Reactions of Lead Tetra-acetate with Substituted Benzaldehyde 5-Phenyl-1,2,4-triazol-3-ylhydrazones

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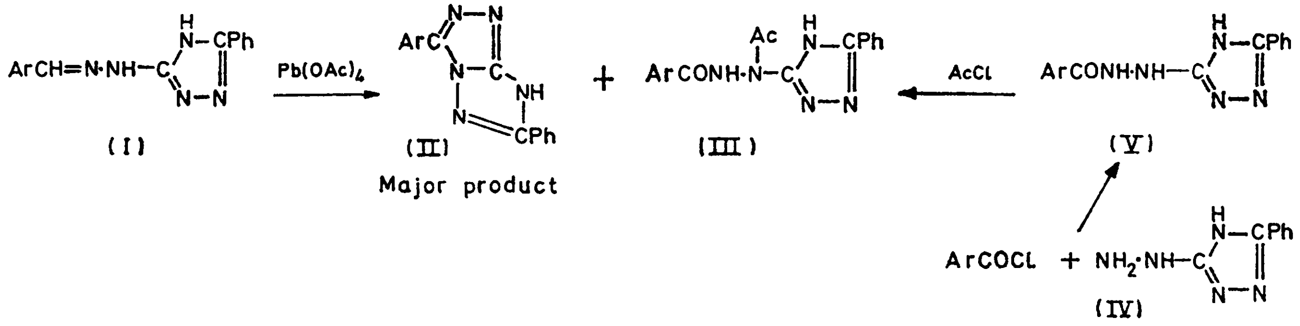
In the reaction of lead tetra-acetate with substituted benzaldehyde 5-phenyl-1,2,4-triazol-3-ylhydrazones the presence of the triazole ring enhanced a cyclisation reaction leading to high yields of 3-aryl-6-phenyl-7*H*-*s*-triazolo-[4,3-*b*]-*s*-triazoles. Low yields of *N*-acetyl-*N'*-aroyl-*N*-(5-phenyl-1,2,4-triazol-3-yl)hydrazines were also isolated from a competitive acetoxylation reaction. The rates of the reaction were rapid, with second-order rate constants *ca.* 160—800 l mol^{-1} s^{-1} at 35° in glacial acetic acid. Substituents in the arylidene ring exerted a small influence ($\rho = -0{\cdot}60$) on the reaction. The mechanism is discussed.

THE reactions of lead tetra-acetate with organic nitrogen compounds have recently undergone a renewal of interest.[1,2] With substituted hydrazones the reaction may yield one or more of five different products.[1-3] Four of these are isomeric compounds derived by replacement of an available hydrogen atom by the elements of an acetoxy-group. These may be azoacetates, acetylhydrazonates, or two different types of *N*-acetylhydrazides.[1-3] The fifth possible product arises from the lead tetra-acetate acting as a dehydrogenating agent particularly with aldehyde hydrazones. When such compounds contain an appropriately located heterocyclic ring oxidative cyclisation to a fused heterocycle may, and often does, occur in competition with the acetoxylation process. In our investigation of the principles governing the balance between cyclisation or acetoxylation in these reactions, we have studied the influence of the heterocyclic ring by using substituted tetrazoles,[3,4] oxadiazole,[5] benzothiazole,[6] and acyclic amido-groups[7] as hydrazone *N*-aryl substituents. This present work concerns the nature of the reaction when the hydrazone *N*-aryl substituent is a 1,2,4-triazole group. The compounds we chose to study were the aromatic aldehyde 5-phenyl-1,2,4-triazol-3-ylhydrazones (I).

