Thallation-Iodination Studies of Heterocyclic Systems

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The thallation-iodination of 3-carbonylindoles (**4a-f**) results in orientation control with substitution occurring at the 4-position (**6a-f**). Also described is the dithallation of *N*-methylpyrrole-2-carboxaldehyde (**2**).

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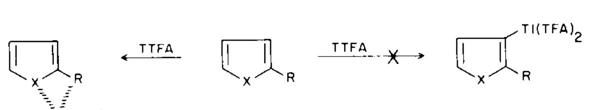
The utility of thallium in organic synthesis has been rapidly and elegantly demonstrated (3) since Taylor and McKillop gave impetus to the methodic study of this interesting element. We have been particularly interested in extending the applications of thallium(III) tris-trifluoroacetate (TTFA) in electrophilic aromatic substitution and recently reported the regiospecific thallation-iodination of certain diarylketones (4). Benzenoid aromatics have received the most attention and the relative lack of reports regarding the thallation of heterocycles (4-8) is particularly noteworthy considering the obvious synthetic advantages which might be gained in this area.

Our initial efforts (1) were directed toward studies of the simpler five-membered ring heterocycles (**1a-f**) having a 2-substituent capable of complexation-orientation of TTFA. Despite the reported mono- (6-8) and even dithallation (7,8) of thiophenes, all attempts to affect reaction of thiophene and furan derivatives **1a-f** with TTFA resulted in recovered starting material. We did note, however, that added TTFA significantly modified the pmr spectra of many substrates, leading us to conclude that possibly both side chain and ring heteroatoms were complexing simultaneously with thallium thus impeding its delivery into the 3-position (Scheme I).

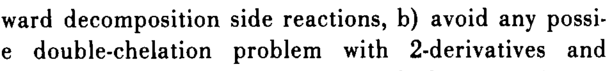
Scheme I



1a, X=S, R=CHO
b, X=S, R=CO$_2$H
c, X=S, R=CO$_2$Et
d, X=S, R=OAc
e, X=O, R=CH$_2$OH
f, X=O, R=CO$_2$Et

Working under this assumption of bidentate chelation, we decided to test an *N*-methylpyrrole derivative as this should both electronically and sterically disfavor complexation at the 1-position. The reaction of *N*-methylpyrrole-2-carboxaldehyde (**2**) was very slow, but use of a 10 molar excess of TTFA allowed the total consumption of starting substrate in 48 hours at room temperature. Attempted isolation of the intermediate led to its decomposition, so the reaction was repeated and treated directly with aqueous potassium iodide. Workup led, unexpectedly, to the isolation of *N*-methyl-3,4-diiodopyrrole-2-carboxaldehyde (**3**) in a 54% yield (Scheme II). For dithallation of **2**, one might predict 3,5-disubstitution, however, assignment of structure **3** was made based upon the observed coupling of H5 with the aldehyde proton (J = 1.5 Hz), which has been studied in this system (9). That dithallation may have occurred is not unique (7,8,10), however, such vicinal substitution would be unprecedented. The treatment of **2** with lesser amounts of TTFA led to decomposition and the simultaneous treatment of TTFA and aqueous potassium idodie led to recovered starting material.

Scheme II



2 3

We next turned out attention to the indole system. Preliminary attempts to thallate indole or 3-alkyl derivatives only resulted in the decomposition of starting materials. We then decided to investigate 3-carbonyl derivatives as we felt this should a) deactivate the system toward decomposition side reactions, b) avoid any possible double-chelation problem with 2-derivatives and c) allow us to study orientation control where sites in two different rings (positions 2 and 4) might compete.

