in yield of 15–20% in the hydrolysis of triphenyltin-lithium.[6] Furthermore, the reaction of phenyllithium (as well as phenylmagnesium bromide) with methyl triphenylgermanecarboxylate has been investigated,[7] and the product obtained was triphenylgermyldiphenylcarbinol, rather than tetraphenylgermane.

It has been concluded, therefore, that the ability of triphenyltin-lithium to act as a metalating agent cannot be precluded in interpreting the results obtained by d'Ans and co-workers[4] since no evidence of an equilibrium has been obtained in any of the reactions of triphenyltin-lithium with carbonyl systems.

EXPERIMENTAL

All melting points reported here are uncorrected. For compounds melting below 250°, the determinations were made in a silicone-oil bath with a 250° thermometer. For high melting compounds a copper block equipped with a 520° thermometer was employed.

Triphenyltin-lithium. Triphenyltin-lithium was prepared through the reaction[8] of phenyllithium with anhydrous tin (II) chloride. A typical 0.045 mole preparation of triphenyltin-lithium was treated with a solution of 13.3 g. (0.045 mole) of triphenylchlorosilane in 100 ml. of ether according to the method previously described.[5,6] After hydrolysis, 19.6 g. (73%) of crude triphenylsilyltriphenyltin was obtained, melting over the range of 277–285°. This compound was recrystallized from benzene to produce 17.7 g. (65%) of pure triphenylsilyltriphenyltin, melting at 287–289°. A mixture melting point with an authentic specimen was not depressed. This experiment indicates the presence of triphenyltin-lithium in a minimum yield of 65%.

Triphenyltin-lithium with diethyl carbonate. Run I. A solution of 2.36 g. (0.02 mole) of diethyl carbonate in 10 ml. of ether was added rapidly to an ethereal suspension of 0.01 mole of triphenyltin-lithium at −10°. Immediately after this addition, a gas was evolved vigorously which blackened a piece of filter paper moistened with a dilute solution of palladium chloride,[9] thus indicating that the gas was carbon monoxide. The stirred reaction mixture was allowed to come to room temperature, and then stirred at room temperature for 1 hr. The mixture was then poured slowly into aqueous ammonium chloride, the insoluble product was removed by filtration, and the two layers were separated. The insoluble product removed after hydrolysis was recrystallized from benzene to obtain 0.55 g. (14%) of tetraphenyltin, melting at 224°. The ethereal layer was dried, then concentrated to obtain 2.01 g. of amorphous material melting over the range 194–207°. Fractional crystallization of this mixture from carbon disulfide, followed by recrystallization of the fractions from benzene gave 1.40 g. (40%) of hexaphenylditin, melting at 231–232°, and 0.32 g. (8%) of additional tetraphenyltin, melting at 222–223°. The total yield of tetraphenyltin was 22%. Mixture melting points with authentic specimens in each case were not depressed.

No evidence of ethyl benzoate, benzophenone or benzoic acid could be found.

Run II. This reaction did not differ essentially from the one described above except in the size of the run. From the reaction of 0.045 mole of triphenyltin-lithium with 10.6 g. (0.09 mole) of diethyl carbonate essentially the same results were obtained. Carbon monoxide was evolved vigorously (palladium chloride test). After hydrolysis and purification of the products, 7.8 g. (50%) of hexaphenylditin, melting at 230–231°, and 3.46 g. (19.5%) of tetraphenyltin, melting at 221–223° were obtained.

No evidence of ethyl benzoate, benzophenone, or benzoic acid could be found.

Triphenyltin-lithium with ethyl chloroformate. Run I. A solution of 9.7 g. (0.09 mole) of freshly distilled ethyl chloroformate in 25 ml. of ether was added all at once to an ethereal suspension containing 0.045 mole of triphenyltin-lithium at room temperature. Carbon monoxide was vigorously evolved (palladium chloride test). The reaction mixture was stirred at room temperature for a period of 2 hr., then hydrolyzed with water, and the products were isolated in the same manner as was described in the reaction of triphenyltin-lithium with diethyl carbonate. After first separating the products by fractional crystallization from carbon disulfide, they were recrystallized from benzene, to produce 1.3 g. (9.2%) of tetraphenyltin and 8.1 g. (51%) of hexaphenylditin. The products obtained melted at 220–222° and 226–227° respectively, and mixture melting points with authentic specimens were not depressed.

No other products were found in the reaction mixture.

Run II. This reaction was carried out under exactly the same conditions as the reaction described in *Run I*, with the single exception that the reversed order of addition was used; *i.e.*, the 0.045 mole of triphenyltin-lithium suspended in ether was added gradually to 9.7 g. (0.09 mole) of ethyl chloroformate in 25 ml. of ether. After hydrolysis, fractional crystallization, and recrystallization as described above, 1.6 g. (11%) of tetraphenyltin and 8.6 g. (54%) of hexaphenylditin were obtained. These products melted at 220–222° and 228–230° respectively.