RESULTS AND DISCUSSION

Course of the Reactions.—When the hydrazones (I) were treated with lead tetra-acetate in acetic acid for 3—4 h at ambient temperature, competing cyclisation and acetoxylation reactions were observed yielding the products (II) and (III) respectively (Scheme 1). The cyclisation was the dominant reaction and only low yields of the *N*-acetylhydrazides (III) were isolated (Table 1). A number of isomeric structures can be postulated for the bicyclic products of the cyclisation reaction. Thus ring closure could theoretically occur at any of the nitrogen atoms of the triazole ring and the primary products of the ring closure could also be isomerised under the reaction conditions to yield new products (*cf.* refs. 8—10). The various possibilities were eliminated and it was confirmed that the reaction involved a clean cyclisation at N-1 of the triazole ring yielding 3-aryl-6-phenyl-7*H*-*s*-triazolo[4,3-*b*]-*s*-triazoles (II) by an unequivocal preparation of these latter products. This involved (Scheme 2) preparation of 4,5-diamino-3-aryl-1,2,4-triazoles (VI) by treating aroylsemicarbazides, or their *S*-methyl derivatives, with hydrazine hydrate, followed by condensation of compounds (VI) with benzoyl chloride in pyridine[11] and



SCHEME 1

a; Ar = p-MeOC$_6$H$_4$
b; Ar = p-MeC$_6$H$_4$
c; Ar = p-Pr^{i}C$_6$H$_4$
d; Ar = Ph
e; Ar = p-ClC$_6$H$_4$
f; Ar = p-BrC$_6$H$_4$
g; Ar = p-NO$_2$C$_6$H$_4$
h; Ar = m-NO$_2$C$_6$H$_4$

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[1] For a review see J. B. Aylward, *Quart. Rev.*, 1971, **25**, 407.

[2] For a review see R. N. Butler, *Chem. and Ind.*, 1968, 437.

[3] F. L. Scott and R. N. Butler, *J. Chem. Soc.* (*C*), 1966, 1202.

[4] R. N. Butler and F. L. Scott, *J. Chem. Soc.* (*C*), 1968, 1711.

[5] R. N. Butler, T. M. Lambe, and F. L. Scott, *J. Chem. Soc.* (*C*), 1972, 269.

[6] R. N. Butler, P. O'Sullivan, and F. L. Scott, *J. Chem. Soc.* (*C*), 1971, 2265.

[7] T. M. Lambe, R. N. Butler, and F. L. Scott, *Chem. and Ind.*, 1971, 996.

[8] R. G. W. Spickett and S. H. B. Wright, *J. Chem. Soc.* (*C*), 1967, 498.

[9] J. Daunis, R. Jacquier, and P. Viallefont, *Bull. Soc. chim. France*, 1969, 2492.

[10] J. Kobe, B. Stanovnik, and M. Tisler, *Tetrahedron*, 1970, **26**, 3357.

[11] E. Hoggarth, *J. Chem. Soc.*, 1950, 614.

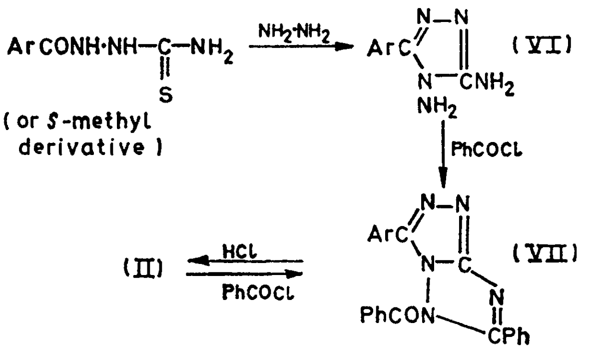
hydrolysis of the resulting benzoyl-*s*-triazolo[4,3-*b*]-*s*-triazoles (VII). The compounds (II) obtained by this procedure were identical with the samples obtained from the lead tetra-acetate reactions. On treatment of the triazolotriazoles (II) with benzoyl chloride the benzoyl derivatives (VII) could be readily obtained. All the intermediates used in this unequivocal preparation have previously been reported and characterised.[11-14] The hydrazone (Id) has previously been treated with lead tetra-acetate by Gehlen[15,16] and Potts and Hirsch.[17] These workers observed an N-1 ring closure yielding compound (IId) but no acetoxylation products were reported. With a series of hydrazones of type (I) where the substituent Ar was held constant as Ph and the substituent in the 5-position was varied, the course of the reaction with lead tetra-acetate again gave predominantly cyclised products.[14,17] The predominance of cyclisation in the triazole case is of interest since oxadiazole,[5] benzothiazole,[6,18] or tetrazole[3,4] rings in place of the triazole-group orient the reaction in favour of acetoxylation.

