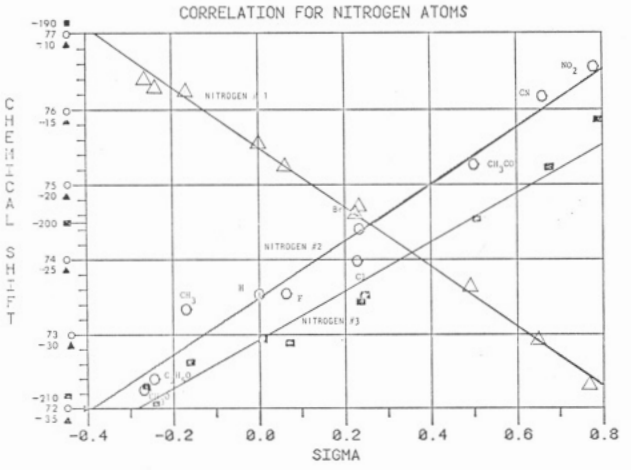

Figure 2. Correlation of N-15 chemical shifts with Hammett σ constants for aryltriazenes: (○) chemical shift for nitrogen atom 2 (r = 0.979), (△) chemical shift for nitrogen atom 1 (r = 0.998), (■) chemical shift for nitrogen atom 3 (r = 0.986).

sensitivity in chemical shift change with the substituent effect, with an overall chemical shift range of 20 ppm on going from methoxy to nitro substituents. The increased shielding of N(1) with increasing substituent electronegativity is consistent with stabilization of the negative charge on N(1) by the substituent in resonance structures B and C. Both N(2) and N(3) are deshielded as the substituent electronegativity increases, as would be expected for nitrogen atoms with positive character as shown for structures B and C in eq 1. The relatively small overall sensitivity (4.2 ppm) of the chemical shifts of N(2) to the substituent effects means that structure B is a minor contributing structure relative to A and C. The N(3) resonance, on the other hand, shows a large chemical shift sensitivity (14.2 ppm), which indicates that structure C is a major contributing member of the conjugated system.

The chemical shift results presented here for N(1), N(2), and N(3) of the triazene system 1, and the polar substituent effects on these shifts, are entirely consistent with the presence of an extended linear π-conjugate system in which N(1) and N(3) exhibit strong negative and positive character, respectively, and in which N(2) displays small but significant positive character.

Experimental Section

1-Phenyl-3,3-pentamethylenetriazenes. The appropriate aromatic amine is diazotized at 0 °C. The resulting aryldiazonium ion mixture is treated with 1.1 equiv of piperidine. The mixture is extracted with ether, filtered, dried, and concentrated to yield the triazene. Triazene purity is at least 95% as determined by ^{1}H and ^{13}C NMR analysis. Yields are 30–95%.

Nuclear magnetic resonance spectra were obtained at 9.04 MHz on a Fourier transform multinuclear FX-90Q instrument without proton decoupling. Solutions of the triazene (40% by weight) in $CDCl_3$ contained in 10-mm sample tubes were measured at 30 °C. Approximately 30 mg of chromium(III) acetate was added to each sample to allow fast pulse repetition times (2 s, 45° pulse). Each sample required 17 000–25 000 scans to obtain spectra of approximately 5:1 signal-to-noise level (8000 Hz spectral width, 32K bits computer). Chemical shifts are reported relative to external $NH_4{}^{15}NO_3$ (17% in 10% HNO_3, 5% H_2O, 85% D_2O), which was measured separately and stored on disc. The instrument computer was set to zero on the standard before each chemical shift was recorded. Chemical shifts obtained in this manner are accurate to ±0.1 ppm.

Acknowledgment. This research was supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society. We thank Ms. Dana Bechtold for the preparation of Figure 2 and Dr. R. E. Viola for advice in obtaining the ^{15}N NMR spectra.

Registry No. 1 (R = CH_3O), 74148-29-1; 1 (R = CH_3CH_2O), 87261-58-3; 1 (R = CH_3), 51274-57-8; 1 (R = H), 16978-76-0; 1 (R = F), 332-01-4; 1 (R = Cl), 62499-15-4; 1 (R = Br), 87261-59-4; 1 (R = CH_3CO), 87261-60-7; 1 (R = CN), 87261-61-8; 1 (R = NO_2), 52010-83-0.