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[7] H. Gilman and C. W. Gerow, *J. Am. Chem. Soc.*, **77**, 5740 (1955).

[8] H. Gilman and S. D. Rosenberg, *J. Am. Chem. Soc.*, **74**, 531 (1952).

[9] R. Nowicki, *Chem. Ztg.*, **35**, 1120 (1911).

Polynitrogen Systems from the Hydrazinocarbonic Acids. Part VIII.[1] The Synthesis and Estimation of Some Nitroguanylhydrazones

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The use of nitroaminoguanidine as a reagent for the characterization of carbonyl compounds[3] has been extended in this present note. In addition an effort was made to utilize the Jamieson iodate technique[4] to estimate some nitroguanylhydrazones.

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[1] Part VII, This Series, F. L. Scott, F. C. Britten and J. Reilly, *J. Org. Chem.*, **21**, 1191 (1956).

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[3] Compare (a) R. A. Henry and G. B. L. Smith, *J. Am. Chem. Soc.*, **74**, 278 (1952); (b) W. F. Whitmore, A. J. Revukas, and G. B. L. Smith, *J. Am. Chem. Soc.*, **57**, 706 (1935); (c) G. B. L. Smith and E. P. Shoub, *J. Am. Chem. Soc.*, **59**, 2077 (1937); (d) W. D. Kumler and P. P. T. Sah, *J. Am. Pharm. Assoc.*, **41**, 375 (1952).

[4] (a) G. I. Keim, R. A. Henry, and G. B. L. Smith, *J. Am. Chem. Soc.*, **72**, 4944 (1950); (b) R. A. Henry, R. C. Makosky, and G. B. L. Smith, *J. Am. Chem. Soc.*, **73**, 474 (1951).

The procedure employed involved hydrolysis by acid of the hydrazones followed by titrimetric determination of the liberated hydrazine function with standard iodate solution. With this technique we found it possible to titrate within ±1% both furfuraldehyde and 4-methoxybenzaldehyde nitroguanylhydrazones. Both of these hydrolyses began very rapidly then slowed and required approximately 9 days to reach an endpoint. Under this same analytical procedure neither the acetone, benzaldehyde, (4-methoxy-3-hydroxy)- or (2-hydroxy)benzaldehyde nitroguanylhydrazones afforded satisfactory titers.[5] Part of these latter anomalously low results may be caused by an internal oxidation-reduction reaction which dissipates the hydrazine function of nitroaminoguanidine. A trial run to confirm this possibility revealed that nitroaminoguanidine in strongly acidic aqueous solution at *ca.* 100° lost its hydrazine function at an approximate rate of 2×10^{-3} sec.$^{-1}$ Under the chosen hydrazone hydrolysis conditions this hydrazine dissipation rate is undoubtedly much slower (the rate being $< 1 \times 10^{-7}$ sec.$^{-1}$ at room temperature) but where the hydrazone hydrolysis rate is comparably slow then loss of hydrazine function becomes evident as a complicating factor in the iodate analyses.

EXPERIMENTAL[6]

Nitroguanylhydrazones. Nitroaminoguanidine was prepared by the method of Henry, Makosky, and Smith.[4b] The new hydrazones synthesized were prepared by the standard methods already described in the literature and are summarized in Table I.

Hydrolysis experiments. The following exemplifies the technique employed. To 0.1002 g. of furfuraldehyde nitroguanylhydrazone were added 20 ml. of water, 30 ml. of concentrated hydrochloric acid, and 10 ml. of chloroform.[7] A few ml. of 0.1*N* potassium iodate solution (standardized against reagent grade hydrazine sulfate), were run in, the mixture was vigorously shaken, and then more iodate was added, dropwise, until the purple color, which had developed in the chloroform layer, had disappeared. The mixture was maintained in a dark press, its temperature being maintained at 15 ± 1°C., and, periodically, further aliquots of standard iodate solution were added, the accepted endpoint each time being a colorless chloroform layer. During each addition, the mixture was well agitated. After nine days, a final titer of iodate equivalent to 0.0600 g. of nitroaminoguanidine was obtained. The calculated quantity of nitroaminoguanidine to be liberated was 0.0605 g. Several repeat experiments with this same hydrazone again afforded accuracy of assay to within ±1%. As already mentioned, the 4-methoxybenzylidene analogue (again with a nine-day period required for attainment of final endpoint), also had the experimental and calculated iodate titers within ±1%. The 2-hydroxybenzylidene nitroguanylhydrazone after 28 days had only liberated approximately half the calculated

