afforded **5b**·H_2O (3.00 g, 53% based on **1b**) as a grayish solid. HPLC indicated 95% purity. The product was shown to be identical with an authentic sample of guanosine H_2O.

Method B. 9-(Phenylmethyl)guanine (5f). **3f** (2.75 g, 10 mmol) and sodium tungstate (0.1 g) were suspended in 6 N sodium hydroxide (20 mL) at 5 °C; 35% hydrogen peroxide (4.0 mL, 44 mmol) was added dropwise at 5–15 °C over 30 min. Water (60 mL) was added to the resulting mixture, and after additional stirring on an ice bath for 1 h, the pH was adjusted to 5 with dilute HCl. The product separated and was isolated by filtration, washed with water, and dried to afford pure **5f** (1.30 g, 54%). The product was identical with **5f** prepared by method A. Compounds **5c–e** were prepared in similar yields by the same procedure.

9-[(2-Hydroxyethoxy)methyl]guanine (Acyclovir) (5h). **3h** (2.59 g, 10.0 mmol) and sodium tungstate (0.05 g) were dissolved in 6 N sodium hydroxide (20 mL) at 5 °C; 35% hydrogen peroxide (4.0 mL, 44 mmol) was added dropwise at 5–15 °C over 15 min, and stirring on an ice bath was continued for additionally 15 min, after which time HPLC indicated formation of the title compound in 59% yield. The pH was adjusted to 5.5 with 4 N acetic acid, and the product was isolated by filtration, washed with water, and dried to afford **5h**·$^3/_4H_2O$ (1.13 g, 50%) as a white solid identical with **5h** prepared by method A.

Registry No. **1a**, 360-97-4; **1**·HCl, 72-40-2; **1b**, 2627-69-2; **1c**, 21343-04-4; **1d**, 67790-32-3; **1e**, 61507-88-8; **1f**, 3815-69-8; **1g**, 118966-30-6; **1h**, 77856-29-2; **1i**, 131490-62-5; **2c**, 131490-63-6; **2d**, 131490-64-7; **2e**, 131490-65-8; **2f**, 131490-66-9; **3c**, 131490-67-0; **3d**, 131490-68-1; **3e**, 131490-69-2; **3f**, 131490-70-5; **3h**, 131490-71-6; **3i**, 131490-72-7; **5b**, 118-00-3; **5c**, 5502-78-3; **5d**, 879-08-3; **5e**, 22917-85-7; **5f**, 14937-72-5; **5h**, 59277-89-3; **5i**, 82410-32-0; MeBr, 74-83-9; PrBr, 106-94-5; $PhCH_2Cl$, 100-44-7; $ClCH_2OCH_2CH_2OAc$, 40510-88-1; EtBr, 74-96-4; $(PhCH_2OCH_2)_2CHOCH_2Cl$, 74564-16-2; PhCONCS, 532-55-8.

1-(Carbazol-9-ylmethyl)benzotriazole Anion: A Formyl Anion Equivalent

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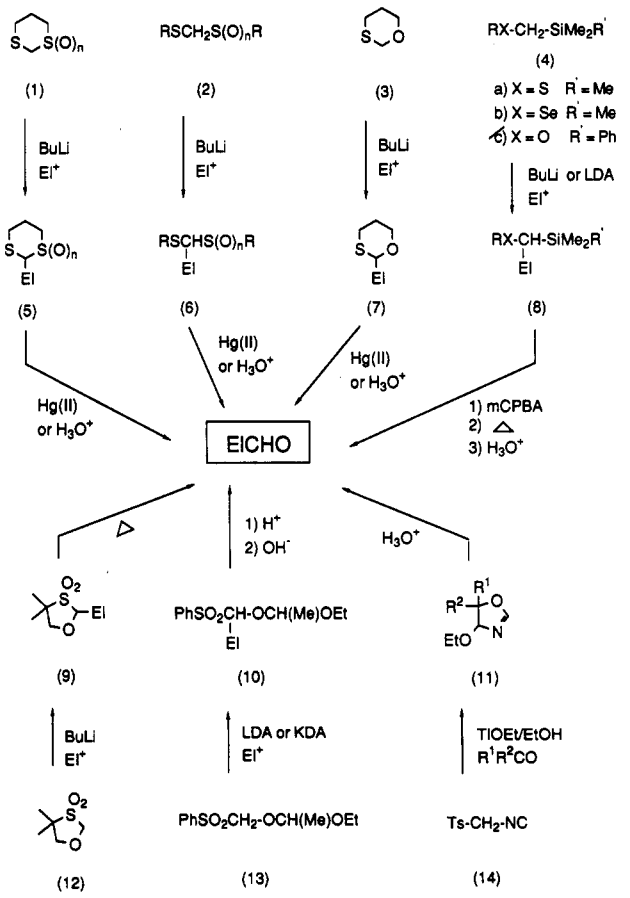
The title anion, readily available as its lithium derivative, smoothly reacts with a wide range of electrophiles to give well-characterized products which are easily hydrolyzed to the corresponding aldehydes in high overall yields. The method is compared with currently available routes.

