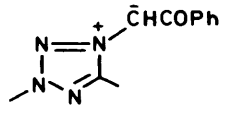
Synthesis and Properties of Tetrazolium *N*-Phenacylides

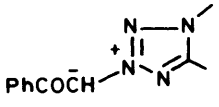
Dietrich Moderhack * and Adalbert Lembcke
Institut für Pharmazeutische Chemie der Technischen Universität, D-3300 Braunschweig, Germany

A number of isomeric tetrazolium 1-phenacylides (**6**) [type (A)] and 3-phenacylides (**7**) [type (B)] have been prepared by deprotonation of the corresponding salts (**3**) and (**4**) and submitted to standard ylide reactions. A comparison of their physicochemical properties as well as their reactivity toward alkali hydroxide and several electrophiles demonstrates that the 3-tetrazoliumyl system as in (B) exerts a stronger electron-withdrawing influence than the 1-tetrazoliumyl system as in (A). Phenacylides of type (C) could not be isolated.

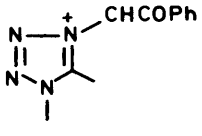
Apart from two long-known classes of tetrazolium *N*-tetrazolides[1,2] and a few tetrazolium *N*-diformylmethylides which have recently been mentioned but without characterisation data,[3] until now there has been no account of the isolation of tetrazolium *N*-ylides. This led us to attempt the synthesis of ylides of type (A), (B), and (C), *i.e.* compounds bearing Kröhnke's[4] classical phenacylide function. Ylides of this type have been obtained from a variety of azoles including pyrazole,[5b] imidazole,[5b] thiazole,[5b] and 1,2,4-triazole.[6]



(A)

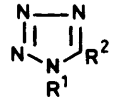


(B)



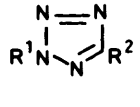
(C)

Synthesis.—Following the general approach to *N*-phenacylides *via* deprotonation of *N*-phenacylazolium salts, we first prepared the respective tetrazolium compounds (**3**), (**4**), and (**5**) by quaternising the starting heterocycles (**1**) and (**2**) (Schemes 1 and 2). Alkylation of (**2**) occurs regiospecifically at N-4 (*cf.*



(1)

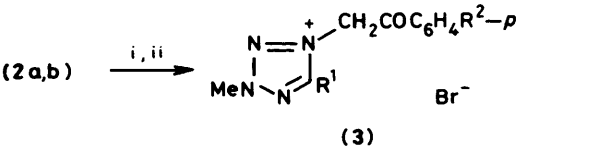
a; R^1 = Me, R^2 = H
b; R^1 = Ph, R^2 = Me
c; R^1 = CH_2COPh, R^2 = H
d; R^1 = $CH_2COC_6H_4Br$-*p*, R^2 = H
e; R^1 = $CH_2COC_6H_4NO_2$-*p*, R^2 = H
f; R^1 = CH_2COPh, R^2 = Me



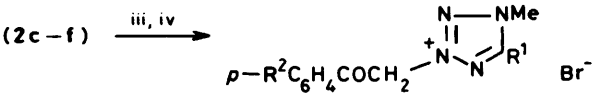
(2)

a; R^1 = Me, R^2 = H
b; R^1 = R^2 = Me
c; R^1 = CH_2COPh, R^2 = H
d; R^1 = $CH_2COC_6H_4Br$-*p*, R^2 = H
e; R^1 = $CH_2COC_6H_4NO_2$-*p*, R^2 = H
f; R^1 = CH_2COPh, R^2 = Me

refs. 7,8) and thus appears to be the most efficient entry into the two series of salts (**3**) and (**4**). However, quaternisation of weak bases such as 2-substituted tetrazoles[9] is a slow process[8b,d] and requires powerful alkylating agents.[7,8a,c,d,10] We found that,



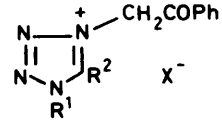
(3)



(4)

a; R^1 = Me, R^2 = H, X = Br
b; R^1 = c-C_6H_{11}, R^2 = Me, X = Br
c; R^1 = Ph, R^2 = Me, X = Br_4
d; R^1 = R^2 = Me, X = Br

Scheme 1. *Reagents:* i, $BrCH_2COC_6H_4R^2$-*p*/$AgBF_4$; ii, anion exchange resin/Br^-; iii, $(MeO)_2SO_2$; iv, see ii



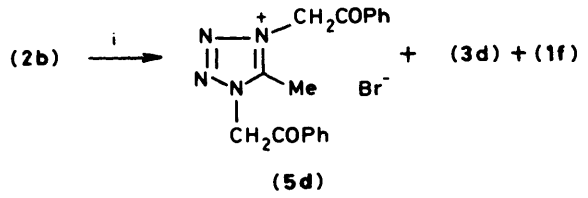
(5)

a; R^1 = R^2 = H
b; R^1 = R^2 = Me, X = Br
c; R^1 = Ph, R^2 = Me, X = BF_4

(**1a**) —i→ (**5a**)
(**1b**) —ii→ (**5c**)
(**1f**) —iii, iv→ (**5b**)

Scheme 2. *Reagents:* i, $BrCH_2COPh$; ii, $BrCH_2COPh$/$AgBF_4$; iii, $(MeO)_2SO_2$; iv, anion exchange resin/Br^-

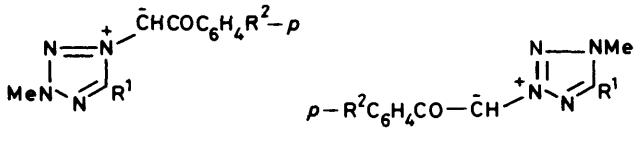
using dimethyl sulphate, the phenacyltetrazoles (**2c**—**f**) are readily quaternised—(**2f**) appreciably faster than (**2c**)—to give, after anion exchange, the desired salts (**4a**—**d**) in excellent yield (Table 4). By contrast, phenacylation of (**2a**,**b**) proceeded well only in the presence of silver tetrafluoroborate.[11] When working without this reagent, serious drawbacks are low reaction rates and, as is illustrated for (**2b**), the formation of substantial amounts of the diphenacyltetrazolium salt (**5d**) (Scheme 3). The 1,4,5-trisubstituted tetrazolium salts (**5b**,**c**) had earlier been made by quaternisation of (**1b**,**f**);[12] (**5a**) was now obtained in like manner. It should be noted that compounds (**5a**—**c**), on account of the ambident behaviour of 1-substituted



Scheme 3. Conditions: i, $BrCH_2COPh$, $MeNO_2$, 60—80 °C, 36—72 h

tetrazoles,[13] were produced along with minor quantities of the corresponding salts of type (**3**) and (**4**), respectively [insignificant amounts of (**4a**) with phenacylation of (**1a**)].

