Isomers of 3-Methylthio-1,5-diarylformazans and their Interconversion in Solution

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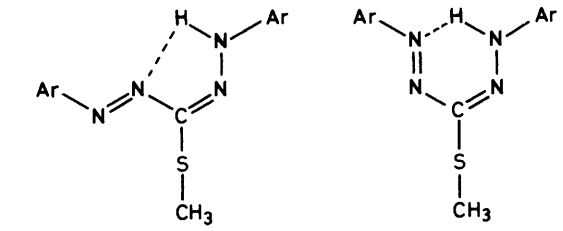
^1H and ^{13}C n.m.r. and i.r. spectroscopic studies, including ^{15}N-labelling, on solutions of ArN:N·C(SR):N·NHAr (Ar = Ph, *p*-, or *o*-tolyl; R = CH_3 or CD_3) taken in conjunction with established *X*-ray crystal structures of pure isomers have made it possible to establish the structural causes responsible for temporal changes in the visible spectra. Relative to the formal C=N double and C–N single bonds the yellow isomer is shown to have a single *anti,s-trans* structure whereas the pink isomer comprises *syn,s-trans* species in rapid tautomeric equilibrium.

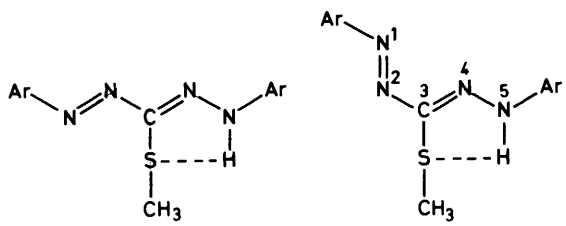
In 1953 Pel'kis [1] reported that methylation of dithizone, PhN:N·C(SH):N·NHPh ⇌ PhN:N·CS·NH·NHPh, gave two isomers, PhN:N·C(SH):N·NMePh and PhN:N·C(SMe):N·NHPh, which were separated by chromatography and which were said to isomerize by the migration of a methyl group from nitrogen to sulphur. One of us,[2] however, obtained only a single pure *S*-methyl derivative by methylating dithizone in alkaline solution with Me_2SO_4, by the action of MeI on silver dithizonate, and (unambiguously) by the action of NaSMe upon 3-chloro-1,5-diphenylformazan, PhN:N·CCl:N·NHPh. Pel'kis later withdrew his earlier observations.[3]

The classical method of determining the structure in potentially tautomeric systems such as dithizone is to compare the parent substance with derivatives in which the structure has been locked unambiguously by methylation into one or other of the possible tautomeric forms. This method fails with dithizone, however, for the visible absorption spectrum of *S*-methyldithizone (3-methylthio-1,5-diphenylformazan) (1), in which the structure should be locked in a thiol form, does not possess a single absorption band that can be correlated with either of the two bands found in the visible spectrum of dithizone, *viz.* at *ca.* 450 or *ca.* 620 nm.[4] On the contrary, although a fresh solution of *S*-methyldithizone (1) in, *e.g.*, chloroform is permanganate pink, with well defined bands at 270 and 550 nm (ε_{550} 1 225 m^2 mol^{-1}), on standing in the dark at room temperature the colour changes to yellow, and the spectrum then shows bands at 280, 420, and 540 nm (ε_{420} 1 775 m^2 mol^{-1}), the band originally at 550 nm becoming less intense as the new band appears at 420 nm. The process is kinetically first-order,[5] and is greatly accelerated by traces of acids and alkalis. The isomerization is reversed on illumination. Analogous effects appear with a number of *S*-alkylated dithizones [3,6] and with many other formazans in general [7-9] where red forms are converted into yellow isomers on standing or on irradiation of solutions in appropriate solvents. *cis–trans* isomerism about the –N=N– bond or *syn–anti* isomerism about the :C=N– bond is thought to be involved.[7-10] Ignoring isomers which scale models show are unlikely to occur owing to serious steric crowding (*i.e.*, all the *cis*-configurations relative to the N=N double bond) leaves four possible isomers (a)—(d) which could result from *syn–anti* isomerism about the C=N double bond and isomerization about the C–N single bond (designated *s-cis* and *s-trans*).