Thallation orientation by carbonyl groups has been limited to reports on carboxylic acids and esters, but our recent results with ketones (4) and aldehyde **2** prompted us to examine the readily obtainable acyl derivatives indole-3-carboxaldehyde (**4a**) and 3-acetylindole (**4e**). Surprisingly, reaction with TTFA in trifluoroacetic acid (TFA) was complete in both cases in less than two hours at room temperature. We then prepared and successfully thallated several methyl derivatives (**4b-d,f**) of these substrates. In all cases, thallation occurred exclusively at the 4-position and the crude intermediates (**5a-f**) were readily transform-

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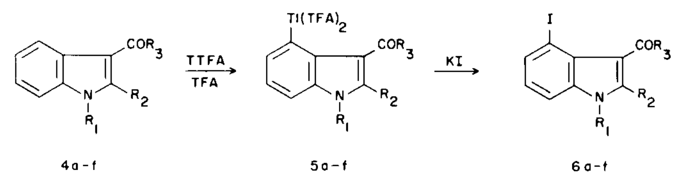
ed into the corresponding 4-iodo derivatives (**6a-f**) by treatment with potassium iodide (Scheme III). Thallation was slower in the case of *N*-methyl derivatives (**4b,d,f**) and with the 1,2-dimethyl derivative **4d** additional steric buttressing makes the reaction incomplete even after prolonged treatment with TTFA.

Scheme III



a; $R_1 = R_2 = R_3 = H$

b; $R_1 = CH_3, R_2 = R_3 = H$

c; $R_2 = CH_3, R_1 = R_3 = H$

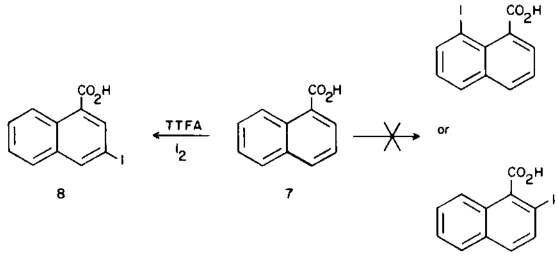
d; $R_1 = R_2 = CH_3, R_3 = H$

e; $R_3 = CH_3, R_1 = R_2 = H$

f; $R_1 = R_3 = CH_3, R_2 = H$

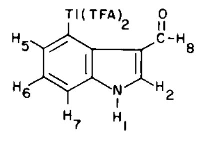
Preferential thallation in the 4-position is easily rationalized by assuming first that thallium coordinates with the carbonyl group and secondly that the two-position is simply more strongly deactivated. Studies of the nitration of aldehydes **4a-d** under a variety of reaction conditions have shown that although the 4-position was never the favored site for substitution, the 2-position was totally unreactive (11-15). Our demonstration of orientation to a "peri" position is in contrast with the results of Carruthers and Pooranamoorthy (16) who showed that thallation-iodination of 1-naphthalenecarboxylic acid (**7**) led neither to 2- nor to 8- substitution, but resulted unexpectedly in the formation of the 3-iodo derivative **8** (Scheme IV).

Scheme IV



The pmr spectral data of compounds **5a-f** and **6a-f** appear at first glance to fit for either a 4- or a 7-substituted indole inasmuch as the remaining three benzene-ring protons are adjacent. A more careful analysis, however, is consistent only with the assigned structures. The pmr spectrum of 4-(3-formylindolyl)thallium (III) bis-trifluoroacetate **5a**, for example, presents the following chemical shifts and coupling constants (Figure I):