TABLE 1

Reactions of hydrazones with lead tetra-acetate to give triazolotriazoles and *N*-acetylhydrazides

	Triazolotriazoles			*N*-Acetylhydrazides				
Hydrazone	Compd.	Yield (%)	M.p. (°C)	Compd.	Yield (%)	M.p. (°C)	k_2/ l mol^{-1} s^{-1} [b]	λk_2/nm [d]
(Ia)	(IIa)	91	267	(IIIa)			792 (±16) [c]	315
(Ib)	(IIb)	88	288	(IIIb)	1·5	228—229	587 (±10)	310
(Ic)	(IIc)	80	233	(IIIc)	8	238	585 (±10)	310
(Id)	(IId)	84	266 [a]	(IIId)	2	225—226	458 (±8)	305
(Ie)	(IIe)	82	326	(IIIe)	9	242	357 (±3)	315
(If)	(IIf)	76	327	(IIIf)	11	261	343 (±6)	320
(Ig)	(IIg)	76	>358	(IIIg)	9	268	182 (±3)	360
(Ih)							167 (±3)	310

[a] Lit.,[11,16,20] m.p. 257, 266, and 268° respectively. [b] Second-order rate constant for the reaction of the hydrazones with lead tetra-acetate in acetic acid at 35°. [c] Values are the mean (and mean deviation) of at least three measurements for the slower rates and five measurements for the faster rates. Reproducible to ±2%. [d] Wavelengths at which the rates were measured. The products displayed minimum absorption at these wavelengths (see text).



SCHEME 2

The structure of the *N*-aroyl-*N'*-acetylhydrazines (III), the minor products of the reaction, was indicated by their i.r. spectra which displayed the strong N–H (3320—3340 cm^{-1}) and the carbonyl doublet (1670—1690 cm^{-1} conjugated; 1715—1730 cm^{-1} unconjugated) absorptions associated with the *N*-acetylhydrazide structure.[3,4,6] A number of the compounds (III) were also prepared by treating the hydrazides (V) [prepared by coupling the hydrazine (IV), from the hydrolysis of compounds (I), with aroyl chlorides] with acetyl chloride thus confirming the structure (III). The possibility that acetylation of a ring nitrogen atom of the triazole ring occurred in this latter reaction is highly unlikely. *N*-Acetyltriazoles are unstable compounds which hydrolyse rapidly in neutral,[19] basic, and acidic media.[20] The compounds (III) were quite stable and showed no tendency for ready hydrolysis.

Mechanism of the Reactions.—Kinetic studies. We examined the kinetics of the reaction of a range of the hydrazones (I) with lead tetra-acetate by following the disappearance of the hydrazone absorption in the 310 nm region (see Table 1 for precise wavelength used for each hydrazone) using glacial acetic acid as solvent at 35°. All the compounds obeyed the Beer–Lambert Law at the wavelengths indicated for the concentration range used, *i.e.* less than 10^{-4}M. The hydrazones (I) showed two absorption bands, $\lambda_{max.}$ 230—242 (log ε 4·19—4·29) and 312—321 nm (4·22—4·32) * and the main products (II) showed a band at $\lambda_{max.}$ 245—258 nm (log ε 3·74—4·38) with a shoulder band between 275 and 280 nm.* Hence, the absorptions of the products did not interfere with the kinetic measurements. The reactions followed second-order kinetics being first order both in hydrazone and lead tetra-acetate. The relevant second-order rate constants are given in Table 1. From these data a Hammett ρ of —0·60 (r = 0·995) was calculated.