TABLE I

SOME NITROGUANYL HYDRAZONES

Carbonyl Compound	Product Formula	Physical Appearance	M.p., °C.	Yield, %	Analyses Carbon Calcd.	Analyses Carbon Found	Analyses Hydrogen Calcd.	Analyses Hydrogen Found	Analyses Nitrogen Calcd.	Analyses Nitrogen Found
Acraldehyde	$C_4H_7N_5O_2$	Cream-colored powder[a]	165	77	30.6	30.6	4.5	4.4	—	—
Alloxane	$C_5H_9N_7O_7$[b]	Salmon-colored powder[c]	198[d]	90	21.5	21.7	3.2	3.2	—	—
Alloxane	$C_5H_5N_7O_5$	Brick-red powder[e]	251	90	24.7	24.8	2.1	2.4	40.3	40.0
4-Aminoacetophenone	$C_9H_{12}N_6O_2$	Yellow microcrystals[f]	203	90	45.8	45.7	5.1	5.0	35.6	35.2
Benzylidene acetone	$C_{11}H_{13}N_5O_2$	Ivory platelets[g]	181	91	53.4	53.6	5.3	5.2	—	—
2,4-Dinitrobenzaldehyde	$C_8H_7N_7O_6$	Cream powder[f]	240	97	32.3	32.9	2.4	2.4	33.0	32.6
Methyl benzyl ketone	$C_{10}H_{13}N_5O_2$	Colorless plates[h]	174[i]	92	51.1	50.9	5.5	5.5	—	—
Methyl nonyl ketone	$C_{12}H_{25}N_5O_2$	White microcrystals[g]	114[j]	80	53.1	52.8	9.2	9.2	—	—
3,4-Dihydroxybenzaldehyde	$C_8H_9N_5O_4$	Yellow flakes[e,f,k]	232	97	40.2	40.1	3.8	3.9	29.3	28.7
Pyruvic aldehyde	$C_5H_{10}N_{10}O_4$[l]	Yellow powder[h]	344[m]	92	21.9	21.5	3.7	3.8	51.1	50.9
2-Thiophene aldehyde	$C_6H_7N_5SO_2$	Lemon, fibrous needles[g]	199	87	33.8	34.2	3.3	3.1	32.9	32.4[n]
Terephthaldehyde	$C_{10}H_{12}N_{10}O_4$[l]	Yellow powder[o]	254[d,p]	92	35.7	36.0	3.6	3.9	—	—

[a] From 50% aqueous ethanol. [b] Physical data recorded are for the dihydrate. [c] Directly as isolated, under the standard conditions, without further purification. [d] Melts with decomposition. [e] From boiling water. [f] From aqueous acetic acid. [g] From 75% ethanol. [h] From absolute ethanol. [i] Darkens prior to melting. [j] Softens at 110°. [k] Photosensitive and readily oxidized. [l] Physical data recorded are for the dihydrazone. [m] Melts with explosive decomposition. [n] Calcd.: S, 15.0. Found: S, 14.9, 15.1. [o] Very insoluble, hence merely washed repeatedly with boiling water and boiling ethanol. [p] M.p. varies markedly with rate of heating.

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[5] Similar difficulties in the estimation of benzaldehydehyde nitroguanylhydrazone have been mentioned in the interesting paper of W. R. McBride, R. A. Henry, and S. Skolnik, *Anal. Chem.*, **25**, 1042 (1953).

[6] All melting points are uncorrected. All microanalyses are by Drs. Wieler and Strauss, Oxford, England.

[7] Purified as described in A. I. Vogel, *A Textbook of Practical Organic Chemistry*, 2nd ed., page 174, Longmans, Green and Co., London, 1951.

quantity of nitroaminoguanidine and its final titer was *ca.* 30% too low. The 3-hydroxy-4-methoxy analogue prove impossible to analyze as after an eight-day period, the chloroform layer acquired a permanent red color which completely obscured the visual endpoint sought. The titrimetric endpoints obtained with both the acetone and benzaldehyde nitroguanylhydrazones were also some 40 and 20% too low respectively.[5] These low values suggested that perhaps nitroaminoguanidine had lost some of its hydrazine function under the given analysis conditions. A trial confirmed that this was possible. Thus, when a number of *ca.* 0.1 g. samples of nitroaminoguanidine, dissolved in 20 ml. of water and 30 ml. of concentrated hydrochloric acid were heated on a steam bath for varying periods of time (5–30 minutes), and then, after quenching the reaction by immersion of the reaction solutions in ice, titrated with iodate as before, a loss of hydrazine function with a rate constant of roughly 2×10^{-3} sec.$^{-1}$ was observed. Under conditions more closely related, temperature-wise, to the hydrazone hydrolyses but involving much greater time intervals (20–90 days) than the previous blank trials, nitroaminoguanidine was again discovered to undergo partial loss of hydrazine function. While this hydrazine dissipation may not be the sole cause of the anomalous iodate values, in any event it can demonstrably be accepted as a factor therein particularly with those hydrazones which prove slowest to hydrolyze.

