612. *Anhydro-compounds from Nitrogen-containing Derivatives of Thioglycollic (Mercaptoacetic) Acid. Part III.* Arylazo-compounds.†*

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Arylazothioalkanoic acids (I) with acid anhydrides in the presence of a tertiary base give monomeric anhydro-compounds which may be regarded as 3-aryl-4-oxo-1-thia(S^{IV})-2 : 3-diazolines‡ (II). Unlike the open-chain acids (I), the anhydro-compounds are very stable, weakly basic substances which undergo characteristic reactions of aromatic systems with electrophilic reagents. Detailed investigations of the anhydro-compound from *p*-tolylazothioglycollic acid (I; Ar = *p*-C_6H_4Me, R = H) support the structure (V) assigned to it.

With boiling sodium ethoxide solution the compound (V) decomposes, yielding 4-oxo-3 : 5-di-*p*-tolyl-1-thia(S^{IV})-2 : 3-diazoline (VII) and 5-mercapto-4-oxo-3-*p*-tolyl-1-thia(S^{IV})-2 : 3-diazoline (IX) which are also prepared by alternative syntheses.

(Arylazothio)acetic acids (I; R = H), which give (arylthio)acetic acids when warmed, were first prepared by Friedländer and Chwala [1] by the reaction of arenediazonium salts with thioglycollic (mercaptoacetic) acid in acid solution. Although these authors reported the isolation of a number of acids, it is difficult to obtain stable acids from certain diazonium compounds. (Phenylazothio)acetic acid (I; Ar = Ph, R = H), for example, although isolable in most experiments, could not be purified and in some cases decomposed spontaneously in the reaction mixture. No (arylazothio)acetic acids could be isolated from reactions involving arenediazonium salts containing *ortho*-substituents, whilst (*p*-nitrophenylazothio)acetic acid, reported [1] as being very stable, occasionally decomposed when kept at room temperature. Variations in stability were also experienced with *p*-chloro- and *p*-bromo-acids even when prepared by apparently the same procedure from the same reagents. No difficulties were experienced in obtaining stable *p*-tolyl-, *p*-methoxyphenyl-, *p*-acetamidophenyl-, and *p*-carboxyphenyl-acids. Thiolactic and thiomandelic acid also gave stable azothio-acids (I; Ar = *p*-C_6H_4Me, R = Me and Ph) respectively.

Like the acids described in Parts I [2] and II,[3] the azothio-acids (I), with the exception of (*p*-nitrophenylazothio)acetic acid which gives an arylated anhydro-derivative, react readily with acetic anhydride and pyridine to give anhydro-compounds by the loss of one mol. of water. Unlike those discussed previously, however, the present compounds are

* Part II, *J.*, 1956, 361.

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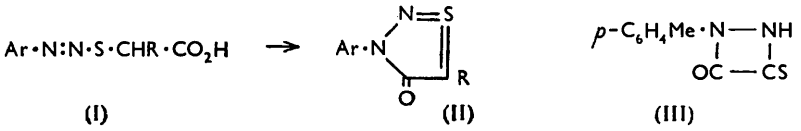
‡ " (S^{IV}) " is used, after consultation with the Editor, to denote the formal quadrivalency of the sulphur atom, which is discussed below.

[1] Friedländer and Chwala, *Monatsh.*, 1907, **28**, 251.

[2] Duffin and Kendall, *J.*, 1951, 734.

[3] *Idem*, *J.*, 1956, 361.

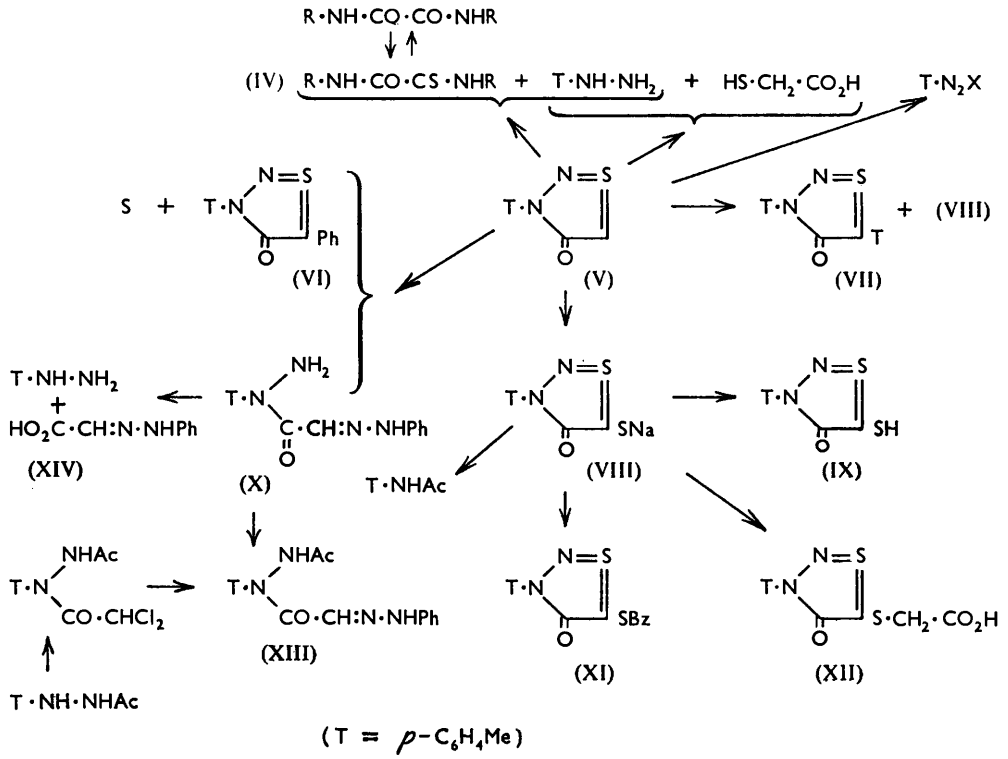
not formed in the absence of a tertiary base. The new compounds are yellow, heat-stable solids which are readily soluble in polar and non-polar solvents and possess two absorption maxima in solution. Like the earlier anhydro-compounds, they show a bathochromic shift of the longer wave absorption maximum of longer wavelength as the polarity of the solvent is decreased. The anhydro-compound from (*p*-tolylazothio)acetic acid, for example,



(I) (II) (III)

gives a colourless aqueous solution and a yellow solution in benzene. In their stability to mineral acids the present anhydro-compounds differ markedly from those described previously, the former being recovered unchanged from boiling 50% sulphuric acid. The compounds derived from the acids (I; R = H), however, although unaffected by boiling alcoholic ammonia and aqueous alkali carbonate, react readily with strong alkali. The present compounds also behave as weak monoacid bases and give double salts with mercuric chloride, thus behaving like 1-thia-2 : 3-diazoles.[4]

Because of its ready accessibility, the anhydro-compound from (*p*-tolylazothio)acetic acid was selected for detailed investigation. It is a weak base which forms colourless