Application of the standard preparative method[14,15] to the salts (**3**) and (**4**) (*i.e.* treatment with an excess of aqueous potassium carbonate in the cold) gave the yellow to red tetrazolium *N*-phenacylides (**6**) and (**7**) as reasonably stable solids (Table 5).*



(**6**) (**7**)

a; $R^1 = R^2 = H$
b; $R^1 = H$, $R^2 = Br$
c; $R^1 = H$, $R^2 = NO_2$
d; $R^1 = Me$, $R^2 = H$

Our efforts to isolate analogous ylides of type (C), however, remained unrewarded. The salt (**5a**), in line with other 1,4-disubstituted tetrazolium compounds having hydrogen in position 5,[7,16] evolved gaseous nitrogen on addition of base. Likewise, no ylide could be obtained from (**5b**), but interestingly this salt, when heated in aqueous hydrogen carbonate, underwent an unexpected ring transformation to produce a 4-imidazolone.[12] Finally, the phenyl substituted tetrazolium salt (**5c**), when treated with potassium carbonate, was hydrolysed to phenyl azide and *N*-phenacylacetamide.[17]

Properties.—Stability as well as reactivity of *N*-ylides largely depend on electronic conditions. In the case of azolium or azinium *N*-ylides (sometimes jointly termed as 'cycloimmonium ylides'[5b–e]), a major stabilising factor is given by resonance interaction between the electron-attracting heterocycle and the carbanionoid lone pair.[5a,c,d] From an inspection of calculated atomic charges for 1,3- and 1,4-dimethyltetrazolium cations[18,19] and also the ensuing discussion[19] of resonance structures of the corresponding methylides it should likewise follow that (i) the electron-withdrawing influence exerted by the tetrazolium rings as in (A), (B), and (C) will decrease in the sequence 1-substituted 3-tetrazoliumyl > 3-substituted 1-tetrazoliumyl > 1-substituted 4-tetrazoliumyl and (ii) the tetrazolium ylide of type (B) constitutes the best stabilised representative of the series. Evidently the majority of our observations described below have a direct bearing on these structural presuppositions.

(1) Rate measurements of H/D exchange of the methylene group in the three isomeric tetrazolium salts (**3d**), (**4d**), and (**5b**) clearly demonstrate that ylide formation is most favoured with (**4d**). Preliminary experiments in neutral deuterium oxide at 32 °C showed half-lives of *ca.* 17 min for (**3d**), 6 min for (**4d**), and 1 h for (**5b**); a similar ratio holds for the triad (**3a**), (**4a**), and (**5a**). This is in accord with literature data[7,17c] pertaining to di- and tri-methyltetrazolium ions which indicate a more rapid exchange with alkyl groups attached to N-3 rather than to N-1. Moreover, there has been found a close correlation between the above H/D exchange results and the pK_a's of our phenacyltetrazolium salts: we determined 8.98, 8.45, 9.64 for (**3a**), (**4a**), (**5a**) and 9.64, 9.05, 10.17 for (**3d**), (**4d**), (**5b**), respectively (all values by potentiometric titration of 0.002 molar solutions with 0.01M-NaOH in water at 20 °C).

(2) The visible absorption band (intramolecular charge-transfer band) of the isomeric ylides (**6a**) and (**7a**) has been studied in solvents of different polarity. Although registered at fairly high frequences compared to (**6a**), the i.c.t. band of (**7a**), quite predictably (*cf.* ref. 20*b*), exhibits a less pronounced (negative) solvatochromism than that of (**6a**) (Table 1). A plot of the transition energies (E_T) of these bands against the empirical solvent polarity (Z)[20a] revealed linear relationships as follows: (**6a**), $E_T = 0.293\ Z + 49.46$ ($r = 0.997$) (2-methylpropan-2-ol neglected); (**7a**), $E_T = 0.142\ Z + 62.54$ ($r = 0.992$) (2-methylpropan-2-ol and acetone neglected).

(3) When comparing the action of alkali hydroxide on isomeric ylides such as (**6a**)/(**7a**), (**6b**)/(**7b**), and (**6c**)/(**7c**), *i.e.* investigating Kröhnke's[4a] 'acid splitting,' it became apparent that all compounds (**7**) have a much higher propensity for giving (**8**) than have the ylides (**6**) (Scheme 4; Table 2).

(4) Treatment with a range of electrophiles has expectedly disclosed that, *vice versa*, the isomers (**6**) react with greater ease. Aroylation of the tetrazolium salts (**3a**) and (**4a**) under Schotten-Baumann conditions in the presence of 2 equiv. of base (*cf.* ref.

Table 1. Charge-transfer band maxima for the ylides (**6a**) and (**7a**) in solvents of decreasing polarity

Solvent (Empirical polarity Z[a])	(6a) $\lambda_{max.}$/nm	(6a) E_T/kcal mol^{-1}	(7a) $\lambda_{max.}$/nm	(7a) E_T/kcal mol^{-1}
Water (94.6)	371	77.1	376	76.0
Ethylene glycol (85.1)	384	74.5	384	74.5
Methanol (83.6)	387	73.9	386	74.1
Ethanol (79.6)	390	73.3	387	73.9
Propan-2-ol (76.3)	396	72.2	388	73.7
2-Methylpropan-2-ol (71.3)	398	71.8	390	73.3
Acetone (65.7)	416	68.7	395	72.4
Methylene chloride (64.2)	420	68.1	400	71.5
Chloroform (63.2)	420	68.1	400	71.5

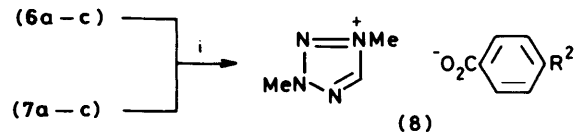
[a] *Cf.* Ref. 20*a*.