We interpret these results in terms of a rate-determining displacement on lead(IV) resulting in a build-up of positive charge along the hydrazone chain (Scheme 3). This is in agreement with ref. 21 where a ρ value of —1·95 was obtained for the effect of *N*-aryl variation in

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* For the *p*-nitro-derivative (Ig) this band appeared at 374 nm and the shoulder band of the triazolotriazole (IIg) was at 324 nm.

[12] E. Hoggarth, *J. Chem. Soc.*, 1950, 1579.

[13] E. Hoggarth, *J. Chem. Soc.*, 1949, 1163.

[14] E. Hoggarth, *J. Chem. Soc.*, 1949, 1918.

[15] H. Gehlen and G. Robisch, *Annalen*, 1962, **660**, 148.

[16] H. Gehlen and F. Lemme, *Annalen*, 1967, **703**, 116.

[17] K. T. Potts and C. Hirsch, *J. Org. Chem.*, 1968, **33**, 143.

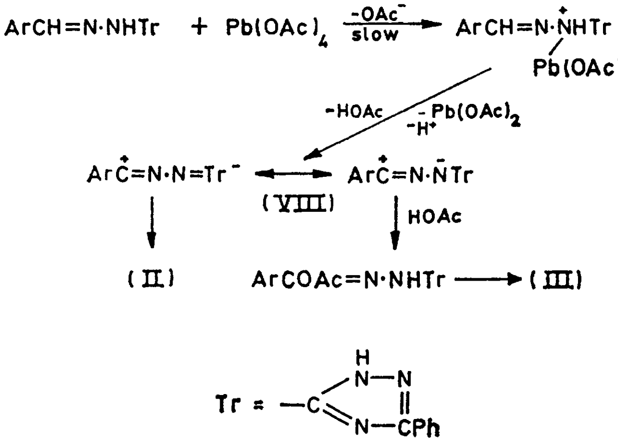
[18] J. D. Bower and F. P. Doyle, *J. Chem. Soc.*, 1957, 727.

[19] B. G. van den Bos, *Rec. Trav. chim.*, 1960, **79**, 836, 1129.

[20] K. T. Potts, *Chem. Rev.*, 1961, **61**, 87.

[21] M. J. Harrison, R. O. C. Norman, and W. A. F. Gladstone. *J. Chem. Soc.* (*C*). 1967, 735.

the reaction of ketone hydrazones with lead tetra-acetate under conditions similar to ours. The data do not allow a distinction between initial attack at the hydrazone NH site (as in Scheme 3) or alternately at the methine carbon atom and arguments for the former [22] and the latter [23] modes of attack have been put forward. Taking the general hydrazone system ArCR=N·NHAr′ and combining Norman *et al.* results [21] with ours gives a *N*-aryl-ρ : *C*-aryl-ρ ratio of 3·25. This is very similar to the corresponding ratios (*ca.* 3·5) which apply for attack on hydrazone systems by electrophiles such as diazonium ion and bromine where methine attack is rate determining. In the present work, therefore, the kinetic data are equally compatible with N- or C-attack. Another mode of reaction involving reversible attack at one site followed by irreversible attack at the other is also a possibility.



SCHEME 3

The subsequent steps of the reaction may involve a nitrilimine intermediate (VIII). Evidence has been quoted for the intermediacy of such a species in lead tetra-acetate oxidations of non-heterocyclic aromatic aldehyde arylhydrazones.[22,24] Attempts to trap such intermediates by treating compound (Id) with lead tetra-acetate in acrylonitrile as solvent proved negative and over 70% of the cyclised product (IId) was obtained. However, the reaction was not clean-cut and it will be studied further. In previous work [6] with heterocyclic benzothiazolylhydrazones such intermediates were also not detected. In the present instance the failure to detect nitrilimine intermediates may indicate that such species are not involved or that the 1,5-dipolar resonance form is highly reactive and yields the compounds (II) through an electrocyclic cyclisation [25] which is more rapid than an intermolecular 1,3-addition reaction. Whatever the precise nature of the steps after the initial attack, these steps make the methine carbon an electrophilic centre and the nearby triazole ring is apparently a powerful and effective nucleophilic competitor for this centre with acetate ion, either inter- or intra-molecularly, being a poor alternative.