On concentrating a solution of *S*-methyldithizone (1) (whether in the pink or yellow form) only the magenta-red solid [diffuse reflectance spectrum (d.r.s.), $\lambda_{max.}$ 550 nm] is deposited. *X*-Ray crystallography [11] shows that the whole molecule is effectively planar and its *syn,s-trans* configuration is represented by structure (1a).



(a) *syn, s-trans* (b) *syn, s-cis*

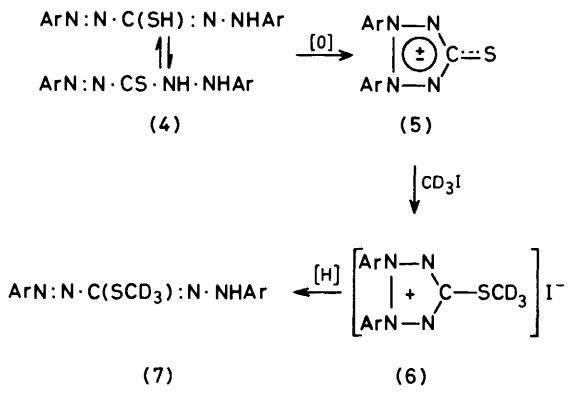


(c) *anti, s-trans* (d) *anti, s-cis*

(1) Ar = Ph
(2) Ar = *p*-tolyl
(3) Ar = *o*-tolyl

The di-*p*-tolyl (2) and di-*o*-tolyl (3) homologues of (1) were prepared in this work by methylating the corresponding ring-substituted dithizones (4; Ar = *p*- or *o*-tolyl) in alkaline solution with dimethyl sulphate. The corresponding SCD_3 analogues (7; Ar = Ph, *p*-, or *o*-tolyl) were synthesized by reacting CD_3I with the 2,3-diaryl-2*H*-tetrazolium-5-thiolates (5) obtained from oxidation of the corresponding substituted dithizones (4) and then reducing the resulting aryltetrazolium iodides (6) with alkaline dextrose. *S*-Methyldithizone (1) labelled at C-3 with ^{13}C and the analogue labelled at

N-1 and N-5 with ^{15}N were also synthesized using this route from the parent labelled dithizone.[12] Details are given in the Experimental section.



RESULTS AND DISCUSSION

The *p*-tolyl homologue (2) crystallizes from ethanol as red needles which dissolve in chloroform to give a pink solution with a single band in the visible spectrum at 550 nm (ε 1 406 m^2 mol^{-1}). On leaving this solution to stand in the dark at room temperature the initially pink solution changed to yellow-brown due to the appearance of a new intense band at 425 nm with a concomitant decrease in the absorbance at longer wavelength, in exact analogy with the behaviour of the unsubstituted *S*-methyldithizone (1). Both compounds exhibit the same sequence of colour changes on isomerization and the rates of change are very easily affected by catalysts. As in the case of (1), the *p*-tolyl homologue (2) crystallizes as a dark red solid by the concentration of solutions of either the pink or the yellow isomer. This red solid redissolves to give a pink solution which again isomerizes to give an equilibrium mixture (isosbestic point 482 nm) of the pink and yellow forms. Addition of a trace of acetic acid converts the pink isomer into the yellow isomer instantly. These spectral changes are depicted in Figure 1. From their similar solution behaviour and identical d.r.s. ($\lambda_{max.}$ 550 nm) it may be presumed that the *p*-tolyl homologue (2) has the same configuration in the solid state as the parent *S*-methyldithizone (1), *viz. syn,s-trans* (2a). The i.r. data (Table) support this assumption.

The *o*-tolyl homologue (3), on the other hand, crystallized from ethanol as yellow plates (d.r.s., $\lambda_{max.}$ 423 nm) and our *X*-ray structural analysis[13] establishes an essentially planar *anti,s-trans* configuration [as (3c)]. A fresh solution in chloroform was bright yellow and the absorption spectrum showed a well defined peak at 420 nm (ε 2 936 m^2 mol^{-1}). During several days in the dark the initially yellow solution in chloroform slowly formed a brown equilibrium mixture with a pink isomer having a peak at 560 nm (isosbestic point 485 nm). Exposure of a fresh yellow solution to sunlight for 30 min gave the pure pink isomer, while addition of a trace of acetic acid caused immediate reversion to a red-brown equilibrium mixture. The preparation of a solid sample of the pink isomer of the *o*-tolyl compound (3) was attempted by concentrating a solution of (3) in the pink form. The solid that separated was yellow-orange and identical with the initial solid product; it underwent the same sequence of colour changes (yellow → brown → pink) when it was redissolved in chloroform. Figure 2 illustrates these changes in the visible spectrum. Recently the crystal structure and some solution properties of *S*-isopropyldithizone, PhN:N·C(SCHMe$_2$):N·NHPh, were reported.[14] The equilibrium for this derivative favours the yellow isomer and it crystallizes in the same *anti,s-trans* configuration [as (c)].