Figure I



5a

H_1 δ 12.6; $J_{TlH_1} = 120$ Hz

H_2 δ 8.50; uncoupled

H_8 δ 9.90; $J_{TlH_8} = 78$ Hz

H_5 δ 7.6; $J_{TlH_5} = 920$ Hz

$J_{H_5H_6} = 8$ Hz

H_6 δ 7.4; $J_{TlH_6} = 280$ Hz

$J_{H_5H_6} = J_{H_6H_7} = 8$ Hz

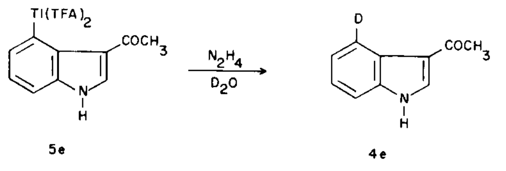
H_7 δ 7.7; $J_{TlH_7} = 125$ Hz

$J_{H_6H_7} = 8$ Hz

A priori, one cannot preclude the possibility of long-range coupling between the aldehyde proton (H_8) and a nucleus at position 7, however, the observed value for J_{TlH_8} of 78 Hz seems more reasonable for thallium in the nearer 4-position. Also, as J_{TlH} values are approximately 130 times larger than corresponding J_{HH} values (17), the value $J_{Tl_4H_1} = 120$ Hz is in accord with the observed $J_{H_1H_4} = 0.8$ Hz for indole (18). And finally, the low-field signal corresponding to the highly deshielded ($\delta > 8$ ppm) 4-protons of 3-carbonylindoles is absent in the spectra of the thallated intermediates. The pmr spectra of the iodo-compounds (**6a-f**) would also be "possible" for 4- or 7-substitution if, again, it were not for the lack of a signal corresponding to a deshielded 4-proton. Also, the close proximity of iodine and the carbonyl group is evidenced by a deshielding, by more than 1 ppm, of the aldehyde protons of **6a-d** relative to the corresponding unsubstituted substrates (**4a-d**), an effect documented for *o*-substituted aromatic aldehydes (19).

Although we felt no doubt remained as to the position of substitution, we accidentally obtained conclusive evidence for our assignments. Investigating the possibility of synthesizing new heterocyclic systems by treating aqueous suspensions of the thallated intermediates with hydrazine, we observed reduction of the Tl-C bond (20), regenerating unsubstituted starting materials. The reduction by hydrazine of thallium(III) sulfate to thallium (I) sulfate has been reported (21). Substituting deuterium oxide (99.8%) for water and using 95% hydrazine, the reduction of **5e** produced "**4e**" (80% yield) with no detectable signal for H-4 in the pmr spectrum and, as expected, a modification of the remaining aromatic multiplet (Scheme V). The reduction also proceeds with **5a**, but the yield is very low as concomitant hydrazone formation appears to be occurring.

Scheme V



5e

4e

We have only investigated the iodination (and reduction) of the thallated intermediates **5a-f**, but presumably the numerous methods available for transforming C-Tl bonds (C-I bonds as well) would be applicable to these and other derivatives, thus providing direct routes to a variety of 4-substituted indoles avoiding more difficult classical syntheses.

EXPERIMENTAL

The ir spectra were obtained on a Perkin-Elmer model PE 180 spectrophotometer. The pmr spectra were recorded on a Hitachi Perkin-Elmer R-20B (60 MHz) nuclear magnetic resonance spectrometer. All melting points are uncorrected. Starting 3-carbonylindoles **4b-f** were prepared according to literature procedures and presented correct melting points and pmr spectra (22-26). Crude arylthallium(III) bis-trifluoroacetates (**5a-f**) were used for pmr spectra and subsequent iodination reactions.

General Methods.

Thallation of 3-Caronylindoles. Method A.

In a 25 ml. flask, protected from light, was placed a mixture of 3 mmoles of indole substrate, 3 mmoles of TTFA and 5 ml. of trifluoroacetic acid. After stirring for 2 hours at room temperature, the mixture was cooled to -10° until crystallization was complete, the supernatent liquid was decanted and the remaining solid washed with 1,2-dichloroethane.

Method B.

In a 25 ml. flask, protected from light, was heated at reflux for two hours a mixture of 3 mmoles of indole substrate, 3 mmoles of TTFA and 10 ml. of trifluoroacetic acid. After cooling, the trifluoroacetic acid was evaporated at reduced pressure, ether added and evaporated at reduced presure (2X) and the remaining solid collected by filtration and washed with ether.

Iodination of Arylthallium(III) Bis-trifluoroacetates. Method C.

A mixture of 1 mmole of arylthallium(III) bis-trifluoroacetate and 1 g. of potassium iodide in 5-10 ml. of water was stirred for 3 hours at room temperature. The reaction mixture was filtered and the precipitate extracted in a Soxhlet apparatus with chloroform. The extract was dried over magnesium sulfate, evaporated, redissolved in chloroform, filtered and evaporated once again.