EXPERIMENTAL

M.p.s were measured with an Electrothermal apparatus. I.r. spectra were measured with a Perkin-Elmer Infracord (model 137E) spectrophotometer with sodium chloride optics. Solids were examined as discs with potassium bromide and as Nujol mulls. U.v. spectra were measured with a Unicam SP 800 spectrophotometer and on a Perkin-Elmer model 137 u.v. spectrophotometer with 95% ethanol and glacial acetic acid as solvents. Microanalytical determinations were carried out by Pascher Microanalytical Laboratories, Bonn, and by Mrs. K. M. Duggan of this Department.

Materials.—All the commercially available compounds were purified before use. Lead tetra-acetate was recrystallised from AnalaR acetic acid containing 5% acetic anhydride and dried over potassium hydroxide pellets *in vacuo*. Analysis (iodine–thiosulphate method) of the sample used for the kinetic studies showed a minimum purity of 99·8%. The triazolylhydrazones (I) were prepared as described by Manchot.[26] Data are in Table 2.

Lead Tetra-acetate Oxidations.—Typically, lead tetra-acetate (3·4 g) was added during 10 min to a solution of benzaldehyde 5-phenyl-1,2,4-triazol-3-ylhydrazone (Id) (2 g) in glacial acetic acid (100 ml) and the mixture was stirred for 4 h at ambient temperature. The white precipitate of the triazolotriazole (IId) (1·2 g), m.p. 266° (from aqueous methanol), was removed and, when the filtrate was treated with water (250 ml), a second crop (512 mg; total yield; 1·712 g, 84%) of this compound was obtained. The mother liquor was extracted with ether (4 × 100 ml). The ether was washed with water, extracted with aqueous sodium carbonate solution (solution A), dried, and evaporated and yielded no residue. The basic solution A was acidified with concentrated hydrochloric acid and extracted with ether (4 × 100 ml). The ether was dried and on evaporation yielded crystals (35 mg, 2%), m.p. 225—226° (from 95% ethanol), of N-*acetyl*-N′-*benzoyl*-N-(5-*phenyl*-1,2,4-*triazol*-3-*yl*)*hydrazine* (IIId). Relevant data for a series of such reactions are in Tables 1 and 2. For the hydrazones (Ic) and (If) the N-*acetylhydrazides* (IIIc) and (IIIf) were best isolated by allowing the aqueous acetic acid mother liquor to stand for *ca.* 10 days, after removal of the second crop of the triazolotriazole, when the compounds (III) precipitated. Compound (IIIa) was not encountered.

Hydrazone (Id) *in Acrylonitrile.*—A solution of the hydrazone (Id) (1 g) in acrylonitrile (230 ml) was treated with lead tetra-acetate (1·7 g) and stirred for 2 h at ambient temperature. The precipitated solid consisted of a lead salt and the triazolotetrazole (IId), the former being removed by leaching with boiling water and small quantities of 10% aqueous alcohol. Evaporation of the acrylonitrile solution yielded a similar residue which was separated by the same procedure. The only identifiable organic product was the triazolotriazole (IId) (71%).

Synthesis and Acetylation of the Hydrazides (V).—(a) 5-*Phenyl*-1,2,4-*triazol*-3-*ylhydrazine* (IV). A suspension of the hydrazone (Id) (7 g) in concentrated hydrochloric acid

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[22] W. A. F. Gladstone, J. B. Aylward, and R. O. C. Norman, *J. Chem. Soc.* (*C*), 1969, 2587.