Table 2. Pseudo first-order rate constants and half-lives of 'acid splitting' (Scheme 4) for the ylides (**6a**—**c**) and (**7a**—**c**) in 0.01M-NaOH at 20 °C

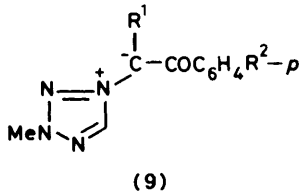
Compd.[a]	$10^2 k_{obs.}$/min^{-1}	$t_{\frac{1}{2}}$/min	k_{rel}[(6):(7)]
(**6a**)	0.395	175.4	1
(**7a**)	17.6	3.9	*ca.* 45
(**6b**)	0.741	93.5	1
(**7b**)	38.0	1.8	*ca.* 51
(**6c**)	(4.36)[b]	(15.9)[b]	1
(**7c**)	71.2	1.0	(*ca.* 16)

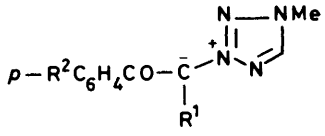
[a] Initial concentration 10^{-4} mol. [b] Plot found linear over one half-life only (*cf.* Experimental section).

* A ready analytical distinction between (**6**) and (**7**) is provided by ^1H n.m.r. and mass spectrometry: compared to ylides (**7**), 5-H of (**6a**—**c**) and N-Me of (**6a**—**d**) are deshielded by 1.4—1.6 and 0.3—0.4 p.p.m., respectively; contrasting with (**6**), no molecular ion peaks were found in case of ylides (**7**) [the same applies to substituted ylides (**10**)].



Scheme 4. Conditions: i, see Table 2

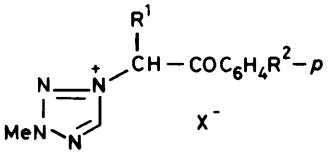

(9)


(10)

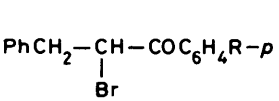
a; R^1 = COC_6H_4Me-*p*, R^2 = H
b; R^1 = COC_6H_4Me-*p*, R^2 = NO_2
c; R^1 = CONHPh, R^2 = H
d; R^1 = CONHPh, R^2 = Br
e; R^1 = CSNHPh, R^2 = NO_2

a; R^1 = COC_6H_4Me-*p*, R^2 = H
b; R^1 = CONHPh, R^2 = H
c; R^1 = CONHPh, R^2 = Br

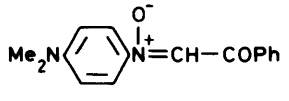
15) led to the ylides (**9a**) and (**10a**) in similar yield (56 and 51%, respectively); however, the formation of (**9a**) occurred much more rapidly. Accordingly, the same experiment with the isomers (**3c**) and (**4c**) succeeded only with the former to give the ylide (**9b**); in the case of (**4c**), the intermediate ylide (**7c**) could not be reacted further. By action of phenyl isocyanate (*cf.* refs. 6*b*,15) on the ylides (**6a,b**) and (**7a,b**) we obtained the carbamoylated derivatives (**9c,d**) and (**10b,c**) in almost quantitative yield; again, the conversion of compounds (**7**) required longer reaction periods (about four times as much). Additional attempts to thiocarbamoylate the nitro substituted ylides (**6c**) and (**7c**) with phenyl isothiocyanate (*cf.* refs. 6*a,b*,15) failed with (**7c**).


(11)

a; R^1 = Me, R^2 = H, X = I
b; R^1 = CH_2Ph, R^2 = Br, X = Br


(12)

a; R = Br
b; R = NO_2


(13)

Alkylation of (**6a**) with methyl iodide and of (**6b**) with benzyl bromide in a way related to an earlier procedure[14b,15] afforded the tetrazolium salts (**11a,b**) in moderate yield (35 and 21%, respectively). By contrast, starting from (**7a**) and methyl iodide as well as from (**6c**), (**7b**) or (**7c**) and benzyl bromide, none of the expected salts could be isolated (although they were detectable by n.m.r.). Apparently, these compounds on account of an increased electron-withdrawal are highly prone to C–N bond cleavage, for we only obtained the α-bromodihydrochalcones (**12a,b**) and the respective methyltetrazoles (**1a**) and (**2a**). A certain, though less marked sensitivity is encountered with the salts (**11a,b**) (*cf.* the low yields): *e.g.*, thermolysis of (**11b**) cleanly generated (**12a**) which, accordingly, has been found as a by-product in the aforementioned reaction of (**6b**) with benzyl bromide.

In a final experiment we submitted the isomeric tetrazolium salts (**3a**) and (**4a**) to the Kröhnke reaction[4a,d] and isolated the corresponding nitrone (**13**)[21] in 56 and 26% yield, respectively.

Our work shows that tetrazolium *N*-phenacylides of type (A) and (B) are well defined compounds having properties that can be correlated with the electron-attracting force of the heterocycle. Further studies will be directed toward the preparation of ylides of type (C).

Experimental

M.p.s were determined on a Kofler microscope and are uncorrected. Spectral data were recorded as follows: i.r. spectra were taken with a Pye-Unicam SP 1100 instrument; ^1H n.m.r. spectra were determined with a Varian EM-390 instrument, ^{13}C n.m.r. spectra were run on Varian XL-100 and Bruker AM-300 or WM-400 instruments (tetramethylsilane as internal standard throughout); mass spectra were determined on a Varian MAT CH-7 instrument; u.v. spectra were taken with a Pye-Unicam SP 800 B spectrophotometer (individual $\varepsilon_{max.}$ values were obtained with a manual Pye-Unicam SP 6-550 UV/VIS instrument).