Enhanced Reducing Properties of Pyridine–Borane Adsorbed on Solid Supports: A Convenient Method for Chemoselective Reduction of Aldehydes

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Among the numerous reagents available for effecting the reduction of a carbonyl moiety to the corresponding alcohol is pyridine–borane. However, the latter is seldom utilized for this transformation since it reduces aldehydes and ketones only at elevated temperature.[1] Recently, one of us, while developing a methodology for the conversion of acid chlorides to the corresponding aldehydes,[2] observed that application of an equimolar mixture of an aldehyde and pyridine–borane to a column of Florisil led instantaneously[3] to a highly exothermic reaction, from which the alcohol corresponding to the aldehyde could be isolated in high yield. Since we have subsequently demonstrated that pyridine–borane remains structurally intact after being adsorbed on Florisil,[4] such results might be rationalized by citing the enhanced reducing properties amine–borane complexes are known[5] to exhibit in the presence of Lewis acids.

In view of the considerable attention focused in recent years on the use of solid supports to modify the reactivity of various reagents,[6] we decided to assess further the enhanced reducing capabilities of pyridine–borane adsorbed on solid supports. Initial experiments were performed by using silica gel to modify the reactivity of the borane complex since until recently[7] not many *reductions* had been examined in the presence of this support. Treatment[8] of a solution of benzaldehyde in cyclohexane with $^1/_3$ molar equiv of pyridine–borane in the presence of silica gel[9] re-

(1) Barnes, R. P.; Graham, J. H.; Taylor, M. D. *J. Org. Chem.* **1958**, *23*, 1561.
(2) Babler, J. H. *Synth. Commun.* **1982**, *12*, 839.
(3) In contrast to these observations, IR analysis of an equimolar mixture of pyridine–borane and *p*-tolualdehyde indicated that no reaction between the neat components had occurred after 2 h at room temperature.
(4) Pyridine–borane, after being adsorbed for 15 min on solid supports such as Florisil, alumina, or silica gel can be recovered in quantitative yield by elution with ether.
(5) Andrews, G. C.; Crawford, T. C. *Tetrahedron Lett.* **1980**, *21*, 693 and references therein.
(6) For a review on organic syntheses using supported reagents, see: McKillop, A.; Young, D. W. *Synthesis* **1979**, 401–422, 481–500.
(7) Lithium aluminum hydride $LiAlH_4$-silica gel has been found to be more selective than $LiAlH_4$ itself and can reduce keto esters to the corresponding hydroxy esters. See: Kamitori, Y.; Hojo, M.; Masuda, R.; Inoue, T.; Izumi, T. *Tetrahedron Lett.* **1982**, *23*, 4585. Silica gel also appears to modify the reduction capability of sodium borohydride. See: Ciurdaru, V.; Hodosan, F. *Rev. Roum. Chim.* **1977**, *22*, 1027.
(8) The standard reduction procedure outlined in the Experimental Section was used for this reaction.
(9) Similar results were obtained with Florisil.

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Table I. Reduction[a] of Representative Aldehydes and Ketones

starting carbonyl compound[b]	reaction time,[c] h	yield,[d] %	product distribution,[e] %		
			alcohol	starting material	all other components
benzaldehyde	5	90	100	0	*f*
p-tolualdehyde	9[g]	89	96	4	*f*
o-chlorobenzaldehyde	4[g]	95	97	3	*f*
m-nitrobenzaldehyde	2.5	77	100	0	*f*
cinnamaldehyde	8[g]	70	100[h]	0	*h*
decanal	3.5	79	>97	0	<3
citral[i]	10	74	>95[j]	0	<5
4-phenyl-2-butanone	2	*k*	<2	>98[l]	*l*
acetophenone	2	*k*	0	100	*l*
cycloheptanone	2	*k*	<2	>98[l]	*l*