Thus, under identical conditions the initially pink (1) or (2) reaches equilibrium with a yellow isomer, while the

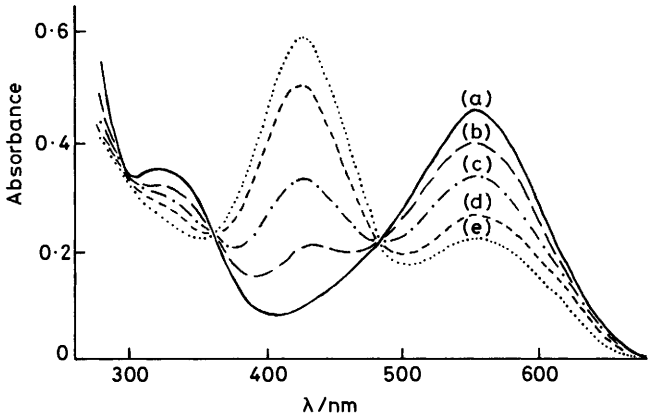


FIGURE 1 Changes in visible absorption spectrum of 3-methylthio-1,5-di-(*p*-tolyl)formazan (2) in chloroform solution (3.28×10^{-5}M). (*a*) Pure pink isomer immediately after preparation, (*b*) after 1 h, (*c*) after 6 h, (*d*) after 24 h, and (*e*) after addition of a trace of acetic acid

^1H Chemical shift values (p.p.m.) of imino and methyl resonances at ambient temperature [δ($CDCl_3$) and, in parentheses, δ(C_6D_6); Me_4Si, 100 MHz]. ν(N–H)/cm^{-1} for KBr pressed disks and CCl_4 solutions

		Solid	Fresh solution		Equilibrium mixture after 70 h	
(1)	–N*H*		10.26	(10.02)	10.26	(10.02)
					9.46	(9.24)
	–SC*H*$_3$		2.54 [a]	(2.29) [a]	2.54 [a]	(2.29) [a]
					2.40 [a]	(1.92) [a]
	ν(N–H)	3 338	3 342		3 342, 3 253	
(2)	–N*H*		10.22	(10.06)	10.19	(10.06)
					9.43	(9.26)
	–SC*H*$_3$		2.52 [a]	(2.32) [a]	2.52 [a]	(2.32) [a]
					2.39 [a,b]	(1.95) [a]
	ArC*H*$_3$		2.39	(2.09)	2.39	(2.09)
					2.42	(2.09) [b]
					2.34	(2.03)
	ν(N–H)	3 341	3 344		3 344, 3 254	
(3)	–N*H*		9.53	(9.41)	9.52	(9.41)
					10.28	(10.21)
	–SC*H*$_3$		2.43 [a]	(1.95) [a]	2.43 [a]	(1.95) [a]
					2.51 [a]	(2.35) [a]
	ArC*H*$_3$		2.40	(1.98)	2.40	(1.98)
			2.72	(2.69)	2.72	(2.69)
					2.53	(2.29)
	ν(N–H)	3 270	3 269		3 269, 3 361	

[a] Resonance disappears in spectrum of SCD_3 analogue. [b] Apparent from peak integration.