Phenacyltetrazoles (**1d—f**) *and* (**2d—f**).—*General procedure.* Following the method described in ref. 22, anhydrous potassium carbonate (0.125 mol) was added portionwise to a refluxing solution of tetrazole[23] or 5-methyltetrazole[24] (0.25 mol) and the respective phenacyl bromide (0.25 mol) in acetone (500 ml). The boiling mixture was stirred for a further 4 h and then poured into cold water (500 ml). Products were collected by filtration and extraction with methylene chloride, respectively. For further work-up see below; data for the compounds are given in Table 3.

(**1d**),(**2d**). The crude product was dissolved in warm acetone. On cooling most of the tetrazole (**1d**) was deposited as needles. The filtrate was concentrated to dryness and the residue chromatographed on silica gel using methylene chloride–acetone (9:1) as eluant to give first (**2d**) and then a second crop of (**1d**).

(**1e**),(**2e**). The crude mixture was directly chromatographed as described before.

(**1f**),(**2f**). The oily product was kept for 12 h at 0 °C when (**1f**) separated as prisms which were collected by filtration. The residual oil was chromatographed on silica gel using benzene–ethyl acetate (1:1) as eluant to yield first (**2f**) and then some more (**1f**).

3-*Methyl- and* 3,5-*Dimethyl*-1-*phenacyltetrazolium Bromides* (**3a—d**): *General procedure.*—A solution of (**2a**)[25] or (**2b**),[26] the respective phenacyl bromide, and silver tetrafluoroborate[11] (0.01 mol each) in anhydrous nitromethane (20 ml) was held at 50—60 °C for 48 h. After evaporation of the solvent, the solid residue was treated with several portions of boiling water. The combined filtrates were allowed to pass a column packed with anion exchange resin containing bromide ion [in the case of (**3b**) at 80 °C]. The resultant solution was concentrated under reduced pressure and the residue crystallised as indicated in Table 4.

1-*Methyl- and* 1,5-*Dimethyl*-3-*phenacyltetrazolium Bromides* (**4a—d**): *General procedure.*—A mixture of the phenacyltetrazole

Table 3. Yields, physical, spectral, and analytical data for the phenacyltetrazoles (**1d—f**) and (**2d—f**)

Compd. (Formula)	Yield (%)	M.p. (°C)	$\delta_H[(CD_3)_2SO]$[a]	$\delta_C[(CD_3)_2SO]$	Elemental analysis (%) Found (required) C	H	N
(**1d**) ($C_9H_7BrN_4O$)	37	186—187[b]	6.37 (CH_2), 9.32 (5-H)	53.9 (t, CH_2), 145.2 (d, C-5)	40.5 (40.5)	2.6 (2.6)	21.0 (21.0)
(**1e**) ($C_9H_7N_5O_3$)	32	197[c]	6.46 (CH_2), 9.33 (5-H)		46.5 (46.4)	3.0 (3.0)	30.1 (30.0)
(**1f**) ($C_{10}H_{10}N_4O$)	46	149[d]	2.49 (Me), 6.33 (CH_2)	8.1 (q, Me), 53.0 (t, CH_2), 153.6 (s, C-5)	59.4 (59.4)	5.0 (5.0)	27.7 (27.7)
(**2d**) ($C_9H_7BrN_4O$)	14	164—165[e]	6.73 (CH_2), 9.16 (5-H)	58.6 (t, CH_2), 153.4 (d, C-5)	40.5 (40.5)	2.6 (2.6)	20.9 (21.0)
(**2e**) ($C_9H_7N_5O_3$)	12	169—170[f]	6.80 (CH_2), 9.09 (5-H)		46.4 (46.4)	2.9 (3.0)	29.9 (30.0)
(**2f**) ($C_{10}H_{10}N_4O$)	17	89—91[g]	2.51 (Me), 6.55 (CH_2)	10.3 (q, Me), 58.4 (t, CH_2), 162.4 (s, C-5)	59.4 (59.4)	4.9 (5.0)	27.6 (27.7)

[a] All signals are singlets. [b] From acetone. [c] From ethyl acetate. [d] From ethanol. [e] From benzene. [f] From propan-2-ol. [g] From benzene–light petroleum.

Table 4. Yields, physical, spectral, and analytical data for the phenacyltetrazolium bromides (**3a—d**), (**4a—d**), and (**5a—d**)

Compd. (Formula)	Yield (%)	M.p. (°C) (decomp.)	$\lambda_{max.}$[a]/nm (log ε)	$\delta_H(CF_3CO_2D)$[b]	$\delta_C[(CD_3)_2SO]$	Elemental analysis (%) Found (required) C	H	N
(**3a**) ($[C_{10}H_{11}N_4O]Br$)	69	138—140[c]	248 (4.16)	4.80 (Me), 6.53 (CH_2), 9.67 (5-H)	44.0 (q, Me), 58.1 (t, CH_2), 150.3 (d, C-5)	42.4 (42.4)	3.8 (3.9)	19.9 (19.8)
(**3b**) ($[C_{10}H_{10}BrN_4O]Br$)	55	171—172[d]	263 (4.24)	4.80 (Me), 6.62 (CH_2), 9.67 (5-H)	43.8 (q, Me), 57.8 (t, CH_2), 150.3 (d, C-5)	33.2 (33.2)	2.8 (2.8)	15.6 (15.5)
(**3c**) ($[C_{10}H_{10}N_5O_3]Br$)	62	153—154[e]	263 (4.16)	4.81 (Me), 6.62 (CH_2), 9.68 (5-H)		36.5 (36.6)	3.1 (3.1)	21.3 (21.3)
(**3d**) ($[C_{11}H_{13}N_4O]Br$)	57	142—146[c]		2.81 (C-Me), 4.67 (N-Me), 6.43 (CH_2)	9.1 (q, C-Me), 43.5 (q, N-Me), 56.7 (t, CH_2), 160.0 (s, C-5)	44.6 (44.5)	4.3 (4.4)	18.7 (18.9)
(**4a**) ($[C_{10}H_{11}N_4O]Br$)	91	121—122[e]	248 (4.17)	4.68 (Me), 6.75 (CH_2), 9.81 (5-H)	38.8 (q, Me), 63.1 (t, CH_2), 150.3 (d, C-5)	42.3 (42.4)	4.0 (3.9)	19.6 (19.8)
(**4b**) ($[C_{10}H_{10}BrN_4O]Br$)·$\frac{1}{2}H_2O$	78	135—137[d]	263 (4.26)	4.67 (Me), 6.70 (CH_2), 9.78 (5-H)	38.8 (q, Me), 62.9 (t, CH_2), 150.3 (d, C-5)	32.3 (32.4)	2.9 (3.0)	15.0 (15.1)
(**4c**) ($[C_{10}H_{10}N_5O_3]Br$)	82	132—134[e]	263 (4.17)	4.71 (Me), 6.86 (CH_2), 9.85 (5-H)		36.4 (36.6)	3.2 (3.1)	21.1 (21.3)
(**4d**) ($[C_{11}H_{13}N_4O]Br$)·$\frac{1}{2}H_2O$	96	115—117[c]		2.95 (C-Me), 4.50 (N-Me), 6.65 (CH_2)	9.5 (q, C-Me), 37.3 (q, N-Me), 62.6 (t, CH_2), 159.7 (s, C-5)	43.1 (43.2)	4.6 (4.6)	18.3 (18.3)
(**5a**) ($[C_{10}H_{11}N_4O]Br$)	90	145—148[c]		4.63 (Me), 6.65 (CH_2), 10.84 (5-H)	38.0 (q, Me), 57.4 (t, CH_2), 144.2 (d, C-5)	42.3 (42.4)	3.8 (3.9)	19.8 (19.8)
(**5d**) ($[C_{18}H_{17}N_4O_2]Br$)·H_2O	see text	133—138[d]		3.02 (Me), 6.48 (2 × CH_2)		51.1 (51.6)	4.6 (4.6)	13.3 (13.4)