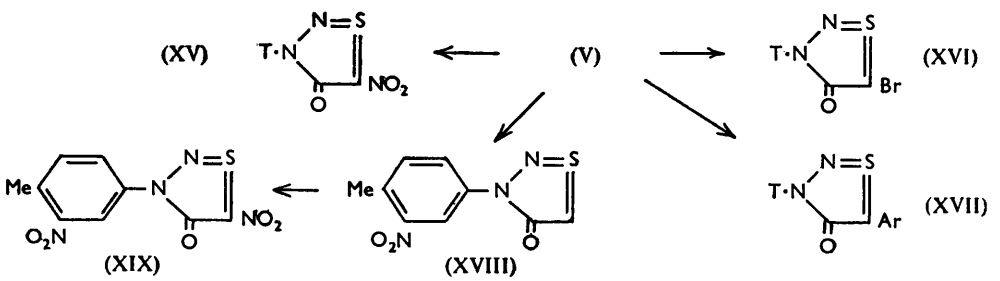
salts (XX) which are decomposed by water and by heat. Although stable to mineral acid, the anhydro-compound is readily reduced with zinc and sulphuric acid to give *p*-tolylhydrazine and thioglycollic acid, indicating that the groupings *p*-$C_6H_4Me{\cdot}N_2{\cdot}$ and ·S·CH·CO· are present in the compound. On oxidation in acetic acid solution the anhydro-compound is gradually decomposed to a toluene-*p*-diazonium salt.

[4] Wolff, *Annalen*, 1902, **325**, 129.

The anhydro-compound, with amines, gives *p*-tolylhydrazine and amides (IV) of monothio-oxalic acid, the structure of the latter being confirmed by synthesis and degradation. The anhydro-compound also reacts rapidly with hydrazine to give *p*-tolylhydrazine, but with phenylhydrazine slowly gives free sulphur, a small quantity of the compound (VI), and a compound $C_{15}H_{16}ON_4$. The last reacts as a hydrazine which has a free amino-group, and is hydrolysed by alkali to glyoxylic acid phenylhydrazone (XIV) and *p*-tolylhydrazine, indicating that it is the phenylhydrazone (X) of glyoxylic acid *N*-*p*-tolylhydrazide. The structure is confirmed by unambiguous synthesis of the acetyl derivative (XIII), which is identical with that obtained from the hydrazide with acetic anhydride. This evidence proves the presence of the grouping *p*-$C_6H_4Me{\cdot}N{<}^{N}_{CO{\cdot}CH:}$ in the anhydro-compound, and suggests a cyclic structure for the latter.

Possible structures are (V) and (III). The latter can be excluded since α-(*p*-tolylazothio)propionic acid (I; Ar = *p*-C_6H_4Me, R = Me) also gives an anhydro-compound with a structure similar to that of the compound from the corresponding acetic acid, as shown by the similarities of ultraviolet absorptions and the products of reduction and oxidation. That no migration of a methyl group has occurred in the compound (II; Ar = *p*-C_6H_4Me, R = Me) is proved by its reaction with hydrazine to give pyruvic acid hydrazone hydrazide. It is concluded therefore that all the anhydro-(arylazothio)acetic acids have the elementary structure of 1-thia-2 : 3-diazole and may be regarded as 3-aryl-4-oxo-1-thia(S^{IV})-2 : 3-diazolines * (II) (cf. Katritzky).[5]

Compounds of this type should possess aromatic properties [6] and, in its chemical behaviour to electrophilic reagents, 4-oxo-3-*p*-tolyl-1-thia(S^{IV})-2 : 3-diazoline (V) behaves like a truly aromatic compound. For example, on bromination it gives the 5-bromo-derivative (XVI) in which the bromine cannot easily be replaced, and on nitration in acetic acid gives the 5-nitro-compound (XV). In sulphuric acid solution it can be mononitrated to give the 3′-nitro-compound (XVIII) or dinitrated to give the 3′ : 5-dinitro-compound (XIX). The preferential nitration in sulphuric acid of the benzene ring appears to be due to salt formation (XX) which reduces the ease of electrophilic attack at the 5-position in the thiadiazole ring. The related 5-methyl compound (II; Ar = *p*-C_6H_4Me, R = Me) in sulphuric acid can be only mononitrated, to the 3′-mononitro-compound (II; Ar = 4-methyl-3-nitrophenyl, R = Me).



Although it has been reported by Wolff [4] that 1-thia-2 : 3-diazoles are unstable to alkali, no investigation of the products of decomposition has been published previously. With hot alcoholic sodium hydroxide or ethoxide the anhydro-compound (V) gives mainly an acidic mixture, together with a non-acidic compound $C_{16}H_{14}ON_2S$. The latter is also obtained by reaction of toluene-*p*-diazonium chloride with the anhydro-compound (V) in neutral or alkaline solution, whilst related compounds (XVII) are obtained from other diazonium salts. That these compounds are 3 : 5-diaryl-4-oxo-1-thia(S^{IV})-2 : 3-diazolines is proved by synthesis and degradation of the 5-phenyl-3-*p*-tolyl compound (VI). This

* See footnote ‡, p. 3189.

[5] Katritzky, *Chem. and Ind.*, 1955, 521.
[6] Bieber, *ibid.*, p. 1055.

is obtained both by the action of acetic anhydride and pyridine on α-phenyl-α-(*p*-tolylazothio)acetic acid and by the reaction of benzenediazonium chloride with 4-oxo-3-*p*-tolyl-1-thia(S^{IV})-2 : 3-diazoline, and is reduced by zinc and hydrochloric acid to phenylacetic acid, *p*-tolylhydrazine, and hydrogen sulphide.

The acidic mixture from the alkaline degradation of the compound (V) has a composition which varies in different experiments, and it cannot be resolved by crystallization. The crude mixture, which is bright yellow, contains a little free sulphur and has an odour of toluene-*p*-thiol. With hydrazine it gives *p*-tolylhydrazine in good yield, whilst with benzylamine it gives monothio-oxaldi(benzylamide) (IV; R = CH_2Ph), indicating that the acidic mixture contains as its main constituent a compound whose structure is similar to that of the original anhydro-compound. Reaction of the acidic mixture with Raney nickel in sodium hydroxide solution gives aceto-*p*-toluidide, *p*-toluidine, ammonia, and sodium acetate. Benzoylation of the acidic mixture in alkaline solution gives a yellow neutral benzoyl derivative $C_{16}H_{12}O_2N_2S_2$, whilst reaction with sodium chloroacetate gives a yellow acid $C_{11}H_{10}O_3N_2S_2$. These compounds are clearly derived from the same compound $C_9H_8ON_2S_2$ which corresponds to the anhydro-compound with an additional atom of sulphur. That their structure is similar to that of the anhydro-compound is shown by the similarity of their absorption spectra (see Table) to that of 5-bromo-4-oxo-3-*p*-tolyl-1-thia(S^{IV})-2 : 3-diazoline (XVI), and by their degradation by hydrazine to *p*-tolylhydrazine.

Light absorptions.