Introduction

As lack of stability greatly limits the use of formyl ($^-$C-H=O) and acyl ($^-$CR=O) anions,[1] various masked synthons have been developed.[2] Important formyl anion equivalents are of the type XYCH$^-$ where X and Y are heteroatoms (Scheme I). Dithioformyls employed include the 1,3-dithione[3] (**1**; n = 0), and bis(alkylthio)[4] (**2**; R = alkyl, n = 0), bis(arylthio)[5] (**2**; R = Ar, n = 0), and cyclic[6] analogues. Thioacetals with one sulfur atom oxidized (e.g., **1**, **2**; n = 1) have also been used.[7] Anions generated by e.g. treatment with n-butyllithium,[8] or by lithium or sodium amide in liquid ammonia,[4] with electrophiles give the corresponding thioacetals (**5–7**), which are converted to the aldehydes by complex formation with a metal ion (usually mercury(II) salts[9]) or by making one sulfur atom more electrophilic through oxidation.[10]

Other sulfur analogues used include 1,3-oxathianes[11] (**3**), α-thio silanes[12] (**4a**), α-functionalized sulfones[13,14] (**12**, **13**)

Scheme I



and TosMIC[15] (**14**). Oxidation of **8** followed by a sila-Pummerer rearrangement affords the *O*-(trimethylsilyl)-

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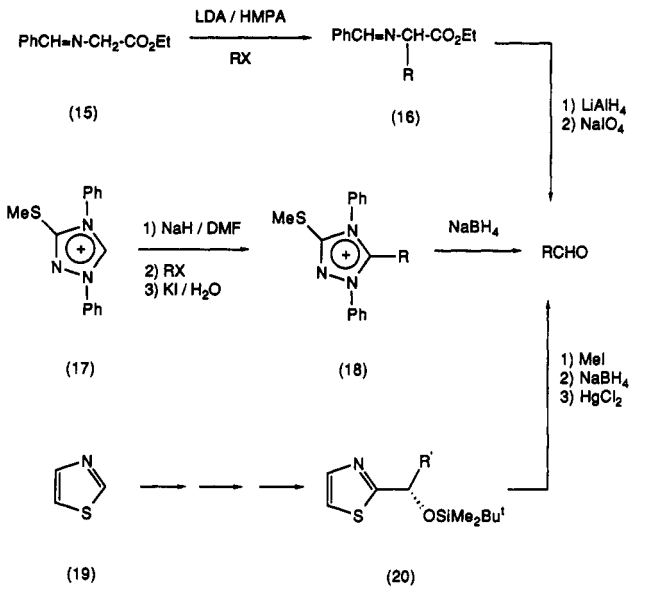
Scheme II