[a] Solvent: 95% EtOH–3M-HCl (100 + 1). [b] All signals are singlets. [c] From ethanol–ether. [d] From water. [e] From ethanol.

(**2c**),[22] (**2e**) or (**2f**) (0.05 mol), and dimethyl sulphate (0.25 mol) was kept at ambient temperature for 48 h; in the case of (**2d**) the mixture was diluted with methanol (25 ml) and stirred. Ether (100 ml) was then added and the product extracted with water. The combined aqueous layers were concentrated to *ca.* one fifth and submitted to the anion exchange procedure as shown for (**3a—d**). For data of compounds see Table 4.

1-*Methyl*-4-*phenacyltetrazolium Bromide* (**5a**).—A solution of (**1a**)* (0.84 g, 0.01 mol) and phenacyl bromide (2.2 g, 0.011 mol) in anhydrous nitromethane (20 ml) was heated to 80 °C for 4 days. The product was isolated by evaporating the solvent under reduced pressure and crystallising the residue from ethanol–ether. Data are given in Table 4.

Treatment of the Tetrazole (**2b**) *with Phenacyl Bromide.*—(a) A solution of (**2b**)[26] (4.9 g, 0.05 mol) and phenacyl bromide (12.5 g, 0.063 mol) in anhydrous nitromethane (10 ml) was held at 60—65 °C for 36 h. On shaking the reaction mixture with ether (30 ml) and water (20 ml), colourless prisms of 5-methyl-1,4-diphenacyltetrazolium bromide (**5d**) separated (1.86 g, 15%; for data see Table 4). From the ethereal layer crystallised some (**1f**) (0.51 g, 5%; for data see Table 3), while the aqueous filtrate of (**5d**), after concentration and addition of acetone, gave (**3d**) as prisms (2.35 g, 16%; for data see Table 4).

(b) From a reaction on the same scale performed at 75—

* Prepared similar to: R. Stollé and F. Henke-Stark, *J. Prakt. Chem.*, 1930, **124**, 261. The by-product (**2a**) has been separated by column chromatography; the data obtained for (**1a**) correspond to those described in ref. 27.

Table 5. Yields, physical, spectral, and analytical data for the tetrazolium phenacylides (**6a**—**d**) and (**7a**—**d**)

Compd. (Formula)	Yield[a] (%)	M.p. (°C) (decomp.)	$\nu_{max.}$(KBr) cm^{-1}	$\lambda_{max.}(H_2O)$ nm (log ε)	*m/z* (70 eV)[b]	δ_H[c]	Elemental analysis (%) Found (required) C	H	N
(**6a**) ($C_{10}H_{10}N_4O$)	98	121—124[d]	1 520	371 (4.15)	202 (M^+, 56%), 160 (68), 105 (100)	4.40 (Me), 7.33 (CH), 11.00 (5-H)	59.4 (59.4)	5.0 (5.0)	27.4 (27.7)
(**6b**) ($C_{10}H_9BrN_4O \cdot \frac{1}{2}H_2O$)	96	144—147[d]	3 450, 1 525	373 (4.20)	282/280 (M^+, 7%), 240/238 (100), 185/183 (94)	4.48 (Me), 7.47 (CH), 11.20 (5-H)	41.4 (41.4)	3.4 (3.5)	19.4 (19.3)
(**6c**) ($C_{10}H_9N_5O_3$)	93	160—161[e]	1 550	390 (4.18)		4.50 (Me), 7.65 (CH), 11.26 (5-H)	48.3 (48.6)	3.6 (3.7)	28.0 (28.3)
(**6d**) ($C_{11}H_{12}N_4O$)	96	132—135[d]	1 525		216 (M^+, 100%), 105 (82)	2.70 (C-Me), 4.51 (N-Me), 7.47 (CH)	60.7 (61.1)	5.6 (5.6)	25.3 (25.9)
(**7a**) ($C_{10}H_{10}N_4O$)	99	124—127[a]	1 535	376 (4.36)	290 (<1%), 276 (4), 248 (22), 220 (5), 171 (8), 146 (76)[f]	4.11 (Me), 7.52 (CH), 9.58 (5-H)	59.2 (59.4)	5.0 (5.0)	27.8 (27.7)
(**7b**) ($C_{10}H_9BrN_4O$)	95	153—155[a]	1 535	378 (4.39)	226/224 (47/53%), 198/196 (17), 185/183 (63), 89 (100), 84 (24)	4.12 (Me), 7.43 (CH), 9.62 (5-H)	42.9 (42.7)	3.4 (3.2)	19.7 (19.9)
(**7c**) ($C_{10}H_9N_5O_3$)	95	171—174[a]	1 555	393 (4.30)		4.16 (Me), 7.54 (CH), 9.68 (5-H)	48.2 (48.6)	3.6 (3.7)	27.6 (28.3)
(**7d**) ($C_{11}H_{12}N_4O$)	93	154—155[a]	1 535		279 (12%), 250 (8), 236 (4), 210 (2), 186 (14), 167 (39)[g]	2.47 (C-Me), 3.98 (N-Me), 7.40 (CH)	60.9 (61.1)	5.6 (5.6)	25.5 (25.9)