[23] P. Bouchet, J. Elguero, and R. Jacquier, *Bull. Soc. chim. France*, 1967, 4716.

[24] W. A. F. Gladstone, *Chem. Comm.*, 1969, 179; J. B. Aylward, *J. Chem. Soc.* (*C*), 1970, 1494.

[25] H. Reimlinger, *Chem. Ber.*, 1970, **103**, 1900.

[26] M. Manchot, *Ber.*, 1910, **43**, 1313.

(450 ml) was heated and steam was passed through the mixture for 5 h. The resulting solution was evaporated under reduced pressure and the residue dissolved in water (30 ml). When the solution was brought to pH 9 with concentrated ammonia and cooled at 0° for 2 h, white crystals (2·9 g) of compound (IV), m.p. 203° (from 95% alcohol) (lit.,[27] 203—205°) (Found: C, 55·1; H, 5·1; N, 40·0. Calc. for $C_8H_9N_5$: C, 54·9; H, 5·1; N, 40·0%), were obtained. Fractional evaporation of the filtrate under reduced pressure yielded successive drops (total yield 3·75 g, 81%).

TABLE 2

Analytical data

Compound (m.p.) [a]	Found (%) C	Found (%) H	Found (%) N	Formula	Required (%) C	Required (%) H	Required (%) N
(Ia) (205)	66·0	5·0	23·9	$C_{16}H_{15}N_5O$	65·5	5·1	23·9
(Ib) (236)	68·8	5·5	25·2	$C_{16}H_{15}N_5$	69·3	5·4	25·3
(Ic) (217)	70·35	6·05	23·2	$C_{18}H_{19}N_5$	70·8	6·2	22·95
(Ie) (258)	60·0	4·2	23·3	$C_{15}H_{12}ClN_5$	60·5	4·0	23·5
(If) (257)	52·2	3·5	20·5	$C_{15}H_{12}BrN_5$	52·6	3·5	20·5
(Ig) (273)	58·3	3·8	27·2	$C_{15}H_{12}N_6O_2$	58·4	3·9	27·3
(Ih) (260)	58·3	3·85	27·7	$C_{15}H_{12}N_6O_2$	58·4	3·9	27·3
(IIa)	66·2	4·4	23·8	$C_{16}H_{13}N_5O$	66·0	4·5	24·05
(IIb)	69·85	4·7	25·7	$C_{16}H_{13}N_5$	69·8	4·7	25·5
(IIc)	71·0	5·6	22·9	$C_{18}H_{17}N_5$	71·3	5·6	23·1
(IIe) [b]	61·2	3·2	23·3	$C_{15}H_{10}ClN_5$	60·9	3·4	23·7
(IIf) [c]	52·6	3·0	20·45	$C_{15}H_{10}BrN_5$	52·9	2·9	20·6
(IIg)	59·3	3·0	27·2	$C_{15}H_{10}N_6O_2$	58·8	3·3	27·45
(IIIb)	64·7	4·8	20·7	$C_{18}H_{17}N_5O_2$	64·5	5·1	20·9
(IIIc)	66·3	5·8	19·5	$C_{20}H_{20}N_5O_2$	66·3	5·5	19·3
(IIId) [d]	63·55	4·5	21·9	$C_{17}H_{15}N_5O_2$	63·5	4·7	21·8
(IIIe) [e]	57·3	3·7	19·7	$C_{17}H_{14}ClNO_2$	57·4	3·9	19·7
(IIIf) [f]	51·4	3·5	17·6	$C_{17}H_{14}BrN_5O_2$	51·0	3·5	17·5
(IIIg) [g]	55·4	4·0	22·85	$C_{17}H_{14}N_6O_2$	55·7	3·8	22·95

[a] Compounds (I) were recrystallised from aqueous ethanol or aqueous acetic acid. [b] Found: Cl, 11·5. Required: Cl, 12·0%. [c] Found: Br, 23·6. Required: Br, 23·5%. [d] Found: O, 10·2. Required: O, 10·0%. [e] Found: Cl, 10·4. Required: Cl, 10·0%. [f] Found: Br, 19·5; O, 8·5. Required: Br, 20·0; O, 8·0%. [g] Found: O, 17·8. Required: O, 17·5%.