Compound	$\lambda_{max.}$ (mμ)	$\lambda_{min.}$ (mμ)
(V) [a]	284 (ε 5350), 394 (ε 7800)	326 (ε 750)
(V) [b]	364 (ε 6200)	315 (ε 1350)
(V)	279 (ε 4880), 370 (ε 7130)	253 (ε 2580), 317 (ε 890)
(II; Ar = *p*-tolyl, R = Me)	278 (ε 4330), 372 (ε 7650)	252 (ε 2500), 318 (ε 1950)
(II; Ar = Ph, R = H)	266 (ε 5880), 368 (ε 7650)	245 (ε 4250), 310 (ε 720)
(XVI)	292 (ε 4760), 391 (ε 8210)	261 (ε 2640), 330 (ε 1600)
(XI)	250 (ε 13,700), 291 (ε 5350),[c] 404 (ε 11,450)	335 (ε 2540)
(XII)	285 (ε 3550), 398 (ε 8920)	265 (ε 3380), 335 (ε 2300)
(VI)	255 (ε 12,800), 290 (ε 4150),[c] 417 (ε 13,700)	345 (ε 1200)
(XV)	234 (ε 14,700), 282 (ε 4020), 437 (ε 20,400)	269 (ε 3700), 353 (ε 1800)
(VIII)	290 (ε 3750), 435 (ε 6050)	272 (ε 3550), 338 (ε 1200)
(IX)	235 (ε 9650) [c] 360 (ε 3750)	320 (ε 2580)

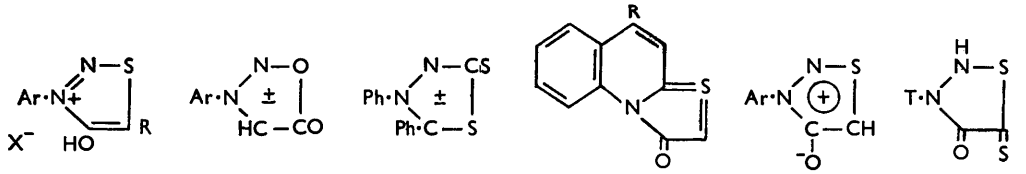
[a] In benzene. [b] In H_2O–pyridine (1 : 1), the remainder in ethanol. [c] Inflexion.

These facts indicate that neither the benzoyl nor the carboxymethyl group is a nitrogen substituent and that the only satisfactory structure for the acidic compound $C_9H_8ON_2S_2$ is 5-mercapto-4-oxo-3-*p*-tolyl-1-thia(S^{IV})-2 : 3-diazoline (IX). The benzoyl derivative is (XI) and the carboxymethyl derivative is (XII). Although these structures could not be confirmed by unambiguous synthesis the mercapto-compound could also be obtained in high yield as its sodium salt (VIII) by heating the original anhydro-compound with sodium disulphide in aqueous ethanol.

Like the anhydro-compounds described in Parts I and II, the sydnones [7] (XXI), and the thiadiazole derivative [8,9] (XXII), the present compounds contain a 5-membered ring system which cannot adequately be represented by a formula with normal valencies. Each ring atom possesses p_z-electrons which, together with the p_z-electron of the exocyclic oxygen atom, will fill 4π-orbitals spreading over the ring and the oxygen atom (cf. Longuet-Higgins).[10] The contribution of the sulphur atom must include that from *d*-orbitals as in the case of thiophen,[11,12] and undoubtedly this contribution would explain the high stability of the present system, when compared with that of the sydnones (cf. the difference between the stability of 1-thia-2 : 3-diazoles and 1-oxa-2 : 3-diazoles [4]). Following the

[7] Baker, Ollis, and Poole, *J.*, 1949, 307.
[8] Busch, *J. prakt. Chem.*, 1903, **67**, 201.
[9] Schönberg, *J.*, 1938, 824.
[10] Longuet-Higgins, *J. Chim. phys.*, 1949, **46**, 246.
[11] Schomaker and Pauling, *J. Amer. Chem. Soc.*, 1939, **61**, 1769.
[12] Longuet-Higgins, *Trans. Faraday Soc.*, 1949, **45**, 173.

present authors' original suggestion (Part I) [2] of a decet of electrons associated with the sulphur atom in the anhydro(quinolylthio)acetic acids, Knott [13] suggested that Schomaker and Pauling's [11] representation of the *dsp*^{2} hybridization [12,14] of the sulphur atom might be applied to these compounds which would be represented as (XXIII). If this type of



(XX) (XXI) (XXII) (XXIII) (XXIV) (XXV)

formulation is extended to the present compounds they would be represented by (II). This formula, we believe, is in agreement with the aromatic properties of the system and its stability. It is of interest that the mercapto-compound (IX), which can be represented by the alternative thione formula (XXV) with " normal " valencies, is unstable while its derivatives, which are stable, possess the fundamental structure of the anhydro-compounds, as shown by their absorption spectra.

Representation of the present anhydro-compounds by (II) *appears* to require *seven* π-electrons in the ring, as in the formula usually written for antipyrine,[6] and not six as for an aromatic sextet, and, although there may be objections to (II) for this reason, we believe that it is a better representation than those suggested for the so-called " cyclic mesoionic " compounds.[5,6,7,15]

According to the most recent suggestion by Baker and Ollis [16] for sydnones the present compounds would be formulated as (XXIV). Such a formulation has, however, unsatisfactory features. It gives the compounds a betaine-like structure which does not accord with their properties, *e.g.*, solubility in non-polar solvents. It also indicates a partial positive charge on each atom of the ring which is clearly at variance with the ease of electrophilic substitution, *e.g.*, bromination and nitration which must require a degree of negativity on the 5-carbon atom.

It is remarkable that, where protonation converts the anhydro-compound into a ring system (XX) which should be aromatic, since it possesses a sextet of electrons, the protonated compounds are only stable in strongly acid solution, and that the salts readily revert to the anhydro-compound although the latter has a structure which does not obviously possess an aromatic sextet.

Experimental

Unless otherwise stated, absorption measurements refer to EtOH solutions.

(*Arylazothio*)*acetic Acids.*—The following exemplifies the procedure: *p*-Toluidine (10·7 g.) in 5N-hydrochloric acid (50 ml.) containing ice (50 g.) was diazotized at 0—5° by sodium nitrite (7·0 g.) in water (20 ml.), and the solution added rapidly to thioglycollic acid (10 g.) in water (100 ml.). After 1 hour's stirring, the precipitated solid was filtered off, dissolved in ether (200 ml.), filtered, and separated from an aqueous layer; the ethereal solution was dried (Na_2SO_4) and evaporated at *ca.* 10° to give (*p*-tolylazothio)acetic acid as buff leaflets, m. p. 55° (decomp.) (17·5 g., 83%).[1]

The following were prepared similarly, all m. p.s being with decomposition: (p-*methoxyphenylazothio*)*acetic acid*, yellow leaflets [from ether by precipitation with light petroleum (b. p. 40—60°)], m. p. 70—71° (68%) (Found: N, 12·1. $C_9H_{10}O_3N_2S$ requires N, 12·4%), (p-*acetamidophenylazothio*)*acetic acid*, yellow needles (from ether), m. p. 105—106° (79%) (Found: N, 16·3. $C_{10}H_{11}O_3N_3S$ requires N, 16·5%), (2-*naphthylazothio*)*acetic acid*, buff leaflets [from ether by precipitation with light petroleum (b. p. 40—60°)], m. p. 75—76° (80%) (Found:

[13] Knott, *J.*, 1955, 918.
[14] Craig, Maccoll, Nyholm, Orgel, and Sutton, *J.*, 1954, 333.
[15] Thomas, *Chem. and Ind.*, 1955, 533.
[16] Baker and Ollis, *ibid.*, p. 910.