[a] Crude product. [b] Ion source temperature (°C): (**6a**), 90; (**6b**), 80; (**6d**), 100; (**7a**), 110; (**7b**), 70; (**7d**), 100. [c] Solvent: $(CD_3)_2SO$ for (**6a**—**d**) and (**7a**—**c**), and $CDCl_3$ for (**7d**). All signals are singlets. Ylidic H which sometimes appeared under multiplet of aromatics was identified by addition of D_2O. [d] From methylene chloride–light petroleum. [e] From ethanol. [f] Further peaks: 118 (40), 105 (86), 90 (100), and 84 (34). [g] Further peaks: 149 (58), 136 (70), 122 (58), 118 (15), 105 (100), and 98 (50).

80 °C for 72 h, higher yields of (**5d**) (4.3 g, 34%) and (**1f**) (0.7 g, 7%) were obtained, whereas only insignificant amounts of (**3d**) were isolated.

3-Methyl- and 3,5-Dimethyltetrazolium 1-Phenacylides (**6a**—**d**); *1-Methyl- and 1,5-Dimethyl-tetrazolium 3-Phenacylides* (**7a**—**d**): *General procedure.*—Potassium carbonate (4.1 g, 0.03 mol) in water (10 ml) was added to the tetrazolium salt (**3a**—**d**) or (**4a**—**d**) (0.01 mol) in water (25—30 ml) at 0 °C with vigorous stirring. The mixtures were stirred at 0 °C for a further 2 h and then the products were collected by filtration or, in the case of (**6d**) and (**7d**), extracted with methylene chloride. The dried ylides were sufficiently pure for further reactions; attempted recrystallisation caused decomposition (**7a**—**d**) or considerable loss of material (**6a**—**d**). For data of compounds see Table 5.

Action of Sodium Hydroxide on the Tetrazolium Bromides (**3a**—**c**) *and* (**4a**—**c**).—(a) The tetrazolium bromide (**3a**) or (**4a**) (0.7 g, 2.5 mmol) was stirred with M-NaOH (50 ml) at ambient temperature for 2 h. After addition of 3M-HCl up to pH 1, extraction with methylene chloride gave benzoic acid (0.3 g, quant.), identified by comparison (m.p., i.r.) with an authentic sample. The aqueous layers were concentrated under reduced pressure to yield a solid residue containing the 1,3-dimethyltetrazolium ion: $\delta_H[(CD_3)_2SO]$ 4.42 (s, 1-Me), 4.69 (s, 3-Me), and 10.54 (s, 5-H) [lit.,[7] (D_2O) 4.6, 4.8, and 10.1].

(b) *Kinetic determinations.* 1.00 ml Portions of 10^{-2} molar stock solutions of (**3a**—**c**) and (**4a**—**c**) in water were diluted to 100.0 ml using 0.01M-NaOH. In these dilutions the change in absorbance (*E*) at wavelengths indicated in Table 5 was observed. Plots of log *E* against time were linear over several half-lives except for (**6c**) (one half-life). For data see Table 2.

3-Methyltetrazolium 1-[α-(4-Methylbenzoyl)phenacylide] (**9a**) *and 1-[α-(4-Methylbenzoyl)-4-nitrophenacylide]* (**9b**).—*p*-Toluoyl chloride (1.7 g, 0.011 mol) in methylene chloride (15 ml) and potassium carbonate (2.8 g, 0.02 mol) in water (10 ml) were added to the tetrazolium salt (**3a**) or (**3b**) (0.01 mol) in water (25 ml). The mixture was stirred at 0 °C until the intermediate solid had disappeared, and after an additional 2 h period of stirring at 0 °C the organic layer was separated. It was then dried (Na_2SO_4) and evaporated to give a pale yellow solid which was recrystallised from methylene chloride–light petroleum to give (i) the phenacylide (**9a**) (1.78 g, 56%) as needles, m.p. 174—176 °C (decomp.) (Found: C, 67.2; H, 4.9; N, 17.4. $C_{18}H_{16}N_4O_2$ requires C, 67.5; H, 5.0; N, 17.5%); $\nu_{max.}$(KBr) 1 515 cm^{-1}; $\delta_H(CDCl_3)$ 2.18 (s, C-Me), 4.58 (s, N-Me), 6.75—7.4 (9 H, m, Ar), and 9.43 (s, 5-H); *m/z* (70 eV, 140 °C) 320 (M^+, 32%), 292 (58), 278 (100), 277 (84), 119 (88), and 84 (25); and (ii) the phenacylide (**9b**) (1.92 g, 51%) as prisms, m.p. 202—205 °C (decomp.) (Found: C, 57.9; H, 4.1; N, 18.8. $C_{18}H_{15}N_5O_4 \cdot \frac{1}{2}H_2O$ requires C, 57.8; H, 4.3; N, 18.7%); $\nu_{max.}$(KBr) 3 420br, 1 530, 1 515, and 1 340 cm^{-1}; $\delta_H[(CD_3)_2SO]$ 2.12 (s, C-Me), 4.74 (s, N-Me), 6.84 (2 H, d) and 7.06 (2 H, d) (AB_q, *J* 8 Hz, Ar), 7.39 (2 H, d) and 7.88 (2 H, d), (AB_q, *J* 9 Hz, Ar), and 10.43 (s, 5-H).