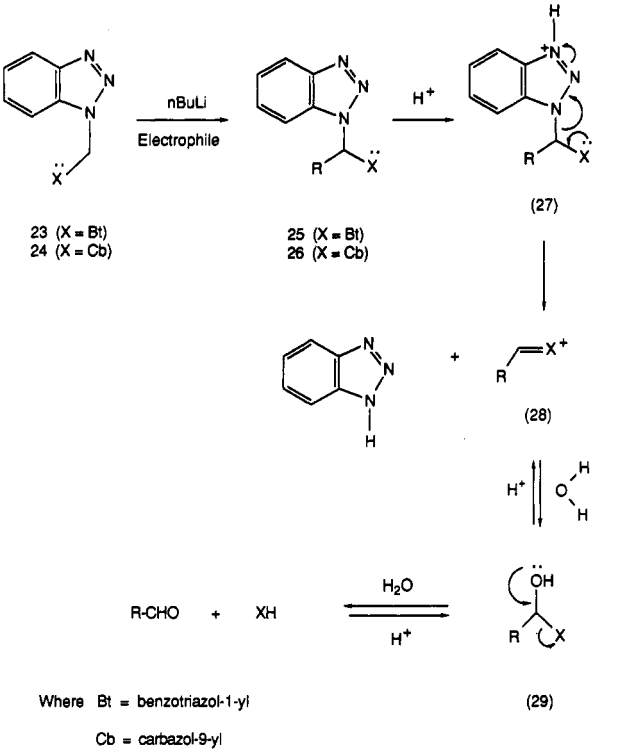


thioacetal;[16] hydrolysis by acid or base then affords the aldehydes. Similarly to the α-thiosilanes, (phenylseleno)(trimethylsilyl)methane (**4b**) has been used.[17] Recently methoxy(phenyldimethylsilyl)methyllithium[18] (**4c**) with carbonyl compounds has afforded β-hydroxy silanes which were converted to the α-hydroxy aldehydes by acetic anhydride, hydrogen peroxide, *m*-chloroperbenzoic acid and bromine, or potassium bromide.

These reactions are subject to various limitations. The hemithioacetal anions **3** react readily with alkyl iodides, but yields with bromides and other types of electrophiles are low to moderate.[11] The α-thio silanes **4a** react only with a limited number of electrophiles to afford **8**, since with carbonyl compounds vinyl sulfides are obtained.[19] For the α-functional sulfones **12**, only the alkyl derivatives **9** have been converted to the aldehydes via pyrolysis.[13] Few examples are known of the linear analogues **13** which require KDA instead of LDA for condensation with carbonyl compounds.[14] TosMIC (**14**) undergoes alkylation under phase-transfer conditions,[20] but for reaction with carbonyl compounds, thallium ethoxide is required to form the oxazoline (**11**) which is hydrolyzed to the α-hydroxy aldehyde.[15] Recently BetMIC (1-benzotriazolylmethyl isocyanide), used in place of TosMIC, did not need thallium for the preparation of α-hydroxy aldehydes.[21]

Another class of formyl anion equivalents X(Y:)C⁻ (Scheme II) require a subsequent reduction step. They include the substituted imines[22] **15** which react with alkyl halides forming intermediates **16**; subsequent reduction with lithium aluminum hydride and sodium periodate

Scheme III



gives modest yields of the aldehydes.[22] 3-(Methylthio)-1,4-diphenyl-*s*-triazolium iodide[23] (**17**) reacts with alkyl halides; reduction of the products with sodium borohydride then affords the aldehydes. However, use of both of these reagents is apparently limited to reactions with alkyl halides as electrophiles. Dondoni[24] et al. have advantageously used thiazole (**19**) which affords a high level of diastereoselectivity during the reduction of acylthiazoles containing an α-chiral center.[25] Deprotection is a one-pot operation requiring a sequence of reagents (methyl iodide, reflux; sodium borohydride, −10 °C; and finally mercury(II) chloride).

As mentioned previously, the formyl carbon is usually attached to two heteroatoms. However, little attention has been paid to systems where the two heteroatoms are parts of separate heterocycles. We now report such a system which can react with a variety of electrophiles followed by hydrolysis of the resulting adducts to afford a series of α-functionalized aldehydes.