N, 10·5. $C_{12}H_{10}O_2N_2S$ requires N, 10·4%), (p-*chlorophenylazothio*)*acetic acid*, yellow leaflets, m. p. 77° (83%) (Found: S, 13·8. $C_8H_7O_2N_2SCl$ requires S, 13·9%), (p-*bromophenylazothio*)-*acetic acid*, yellow leaflets, m. p. 91° (77%) (Found: S, 11·8. $C_8H_7O_2N_2SBr$ requires S, 11·6%), and (p-*carboxyphenylazothio*)*acetic acid*, buff, m. p. 152° (96%) (Found: N, 11·3. $C_9H_8O_4N_2S$ requires N, 11·6%). Diazotized *p*-toluidine with thiolactic acid gave α-(p-*tolylazothio*)*propionic acid*, yellow leaflets [from ether by precipitation with light petroleum (b. p. 40—60°)], m. p. 69° (58%) (Found: N, 12·3. $C_{10}H_{12}O_2N_2S$ requires N, 12·4%) [$\lambda_{max.}$ 325 mμ (ε 14,900)], and with thiomandelic acid gave α-p-(*tolylazothio*)*phenylacetic acid*, yellow leaflets (from ether), m. p. 80° (75%) (Found: N, 9·7. $C_{15}H_{14}O_2N_2S$ requires N, 9·8%).

4-*Oxo*-3-*phenyl*-1-*thia*(S^{IV})-2 : 3-*diazoline*.—Aniline (1·86 g.) in 5N-hydrochloric acid (10 ml.) was diazotized with sodium nitrite (1·5 g.) in water (10 ml.). This solution was added to thioglycollic acid (2·0 g.) and crystalline sodium acetate (1·36 g.) in water (50 ml.) at 0°. After 15 min., the precipitated solid was filtered off, washed with water, and pressed between filter papers. The solid (2·4 g.) was added to pyridine (4 ml.) and acetic anhydride (12 ml.) at 0° and left for 3 days. Water (50 ml.) was added and the resulting solution evaporated *in vacuo*, to leave an oil which was extracted (3 × 20 ml.) with boiling *cyclo*hexane which, on cooling, gave a solid; recrystallized from *cyclo*hexane this gave the *anhydro-compound* as pale yellow needles, m. p. 65° (0·27 g., 8%) (Found: S, 17·85. $C_8H_6ON_2S$ requires S, 17·95%).

4-*Oxo*-3-p-*tolyl*-1-*thia*(S^{IV})-2 : 3-*diazoline*.—(*p*-Tolylazothio)acetic acid (50 g.) was added gradually to acetic anhydride (150 ml.) and pyridine (50 ml.) at 0—5°. After 15 min., crystals were precipitated which were filtered off, washed with ether, and recrystallized from *cyclo*hexane, to give the *anhydro-compound* as yellow needles, m. p. 121° (22 g., 48%) [Found: C, 56·5; H, 4·35; N, 14·8; S, 16·7%; *M* (ebullioscopic), in C_6H_6 194, in EtOH 196, in AcOH 190, (Rast) 198. $C_9H_8ON_2S$ requires C, 56·3; H, 4·15; N, 14·6; S, 16·7%; *M*, 192].

Other *anhydro-compounds* obtained by similar processes are tabulated.

Anhydro-compounds (II).

				Found				Required (%)		
Ar	R	M. p.	Yield (%)	C	H	S	Formula	C	H	S
p-C_6H_4Br	H	143°	80 [a]	37·6	2·2	12·2	$C_8H_5ON_2SBr$	37·4	1·95	12·4
p-C_6H_4Cl	H	159	73 [a]	45·2	2·35	15·25	$C_8H_5ON_2SCl$	45·3	2·35	15·1
p-$C_6H_4{\cdot}CO_2H$ ...	H	256	32 [g]	—	—	14·4	$C_9H_6O_3N_2S$	48·7	2·7	14·4
p-$C_6H_4{\cdot}OMe$	H	150	53 [c]	52·0	3·9	15·2	$C_9H_8O_2N_2S$	51·95	3·85	15·4
p-$C_6H_4{\cdot}NHAc$ ...	H	220	23 [d]	—	—	13·9	$C_{10}H_9O_2N_3S$	51·2	2·85	14·0
p-C_6H_4Me	Ph	173	31 [f]	66·9	4·7	11·85	$C_{15}H_{12}ON_2S$	67·2	4·5	11·9
p-C_6H_4Me	Me	99	25 [e]	58·1	4·75	15·8	$C_{10}H_{10}ON_2S$	58·3	4·85	15·6
2-$C_{10}H_7$	H	102	36 [b]	—	—	14·0	$C_{12}H_8ON_2S$	63·2	3·5	14·05

[a] Yellow needles from benzene. [b] Yellow needles from benzene–light petroleum. [c] Yellow plates from benzene. [d] Orange needles from ethanol. [e] Yellow needles from *cyclo*hexane. [f] Yellow leaflets from ethanol. [g] Insoluble in usual solvents; purified by dissolution in alkali and reprecipitation by acid.

Action of Acetic Anhydride–Pyridine on (p-*Nitrophenylazothio*)*acetic Acid*.—The acid [1] (4 g.) was added to pyridine (5 ml.) and acetic anhydride (12 ml.) at 0°. The mixture was allowed to warm to room temperature and cooled again to 0°, to give a solid which was filtered off, washed with ethanol, and dried (1·1 g.; m. p. 80—90°). This solid was boiled with carbon tetrachloride to leave an insoluble orange material while the filtered solvent, on cooling, gave pale yellow crystals which, recrystallized from water, gave (*p*-nitrophenylthio)acetic acid [1] as yellow needles, m. p. 157° (0·4 g., 12%) (Found: S, 15·1. Calc. for $C_8H_7O_4NS$: S, 14·9%). The orange solid was recrystallized from acetic acid, to give 3 : 5-*di*-p-*nitrophenyl*-4-*oxo*-2-*thia*(S^{IV})-2 : 3-*diazoline* as orange needles, m. p. 295° (0·25 g., 14%) (Found: S, 9·15. $C_{14}H_8O_5N_4S$ requires S, 9·25%).

3-p-*Aminophenyl*-4-*oxo*-1-*thia*(S^{IV})-2 : 3-*diazoline*.—3-*p*-Acetamidophenyl-4-oxo-1-thia(S^{IV})-2 : 3-diazoline (2·0 g.) and 10N-hydrochloric acid (10 ml.) were heated on a steam-bath for 1 hr. After dilution with water, the solution was neutralized by sodium carbonate, a solid being precipitated which was filtered off and recrystallized from ethanol, to give the pure *amine* as orange needles, m. p. 197° (1·38 g., 84%) (Found: S, 16·7. $C_8H_7ON_3S$ requires S, 16·5%).

