupling constant, 4.9 Hz, is observable in DMSO-d_6 but not in deuteriochloroform, and is characteristic for the NH-CH_3 group (10-12).

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(13) The hydrolysis was carried out with the mixture of both salts **3f** and **4f**, and the compounds were not separated. The nmr data for **12** were thus obtained in a mixture of compounds **9** and **12**.

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