1-Methyltetrazolium 3-[α-(4-Methylbenzoyl)phenacylide] (**10a**).—A similar treatment of the isomeric tetrazolium salt (**4a**) gave the product (1.69 g, 53%) as fine needles, m.p. 194—196 °C (decomp.) (from methylene chloride–light petroleum) (Found: C, 67.6; H, 5.0; N, 17.2. $C_{18}H_{16}N_4O_2$ requires C, 67.5; H, 5.0; N, 17.5%); $\nu_{max.}$(KBr) 1 535 cm^{-1}; $\delta_H[(CD_3)_2SO]$ 2.21 (s, C-Me), 4.43 (s, N-Me), 6.85—7.35 (9 H, m, Ar), and 10.20 (s, 5-H) (disappeared on addition of deuterium oxide); *m/z* (70 eV, 170 °C) 368 (1%), 354 (1), 319 (2), 292 (62), 236 (100), 192 (66), 178 (42), 165 (55), 119 (90), 105 (91), and 84 (16).

3-Methyltetrazolium 1-[α-(Phenylcarbamoyl)phenacylide] (**9c**) *and 1-[4-Bromo-α-(phenylcarbamoyl)phenacylide]* (**9d**).—Phenyl isocyanate (1.3 g, 0.011 mol) in methylene chloride (5 ml) was added to a suspension of the ylide (**6a**) or (**6b**) (0.01 mol) in methylene chloride (25 ml). The mixture was stirred at

ambient temperature until a clear solution had formed; 2 h later the solvent was evaporated and the residue crystallised from methylene chloride–light petroleum to give (i) the phenacylide (**9c**) (3.1 g, 96%) as yellow plates, m.p. 134—135 °C (decomp.) (Found: C, 63.2; H, 4.7; N, 21.5. $C_{17}H_{15}N_5O_2$ requires C, 63.5; H, 4.7; N, 21.8%); $\nu_{max.}$(KBr) 1 625 and 1 530 cm^{-1}; $\delta_H(CDCl_3)$ 4.20 (s, Me), 6.85—7.75 (10 H, m, Ar), 9.29 (s, 5-H), and 12.05 (br s, NH) (disappeared on addition of deuterium oxide); $\delta_C[(CD_3)_2SO]$ 42.9 (q, Me), 100.2 (s, ylidic C), 152.2 (d, C-5), 162.6 (s, amidic CO), and 178.4 (s, enolic CO); *m/z* (70 eV, 120 °C) 321 (M^+, 8%), 293 (8), 212 (19), and 105 (100); and (ii) the phenacylide (**9d**) (4.1 g, 93%) as yellow prisms, m.p. 145—147 °C (decomp). (Found: C, 47.4; H, 3.4; N, 16.1. $C_{17}H_{14}BrN_5O_2 \cdot \frac{1}{2}CH_2Cl_2$ requires C, 47.5; H, 3.4; N, 15.8%); $\nu_{max.}$(KBr) 1 640 and 1 530 cm^{-1}; $\delta_H(CDCl_3)$ 4.29 (s, Me), 5.28 (1 H, s, $\frac{1}{2}CH_2Cl_2$), 6.85—7.75 (9 H, m, Ar), 9.38 (s, 5-H), and 11.96 (br s, NH) (disappeared on addition of deuterium oxide).

1-*Methyltetrazolium* 3-[α-(*Phenylcarbamoyl*)*phenacylide*] (**10b**) *and* 3-[4-*Bromo*-α-(*phenylcarbamoyl*)*phenacylide*] (**10c**).—A similar treatment of the isomeric ylide (**7a**) or (**7b**) gave (i) the product (**10b**) (3.08 g, 93%) as yellow plates, m.p. 109—112 °C (decomp.) (from methylene chloride–light petroleum) (Found: C, 62.1; H, 4.8; N, 21.2. $C_{17}H_{15}N_5O_2 \cdot \frac{1}{2}H_2O$ requires C, 61.8; H, 4.9; N, 21.2%); $\nu_{max.}$(KBr) 3 450br, 1 635, and 1 535 cm^{-1}; $\delta_H(CDCl_3)$ 3.97 (s, Me), 6.9—7.75 (10 H, m, Ar), 9.71 (s, 5-H), and 12.05 (s, NH) (disappeared on addition of deuterium oxide); $\delta_C[(CD_3)_2SO]$ 37.8 (q, Me), 105.3 (s, ylidic C), 148.4 (d, C-5), 162.6 (s, amidic CO), and 178.4 (s, enolic CO); *m/z* (70 eV, 150 °C) 364 (5%), 340 (4), 307 (5), 287 (9), 265 (12), 220 (23), 192 (17), 180 (35), 174 (28), 159 (28), 146 (46), 131 (24), 119 (85), 105 (100), and 84 (16); and (ii) the product (**10c**) (3.78 g, 92%) as yellow needles, m.p. 167—168 °C (decomp.) (from methylene chloride–light petroleum) (Found: C, 49.9; H, 3.5; N, 17.1. $C_{17}H_{14}BrN_5O_2 \cdot \frac{1}{2}H_2O$ requires C, 49.9; H, 3.7; N, 17.1%); $\nu_{max.}$(KBr) 3 450br, 1 635, and 1 530 cm^{-1}; $\delta_H[(CD_3)_2SO]$ 4.33 (s, Me), 6.85—7.7 (9 H, m, Ar), 10.06 (s, 5-H), and 12.10 (s, NH) (these latter signals disappeared on addition of deuterium oxide).

3-*Methyltetrazolium* 1-[4-*Nitro*-α-(*phenylthiocarbamoyl*)-*phenacylide*] (**9e**).—Use of phenyl isothiocyanate (1.5 g, 0.011 mol) in place of phenyl isocyanate under the same conditions as described above gave with the ylide (**6c**) the title compound (1.64 g, 43%) as yellow needles, m.p. 166—168 °C (decomp.) (from methylene chloride–light petroleum) (Found: C, 53.5; H, 3.7; N, 21.4. $C_{17}H_{14}N_6O_3S$ requires C, 53.4; H, 3.7; N, 22.0%); $\nu_{max.}$(KBr) 1 515, 1 505, and 1 340 cm^{-1}; $\delta_H[(CD_3)_2SO]$ 4.63 (s, Me), 7.1—8.25 (9 H, m, Ar), 10.53 (s, 5-H), and 14.1 (br s, NH) (these latter signals disappeared on addition of deuterium oxide).