4-*Hydroxy*-3-p-*tolyl*-1-*thia*-2 : 3-*diazolium Chloride*.—4-Oxo-3-*p*-tolyl-1-thia(S^{IV})-2 : 3-diazoline (5 g.) in dry ether (25 ml.) and chloroform (50 ml.) was saturated at 0° with dry hydrogen chloride. After 60 hr., the solution was evaporated at 20°/15 mm. to give a sticky solid which, twice recrystallized from acetone, gave the *chloride* as colourless needles, m. p. 138—140° (3·0 g.,

51%) (Found: S, 14·0; Cl, 15·5. $C_9H_9ON_2SCl$ requires S, 14·0; Cl, 15·5%). On contact with water or when dried *in vacuo* at elevated temperatures the chloride rapidly reverted to the anhydro-compound.

Mercuric Chloride Adduct of 4-*Oxo*-3-p-*tolyl*-1-*thia*(S^{IV})-2 : 3-*diazoline*.—The anhydro-compound (1·5 g.) was added to a solution of mercuric chloride (2·1 g.) in ethanol (20 ml.) and the mixture boiled for 5 min. and cooled to precipitate a solid. Recrystallization from ethanol gave the *adduct* as pale yellow needles, m. p. 130° (2·2 g., 78%) (Found: S, 6·65. $C_9H_8ON_2S,HgCl_2$ requires S, 6·65%).

Reduction of 4-*Oxo*-3-p-*tolyl*-1-*thia*(S^{IV})-2 : 3-*diazoline*.—Granulated zinc (10 g.) was added gradually to the anhydro-compound (5·0 g.) and 5N-sulphuric acid (5 ml.). When the resulting vigorous reaction had subsided, the mixture was warmed on a steam-bath for 1 hr., filtered, and made alkaline with sodium hydroxide. Ether-extraction (4 × 100 ml.) gave *p*-tolylhydrazine (2·6 g., 85%) (*m*-nitrobenzylidene derivative, m. p. and mixed m. p. 150°). The aqueous solution was re-acidified with sulphuric acid and extracted continuously with ether, to give thioglycollic acid (91% by iodine estimation).

A similar reduction of 5-methyl-4-oxo-3-*p*-tolyl-1-thia(S^{IV})-2 : 3-diazoline gave *p*-tolylhydrazine (78%) and thiolactic acid (85%).

Oxidation of 4-*Oxo*-3-p-*tolyl*-1-*thia*(S^{IV})-2 : 3-*diazoline*.—Chromium trioxide (1·0 g.) in acetic acid (10 ml.) was added to the anhydro-compound (1·92 g.) in acetic acid (10 ml.) and propionic acid (5 ml.) at 0°. After 16 hr. at 0° the solution was diluted with water (100 ml.). A precipitated solid was filtered off, which was unstable and decomposed on storage. The filtrate was added to β-naphthol (1·0 g.) in 10% aqueous sodium hydroxide (200 ml.), precipitating 1-*p*-tolylazo-2-naphthol (0·45 g., 18%). Potassium permanganate, in the presence of sulphuric acid, gave similar results, but ferric chloride was without action.

The oxidation of the 5-methyl anhydro-compound likewise gave toluene-*p*-diazonium salts.

Action of Sulphuric Acid on 4-*Oxo*-3-p-*tolyl*-1-*thia*(S^{IV})-2 : 3-*diazoline*.—Sulphuric acid (*d* 1·84) (10 ml.), water (10 ml.), and the anhydro-compound (5·0 g.) were mixed, rapidly giving a colourless solution. The solution was boiled under reflux for 20 hr. and diluted with water (100 ml.), to give the unchanged anhydro-compound (4·7 g., 94%), m. p. and mixed m. p. 121°.

Action of Amines on 4-*Oxo*-3-p-*tolyl*-1-*thia*(S^{IV})-2 : 3-*diazoline*.—*With benzylamine*. (i) The anhydro-compound (5·0 g.) and benzylamine (25 ml.) were heated for 4 hr. in an oil-bath at 140°, diluted with water (100 ml.), and steam-distilled (distillate 200 ml.). The residue was cooled and the resulting solid recrystallized from ethanol, to give *monothio-oxaldi*(*benzylamide*) as pale yellow needles, m. p. 121° (3·9 g., 53%) [Found: C, 66·3; H, 5·55; N, 10·0; S, 11·5%; *M* (Rast), 277. $C_{16}H_{16}ON_2S$ requires C, 67·6; H, 5·65; N, 9·85; S, 11·25%; *M*, 284], identical with the compound obtained as follows: Oxaldi(benzylamide) [17] (13·4 g.), phosphorus pentasulphide (3·0 g.), and pyridine (50 ml.) were boiled under reflux for 3 hr., then diluted with water (200 ml.). The resulting solid was filtered off and recrystallized from ethanol, to give monothio-oxaldi(benzylamide) (8·3 g., 58%). Boiling 5% aqueous ethanolic sodium hydroxide slowly reconverted the monothioamide into oxaldi(benzylamide), colourless plates (from dioxan), m. p. and mixed m. p. 220°. (ii) The anhydro-compound (5·0 g.), benzylamine (5 ml.), and ethanol (20 ml.) were boiled under reflux for 48 hr. On cooling, monothio-oxaldi(benzylamide) (4·2 g., 57%) crystallized. Dilution of the mother-liquors with water and evaporation of the ethanol gave crude *p*-tolylhydrazine, identified as *m*-nitrobenzylidene-*p*-tolylhydrazine, m. p. and mixed m. p. 150° (3·8 g., 57%).

By a process similar to (i) above, the anhydro-compound with *cyclo*hexylamine gave *monothio-oxaldi*(cyclo*hexylamide*) obtained from ethanol as yellow needles, m. p. 173° (71%) (Found: C, 62·4; H, 8·8; N, 10·5; S, 12·1. $C_{14}H_{24}ON_2S$ requires C, 62·7; H, 8·95; N, 10·45; S, 11·95%), and with *p*-anisidine gave *monothio-oxaldi*-(p-*anisidide*), yellow needles (from ethanol), m. p. 153° (73%) (Found: C, 61·0; H, 5·4; N, 8·9; S, 9·95. $C_{10}H_{16}O_3N_2S$ requires C, 60·8; H, 5·1; N, 8·85; S, 10·1%).

Action of Hydrazine on 4-*Oxo*-3-p-*tolyl*-1-*thia*(S^{IV})-2 : 3-*diazoline*.—The anhydro-compound (5·0 g.), ethanol (20 ml.), and 90% hydrazine hydrate (10 ml.) were boiled under reflux for 1 hr., hydrogen sulphide being evolved. After dilution with water (50 ml.), the ethanol was removed by evaporation and the residue extracted with ether, to give *p*-tolylhydrazine (2·4 g., 78%) (*m*-nitrobenzylidene derivative, m. p. and mixed m. p. 150°).