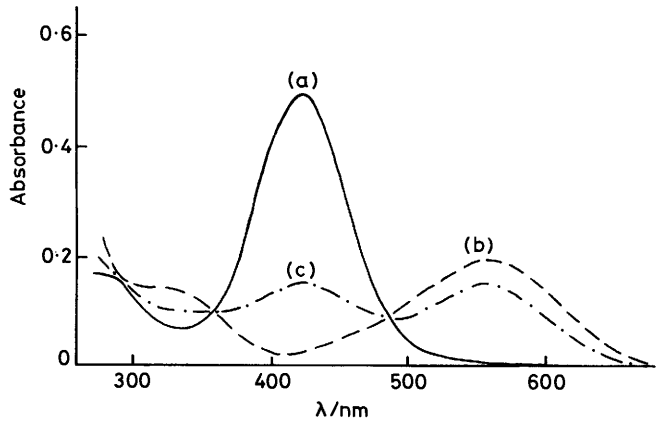
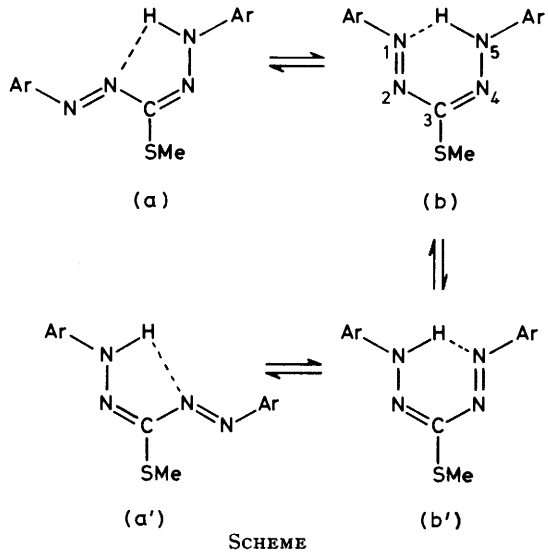


FIGURE 2 Changes in visible absorption spectrum of 3-methylthio-1,5-di-(*o*-tolyl)formazan (3) in chloroform solution (3.35×10^{-5}M). (*a*) Pure yellow isomer immediately after preparation, (*b*) after exposure to direct sunlight for 3 h (pink isomer), and (*c*) after 2 days in the dark (equilibrium mixture of yellow and pink isomers)

initially yellow (3) reaches equilibrium with a pink isomer: presumably the pink isomers of (1)—(3) are isostructural, as are all the yellow isomers of the compounds. This was demonstrated by ^{1}H n.m.r. spectroscopy, where in addition to measurements on (1)—(3) the corresponding SCD_3 analogues (7; Ar = Ph, *p*-, or *o*-tolyl) were examined in order to facilitate unambiguous assignment of the methyl resonances (Table). The results obtained from both chloroform and benzene solutions afforded the same conclusions, the benzene solution spectra showing better separation of the methyl resonances.

In a freshly prepared (pink) solution of (2) the *p*-tolyl methyl groups give rise to a single resonance integrating for 6 H. Their equivalence is consistent with the closed-ring *syn,s-cis* configuration (2b) with its internal hydrogen bridge. This structure is known in many formazans to exist in very rapid equilibrium with its tautomer, as (b) ⇌ (b') (Scheme).[8,9,15,16] This is supported by preparing (1) with the terminal nitrogens N-1 and N-5 enriched with 96 atom % ^{15}N, whereupon the imino proton N*H* line at δ($CDCl_3$) 10.26 becomes a triplet (1 : 2 : 1) with an apparent coupling constant of 47.6 Hz (unchanged at −40 °C). This falls outside the normal range of $^1J(^{15}N-H)$ values (*ca.* 90 Hz for structurally related compounds)[17,18] and indicates an averaging of the ^{15}N–H coupling over two chemically equivalent nitrogen sites consistent with a very rapid tautomeric equilibrium. However, formazans known to have this structure in the solid state[16,19] show the imino proton at δ($CDCl_3$) 14—16 and ν(N–H) *ca.* 3 030 cm^{-1} (if observed)[8,20] in fresh solutions. Spectroscopic data for (1)—(3) do not provide evidence for such strong hydrogen bonding either in the solid state or in solution (Table) and configuration (2a) [already shown to exist in crystals of (1)][11] should be considered, the equivalence of the two Me groups being achieved by interconversion, fast on the n.m.r. time scale, between two equivalent forms of (2a) by rotation about the C–N single bond (*trans* → *cis*) to give the *syn,s-cis* structure (2b) as an intermediate.

This equilibrium (a) ⇌ (b) ⇌ (b') ⇌ (a') (Scheme) still accounts for the N*H* triplet and apparently halved ^{15}N–H coupling value in the ^{1}H n.m.r. spectrum of the ^{15}N-labelled (1). An interesting feature of this spectrum is a very low intensity doublet (*J* 47.6 Hz) centred at the same chemical shift as the triplet. This arises because the compound was labelled with 96 atom % ^{15}N and the presence of 4 atom % ^{14}N gives rise to a low intensity doublet corresponding to the situation where only one terminal nitrogen (N-1 or N-5) is labelled with ^{15}N.