Benzotriazole is a readily available precursor forming Mannich adducts with aldehydes and amines,[26,27] amides,[28] and many other nitrogen systems. The high electron withdrawing nature of benzotriazole also makes it a good leaving group which has been displaced by a variety of nucleophiles.[29] Benzotriazolyl groups have also been removed under acidic conditions as seen in the hydrolysis of *p*-[bis(benzotriazol-1-yl)methyl]toluene derivatives **21** to afford aryl ketones[30] or in tris(benzotriazolyl)methyl

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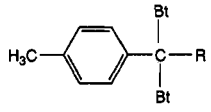
Table I. Reaction of Bis(benzotriazol-1-yl)methane (23) and 1-(Carbazol-9-ylmethyl)benzotriazole (24) with Electrophiles (23 → 25) and (24 → 26), Respectively

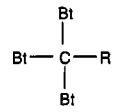
compd	electrophile [E]	yield (%)	mp (°C)	crystal form (recryst solvent)	molecular formula	found (required)
25a	$PhCH_2Br$ [$PhCH_2$]	46	182–184	microcrystals (MeOH)	$C_{27}H_{22}N_6$	75.01 5.10 19.95 (75.33 5.15 19.52)
25b	4-Me-C_6H_4CHO [4-Me-$C_6H_4CH(OH)$]	70	197–199	microcrystals (MeOH)	$C_{21}H_{18}N_6O$	67.87 4.88 22.82 (68.11 4.86 22.70)
25c	4-Me-C_6H_4COOEt [4-Me-C_6H_4CO]	76	181–183	microcrystals (MeOH)	$C_{21}H_{16}N_6O$	68.41 4.26 22.93 (68.48 4.35 22.83)
26a	$PhCH_2Br$ [$PhCH_2$]	81	129–130	plates (MeOH)	$C_{26}H_{20}N_4$	[32]
26b	4-Br-$C_6H_4CH_2Br$ [4-Br-$C_6H_4CH_2$]	78	141–142	needles (MeOH)	$C_{26}H_{19}BrN_4$	66.56 4.06 11.80 (66.82 4.10 11.99)
26c	n-$C_8H_{17}Br$ [n-C_8H_{17}]	71	112–114	microcrystals [a]	$C_{27}H_{30}N_4$	79.41 7.21 13.38 (79.02 7.32 13.66)
26d	n-C_4H_9I [n-C_4H_9]	84	135–137	needles (MeOH)	$C_{23}H_{22}N_4$	77.90 6.23 15.89 (77.97 6.21 15.82)
26e	4-Me-C_6H_4CHO [4-Me-$C_6H_4CH(OH)$]	82	234–235	needles (MeOH)	$C_{27}H_{22}N_4O$	[32]
26f	$(CH_3)_2CHCHO$ [$(CH_3)_2CHCH(OH)$]	91	222–224	plates (MeOH)	$C_{23}H_{22}N_4O$	[32]
26g	$(CH_3)_3CCHO$ [$(CH_3)_3CCH(OH)$]	96	218–220	plates (MeOH/AcOEt)	$C_{24}H_{24}N_4O$	75.35 6.41 14.70 (75.00 6.25 14.58)
26h	$(C_2H_5)CO$ [$(C_2H_5)_2C(OH)$]	86	154–156	plates (petroleum ether/ether)	$C_{24}H_{24}N_4O$	74.78 6.34 14.55 (74.97 6.29 14.57)
26i	$(CH_2)_5CO$ [$(CH_2)_5C(OH)$]	91	194–196	plates (MeOH)	$C_{25}H_{24}N_4O$	75.85 6.18 14.27 (75.73 6.10 14.13)
26j	$(CH_2)_4CO$ [$(CH_2)_4C(OH)$]	84	197–198	plates (MeOH)	$C_{24}H_{22}N_4O$	75.34 5.78 14.96 (75.37 5.80 14.65)
26k	PhNCS [PhNHC(=S)]	78	178–179	plates (MeOH/AcOEt)	$C_{26}H_{19}N_5S$	72.14 4.37 16.29 (72.03 4.42 16.15)
26l	PhNCO [PhNHC(=O)]	93	201–202	plates (MeOH)	$C_{26}H_{19}N_5O$	74.52 4.51 16.84 (74.80 4.59 16.78)
26m	$PhCO_2C_2H_5$ [PhC(=O)]	88	89–90	plates (petroleum ether/ether)	$C_{26}H_{18}N_4O$	[32]
26n	$(Ph)_2C{=}O$ [$(Ph)_2C(OH)$]	94	193–194	plates (MeOH/AcOEt)	$C_{32}H_{24}N_4O$	80.29 5.04 11.59 (79.98 5.03 11.66)