3-*Methyl*-1-(α-*methylphenacyl*)*tetrazolium Iodide* (**11a**).—The ylide (**6a**) (1.0 g, 5 mmol) and methyl iodide (1.2 g, *ca.* 8 mmol) in pure dimethylformamide (DMF) (30 ml) were stirred at ambient temperature for 24 h. Evaporation under reduced pressure (bath at 70 °C) gave a residue which was crystallised from ethanol–ether to give the product (0.6 g, 35%) as coarse prisms, m.p. 118—120 °C (decomp.) (Found: C, 38.7; H, 3.8; N, 16.3. $[C_{11}H_{13}N_4O]I$ requires C, 38.4; H, 3.8; N, 16.3%); $\nu_{max.}$(KBr) 1 695 cm^{-1}; $\delta_H(CF_3CO_2H)$ 2.22 (d, *J* 8 Hz, C-Me), 4.80 (s, N-Me), 7.28 (q, *J* 8 Hz, C*H*-Me), 7.55—8.25 (5 H, m, Ar), and 9.93 (s, 5-H); $\delta_C[(CD_3)_2SO]$ 17.3 (q, C-*C*H_3), 43.7 (q, N-Me), 63.5 (d, *C*H-Me), 149.1 (d, C-5), and 191.8 (s, C=O); *m/z* (70 eV, 100 °C) 260 (63%), 142 (86), and 105 (100). In the filtrate of (**11a**) some tetrazole (**2a**) was detected by t.l.c.

1-(α-*Benzyl*-4-*bromophenacyl*)-3-*methyltetrazolium Bromide* (**11b**).—The ylide (**6b**) (1.45 g, 5 mmol) and benzyl bromide (1.0 g, *ca.* 6 mmol) in DMF (50 ml) were treated as above for 5 days. The product (0.5 g, 21%) was obtained as fine needles, m.p. 98—100 °C (decomp.) (from ethanol–ether) (Found: C, 43.6; H, 3.8; N, 11.9. $[C_{17}H_{16}BrN_4O]Br \cdot H_2O$ requires C, 43.4; H, 3.9; N, 11.9%); $\nu_{max.}$(KBr) 3 460br and 1 695 cm^{-1}; $\delta_H(CF_3CO_2D)$ 3.7—3.95 (m, CH_2), 4.75 (s, Me), 7.1—7.4 (5 H, m, Ar), 7.47 (t, *J* 7 Hz, $PhCH_2CH$), 7.76 (2 H, d) and 7.97 (2 H, d) (AB_q, *J* 8 Hz, Ar), and 9.81 (s, 5-H); *m/z* (70 eV, 110 °C) 289/287 (100%), 208 (59), and 185/183 (91/95).

The filtrate of (**11b**) was concentrated and the residue dissolved in methanol. On cooling, 2-bromo-1-(4-bromophenyl)-3-phenylpropan-1-one (**12a**) (0.3 g, 16%) separated as prisms, m.p. 86 °C* (Found: C, 48.7; H, 3.2. $C_{15}H_{12}Br_2O$ requires C, 49.0; H, 3.3%); $\nu_{max.}$(KBr) 1 680 cm^{-1}; $\delta_H(CDCl_3)$ 3.34, 3.36, and 5.23 (3 H, ABX, J_{AB}, 18 Hz, $J_{AX,BX}$ 7.2 Hz, $CHCH_2$), 7.27 (5 H, s, Ar), and 7.56 (2 H, d) and 7.82 (2 H, d) (AB_q, *J* 9 Hz, Ar); *m/z* (70 eV, 50 °C) 289/287 (87/83%) and 185/183 (100/93).

Treatment of the Ylide (**6c**) *with Benzyl Bromide*.—A similar reaction of the ylide (**6c**) (1.24 g, 5 mmol) with benzyl bromide (1.0 g, *ca.* 6 mmol) in DMF (50 ml) only gave 2-bromo-1-(4-nitrophenyl)-3-phenylpropan-1-one (**12b**) (0.82 g, 49%) as plates, m.p. 84 °C (from methanol) (Found: C, 54.3; H, 3.8; N, 4.1. $C_{15}H_{12}BrNO_3$ requires C, 53.9; H, 3.6; N, 4.2%); $\nu_{max.}$(KBr) 1 690, 1 530, and 1 350 cm^{-1}; $\delta_H(CDCl_3)$ 3.36, 3.68, and 5.27 (3 H, ABX, J_{AB} 18 Hz, $J_{AX,BX}$ 7.2 Hz, $CHCH_2$), 7.30 (5 H, s, Ar), and 8.08 (2 H, d) and 8.28 (2 H, d) (AB_q, *J* 9 Hz, Ar).

Treatment of the Ylides (**7b,c**) *with Benzyl Bromide*.—Following the procedure as above, the crude product was chromatographed on silica gel: with methylene chloride as first eluant, the products (**12a**) (0.93 g, 51%) and (**12b**) (0.91 g, 54%), respectively, were obtained; then using methanol, some tetrazole (**1a**) was eluted [identified by comparison (m.p., i.r., t.l.c.) with an authentic sample †].

Reaction of the Tetrazolium Salts (**3a**) *and* (**4a**) *with* N,N-*Dimethyl*-4-*nitrosoaniline*.—Potassium carbonate (0.28 g, 2 mmol) in water (2 ml) was added at 0 °C to a mixture of the tetrazolium salt (**3a**) or (**4a**) (0.57 g, 2 mmol) in water (5 ml) and *N,N*-dimethyl-4-nitrosoaniline (0.3 g, 2 mmol) in ethanol (8 ml). After 12 h at 0 °C, 4-dimethylamino-*N*-phenacylideneaniline *N*-oxide (**13**) [0.30 g (56%) and 0.14 g (26%), respectively] was collected by filtration; red needles, m.p. 112—113 °C (decomp.) (from ethanol) (lit.,[21] 109—110 °C).

* This compound has been mentioned in ref. 28 without characteristics.

† See footnote on p. 1160.

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