Method D.

A mixture of 1 mmole of arylthallium(III) bis-trifluoroacetate and 1 g. of potassium iodide in 5-10 ml. of water was stirred for 3 hours at room temperature. The mixture was extracted with chloroform, dried over magnesium sulfate and then evaporated at reduced pressure. The residue was redissolved in chloroform, filtered and evaporated once again.

N-Methyl-3,4-diiodopyrrole-2-Carboxaldehyde (3).

A mixture of 1.1 g. (0.01 mole) of *N*-methylpyrrole-2-carboxaldehyde (**2**) and 54 g. (0.1 mole) of TTFA in 100 ml. of trifluoroacetic acid was allowed to stand at room temperature for 48 hours in a closed flask protected from light. A solution of 3 g. of potassium iodide in 50 ml. of water was then added, the mixture stirred for 10 minutes and then decolorized by addition of small portions of sodium metabisulfite. The mixture was extracted with ether (5 × 50 ml.) and the combined extracts washed with water (5 × 50 ml.) then with 50 ml. of a 5% aqueous sodium bicarbonate solution. After drying over magnesium sulfate and evaporation of solvent, the solid residue was chromatographed over silica gel with benzene and the product recrystallized from ethanol giving 1.94 g. (54%) of colorless crystals, m.p. 143°; ir (potassium bromide): 3120 cm^{-1} (C*H*O) and 1655 cm^{-1} (C=O); pmr (deuteriochloroform): δ 9.50 (d, 1, CHO, J = 1.5 Hz), 7.32 (d, 1, ArH, J = 1.5 Hz) and 3.98 (s, 3, CH_3).

Anal. Calcd. for $C_6H_5NI_2O$: C, 19.97; H, 1.40; N, 3.88. Found: C, 19.85; H, 1.29; N, 3.78.

4-(3-Formylindolyl)thallium(III) Bis-trifluoroacetate (5a).

Prepared by Method A, there was obtained 1.12 g. (65%) of colorless crystals, m.p. 210-220° dec.; pmr (dimethylsulfoxide-d_6): δ 12.6 (d, 1, H_1, J_{TlH_1} = 120 Hz), 9.9 (d, 1, CHO, J_{TlH} = 78 Hz), 8.50 (s, 1, H_2), 7.7 (dd, 1, H_7, J_{TlH_7} = 125 Hz, $J_{6,7}$ = 8 Hz), 7.6 (dd, 1, H_5, J_{TlH_5} = 920 Hz, $J_{5,6}$ = 8 Hz) and 7.4 (dt, 1, H_6, J_{TlH_6} = 280 Hz, $J_{5,6}$ = 8 Hz, $J_{6,7}$ = 8 Hz).

4-*N*-Methyl-3-formylindolyl)thallium(III) Bis-trifluoroacetate (5b).

Prepared by Method B, there was obtained 1.08 g. (62%) of colorless crystals, m.p. 240-250° dec.

4-(2-Methyl-3-formylindolyl)thallium(III) Bis-trifluoroacetate (5c).

Prepared by Method A, there was obtained 1.45 g. (82%) of a colorless solid, m.p. 250-270° dec.

4-(1,2-Dimethyl-3-formylindolyl)thallium(III) Bis-trifluoroacetate (5d).

In a 25 ml. flask, protected from light, was placed a mixture of 0.53 g. of **4d**, 1.63 g. of TTFA and 5 ml. of trifluoroacetic acid which was maintained at room temperature for 16 hours. The mixture was then diluted with 5 ml. of water and maintained at 0° until crystallization was complete. After filtration and washing with ether, there was obtained 1.1 g. (61%) of colorless crystals, m.p. 180-200° dec.

4-(3-Acetylindolyl)thallium(III) Bis-trifluoroacetate (5e).