SCHEME

As the solution of (2a) gradually changes colour from pink to brown, two new *p*-tolyl Me resonances slowly develop until after 3 days in the dark three *p*-tolyl Me lines are found (Table), still integrating *in toto* for 6 H. The new resonances are attributed to the magnetically non-equivalent *p*-tolyl Me groups of isomer (2c) produced by a *syn* → *anti* isomerization about the formal C=N double bond. This would result in two rotamers, (2c) ⇌ (2d), but structure (2d) will be less favoured owing to the close proximity of the lone pairs of electrons on N-1 and N-4. The ^{1}H n.m.r. spectrum of a $CDCl_3$ solution of the ^{15}N-labelled *S*-methyldithizone (1) after 3 days in the dark shows the imino proton resonance shifted upfield to δ 9.46 where it now appears as a doublet with $^1J(^{15}N-H)$ 92.2 Hz. This doublet, which shows the imino proton coupling to only one ^{15}N atom (without any fast intramolecular proton exchange) is superimposed upon the triplet of the fresh solution. The coupling constant value is normal and provides conclusive evidence for the single *anti,s-trans* configuration (c) as the yellow isomer, with the possibility of a contribution from the less favoured *s-cis* rotamer. Once again the spectrum at −40 °C was identical with that at ambient temperature.

The magnetically non-equivalent *o*-tolyl Me groups in a fresh (yellow) solution of (3) show two resonances of equal intensity (Table) derived from the structure (3c), as expected from the *X*-ray analysis of the yellow

crystals of (3).[13] On standing in the dark isomerization about the C=N bond occurs yielding the pink *syn,s-trans* (3a) tautomeric system (a) ⇌ (b) ⇌ (b′) ⇌ (a′) (Scheme) which gives rise to an additional *o*-tolyl Me resonance in the spectrum of the equilibrium mixture, the *o*-tolyl Me peaks still integrating for 6 H *in toto*. During the isomerization (3c) → (3a) a new SMe resonance appears at virtually the same chemical shift value as that given by a fresh solution of (2a); the isomerization (2a) → (2c) gives a new SMe line corresponding to a fresh solution of (3c) (Table). Since the equilibrium mixture in either case contains approximately equal proportions of the two isomers, their ^{1}H n.m.r. spectra are very similar, contrasting mainly in the difference in chemical shifts of the two *o*-tolyl Me resonances [(3c); *e.g.*, C_6D_6 2.69—1.98 = 0.71 p.p.m.] compared with the smaller difference in those of *p*-tolyl in the same configuration [(2c); 2.09 — 2.03 = 0.06 p.p.m.], presumably owing to the magnetic anisotropy effect of the azo-group on one of the *o*-tolyl Me groups.

The broad-band ^{1}H-decoupled ^{13}C n.m.r. spectrum of a fresh (pink) $CDCl_3$ solution of *S*-methyldithizone (1) labelled at C-3 with 91 atom % ^{13}C shows a peak at 146.3 p.p.m. downfield from Me_4Si which diminishes in intensity as a new peak grows at 147.4 p.p.m. due to the formation of the yellow isomer. The ^{1}H-coupled spectrum, obtained by gated proton irradiation [21] of the equilibrium solution, shows each C-3 peak split into a pseudo-triplet. Coupling to both the SMe protons and the NH proton is suggested by the asymmetry of the 'triplets' (each peak showing splittings of 2.9 and 4.4 Hz) which are probably unresolved superimpositions of a quartet (from SMe) and a doublet (from NH). Coupling of ^{13}C-3 to both groups was unambiguously confirmed when the ^{1}H n.m.r. spectrum of the ^{13}C-labelled (1) was measured in $CDCl_3$. This shows the two SMe peaks arising from the two isomers as doublets with the same three-bond coupling constant ^3J(H–C–S–^{13}C) of 3.7 Hz. Both N*H* peaks also appear as doublets but with different coupling values. The ^3J(H–N–N–^{13}C) value for the pink isomer (1a) is 2.8 Hz while that for the yellow isomer (1c) is 4.5 Hz. These values differ because the coupling is transmitted through bonds which are directly involved in the isomerization [with a rapid tautomeric equilibrium present in (1a)], whereas the ^3J(H–C–S–^{13}C) values are identical since the SCH_3 part of the molecule is not greatly affected by the isomerization.

