from a mixture of isopropyl ether and hexane afforded 1.35 g (92%) of pale yellow needles, mp 139–141°.

Anal. Calcd for $C_{15}H_{17}N_5O_3$: C, 57.13; H, 5.43; N, 22.21. Found: C, 56.90; H, 5.42; N, 21.93.

2-Phenyl-4-amino-6-methylpteridine (**9b**).—A solution of 1.0 g of **6b** in 100 ml of ethanol was hydrogenated over 100 mg of 10% Pd/C at room temperature and 50 psi of hydrogen pressure until the uptake of hydrogen ceased. The catalyst was removed by filtration and the solution was evaporated under reduced pressure to afford a yellow oil. This was dissolved in 100 ml of water to which had been added several drops of concentrated hydrochloric acid. The solution was kept at room temperature under an atmosphere of nitrogen overnight. The solution was neutralized with aqueous sodium bicarbonate solution, and the yellow solid which formed was collected by filtration and treated with activated manganese dioxide in THF containing magnesium sulfate. After several hours, the solution was filtered and evaporated and the resulting dark oil was dissolved in cold dilute hydrochloric acid to give a homogeneous solution which was decolorized with charcoal and neutralized with aqueous sodium bicarbonate. The resulting precipitate was collected by filtration and recrystallized from methanol to afford 0.51 g (60%) of pale yellow plates, mp 242–244° (lit.[7] mp 240–241°). Its nmr spectrum was identical with the reported spectrum.[6]

5-Phenyl-7-acetylhydrazinofurazano[3,4-*d*]pyrimidine (**10a**).—A suspension of 2.00 g (9.38 mmol) of 5-phenyl-7-aminofurazano-[3,4-*d*]pyrimidine (**1**) and 3.44 g (46.8 mmol) of acethydrazide in 40 ml of 1 *N* ethanolic hydrogen chloride was stirred at room temperature for 24 hr and filtered, and the collected solid was recrystallized from ethanol to give 1.58 g (63%) of fine yellow needles, mp 266–267° dec.

Anal. Calcd for $C_{12}H_{10}N_6O_2$: C, 53.33; H, 3.73; N, 31.10. Found: C, 53.50; H, 3.83; N, 31.32.

5-Amino-3-methyl-7-phenylpyrimido[5,4-*e*]-*as*-triazine (**12a**).—A suspension of 0.30 g (1.11 mmol) of **10a** in 25 ml of ethanol containing 0.05 g of 10% Pd/C and 1.1 ml of 1 *N* ethanolic hydrogen chloride was shaken under 1 atm of hydrogen at room temperature until the hydrogen uptake ceased. The mixture was then refluxed for 2 hr and cooled, isoamyl nitrite (0.30 ml) was added, and stirring was continued for 16 hr at room temperature. Filtration through a Celite pad, evaporation of the filtrate under reduced pressure, and addition of water afforded an orange solid which was recrystallized from aqueous dimethylformamide to give 0.14 g (53%) of orange needles: mp 237° dec; uv $\lambda_{\max}^{C_2H_5OH}$ 2.51 nm (log ϵ 3.73), 290 (3.93), 382 (2.96); nmr (DMSO-d_6) δ 3.08 (3 H, s), 7.6 (3 H, m), 8.5 (2 H, m), 9.0 (2 H, br, NH_2).

Anal. Calcd for $C_{12}H_{10}N_6$: C, 60.49; H, 4.23; N, 35.28. Found: C, 60.21; H, 4.08; N, 35.28.

5-Phenyl-7-benzoylhydrazinofurazano[3,4-*d*]pyrimidine (**10b**).—A suspension of 0.50 g (2.32 mmol) of **1** and 1.59 g (11.7 mmol) of benzhydrazide in 15 ml of 1 *N* ethanolic hydrogen chloride was stirred for 24 hr at room temperature and then filtered. The collected solid was recrystallized from ethanol to give 0.42 g (54%) of powdery flakes, mp 258–259° dec.

Anal. Calcd for $C_{17}H_{12}N_6O_2$: C, 61.44; H, 3.64; N, 25.29. Found: C, 61.64; H, 3.53; N, 25.02.

5-Amino-3,7-diphenylpyrimido[5,4-*e*]-*as*-triazine (**12b**).—A suspension of 0.25 g (0.75 mmol) of **10a** in 25 ml of ethanol containing 10% Pd/C was shaken under 1 atm of hydrogen at room temperature until hydrogen uptake ceased, 5 ml of 1 *N* ethanolic hydrogen chloride was added, the mixture was heated to boiling and filtered through Celite, and the filtrate then refluxed for 2 hr. Isoamyl nitrite (0.25 ml) was added, and the mixture was stirred for 24 hr at room temperature, neutralized with sodium bicarbonate, and concentrated to dryness under reduced pressure. The residue was triturated with water and then filtered. Recrystallization of the collected solid from aqueous dimethylformamide gave 0.18 g (80%) of fine yellow plates: mp >300°; uv $\lambda_{\max}^{C_2H_5OH}$ 254 nm (log ϵ 3.70), 307 (4.22), 396 (3.34); nmr (DMSO-d_6) δ 7.68, 8.5–9.0 (12 H, m).