Prepared by Method A, there was obtained 0.98 g. (55%) of colorless crystals, m.p. 220-225° dec.; pmr (dimethylsulfoxide-d_6): δ 12.8 (d, 1, H_1, J_{TlH_1} = 150 Hz), 8.65 (d, 1, H_2, $J_{1,2}$ = 4 Hz), 7.7 (d, 1, H_6; J_{TlH_6} = 360 Hz), 7.6 (d, 1, H_7, J_{TlH_7} = 150 Hz), 7.1 (d, 1, H_5, J_{TlH_5} = 1080 Hz) and 2.5 (s, 3, CH_3).

4-(*N*-Methyl-3-acetylindolyl)thallium(III) Bis-trifluoroacetate (5f).

Prepared by Method B, there was obtained 1.0 g. (57%) of a colorless solid, m.p. 180-200° dec.

4-Iodoindole-3-Carboxaldehyde (6a).

Prepared by Method C, there was obtained 0.16 g. (60%) of off-white crystals, m.p. 182-183°; ir (potassium bromide): 3170 cm^{-1} (NH) and 1630 cm^{-1} (C=O); pmr (acetone-d_6): δ 11.08 (s, 1, CHO); 8.21 (d, 1, H_2, $J_{1,2}$ = 4 Hz), 7.7 (dd, 1, H_5, $J_{5,6}$ = 7.5 Hz; $J_{5,7}$ = 1.5 Hz), 7.65 (dd, 1, H_7, $J_{6,7}$ = 7.5 Hz; $J_{5,7}$ = 1.5 Hz) and 6.97 (dd, 1, H_6, $J_{5,6}$ = 7.5 Hz, $J_{6,7}$ = 7.5 Hz).

Anal. Calcd. for C_9H_6NIO: C, 39.88; H, 2.23; N, 5.17. Found: C, 40.13; H, 2.28; N, 4.88.

N-Methyl-4-iodoindole-3-carboxaldehyde (6b).

Prepared by Method C, there was obtained 0.185 g. (65%) of a tan solid, m.p. 146-148°; ir (potassium bromide): 1650 cm^{-1} (C=O); pmr (deuteriochloroform): δ 11.05 (s, 1, CHO), 7.85 (s, 1, H_2), 7.7 (dd, 1, H_5, $J_{5,6}$ = 7.5 Hz; $J_{5,7}$ 1.5 Hz), 7.32 (dd, 1, H_7, $J_{6,7}$ = 7.5 Hz; $J_{5,7}$ = 1.5 Hz), 6.93 (dd, 1, H_6, $J_{5,6}$ = 7.5 Hz; $J_{6,7}$ = 7.5 Hz) and 3.8 (s, 3, CH_3).

Anal. Calcd. for $C_{10}H_8NIO$: C, 42.13; H, 2.83; N, 4.91. Found: C, 42.17; H, 2.95; N, 5.10.

2-Methyl-4-iodoindole-3-carboxaldehyde (6c).

Prepared by Method C, there was obtained 0.172 g. (60%) of light-tan solid, m.p. 172-174°; ir (potassium bromide): 3100 cm^{-1} (NH) and 1625 cm^{-1} (C=O); pmr (acetone-d_6): δ 11.9 (bs, 1, H_1), 11.23 (s, 1, CHO), 7.68 (dd, 1, H_5, $J_{5,6}$ = 7 5 Hz; $J_{5,7}$ = 1.5 Hz), 7.5 (dd, 1, H_7, $J_{6,7}$ = 7.5 Hz; $J_{5,7}$ = 1.5 Hz), 6.87 (dd, 1, H_6, $J_{5,6}$ = 7.5 Hz, $J_{6,7}$ = 7.5 Hz) and 2.75 (s, 3, CH_3).

Anal. Calcd. for $C_{10}H_8NIO$: C, 42.13; H, 2.83; N, 4.91. Found: C, 41.76; H, 2.68; N, 4.84.

1,2-Dimethyl-4-iodoindole-3-carboxaldehyde (6d).