[a] By column chromatography (hexane–chloroform, 1:1).

derivatives (**22**) to form carboxylic acids.[31] It was believed that other bis(*N*-heteroaryl)methyl derivatives could be similarly hydrolyzed to afford aldehydes.



(21)



(22)

Results and Discussion

Bis(benzotriazol-1-yl)methane (**23**) undergoes smooth lithiation with *n*-butyllithium at −78 °C and the anion reacted with benzyl bromide and carbonyl compounds to form the corresponding adducts (**25**) (Scheme III) in yields of 46–76% (see Table I). With benzyl bromide, only the disubstituted adduct was obtained. However, attempts to hydrolyze the adducts using conditions ranging from 1 to 10 M hydrochloric acid in tetrahydrofuran, reflux conditions or using 55% sulfuric acid still failed to generate the aldehydes (or in the case of **25a**, the ketone) satisfactorily. Benzotriazole is electron-withdrawing in nature and evidently there is insufficient nucleophilic assistance from the one benzotriazole moiety to displace the second protonated benzotriazole from the intermediate (**27**) when R = alkyl or acyl, in contrast to the success of such hydrolysis when R = aryl[30] as mentioned above.

We selected carbazole as the other heterocycle which with a greater electron donor effect should assist in the displacement of benzotriazole but not simultaneously deactivate the methylene group towards lithiation (Scheme III). Indeed, 1-(carbazol-9-ylmethyl)benzotriazole (**24**) was previously shown to undergo easy metalation, and we reported reactions of the anion with benzyl bromide, isobutyraldehyde, and ethyl benzoate to afford the adducts **26** in good yields.[32] We now show that the anion of **24** reacts with a wide range of alkyl halides, aldehydes, ketones, esters, isocyanates, and isothiocyanates to form the corresponding products in good yields. Furthermore, as expected, these derivatives can be rapidly and smoothly hydrolyzed to the corresponding aldehydes by dilute mineral acid at ambient temperature.

The reaction of 1-(carbazol-9-ylmethyl)benzotriazole (**24**) with *n*-butyllithium at −78 °C in tetrahydrofuran affords a pale yellow solution of the anion. Subsequent treatment with various electrophiles (see Table I) yielded 71–96% of pure crystalline products which were characterized by their microanalyses data and ^1H and ^{13}C NMR spectra (Tables II and III in the supplementary material). Absence of the methylene carbon resonance at 54.4 ppm in the ^{13}C NMR spectra of the crude products indicated the reactions went to completion. The corresponding methine carbon of the pure products resonated downfield between 67 and 75 ppm.

Hydrolysis of the benzoyl derivatives **26m** with 4 equiv of 10 M hydrochloric acid in methanol afforded 9-(α-methoxyphenacyl)carbazole (**30**) as a colorless oil upon workup (Scheme IV). The ^1H and ^{13}C NMR spectra

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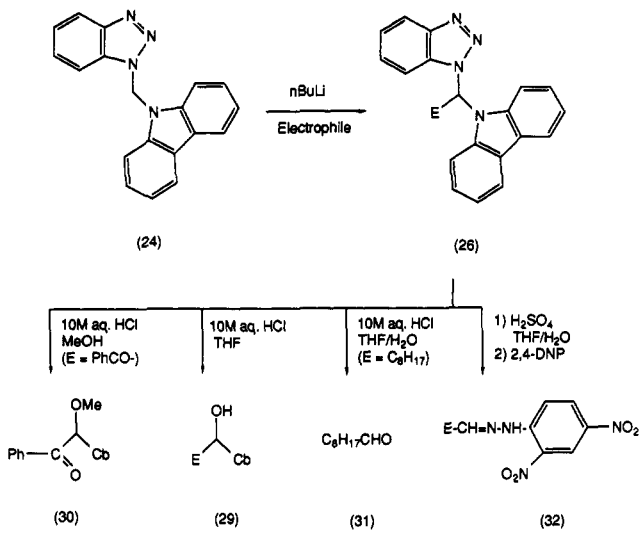
Table IV. Hydrolysis of Adducts 26a–l to the Aldehydes [E-CH=N-NH-C_6H_3-2,4-$(NO_2)_2$] (32a–l)