Anal. Calcd for $C_{17}H_{12}N_6$: C, 67.99; H, 4.03; N, 27.99. Found: C, 67.70; H, 4.15; N, 27.98.

Registry No.—**1**, 30720-36-6; **6a**, 39550-16-8; **6b**, 39550-17-9; **7a**, 39550-18-0; **9a**, 1084-59-9; **9b**, 19830-37-6; **10a**, 39550-21-5; **10b**, 39550-22-6; **12a**, 39550-23-7; **12b**, 39550-24-8; aminoacetaldehyde diethyl acetal, 645-36-3; aminoacetone diethyl acetal, 39550-25-9; acethydrazide, 1068-57-1.

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Reactions of Vinyl Acetate with Carbazole

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Organic transformations brought about by thallium(I) and thallium(III) compounds have received considerable attention.[1] Recently we have demonstrated the usefulness of thallium(I) ethoxide as a base for the alkylation, under mild conditions, of carbazole, phenothiazine, and to a lesser extent 5*H*-dibenz[*b*,*f*]-azepine.[2] A notable feature of this reaction is that alkylation employing thallium(I) ethoxide as the base, unlike those employing potassium metal or potassium amide, is subject to steric limitations, and can only be used for the introduction of primary alkyl groups.

We now wish to report a further instance of the differing behavior of carbazole in reactions induced by potassium hydroxide and thallium(I) ethoxide, respectively.

Lopatinski, *et al.*,[3] have shown that carbazole, vinyl acetate, and potassium hydroxide react in acetone at −10 to −20° to afford *N*-(α-acetoxyethyl)carbazole (**1a**). We have repeated this reaction and confirmed the identity of the product **1a**, although the reaction is best carried out below −30°. Upon treatment with methanol the ester **1a** is converted to *N*-(α-methoxyethyl)carbazole (**1b**), and this product was found to be identical with authentic material prepared from methanol and *N*-vinylcarbazole.[4]

In complete contrast, the reaction of vinyl acetate with carbazole and thallium(I) ethoxide at room temperature in DMF–ether afforded *N*-acetylcarbazole (57%) together with an insoluble, light-sensitive thallium compound. This material was tentatively identified as vinyloxythallium(I) (**3**); however, during subsequent manipulation of this unstable compound an insertion reaction[5] with atmospheric carbon dioxide occurred producing vinylcarbonatothallium (**4**). The infrared spectrum of **4** showed bands at 1550 (br) and 1020 and 920 cm^{-1}, appropriate to a carbonato[6] and vinyl group, respectively. No molecular ion could be detected in the mass spectrum; however, an ion at *m/e* 249 was identified as $^{205}TlCO_2$ by accurate mass measurement.

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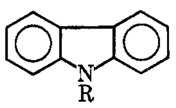
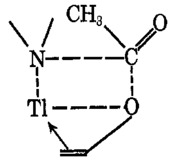
It is proposed that the thallium(I)-induced reaction of carbazole and vinyl acetate occurs *via* a four-center transition state (**2**) in which an important factor is coordination between the vinyl group and thallium,[7] since this reaction fails when the substrate is a simple ester, *e.g.*, ethyl acetate, or a sterically hindered ester, *e.g.*, vinyl pivalate or vinyl benzoate.



1a, R = CHMeOCOMe
b, R = CHMeOMe
c, R = COMe



2

$CH_2{=}CHOTl$

3

$CH_2{=}CHOCO_2Tl$

4

The potassium-induced reaction is envisaged as occurring *via* addition of potassium carbazole to the carbonyl group of vinyl acetate, and subsequent attack by a carbazolyl anion at the activated α-carbon atom (*cf.*[8] reactivity of vinyl ethers toward nucleophiles); likewise this reaction fails with sterically hindered esters (vinyl pivalate).

The differing mechanisms which operate for the thallium(I)- and potassium-induced reactions are seen to reflect the bonding in the respective metal–nitrogen bonds. Gray[9] has interpreted the somewhat short Tl–N distance (2.98 Å) in thallium(I) azide (*cf.* K–N 2.96 Å in potassium azide; ionic radii Tl^+ 1.49, K^+ 1.33) as indicating that the thallium–nitrogen bond is partially covalent. Further evidence in support of the proposed four-center reaction mechanism is available from Pearson's hard–soft acid–base principle.[10] Thallium(I) is a soft Lewis acid, whereas potassium (K^+) is a hard Lewis acid, and the former would be expected to exhibit a much greater tendency to coordinate to the vinyl group.