Prepared by Method C, there was obtained 0.160 g. (54%) of light-tan solid contaminated with a small amount of **4d**. Recrystallization from carbon tetrachloride furnished off-white crystals, m.p. 140-142°; ir (potassium bromide): 1640 cm^{-1} (C=O); pmr (deuteriochloroform): δ 11.2 (s, 1, CHO), 7.63 (dd, 1, H_5, $J_{5,6}$ = 7.5 Hz; $J_{5,7}$ = 1.5 Hz), 7.33 (dd, 1,

H_7, $J_{6,7}$ = 7.5 Hz; $J_{5,7}$ = 1.5 Hz), 6.83 (dd, 1, H_6, $J_{5,6}$ = 7.5 Hz, $J_{6,7}$ = 7.5 Hz), 3.62 (s, 3, NCH_3) and 2.69 (s, 3, CH_3).

Anal. Calcd. for $C_{11}H_{10}NIO$: C, 44.17; H, 3.37; N, 4.68. Found: C, 44.02; H, 3.18; N, 4.58.

4-Iodo-3-acetylindole (**6e**).

Prepared by Method D, there was obtained 0.125 g. (75%) of off-white crystals, m.p. 204-206° dec.; ir (potassium bromide): 3150 cm^{-1} (NH) and 1640 cm^{-1} (C=O); pmr (dimethylsulfoxide-d_6): δ 12.1 (bs, 1, H_1), 8.3 (d, 1, H_2, $J_{1,2}$ = 4 Hz), 7.7 (dd, 1, H_5, $J_{5,6}$ = 7.5 Hz; $J_{5,7}$ = 1.5 Hz), 7.5 (dd, 1, H_7, $J_{6,7}$ = 7.5 Hz; $J_{5,7}$ = 1.5 Hz), 6.9 (dd, 1, H_6, $J_{5,6}$ = 7.5 Hz; $J_{6,7}$ = 7.5 Hz) and 2.5 (s, 3, CH_3).

Anal. Calcd. for $C_{10}H_8NIO$: C, 42.13; H, 2.85; N, 4.91. Found: C, 41.94; H, 3.00; N, 4.85.

N-Methyl-4-iodo-3-acetylindole (**6f**).

Prepared by Method D, there was obtained 0.20 g. (67%) of an off-white solid, m.p. 135-136°; ir (potassium bromide): 1650 cm^{-1} (C=O); pmr (deuteriochloroform): δ 7.75 (dd, 1, H_5, $J_{5,6}$ = 7.5 Hz; $J_{5,7}$ = 1.5 Hz), 7.55 (s, 1, H_2), 7.22 (dd, 1, H_7, $J_{6,7}$ = 7.5 Hz; $J_{5,7}$ = 1.5 Hz), 6.87 (dd, 1, H_6, $J_{5,6}$ = 7.5 Hz; $J_{6,7}$ = 7.5 Hz), 3.71 (s, 3, NCH_3) and 2.58 (s, 3, CH_3).

Anal. Calcd. for $C_{11}H_{10}NIO$: C, 44.17; H, 3.37; N, 4.68. Found: C, 43.87; H, 3.52; N, 4.41.

Reduction of **5e** with Hydrazine in Water.

A mixture of 0.59 g. of **5e**, 0.3 ml. of 85% hydrazine hydrate and 5 ml. of water was stirred at room temperature for 1 hour. The mixture was extracted with chloroform (2 × 25 ml.) and the combined extracts washed with water (2 × 50 ml.), dried over magnesium sulfate and evaporated furnishing 127 mg. (80%) of 3-acetylindole (**4e**) identical in all respects with an authentic sample; m.p. 190-192° (lit. (27) 191-193°).

Reduction of **5e** with Hydrazine in Deuterium Oxide.