product	E	method	yield (%)	mp (°C)	lit. mp (°C)	molecular formula	found (required)
32a	$PhCH_2$	A	78	134–136	120–121[a]	$C_{14}H_{12}N_4O_4$	55.72 3.92 18.59 (56.00 4.00 18.67)
32b	4-Br-$C_6H_4CH_2$	B	81	153–154	–	$C_{14}H_{12}BrN_4O_4$	43.84 2.79 14.71 (44.15 2.92 14.78)
32c	*n*-C_8H_{17}	A	67	103–104	106[b]	$C_{15}H_{22}N_4O_4$	56.19 6.95 17.47 (55.89 6.88 17.38)
32d	*n*-C_4H_9	B	83	107–108	102–104[c]	$C_{11}H_{14}N_4O_4$	– – –
32e	4-Me-$C_6H_4CH(OH)$	B	42	178–179	–	$C_{15}H_{14}N_4O_5$	54.83 4.17 17.19 (54.55 4.27 16.96)
32f	$(CH_3)_2CHCH(OH)$	B	76	131–132	–	$C_{11}H_{14}N_4O_5$	46.85 4.97 20.13 (46.81 5.00 19.95)
32g	$(CH_3)_3CCH(OH)$	B	71	155–156	–	$C_{12}H_{16}N_4O_5$	48.81 5.44 19.19 (48.65 5.41 18.92)
32h	$(C_2H_5)_2C(OH)$	B	73	182–184	–	$C_{12}H_{16}N_4O_5$	48.72 5.44 19.20 (48.65 5.41 18.92)
32i	$(CH_2)_5C(OH)$	B	71	171–172	217–218[d]	$C_{13}H_{16}N_4O_5$	50.65 5.24 18.35 (50.65 5.23 18.17)
32j	$(CH_2)_4C(OH)$	B	61	182–184	–	$C_{12}H_{14}N_4O_5$	48.26 4.70 19.17 (48.58 4.80 19.04)
32k	PhNHC(=S)	B	70	247–249	–	$C_{14}H_{11}N_5O_4S$	48.48 3.21 20.64 (48.69 3.21 20.28)
32l	PhNHC(=O)	A	68	266–268	–	$C_{14}H_{11}N_5O_5$	51.02 3.24 21.39 (51.07 3.37 21.27)

[a] Meyers, A. I.; Collington, E. W. *J. Am. Chem. Soc.* **1970**, *92*, 6676. [b] Malone, C. R.; Meyers, A. I. *J. Org. Chem.* **1974**, *39*, 623. [c] Meyers, A. I.; Nabeya, A.; Adickes, H. W.; Politzer, I. R.; Malone, G. R.; Kovelesky, A. C.; Nolen, R. L.; Portnoy, R. C. *J. Org. Chem.* **1973**, *38*, 36. [d] Reference 15c.

Scheme IV



displayed signals corresponding to carbazole but indicated the absence of a benzotriazole group. The presence of a new singlet at 3.25 ppm in the proton spectrum and at 55.8 ppm in the carbon spectrum indicated displacement of benzotriazole by the methoxy group forming **30**.

When methanol was replaced by tetrahydrofuran, the NMR of the unstable product indicated it to be *N*-(α-hydroxyphenacyl)carbazole (**29**; E = PhCO). The absences of benzotriazole resonances and the downfield shift of the N-C_α carbon to 87.9 ppm confirmed the suspicion. For the benzyl derivative **29** (E = $PhCH_2$), in addition to the similar downfield shift of the N-C_α carbon in the ^{13}C NMR spectrum, an aldehyde resonance at 193.8 ppm was also detected. The corresponding aldehyde signal at 9.6 ppm in the ^1H NMR indicated that it was formed in ca. 5% yield.