Action of Hydrazine on 5-*Methyl*-4-*oxo*-3-p-*tolyl*-1-*thia*(S^{IV})-2 : 3-*diazoline*.—The anhydro-compound (2·0 g.), ethanol (10 ml.), and 90% hydrazine hydrate (5 ml.) were boiled under

[17] Strakosch, *Ber.*, 1872, **5**, 694.

reflux for 1 hr., during which hydrogen sulphide was evolved. Water (50 ml.) was added, the ethanol removed, the solution extracted with ether (2 × 20 ml.), and the ether extracts were evaporated. The residue was dissolved in ethanol (10 ml.), and *m*-nitrobenzaldehyde (2·0 g.) and a few drops of acetic acid were added, 1-*m*-nitrobenzylidene-2-*p*-tolylhydrazine being obtained (1·65 g., 67%), m. p. and mixed m. p. 150°. The aqueous layer from the ether-extraction gave, on evaporation, an oil which was dissolved in benzene. Addition of light petroleum (b. p. 60—80°) precipitated a solid which was recrystallized from ethanol, to give *pyruvic acid hydrazide hydrazone* as colourless needles, m. p. 145° (0·3 g., 27%) (Found: C, 30·95; H, 7·0. $C_3H_8ON_4$ requires C, 31·0; H, 6·9%), identical with the compound prepared as follows: Mixing ethyl pyruvate (13·4 g.) and 90% hydrazine hydrate (20 ml.) caused an exothermic reaction. The mixture was then boiled under reflux for 16 hr., and cooled, giving the crystalline hydrazide which recrystallized from ethanol as colourless needles, m. p. 143° (5·5 g., 41%). Its m-*nitrobenzylidene derivative* was obtained from ethanol as pale yellow needles, m. p. 185° (Found: N, 27·9. $C_{10}H_{11}O_3N_5$ requires N, 28·1%).

Action of Phenylhydrazine on 4-*Oxo*-3-p-*tolyl*-1-*thia*(S^{IV})-2 : 3-*diazoline*.—The anhydro-compound (9·5 g.), phenylhydrazine (10 ml.), and ethanol (40 ml.) were boiled under reflux for 48 hr. On cooling, sulphur was rapidly precipitated and was filtered off (1·02 g., 64%). The filtrate was evaporated and benzene added to the residue, which then crystallized. Recrystallization from methanol gave the *glyoxylic acid* N-p-*tolylhydrazide phenylhydrazone* as buff leaflets, m. p. 173° (5·1 g., 39%) (Found: C, 66·5; H, 5·95; N, 20·9. $C_{15}H_{16}ON_4$ requires C, 67·1; H, 5·95; N, 20·9%) which, with acetic anhydride, gave *glyoxylic acid* N′-*acetyl*-N-p-*tolylhydrazide phenylhydrazone*, colourless needles (from aqueous ethanol), m. p. 196° (Found: N, 18·05. $C_{17}H_{18}O_2N_4$ requires N, 18·1%), and with *m*-nitrobenzaldehyde gave *glyoxylic acid* N′-m-*nitrobenzylidene*-N-p-*tolylhydrazide phenylhydrazone* as pale yellow leaflets, m. p. 209° (decomp.) (Found: C, 65·55; H, 4·9. $C_{22}H_{19}O_3N_5$ requires C, 65·8; H, 4·75%). Evaporation of the benzene filtrate gave a thick oil which on trituration with ethanol gave a solid which recrystallized from ethanol, to give 4-oxo-5-phenyl-3-*p*-tolyl-1-thia(S^{IV})-2 : 3-diazoline as yellow leaflets, m. p. 173° (0·12 g.), identical with that obtained above. The combined ethanol washings and mother-liquors were evaporated, and the solid residue was recrystallized from light petroleum, to give a substance of unknown constitution as pale yellow needles, m. p. 94° (0·71 g.) (Found: C, 68·65; H, 8·2; N, 19·8%; S, 0) ($\lambda_{max.}$ 295 and 351 mμ, the latter possessing a high extinction coefficient).

Hydrolysis of Glyoxylic Acid N-p-*Tolylhydrazide Phenylhydrazone*.—The hydrazone (2·8 g.), 10% aqueous sodium hydroxide (10 ml.), and ethanol (5 ml.) were boiled under reflux for 1 hr. The cooled mixture was extracted with ether (3 × 50 ml.), the residue from the combined extracts, after evaporation, was dissolved in ethanol (30 ml.), and *m*-nitrobenzaldehyde (1·5 g.) and acetic acid (0·1 ml.) were added. After boiling for 1 min., the solution was cooled, to give *N*-*m*-nitrobenzylidene-*N*′-*p*-tolylhydrazine, m. p. and mixed m. p. 150° (1·8 g., 68%). The aqueous solution from the hydrolysis was cooled and acidified with 2N-hydrochloric acid, to give glyoxylic acid phenylhydrazone, m. p. 138° (1·0 g., 58%), identical with the authentic material.[18]

Unambiguous Synthesis of Glyoxylic Acid N′-*Acetyl*-N-p-*tolylhydrazide Phenylhydrazone*.—Dichloroacetyl chloride (14·8 g.) was added to *N*-acetyl-*N*′-*p*-tolylhydrazine (16·4 g.)[19] in dry benzene (80 ml.), and the mixture boiled under reflux for 2 hr. On cooling, the crystalline N′-*acetyl*-N-p-*tolylhydrazide* of dichloroacetic acid was deposited. This recrystallized as colourless needles, m. p. 152—153° (17 g., 62%) (Found: N, 10·4; Cl, 25·6. $C_{11}H_{12}O_2N_2Cl_2$ requires N, 10·2; Cl, 25·8%). This compound (10 g.), phenylhydrazine (11 ml.), and ethanol (50 ml.) were boiled under reflux for 24 hr. Dilution with water (200 ml.) precipitated an oil which crystallized on addition of benzene. Recrystallization from ethanol gave glyoxylic acid *N*′-acetyl-*N*-*p*-tolylhydrazide phenylhydrazone as colourless needles, m. p. and mixed m. p. 196° (5·3 g., 44%) (Found: N, 18·1%).

Bromination of 4-*Oxo*-3-p-*tolyl*-1-*thia*(S^{IV})-2 : 3-*diazoline*.—The anhydro-compound (4·5 g.), anhydrous sodium acetate (5·0 g.), and acetic acid (50 ml.) were stirred and bromine (2·6 ml.) was added slowly at room temperature. The mixture was warmed for 5 min. on a steam-bath and diluted with water (300 ml.), a solid being precipitated. Recrystallization from ethanol gave the 5-*bromo-derivative* as orange leaflets, m. p. 125° (3·1 g., 48%), which became pink in air (Found: C, 40·1; H, 2·8; S, 12·1. $C_9H_7ON_2SBr$ requires C, 39·95; H, 2·6; S, 11·8%).

[18] Nölting and Collin, *Ber.*, 1884, **17**, 261.
[19] Busch and Meussdorffer, *J. prakt. Chem.*, 1907, 2, **75**, 133.

Nitration of 4-*Oxo*-3-p-*tolyl*-1-*thia*(S^{IV})-2 : 3-*diazoline*.—(*a*) The anhydro-compound (19·2 g.) was stirred with sulphuric acid (*d* 1·84) (200 ml.) until all had dissolved, then the whole was cooled to −5°. Nitric acid (*d* 1·42) (10 ml.) and sulphuric acid (*d* 1·84) (50 ml.) were added with stirring at −5° to −1° during 45 min. The mixture was stirred for a further 30 min. and poured on ice. The precipitated solid recrystallized from ethanol, to give 3-(4-*methyl*-3-*nitrophenyl*)-4-*oxo*-1-*thia*(S^{IV})-2 : 3-*diazoline* as orange needles, m. p. 154° (16·0 g., 68%) (Found : S, 13·5. $C_9H_7O_3N_3S$ requires S, 13·5%).