The approach to an equilibrium mixture starting from either the *syn,s-trans* (2a) or the *anti,s-trans* (3c) isomer can be followed clearly by observation of the ν(N–H) stretching frequency: the intramolecular N–H • • • N and N–H • • • S hydrogen bonds differ significantly in strength and show a separation in ν(N–H) of *ca.* 90 cm^{-1} (Table). The change in the position of the imino proton resonance (Table) also reflects this difference in internal hydrogen bonding.

The present assignments correct those proposed in 1966 by Burns and Duncan [10] which were, however, based upon rather limited measurements.

EXPERIMENTAL

Scrupulously clean glassware, n.m.r. tubes, and i.r. and optical cells were used throughout to eliminate traces of impurity which would catalyse the isomerization processes being studied. All solvents used for spectroscopic work were dry and of spectroscopic grade. Visible absorption spectra were recorded on a Varian Superscan 3 instrument using 1.00 cm matched quartz cells. Diffuse reflectance spectra were taken as Nujol mulls on filter paper using a Beckman DK-2A ratio recording spectrophotometer in the reflectance mode. I.r. spectra were recorded as CCl_4 solutions in new matched NaCl solution cells with a 0.5 mm path length or as KBr pressed disks using a Perkin-Elmer 180 spectrophotometer. ^{1}H N.m.r. spectra were obtained at 100 MHz on a Varian XL-100 continuous wave spectrometer at ambient temperature (*ca.* 32 °C) and at −40 °C. Chemical shifts are quoted relative to Me_4Si and are accurate to ±0.05 p.p.m., while coupling constants are estimated to ±0.5 Hz. ^{13}C N.m.r. spectra were measured on a Bruker WH-90DS Fourier transform spectrometer operating at 22.63 MHz and ambient temperature *ca.* 40 °C. Chemical shifts were recorded relative to the $CDCl_3$ signal and related to the standard Me_4Si using the conversion $\delta(Me_4Si) = \delta(CDCl_3) + 76.9$ p.p.m.; [22] they are accurate to an estimated 0.1 p.p.m. The use of shiftless relaxation agents was prohibited by their catalytic effect on the isomerization being monitored.

Preparations.—*3-Methylthio-1,5-diphenylformazan* (1). A solution of Merck analytical reagent grade dithizone (5.0 g) in dilute aqueous alkali (15 cm^3 of 2M-NaOH solution and 50 cm^3 of water) was shaken well with dimethyl sulphate (2.6 g, 1.9 cm^3) in a glass-stoppered flask. The initial orange colour of the solution rapidly disappeared and a black solid separated almost immediately. A further portion of NaOH solution was added (15 cm^3 of 2M), and the mixture was heated gently on a water-bath for 30 min to destroy any excess of Me_2SO_4. On cooling, the mixture was extracted with successive quantities of chloroform and the combined organic extract was washed several times with dilute aqueous ammonia solution to remove unmethylated dithizone, and then with water and finally the organic extract was dried (Na_2SO_4). Removal of the solvent left impure (1) which was purified by chromatography on neutral alumina. Carbon tetrachloride was found to be a suitable solvent for introduction of the material on the top of the column, and elution was performed with benzene. The main band which developed was dark brown in colour; it was preceded by a faint pink band and followed by one of a lighter brown. While the main band was moving off the column the eluant was collected; subsequent removal of the solvent gave the desired solid product (1). Recrystallization from ethanol gave sharp black needles with a bronze reflex (2.85 g, 54.0% yield), m.p. 118—120 °C (decomp.) (lit.,[2] 119—120 °C) (Found: C, 62.3; H, 5.35; N, 20.8. Calc. for $C_{14}H_{14}N_4S$: C, 62.2; H, 5.2; N, 20.7%).

3-Methylthio-1,5-di-(p-tolyl)formazan (2) was prepared in the same way as (1) above by methylation of the *p*-tolyl homologue (1.0 g) of dithizone.[12] The crude product obtained was purified by column chromatography and recrystallized twice from ethanol to yield sharp deep red *needles* (0.47 g, 45.0% yield), m.p. 128—130 °C (decomp.) (Found: C, 64.5; H, 6.2; N, 18.7. $C_{16}H_{18}N_4S$ requires C, 64.4; H, 6.1; N, 18.8%).