Such adducts of carbazole with aldehydes have not previously been reported. However, Anfinogenov[33] et al. reacted carbazole with aliphatic aldehydes and alcohols in acid to give the carbenium-immonium ion **28** in the slow step which then added the alcohol.

The isolation of **29** is in agreement with our findings involving attack of methanol on **28** affording **30**. In tetrahydrofuran, the semiaminal **29** is mainly obtained (obviously from the small amount of water present in the 10 M HCl solution). A larger amount of water shifted the equilibrium further, affording the aldehyde in a yield of 40%. From the octyl derivative **26c**, the corresponding nonyl aldehyde (**31**) was isolated (57%). The other aldehydes were trapped prior to isolation. Thus treatment of the adducts with concentrated sulfuric acid in THF/H_2O (2:1) in the presence of 2,4-dinitrophenylhydrazine (DNP), or addition of DNP in 10% perchloric acid to the reaction solution after 24 h, afforded the corresponding hydrazones (**32**) in yields of 61–83% (Table IV). The hydrazones were characterized by their ^1H and ^{13}C NMR and by their CHN analyses (see Tables IV–VI, Tables V and VI are found in the supplementary material). Sparse literature data for some of these hydrazones was in agreement with our findings.

Conclusions

The single step used in the present procedure makes it more attractive than those requiring multiple steps for the formation of the aldehydes. Our use of aqueous acid is also preferable to mercury reagents, thermolysis, or strong reducing agents. Oxidized thioacetals (**5**, **6**) are indeed hydrolyzed under mild acid conditions; however, hydrolysis of some of these adducts afforded α-hydroxy ketones (i.e. $ArCOCH_2OH$) rather than the expected ArCH(OH)CHO, although copper(II) chloride or triethyl orthoformate circumvented this problem.[34] The hydrolysis of the TosMIC oxazole (**11**) does occur with dilute hydrochloric acid in THF at room temperature, but this method is applicable only to α-hydroxy aldehydes.

The 1-(carbazol-9-ylmethyl)benzotriazole system, which is the first formyl anion equivalent developed from a

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heterocycle-activated methane, is attractive due to the relatively mild single-step hydrolysis conditions employed without the use of exotic reagents and of the variety of electrophiles that can be utilized.

Experimental Section

Melting points were determined on a bristoline hot-stage microscope and are uncorrected. ^1H (300 MHz) NMR spectra were recorded on a Varian VXR-300 (FT mode) spectrometer with Me_4Si as internal standard. ^{13}C NMR spectra were recorded at 75 MHz on the same instrument using solvent peaks ($CDCl_3$, δ 77.0 or DMSO-d_6, δ 39.5) as references. Elemental analyses (C, H, N) were carried out using a Carlo Erba 1106 elemental analyzer under the supervision of Dr. D. Powell, University of Florida. Tetrahydrofuran (THF) was freshly distilled from sodium benzophenone. All moisture-sensitive reactions were carried out in a dry argon atmosphere.

The following compound was prepared by a known literature procedure: **bis(benzotriazol-1-yl)methane (23)**, mp 191–193 °C (lit.[35] mp 192–193 °C).

1-(Carbazol-9-ylmethyl)benzotriazole (28). To a solution of carbazole (6.7 g, 40 mmol) in DMSO (30 mL) was added powdered NaOH (3.2 g, 80 mmol). The mixture was heated to 50–60 °C and kept for 2 h at that temperature. 1-(Chloromethyl)benzotriazole (6.7 g, 40 mmol) was then added to the above solution, and the system was stirred for an additional 2 h at 50–60 °C. After cooling, the reaction mixture was poured into ice (100 g), and the precipitate was filtered off, washed with water (3 × 50 mL), and dried. The pale solid thus obtained was triturated with benzene to give the pure product (12 g, 80%), mp 193–195 °C (lit.[32] mp 194–196 °C).