[a] All reactions were run for the specified time by using the standard reduction procedure described in the Experimental Section. [b] Available from Aldrich Chemical Co., Milwaukee, WI. [c] After a reaction time of 2 h, NMR analysis of the crude product (still contaminated with pyridine–borane) indicated that each of the aldehyde substrates had been reduced to the extent of >70%. In sharp contrast, after a similar reaction time little if any (<2%) alcohol could be detected by IR and NMR analysis of the crude product mixture derived from three representative ketones. [d] Determined after removal of any excess pyridine–borane by using the method outlined in the Experimental Section. The product mixtures derived from cinnamaldehyde, decanal and citral were further purified by evaporative distillation. [e] For cinnamaldehyde, decanal, and citral, these ratios were determined by both NMR and VPC analysis (6 ft × $^1/_8$ in. column packed with 5% OV-17 on 100–120 mesh Gas Chrom Q). Each major component was further identified by coinjection with a known sample. For benzaldehyde, *p*-tolualdehyde, *o*-chlorobenzaldehyde, and *m*-nitrobenzaldehyde, these ratios were determined by NMR analysis (CHO vs. CH_2OH signals). [f] The IR and NMR spectral properties of each of these alcohol products were identical with those exhibited by the authentic compounds sold by Aldrich Chemical Co. [g] After a reaction time of 2 h, NMR analysis of the crude product indicated the presence of 8%, 20%, and 20% starting aldehyde for the reductions involving *o*-chlorobenzaldehyde, *p*-tolualdehyde, and cinnamaldehyde, respectively. [h] NMR and VPC analyses indicated the alcohol product to be a 16:1 mixture of cinnamyl alcohol and 3-phenyl-1-propanol, respectively; the latter presumably arising from initial 1,4-reduction of the α,β-unsaturated aldehyde. [i] A mixture of *E*:*Z* stereoisomers, as sold by Aldrich Chemical Co. [j] NMR and VPC analysis indicated the alcohol product to be a 55:45 mixture of 3,7-dimethyl-2(*E*,*Z*),6-octadien-1-ol and citronellol, respectively, the latter presumably arising from initial 1,4-reduction of citral. [k] The crude product consisted of a mixture of starting ketone and pyridine–borane. Since the latter is known to reduce ketones at elevated temperature[1] or in the presence of acids,[5] no attempt was made to separate these two components. [l] NMR spectra indicated the virtual absence of alcohol and were identical with those exhibited by an authentic mixture of pyridine–borane and the ketone substrate. IR analysis indicated a trace (<2%) of alcohol in the products obtained from 4-phenyl-2-butanone and cycloheptanone.

sulted in >95% reduction of the aldehyde after 45 min at room temperature—an indication that full utilization of the available hydride was possible under such reaction conditions.

Encouraged by the above results, we explored similar reaction conditions ($^1/_3$ molar equiv of pyridine–borane, silica gel, cyclohexane, 20 °C) with 4-phenyl-2-butanone. Although the reduction occurred more slowly, nevertheless, 4-phenyl-2-butanol comprised >40% of the product mixture[10] after a reaction time of 2 h. To our amazement, however, treatment of this ketone with pyridine–borane in the presence of activated alumina,[11] resulted in only a trace (<2%) of any reduction product after 2 h at room temperature, whereas under similar conditions reduction of benzaldehyde was nearly quantitative (95%).

A detailed study was undertaken to ascertain further the selectivity of pyridine–borane/alumina in the reduction of carbonyl substrates. As can be seen in Table I, virtually no reduction of three representative ketones occurred after a reaction time sufficient to reduce most aldehydes. To substantiate further the chemoselectivity of this reagent, we treated *p*-tolualdehyde with ~$^1/_3$ molar equiv of pyridine–borane/alumina in the presence of a molar equivalent of acetophenone. As the results in the Experimental Section demonstrate, >95% aldehyde but less than 2% ketone reduction occurred when using this reagent—an indication of its potential for selective carbonyl reductions.[12] A further indication of the selectivity of pyridine–borane/alumina was its failure to reduce hydrocinnamonitrile and methyl caprylate after 2 h at 20 °C.

Although other metal hydride reagents supported on a solid surface have been used for selective reduction of aldehydes in the presence of ketones, the chemoselectivity reported for such competitive reductions has generally[13] been inferior to that which we observed using pyridine–borane in the presence of activated alumina. For example, de Mayo and co-workers[14] treated an equimolar mixture of benzaldehyde and methyl naphthyl ketone with 1.05 equiv of tributyltin hydride in the presence of silica gel—conditions that led to 97% and 8% reduction of the aldehyde and ketone, respectively. The chemoselectivity exhibited by pyridine–borane/alumina is quite remarkable in view of the latter results when one considers that *p*-tolualdehyde is less reactive than benzaldehyde with this reagent (Table I, entries 1 and 2). However, even more

(10) Use of Florisil in place of silica gel slowed the reaction slightly (i.e., 25% vs. 40% reduction after 2 h). A more dramatic effect on the rate of reaction was seen when ethyl ether (in which pyridine borane is soluble) was used as the solvent in lieu of cyclohexane. Such conditions (pyridine–borane, silica gel or Florisil, ethyl ether, 20 °C, 2 h) resulted in little (<5%) reduction of 4-phenyl-2-butanone.

(11) See the Experimental Section for the specific type of alumina and its supplier.