3-Methylthio-1,5-di-(o-tolyl)formazan (3) was prepared

analogously to (2) above and recrystallized twice from ethanol to give yellow-orange *plates* (0.52 g, 49.8% yield), m.p. 130—133 °C (decomp.) (Found: C, 64.3; H, 6.0; N, 18.7. $C_{16}H_{18}N_4S$ requires C, 64.4; H, 6.1; N, 18.8%).

2,3-*Diphenyl*-2H-*tetrazolium*-5-*thiolate* (5; Ar = Ph). A solution of dithizone (1.0 g) in chloroform (300 cm^3) was stirred mechanically for 2 h with a solution of potassium hexacyanoferrate(III) (3.2 g) and potassium carbonate (3.0 g) in distilled water (100 cm^3). The organic layer was removed, dried (Na_2SO_4), and the solvent allowed to evaporate at room temperature. The residue was taken up in boiling ethanol, treated with animal charcoal, filtered, and allowed to cool overnight to yield orange-red crystals (0.65 g, 65% yield), m.p. 173 °C (decomp.) [lit.,[4] 173 °C (decomp.)] (Found: C, 61.2; H, 4.0; N, 21.85. Calc. for $C_{13}H_{10}N_4S$: C, 61.4; H, 4.0; N, 22.0%).

The di-(*p*-tolyl) and di-(*o*-tolyl) homologues (5, Ar = *p*- or *o*-tolyl) were similarly prepared in 34 and 29% yield, respectively, from the corresponding substituted dithizones. The ^{13}C- and ^{15}N-labelled analogues of (5; Ar = Ph) were also prepared in this way, again from the corresponding labelled dithizones, in 67 and 63% yields, respectively.[12] These intermediates were all recrystallized but not analysed before continuing with the following stage.

2,3-*Diphenyl*-5-*trideuteriomethylthiotetrazolium iodide* (6; Ar = Ph). A solution of the mesoionic (5; Ar = Ph) (0.48 g) and trideuteriomethyl iodide (0.23 g) in chloroform (30 cm^3) was gently boiled under reflux for 1 h during which time the colour of the solution changed from orange-red to dark brown. The solution was treated with animal charcoal and filtered; on cooling a precipitate formed which was yellow when isolated and washed with chloroform. Recrystallization from a boiling ethanol–diethyl ether mixture (3 : 1) gave pale yellow crystals (0.67 g, 89.5% yield).

The di-(*p*-tolyl) and di-(*o*-tolyl) homologues (6; Ar = *p*- or *o*-tolyl) were similarly prepared from the corresponding substituted dehydrodithizones in similar yield, except that the *o*-tolyl homologue could not be crystallized; however, the oil was successfully used in the subsequent stage of the synthesis (below). The ^{13}C- and ^{15}N-labelled analogues of the diphenyltetrazolium iodide were similarly prepared from the corresponding labelled dehydrodithizone using CH_3I in place of CD_3I.

1,5-*Diphenyl*-3-*trideuteriomethylthioformazan* (7; Ar = Ph). A solution of 5-deuteriomethylthio-2,3-diphenyltetrazolium iodide (6; Ar = Ph) (0.50 g), sodium hydroxide (0.25 g), and dextrose (2.0 g) in distilled water (100 cm^3) was warmed gently for a few minutes with vigorous stirring until a dark brown flocculent precipitate started to separate. On cooling in ice and acidification with dilute sulphuric acid the entire yield separated and was collected, dried, and recrystallized from ethanol to give the SCD_3 analogue of (1). T.l.c. showed that the product needed no further purification (0.21 g, 62.1% yield).

The di-(*p*-tolyl) and di-(*o*-tolyl) homologues (7; Ar = *p*- or *o*-tolyl) were similarly prepared from the corresponding 5-trideuteriomethylthio-2,3-diaryltetrazolium iodides in similar yields. The di-(*o*-tolyl)tetrazolium iodide, which was obtained as an oil (above), was dissolved in ethanol and used in this synthesis successfully to give the required product. The ^{13}C- and ^{15}N-analogues of (1) were also prepared in this way from the corresponding labelled (but not deuteriated) diphenyltetrazolium iodides synthesized above.

We are indebted to Dr. K. R. Koch for helpful discussions and to Dr. A. H. Nabilsi for preliminary measurements. The University of Cape Town and the C.S.I.R. (Pretoria) are thanked for their financial assistance.

[2/304 *Received*, 18*th February*, 1982]

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