It is interesting to note that reaction of carbazole with vinyl acetate catalyzed by mercury(II) compounds yields exclusively *N*-vinylcarbazole.[11]

Experimental Section

Ir spectra were recorded for Nujol mulls. Mass spectra were measured by the Physico-Chemical Measurements Unit, Harwell. ^1H nmr spectra were recorded at 60 MHz with tetramethylsilane as internal standard.

N-Acetylcarbazole, mp 68–69° (lit.[12] mp 68–69°), was prepared from carbazole and acetic anhydride, as described.[11] *N*-(α-Methoxyethyl)carbazole, mp 88–90° (lit.[4] mp 89–90), was prepared from *N*-vinylcarbazole and methanol.

***N*-(α-Acetoxyethyl)carbazole.**—Vinyl acetate (10 g) was added dropwise to a stirred mixture of carbazole (10 g) and powdered potassium hydroxide (0.5 g) in acetone (25 ml) cooled in a carbon tetrachloride–Dry Ice bath (*ca.* −35°). The reaction mixture was stirred for 2 hr and then allowed to warm up to room temperature and filtered. The filtrate was evaporated and the resulting oil was recrystallized from petrol (bp 40–60°) to afford *N*-(α-acetoxyethyl)carbazole[13] (8.5 g, 57%): mp 87–88° (lit.[3] mp 85–87°); ν_{max} 1745, 1730 (C=O), 1598, 1490, 1335, 1238, 1210, 1155, 1085, 1058, 1010, 985, 920, 750, and 720 cm^{-1}; nmr τ [$(CD_3)_2CO$] 1.9–3.0 (9 H, m, ArH and NCHO–), 8.05 (3 H, s, $COCH_3$), and 8.16 (3 H, d, J = 7 Hz, CH_3); mass spectrum *m/e* (rel intensity) 253 (M^+, 12), 194 ($M - MeCO_2$, 20), 193 ($M - C_2H_4O_2$, 42), 192 (10), 168 (12), 167 ($M - C_4H_6O_2$, 100), 166 (14), 140 (20), and 139 (10).

N-(α-Acetoxyethyl)carbazole was refluxed in methanol for 0.5 hr to afford *N*-(α-methoxyethyl)carbazole, mp and mmp 86–88° (lit.[4] mp 89–90°), from methanol: nmr [$(CD_3)_2CO$] 1.9–3.1 (8 H, m, ArH), 4.55 (1 H, q, J = 7 Hz, NCHO), 6.91 (3 H, s, $COCH_3$), and 8.32 (3 H, d, CH_3).

Reaction of Vinyl Acetate with Carbazole and Thallium(I) Ethoxide.—Thallium(I) ethoxide (3.0 g) was added to a solution of carbazole (1.7 g) in DMF–ether (25 ml, 1:1 v/v), and the mixture was stirred at room temperature for 0.5 hr. Vinyl acetate (4.0 g) was then added and the mixture was stirred at room temperature for a further 2 hr, during which time a white precipitate was deposited. The reaction mixture was filtered free of solid material and poured into water, and the aqueous mixture was extracted with ether and dried ($MgSO_4$). Evaporation afforded an oil which was recrystallized from aqueous methanol to give *N*-acetylcarbazole (1.2 g, 57%), mp and mmp 68–70° (lit.[12] mp 68–69°).

The precipitate (1.0 g), mp 80–85° dec, which discolored upon standing in daylight, was tentatively identified as vinyloxythallium(I). *Anal.* Calcd for C_2H_3TlO: C, 9.7; H, 1.2. Found: C, 9.7, H, 1.2. Upon standing this material reacted with carbon dioxide (air) to form vinylcarbonatothallium: ν_{max} 1620–1500 (br, carbonate), 1285, 1210, 1015, 950, and 920 cm^{-1} (vinyl); mass spectrum *m/e* (rel intensity) 249/247 ($M - C_2H_3O$, 23/5), 221/219 ($M - C_3H_3O_2$, 2/1), 205/203 (100/47, $^{205}Tl^+/^{203}Tl^+$), 60 (60), 45 (72), and 43 (81); measured mass 246.9621 (calcd for $CO_2{}^{203}Tl$, 246.9631).

Registry No.—**3**, 39542-29-5; **4**, 39542-30-8; vinyl acetate, 108-05-4; carbazole, 86-74-8; thallium(I) ethoxide, 20398-06-5.

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(13) This material was stored below 5°.

A Novel Aryl Cyanide Synthesis Using Trichloroacetonitrile

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Although there exist a great number of ways to effect dehydration of aldoximes, interest in this area remains unabated.[1] Since most methods either utilize acidic reagents or are attended by the generation of acidic side products which might be detrimental to sensitive molecules, the development of procedures involving strictly neutral conditions is highly desirable. We wish to report a novel method for converting aryl aldoximes to the corresponding cyanides which fulfills this criterion; furthermore, the present procedure is simple, efficient, and economical.

Trichloroacetonitrile exhibits a remarkable capability of mediating the replacement of a hydroxy group by chlorine[2] under very mild conditions; it is also useful

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