(b) *Hydrazides* (V).—Each of the compounds (V) isolated from the following reactions was hygroscopic. In the analytical data the loss of weight (%) on drying is given as % H_2O.

Benzoyl chloride (0·33 ml) was added with vigorous shaking to a solution of compound (IV) (400 mg) in ice-cold pyridine (20 ml) and the mixture was allowed to stand for 16 h at ambient temperature, poured into ice–water (400 ml), and allowed to stand for 3 days at 0°. The brownish solid (filtrate A), which separated, was extracted with small quantities of water (8 × 20 ml). Evaporation of the extracts yielded the monohydrate of *N*-benzoyl-*N'*-(5-phenyl-1,2,4-triazol-3-yl)hydrazine (Vd) (286 mg, 42%), 215° (from aqueous alcohol) (lit.,[16] 214—216°) (Found: C, 64·5; H, 4·6; N, 25·0; H_2O, 6·2. Calc. for $C_{15}H_{13}N_5O_2H_2O$: C, 64·5; H, 4·7; N, 25·1; H_2O, 6·1%). The water-insoluble material was a gummy residue from which no further pure products could be obtained. Acidification followed by extraction with ether of filtrate A also yielded no further pure products. A similar reaction using *p*-chlorobenzoyl chloride yielded N-p-*chlorobenzoyl*-N'-(3-*phenyl*-1,2,4-*triazol*-5-*yl*)*hydrazine monohydrate* (Ve) (58%), m.p. 255—256° (from 95% alcohol) (Found: C, 57·35; H, 3·7; Cl, 11·5; N, 22·6; O, 5·4; H_2O, 5·2. $C_{15}H_{12}ClN_5,H_2O$ requires C, 57·4; H, 3·8; Cl, 11·3; N, 22·3; O, 5·1; H_2O, 5·4%).

(c) Separate solutions of the compounds (Vd) (150 mg) and (Ve) (150 mg) in mixtures of glacial acetic acid (35 ml) and acetyl chloride (10 ml) were heated under reflux for 30 min, allowed to stand for 12 h at ambient temperature and treated with water (100 ml). When the resulting solutions were extracted with ether, the ethereal layers contained the N-*acetylhydrazides* (IIId) (86%) and (IIIe) (96%). Relevant data are in Tables 1 and 2.

3-*Aryl*-6-*phenyl*-7H-s-*triazolo*[4,3-b]-s-*triazoles*.— 4,5-*Diamino*-3-*aryl*-1,2,4-*triazoles* (VI). The compounds (VIb), m.p. 236—237° (from water) (Found: C, 57·2; H, 5·8; N, 37·2. $C_9H_{11}N_5$ requires C, 57·1; H, 5·8; N, 37·0%), and (VId), m.p. 224° (lit.,[12] 223°) (Found: C, 54·44; H, 5·2; N, 40·3. Calc. for $C_8H_9N_5$: C, 54·9; H, 5·1; N, 40·0%) were prepared by treating the corresponding aroyl thiosemicarbazides [13] with hydrazine hydrate as previously described.[12] To obtain the compounds (VIa), m.p. 243° (from water) (lit.,[12] 242°) (Found: C, 53·0; H, 5·45; N, 33·8. Calc. for $C_9H_{11}N_5O$: C, 52·7; H, 5·4; N, 34·1%), and (VIe), m.p. 237° (from water) (lit.,[12] 236°) (Found: C, 45·7; H, 3·65; N, 33·6. Calc. for $C_8H_8ClN_5$: C, 45·8; H, 3·8; N, 33·4%) it was necessary to use 1-aroyl-*S*-methylisothiosemicarbazides [14] in the reaction with hydrazine. In these latter reactions by doubling the quantity of hydrazine hydrate, which was previously used,[12] higher yields of the diaminotriazoles were obtained at the expense of the other side products.