(*b*) The anhydro-compound (4·5 g.) was dissolved in sulphuric acid (*d* 1·84) (50 ml.), and nitric acid (*d* 1·42) (6·0 ml.) was added with stirring at 12—15° during 15 min. The mixture was stirred for 45 min. and diluted with ice, to precipitate an orange solid which was filtered off and recrystallized from ethanol, giving 3-(4-*methyl*-3-*nitrophenyl*)-5-*nitro*-4-*oxo*-1-*thia*(S^{IV})-2 : 3-*diazoline* as orange needles, m. p. 125° (decomp.) (3·9 g., 49%) (Found : N, 19·9. $C_9H_6O_5N_4S$ requires N, 19·9%).

(*c*) Three experiments were carried out in each of which the anhydro-compound (1·92 g.), acetic acid (10 ml.), and propionic acid (5·0 ml.) were cooled to −2°, and nitric acid (*d* 1·42) (0·7 ml.) and acetic acid (5 ml.) added with stirring. The first mixture was immediately diluted with water (250 ml.), and the resulting solution added to β-naphthol (2·0 g.) in 10% aqueous sodium hydroxide (200 ml.), to precipitate unchanged anhydro-compound (1·7 g., 86%). The second mixture was similarly diluted after 1 hr. at 0° and added to alkaline β-naphthol, to give a solid which was separated by hot *cyclo*hexane into unchanged anhydro-compound (1·2 g., 60%) and 1-*p*-tolylazo-2-naphthol, m. p. and mixed m. p. 134° (0·26 g., 10%). The third was diluted after 20 hr. at 0°, to precipitate an orange solid which was filtered off, washed with water, dried, and recrystallized from ethanol, giving 5-*nitro*-4-*oxo*-3-p-*tolyl*-1-*thia*(S^{IV})-2 : 3-*diazoline* as orange-yellow needles, m. p. 146° (explosion) (0·45 g., 19%) [Found : S, 14·2%; *M* (ebullioscopic in benzene), 239. $C_9H_7O_3N_3S$ requires S, 13·5%; *M*, 237]. The aqueous filtrate was added at 0° to alkaline β-naphthol, to give 1-*p*-tolylazo-2-naphthol (1·9 g., 72%).

Action of Nitric Acid on 5-*Methyl*-4-*oxo*-3-p-*tolyl*-1-*thia*(S^{IV})-2 : 3-*diazoline*.—(*a*) The anhydro-compound (1·02 g. and concentrated sulphuric acid (10 ml.) were cooled to 0° and nitric acid (*d* 1·43) (0·37 ml.) and concentrated sulphuric acid (2·5 ml.) added with stirring. After 1 hr. the mixture was added to ice, and the precipitated solid recrystallized from ethanol, to give 5-*methyl*-3-(4-*methyl*-3-*nitrophenyl*)-4-*oxo*-1-*thia*(S^{IV})-2 : 3-*diazoline* as yellow needles, m. p. 152° (0·55 g., 44%) (Found : S, 12·65. $C_{10}H_9O_3N_3S$ requires S, 12·7%).

(*b*) Nitric acid (*d* 1·42) (0·7 ml.) and acetic acid (5 ml.) were added to the anhydro-compound (2·06 g.) in acetic acid (10 ml.) and propionic acid (5 ml.) at 0°. After 15 hr. the solution was diluted with water and filtered from a little tar. Addition to a solution of β-naphthol (2·0 g.) in 10% aqueous sodium hydroxide (200 ml.) precipitated 1-*p*-tolylazo-2-naphthol (1·1 g., 44%).

Action of Hydrazine on Bromo- and Nitro-anhydro-compounds.—By a similar process to that described above, 5-bromo- and 5-nitro-4-oxo-3-*p*-tolyl-1-thia(S^{IV})-2 : 3-diazoline gave *p*-tolylhydrazine, identified as its *m*-nitrobenzylidene derivative, 75% and 42% respectively. 3-(4-Methyl-3-nitrophenyl)-, 3-(4-methyl-3-nitrophenyl)-5-nitro-, and 5-methyl-3-(4-methyl-3-nitrophenyl)-4-oxo-thia(S^{IV})-2 : 3-diazoline gave 4-methyl-3-nitrophenylhydrazine, identified as its m-*nitrobenzylidene derivative* which was obtained from ethanol as orange needles, m. p. 189° (77%, 65%, and 53% respectively) (Found : N, 19·0. $C_{14}H_{12}O_4N_4$ requires N, 18·7%), identical with the authentic material prepared as follows : 4-Amino-2-nitrotoluene [20] was diazotized in 2·5N-hydrochloric acid (10·3 ml.) with sodium nitrite (0·7 g.) in water (1·5 ml.), and stannous chloride (6·1 g.) in 10N-hydrochloric acid (7·6 ml.) was added gradually to the solution at 5°. The resulting precipitate was filtered off, dissolved in water, and made alkaline with 10N-sodium hydroxide (10 ml.). Extraction with ether, followed by evaporation, gave a solid which recrystallized from benzene–light petroleum (b. p. 60—80°), to give 4-*methyl*-3-*nitrophenylhydrazine* as orange needles, m. p. 82° (0·47 g., 29%) (Found : N, 25·2. $C_7H_9O_2N_3$ requires N, 25·1%). Its *m*-nitrobenzylidene derivative, m. p. 189°, was identical with that obtained as above.

Action of Sodium Ethoxide on 4-*Oxo*-3-p-*tolyl*-1-*thia*(S^{IV})-2 : 3-*diazoline*.—The anhydro-compound (10·0 g.) and sodium (1·2 g.) in ethanol (50 ml.) were boiled under reflux for 1 hr., the solution diluted with water (100 ml.), and the ethanol distilled off; a solid separated. Filtration and recrystallization from benzene gave 4-*oxo*-3 : 5-*di*-p-*tolyl*-1-*thia*(S^{IV})-2 : 3-*diazoline* as orange leaflets, m. p. 182° (1·5 g., 22%) [Found : C, 68·5; H, 5·05; N, 9·95; S, 11·15%; *M* (ebullioscopic in EtOH), 287. $C_{16}H_{14}ON_2S$ requires C, 68·1; H, 5·0; N, 9·95;

[20] Gattermann, Johnson, and Hölzle, *Ber.*, 1892, **25**, 1080.

S, 11·4%; *M*, 282]. The aqueous filtrate was acidified at 0° by addition of 2N-hydrochloric acid to give a yellow precipitate which was collected, washed with water, and dried *in vacuo* (8·5 g.), m. p. about 90° (Found: C, 53·25; H, 4·35; N, 13·35; S, 18·0%; equiv., 209, 217). From similar experiments acidic mixtures were obtained with different analyses. The acidic mixture could not be crystallized since, although soluble in most solvents, it appeared to decompose when warmed.

Action of benzylamine on "acidic mixture." The acidic mixture (2·5 g.) from the above experiment, and benzylamine (5 ml.) were heated at 140° for 1 hr. Dilution with water (100 ml.) precipitated a solid which was filtered off and recrystallized from ethanol, to give monothiooxaldi(benzylamide), m. p. 121° (1·13 g.), identical with that obtained as above.