A 0.59 g. sample of **5e** was added to a mixture (equilibrated for 24 hours) of 0.1 ml. of 95% hydrazine and 5 ml. of deuterium oxide (99.8%) and stirred for 1 hour. The mixture was then extracted with chloroform (2 × 25 ml.) and the combined extracts washed with water (2 × 50 ml.), dried over magnesium sulfate and evaporated furnishing 130 mg. (82%) of 4-deuterio-3-acetylindole with tlc behavior identical to **4e**, m.p. 189-192°; pmr (acetic acid-d_6): δ 8.08 (s, 1, H_2), 7.1-7.6 (m, 3, ArH) and 2.53 (s, 3, CH_3).

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REFERENCES AND NOTES

(1) V. M. S. carried out the studies on the thiophene, furan and pyrrole systems.

(2) M. C. S. made the initial investigations of the indole system.

(3) A. McKillop and E. C. Taylor, *Chem. Br.*, **9**, 4 (1973).

(4) R. A. Hollins and V. M. Salim, *Tetrahedron Letters* 591 (1979).

(5) H. Gilman and R. K. Abbott, Jr., *J. Am. Chem. Soc.*, **65**, 122 (1943).

(6) A. McKillop, J. S. Fowler, M. J. Zelesko, J. D. Hunt, E. C. Taylor and G. M. McGillivray, *Tetrahedron Letters*, 2427 (1969).

(7) A. McKillop, J. S. Fowler, M. J. Zelesko, J. D. Hunt, E. C. Taylor, F. Kienzle and G. McGillivray, *J. Am. Chem. Soc.*, **93**, 4841 (1971).

(8) G. B. Deacon, D. Tunaley and in part R. N. M. Smith, *J. Organomet. Chem.*, **144**, 111 (1978).

(9) T. J. Batterham, "NMR Spectra of Simple Heterocycles", E. C. Taylor and A. Weissberger, Eds., Wiley-Interscience, New York, N. Y., 1973, Ch. 3.

(10) G. B. Deacon, R. N. M. Smith and D. Tunaley, *J. Organomet Chem.*, **114**, Cl (1976).

(11) A. Da Settimo, *Gazz. Chim. Ital.*, **92**, 150 (1962).

(12) G. Berti, A. Da Settimo and D. Livi, *Tetrahedron*, **20**, 1397 (1964).

(13) A. Da Settimo and M. F. Saettone, *ibid.*, **21**, 1923 (1965).

(14) W. E. Noland and R. D. Rieke, *J. Org. Chem.*, **27**, 2250 (1962).

(15) W. E. Noland, L. R. Smith and K. R. Rush, *ibid.*, **30**, 3457 (1965).

(16) N. Carruthers and R. Pooranamoorthy, *J. Chem. Soc., Perkin Trans. I*, 2405 (1974).

(17) A. McKillop, J. D. Hunt and E. C. Taylor, *J. Organomet. Chem.*, **24**, 77 (1970).

(18) A. R. Katritzky and A. J. Boulton in "Advances in Heterocyclic Chemistry", S. P. Hiremath and R. S. Hosmane, Eds., Vol. 15, 287 (1973).

(19) R. E. Klinck and J. B. Stothers, *Can. J. Chem.*, **40**, 1071 (1962).

(20) The manuscript is in preparation on the general applicability of this reaction.

(21) A. G. Lee, "The Chemistry of Thallium", Elsevier Publishing Company, New York, N. Y., 1971.

(22) P. N. James and H. R. Snyder, "Organic Syntheses", Col. Vol. IV, Wiley, New York, N. Y., 1963, p. 539.

(23) R. C. Blume and H. G. Lindwall, *J. Org. Chem.*, **10**, 255 (1945).

(24) E. Leete, *J. Am. Chem. Soc.*, **81**, 6025 (1959).

(25) H. Wieland, W. Konz and H. Mittasch, *Ann. Chem.*, **513**, 1 (1934).

(26) Y. A. Baskakov and N. N. M. Solbrinik, *Sb. Statei Obshch. Khim., Adad. Nauk, USSR*, **1**, 712 (1953).

(27) W. C. Anthony, *J. Org. Chem.*, **25**, 2049 (1960).