Treatment of diaminotriazoles (VI) *with aroyl chlorides*. Typically, a solution of compound (VId) (300 mg) in benzoyl chloride (1 ml) and pyridine (10 ml) was heated under reflux for 9·5 h, cooled, and treated with water (12 ml). The monobenzoyl derivative of 3,6-diphenyl-7*H*-*s*-triazolo-[4,3-*b*]-*s*-triazole (VIId) (82%), m.p. 200° (from absolute alcohol) (lit.,[11] 196—198°) (Found: C, 71·9; H, 4·3; N, 18·9. Calc. for $C_{22}H_{15}N_5O$: C, 72·3; H, 4·1; N, 19·2%) separated. Similarly prepared were the following: (i) 3-p-*chlorophenyl derivative* (VIIe) (93%), m.p. 185° (shrinking 140°) (from absolute alcohol) (Found: C, 66·3; H, 3·4; Cl, 9·0; N, 17·5. $C_{22}H_{15}ClN_5O$ requires C, 66·1; H, 3·5;

[27] H. Gehlen and N. Pollok, East Ger. P. 36,433/1965 (*Chem. Abs.*, 1965, **63**, 13,275*d*).

Cl, 8·9; N, 17·5%); (ii) 3-p-*tolyl derivative* (VIIb) (85%), m.p. 221—222° (from absolute alcohol) (Found: C, 73·1; H, 4·5; N, 18·3. $C_{23}H_{17}N_5O$ requires C, 72·8; H, 4·5; N, 18·5%); and (iii) 3-p-*methoxy-derivative* (VIIa) (98%), m.p. 223° (from absolute alcohol) (Found: C, 69·7; H, 4·3; N, 17·9. $C_{23}H_{17}N_5O_2$ requires C, 70·0; H, 4·3; N, 17·7%).

When the compounds (VII) (250 mg) were heated under reflux in mixtures of concentrated hydrochloric acid (1 ml) and 2-ethoxyethanol (10 ml) for 2·5 h and the resulting solutions were evaporated to low volume under reduced pressure, cooled, and neutralised with potassium hydrogen carbonate solution, the triazolotriazoles (II) were obtained in yields greater than 90%. The samples obtained by this procedure were identical (mixed m.p. and i.r. spectra) with those obtained from the lead tetra-acetate reactions.

When the triazolotriazoles (II) were stirred with benzoyl chloride in pyridine at −5° for 14 h, the monobenzoyl derivatives (VII) were obtained in yields of *ca.* 50%.

Kinetic Measurements.—The rates of the lead tetra-acetate oxidations were determined by following the disappearance of the hydrazone absorptions at the wavelengths indicated in Table 1, using a Unicam SP 800B spectrophotometer with an SP 870 constant temperature cell housing an SP 875 electrical control unit. Rate constants, determined at 35 ± 0·2° in glacial acetic acid, are shown in Table 1. Absorption by the products did not interfere with the rate measurements at the wavelengths chosen. The technique employed for the measurements was that developed by King.[28] The concentration of both reactants was 10^{-4}M and all the solutions obeyed the Beer–Lambert Law. The rates were too rapid for mixing of the solutions outside the reaction cell and this was performed quickly in the cell itself. This contrasts with the slower rates observed by Norman and his co-workers.[21] In separate experiments, repeated scanning of reaction solutions over the range 250—450 nm failed to detect absorptions due to any intermediates of the reaction.

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[28] E. L. King, *J. Amer. Chem. Soc.*, 1952, **74**, 563.