Action of hydrazine on the "acidic mixture." The acidic mixture (2·5 g.), 90% hydrazine hydrate (10 ml.), and ethanol (10 ml.) were boiled under reflux for 20 hr. Water (50 ml.) was added, ethanol removed, and the residue extracted with ether (3 × 25 ml.). Removal of the ether gave *p*-tolylhydrazine (1·2 g.) (*m*-nitrobenzylidene derivative, m. p. and mixed m. p. 150°).

Action of Raney nickel on the "acidic mixture." The acidic mixture (8·0 g.) in 1% aqueous sodium hydroxide (200 ml.) and Raney nickel (prepared from 37 g. of the alloy by Brown's method [21]) were boiled under reflux for 2 hr., during which time ammonia was evolved. The mixture was filtered hot and the nickel washed with hot water. The filtrate, on cooling, afforded aceto-*p*-toluidide (1·5 g.), m. p. and mixed m. p. 147°, and ether-extraction gave *p*-toluidine, m. p. and mixed m. p. 41° (1·15 g.). Acidification of the alkaline solution gave a tarry acid (2·2 g.; m. p. 100—120°) from which, by extraction with boiling water, a *substance* was obtained which recrystallized from water to give colourless needles, m. p. 255° (0·12 g.) (Found: C, 59·35; H, 4·8%). Steam-distillation of the acidified solution gave a distillate containing acetic acid.

Benzoylation of the "acidic mixture." The acidic mixture (8·0 g.) in 5% aqueous sodium hydroxide (165 ml.) was shaken for 1 hr. with benzoyl chloride (8 ml.). The precipitated yellow solid was filtered off, washed with ethanol, and recrystallized from xylene, to give **5-*benzoylthio*-4-*oxo*-3-p-*tolyl*-1-*thia*(S^{IV})-2 : 3-*diazoline*** as yellow leaflets, m. p. 201° (1·6 g.) (Found: C, 58·8; H, 3·95; N, 8·55; S, 19·73. $C_{16}H_{12}O_2N_2S_2$ requires C, 58·5; H, 3·7; N, 8·55; S, 19·55%).

Carboxymethylation of "acidic mixture." The acidic mixture (8·0 g.), chloroacetic acid (4·75 g.), and N-aqueous sodium hydroxide (100 ml.) were heated for 1 hr. at 100°. The cooled solution was acidified with dilute sulphuric acid, an oil being precipitated. Crystallization from ethyl acetate gave *5-carboxymethylthio-4-oxo*-3-p-*tolyl*-1-*thia*(S^{IV})-2 : 3-*diazoline* as pale yellow needles, m. p. 177° (3·2 g.) (Found: C, 46·7; H, 3·25; N, 9·95; S, 22·95. $C_{11}H_{10}O_3N_2S_2$ requires C, 46·8; H, 3·5; N, 9·95; S, 22·75%).

5-Mercapto-4-oxo-3-p-*tolyl*-1-*thia*(S^{IV})-2 : 3-*diazoline*.—Sulphur (1·6 g.), dissolved in a warm solution of crystalline sodium sulphide (12·0 g.) in ethanol (20 ml.), was added to 4-oxo-3-*p*-tolyl-1-thia(S^{IV})-2 : 3-diazoline (9·0 g.) in ethanol (100 ml.). After boiling under reflux for 90 min., the deep yellow solution was diluted with water (100 ml.) and evaporated *in vacuo* until a yellow solid was precipitated. The mixture was cooled, the solid removed, and the filtrate mixed with saturated sodium chloride solution to give a second crop. The combined solids were dissolved in water (80 ml.), filtered to remove a little tar, and diluted with sodium chloride solution, to give the *sodium salt* as bright yellow leaflets, m. p. 180° (8·5 g., 70%) (Found: N, 10·9; S, 25·55. $C_9H_7ON_2S_2Na$ requires N, 11·4; S, 25·9%), from which 5-carboxymethylthio- (60%) and 5-benzoylthio-4-oxo-3-*p*-tolyl-1-thia(S^{IV})-2 : 3-diazoline (46%) were obtained, identical with the compounds described above.

Acidification of an aqueous solution of the sodium salt of the mercapto-compound gave *5-mercapto-4-oxo*-3-p-*tolyl*-1-*thia*-(S^{IV})-2 : 3-*diazoline* as a yellow powder, m. p. 90° (decomp.) (Found: S, 28·35. $C_9H_8ON_2S_2$ requires S, 28·6%).

Arylation of 4-Oxo-3-p-*tolyl*-1-*thia*(S^{IV})-2 : 3-*diazoline*.—The anhydro-compound (1·9 g.) in pyridine (10 ml.) was cooled to 5°, and a solution of diazotized *p*-toluidine from the amine (1·07 g.), 5N-hydrochloric acid (5·0 ml.), and sodium nitrite (0·75 g.) in water (2 ml.) added gradually. Nitrogen was evolved and a solid slowly precipitated. After 1 hr., the solid was collected and recrystallized from benzene, to give 4-oxo-3 : 5-di-*p*-tolyl-1-thia(S^{IV})-2 : 3-diazoline as orange leaflets, m. p. 182° (0·46 g., 17%) (Found: C, 67·9; H, 5·0; N, 10·1; S, 11·6%), identical with the compound described above.

The same product (14%) was obtained when the reaction was carried out in 10% alcoholic

[21] Brown, *J. Soc. Chem. Ind.*, 1950, **69**, 355.

sodium hydroxide, and similar reactions with diatotized aniline gave anhydro-5-phenyl- (21%) (cf. Table), with *p*-anisidine gave 5-p-*methoxyphenyl*- (from ethanol), yellow plates, m. p. 154° (18%) (Found: S, 10·65. $C_{16}H_{14}O_2N_2S$ requires S, 10·7%), and with *p*-nitroaniline gave 5-p-*nitrophenyl*-4-*oxo*-3-p-*tolyl*-1-*thia*(S^{IV})-2 : 3-*diazoline* (from ethanol), orange needles, m. p. 170° (19%) (Found: C, 57·65; H, 3·7; S, 10·2. $C_{15}H_{11}O_3N_3S$ requires C, 57·6; H, 3·55; S, 10·2%).

Reduction of 4-*Oxo*-5-*phenyl*-3-p-*tolyl*-1-*thia*(S^{IV})-2 : 3-*diazoline*.—The anhydro-compound (2·1 g.), ethanol (20 ml.), water (20 ml.), 10N-hydrochloric acid (12 ml.), and granulated zinc (8 g.) were boiled for 20 hr. The ethanol was removed and the residue extracted with ether. The aqueous acid solution was made alkaline with sodium hydroxide and extracted with ether, the ether removed, and *m*-nitrobenzaldehyde added to the residue in ethanol, to give *N*-*m*-nitrobenzylidene-*N'*-*p*-tolylhydrazine, m. p. and mixed m. p. 153° (1·4 g., 70%). The original ether extract was evaporated, giving an oil which was heated to 100° with 10% aqueous sodium hydroxide (5 ml.) for 1 hr., acidified with 2N-sulphuric acid, and extracted with ether. Distillation of the ether extracts gave phenylacetic acid, b. p. 160—162°/15 mm., m. p. and mixed m. p. 75° (0·6 g., 60%).

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