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Polynitrogen Systems from the Hydrazinocarbonic Acids. Part IX.[1] The Synthesis and Bromination of Some 5-Tetrazolyl- and Related -hydrazones

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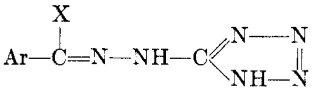
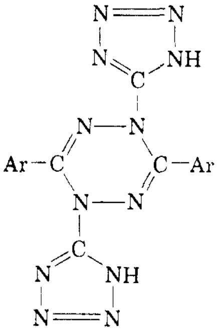
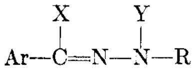
We have developed the utility of 5-hydrazinotetrazole as a means of characterizing carbonyl compounds somewhat more fully than the scattered literature data[3] thereon previously achieved. Some preliminary observations have also been made on the possibility of ω-bromination of the 5-tetrazolylhydrazones (I). The reactions encountered with the benzylidene derivative (IA) typify the complexities involved. When IA was brominated under the standard conditions utilized, namely, using equimolar quantities of bromine and hydrazone in glacial acetic acid solution (or suspension) at room temperature, it formed apparently the crude ω-bromo derivative (IB). This when crystallized from anhydrous chloroform was obtained pure. When it was boiled in glacial acetic acid, it dehalogenated and reverted to the parent hydrazone (IA). When refluxed in 50% aqueous ethanol for a few minutes IB was oxidized and the hydrogen-abstracted derivative so isolated may possibly be the tetrazine (IIA).[4] When IA was treated with an excess of bromine, again in glacial acetic acid medium, considerable hydrolysis of the hydrazone accompanied the ω-bromination effected. Finally, when IA was allowed to react in an excess of bromine without any additional solvent ring—as well as ω—bromination occurred, yielding most probably IC. The 3-nitrobenzylidene analogue of IA, *viz.*,



I, A, Ar = C_6H_5, X = H;
B, Ar = C_6H_5, X = Br;
C, Ar = 4(?)Br—C_6H_4, X = Br;
D, Ar = 3—NO_2—C_6H_4, X = H

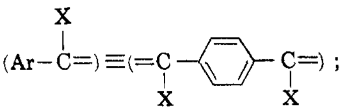


II, A, Ar = C_6H_5;
B, Ar = 3—NO_2—C_6H_4



$$\mathrm{Ar{-}\overset{\overset{\large X}{|}}{C}{=}N{-}\overset{\overset{\large Y}{|}}{N}{-}R}$$

III, A, X = Br, Y = H;
B*, R = C(=NH)—NH—NO_2;

C*,  ;

D, X = H, Y = C(=O)—C_6H_5, R = C(=NH)—NH—C(=O)—C_6H_5;
E, X = NH_2, Y and R as in D;
For substances starred (*), X = Y = H

$(Ar—CH=N—NH—)_2C=N—R$
IV, A, R = H;
B, R = (—N=CH—Ar).

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(2) To whom inquiries concerning reprints are to be sent. Present address, Department of Chemistry, University of California, Los Angeles 24, Calif.

(3) *Vide* (a) J. Thiele and H. Ingle, *Ann.*, **287**, 233 (1895); (b) J. Thiele and J. T. Marais, *Ann.*, **273**, 144 (1893); (c) J. Thiele, *Ann.*, **303**, 66 (1898); (d) K. A. Hofmann, H. Hock, and H. Kirmreuther, *Ann.*, **380**, 131 (1911); (e) F. L. Scott, D. G. O'Donovan, and J. Reilly, *J. Appl. Chem.*, **2**, 368 (1952).

(4) Compare: F. D. Chattaway and A. J. Walker, *J. Chem. Soc.*, **127**, 975, 1687 (1925); F. D. Chattaway and A. B. Adamson, *J. Chem. Soc.*, 157, 843 (1930); F. D. Chattaway and G. D. Parkes, *J. Chem. Soc.*, 113 (1926); F. D. Chattaway, T. Deighton, and A. Adair, *J. Chem. Soc.*, 1925 (1931); F. D. Chattaway and A. B. Adamson, *J. Chem. Soc.*, 2787, 2792 (1931); F. D. Chattaway and H. Irving, *J. Chem. Soc.*, 90 (1935).