General Procedure for the Lithiation of Bis(benzotriazol-1-yl)methane (23) and 1-(Carbazol-9-ylmethyl)benzotriazole (25) and Reaction with Electrophiles. To a solution of **23** or **25** (10 mmol) in dry THF (80 mL) was added *n*-BuLi (2.5 M in hexane; 4.4 mL, 11 mmol) at −78 °C. The solution was stirred at −78 °C for 2 h, and then the corresponding electrophile (11 mmol) in THF (10 mL) was added. The mixture was stirred at −78 °C for 4 h and then at room temperature for 12 h. The reaction mixture was poured into saturated aqueous NH_4Cl (40 mL), and the aqueous layer was extracted with diethyl ether (3 × 30 mL). The combined organic layers were washed with water (1 × 25 mL) and dried ($MgSO_4$), and the solvent was evaporated under reduced pressure to afford the crude products which were then purified to give analytically pure products (Tables I–III).

General Procedure for the Hydrolysis of the Intermediates (26a–l). Method A. To a solution of the intermediate **26** (2.5 mmol) in THF (20 mL) and H_2O (10 mL) was added concentrated H_2SO_4 (0.5 mL). The solution was stirred at room temperature for 30 min, and then 2,4-dinitrophenylhydrazine (2.5 mmol) was added. The mixture was stirred at room temperature for 24 h and extracted with Et_2O (3 × 25 mL). The etheral layer was dried ($MgSO_4$) and evaporated under reduced pressure to give a yellow solid, which was then recrystallized from appropriate solvents to afford the pure product.

Method B. The hydrolysis conditions were similar to method A, but 2,4-dinitrophenylhydrazine in 10% $HClO_4$ was added to the reaction solution which had been previously stirred at room temperature for 24 h (Tables IV–VI).

9-(α-Methoxyphenacyl)carbazole (30). A mixture of 1-(benzoylcarbazol-9-ylmethyl)benzotriazole (**26m**) (1.0 g, 2.4 mmol), 10 M HCl (0.5 mL), and MeOH (30 mL) was heated under reflux for 3 h. Evaporation of the solvent gave an oil which was extracted with Et_2O (2 × 25 mL), and the combined organic layer was washed with water (3 × 5 mL) and dried ($MgSO_4$). Evaporation of the solvent under reduced pressure afforded an oil which was purified by column chromatography (chlorform/hexane, 2/1) to give the product as a pale yellow oil (0.66 g, 87%): ^1H NMR ($CDCl_3$) δ 8.0–7.75 (m, 4 H), 7.6–7.05 (m, 9 H), 6.73 (s, 1 H), and 3.25 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 191.6, 139.4, 134.1, 133.5, 128.2, 126.1, 123.7, 120.3, 120.2, 84.5, 55.8. $C_{21}H_{17}N_{10}O_2$ requires M^+ m/z 315.1259, found M^+ m/z 315.1252.

Nonyl Aldehyde (31). The octyl derivative **26c** (2.0 g, 4.88 mmol) was dissolved in THF (30 mL), and then HCl (10 M; 2 mL) and H_2O (15 mL) were added. The solution was stirred at ambient temperature for 24 h. Et_2O (30 mL) was then added, and the layers were separated. The aqueous fraction was washed with Et_2O (3 × 25 mL), the combined organic fraction was washed with water (2 × 15 mL) and dried ($MgSO_4$), and the solvent was removed under reduced pressure. The residue was extracted with hexanes (4 × 25 mL), and the solvent was removed under reduced pressure. The crude product was then purified by column chromatography (hexane–$CHCl_3$, 2:1) to give 0.4 g (57%) of **31** as a colorless liquid: bp 77–79 °C (15 mmHg) (lit.[36] bp 49–52 °C (1 mmHg)).

Supplementary Material Available: ^1H and ^{13}C NMR spectra for compound **30** and ^1H and ^{13}C NMR spectral data for compounds **25a–c** and **26a–n** (Tables II and III, respectively) and for compounds **32a–l** (Tables V and VI) (7 pages). Ordering information is given on any current masthead page.

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