(12) Among the most recent reagents developed for chemoselective reduction of aldehydes in the presence of ketones is the sterically hindered lithium tris[(3-ethyl-3-pentyl)oxy]aluminum hydride. See: Krishnamurthy, S. *J. Org. Chem.* **1981**, *46*, 4628. For other methods for reduction of aldehydes in the presence of ketones, see: Babler, J. H.; Invergo, B. J. *Tetrahedron Lett.* **1981**, *22*, 621 and references in footnote 13 of that paper.

(13) Lithium borohydride adsorbed on certain types of molecular sieves has been shown to exhibit remarkable selectivity toward the reduction of aldehydes in the presence of ketones. However, the study was limited to two relatively simple aliphatic aldehydes and extensive formation of polymeric byproducts was observed. Furthermore, some destruction (but not reduction) of the starting ketones under the reaction conditions was noted. See: Risbood, P. A.; Ruthven, D. M. *J. Org. Chem.* **1979**, *44*, 3969.

(14) Fung, N. Y. M.; de Mayo, P.; Schauble, J. H.; Weedon, A. C. *J. Org. Chem.* **1978**, *43*, 3977.

amazing about our experimental results is the fact that the reverse selectivity (i.e., more rapid reduction of acetophenone) using pyridine–borane in chloroform solution has been reported.![15]

In conclusion, pyridine–borane adsorbed on solid supports such as alumina or silica gel offers several advantages in the reduction of carbonyl compounds. Such reactions appear to be more selective[16] than the corresponding homogeneous reactions; they are easy to conduct since the reagent is air-stable; they can be effected with nearly quantitative[17] utilization of the available hydride; and in the absence of excess reducing agent, reaction workup is simplified, with the product being recovered after filtration. Furthermore, the chemoselectivity exhibited by this supported reagent compares favorably with that reported for other available reagents used to effect selective carbonyl reductions.

Experimental Section

General Methods. Reactions were carried out under a nitrogen atmosphere. Alumina (activated, chromatographic grade, 80–325 mesh, catalog no. AX0611) was purchased from MCB Manufacturing Chemists, Inc., Gibbstown, NJ; and silica gel (Baker analyzed, 40–140 mesh) was obtained from J.T. Baker Chemical Co. Florisil (60–100 mesh) was purchased from Fisher Scientific Company. In those reactions utilizing an excess of pyridine–borane, products were recovered from the ether extracts after drying the organic layer over anhydrous magnesium sulfate and removal of the solvent by using a rotary evaporator under reduced pressure. Evaporative distillation refers to bulb-to-bulb (Kugelrohr) short-path distillation. ^{1}H NMR spectra were recorded with a Varian EM-360 spectrometer, and infrared spectra were obtained on a Beckman Acculab 1 spectrophotometer. Vapor-phase chromatography (VPC) was performed on a Hewlett-Packard 5750 chromatograph. Where indicated (Table I), percentages refer to peak areas without correction for response factors relative to an internal standard.

Standard Reduction Procedure. To a 100-mL flask containing a stirring bar and 10 mL of activated alumina were added in succession 0.25 mL (2.47 mmol) of pyridine–borane,[18] 10 mL of cyclohexane,[19] and 6.0–6.5 mmol[20] of the carbonyl substrate. This mixture was then stirred vigorously at room temperature for the time specified in Table I, after which it was diluted with 25 mL of solvent ether and the alumina removed by filtration. The alumina was washed with ether (3 × 10 mL) to ensure quantitative recovery of the product, and the combined organic filtrate was washed with 10% aqueous sodium chloride (2 × 25 mL) and saturated brine (25 mL) in successive order. The product was isolated from the organic layer as described in the General Methods section. The primary alcohols obtained by reduction of the aldehydes listed in Table I were separated[21] from any residual pyridine–borane by treatment of the crude product with 6 mL of 1:1 (v/v) tetrahydrofuran: 4 M aqueous hydrochloric acid at room temperature for approximately 5 min. The alcohol was recovered by dilution of this mixture with 25 mL of saturated brine and extraction with ether, followed by washing of the organic layer with 1:1 (v/v) 1 M aqueous sodium hydroxide, saturated brine (20 mL), 10% aqueous sodium chloride (20 mL), and saturated brine (20 mL), in successive order. The product was isolated from the organic extract in the usual manner and, if necessary, purified by evaporative distillation.

Reduction of an Aldehyde with a Limited Amount of Pyridine–Borane. A mixture of 10 mL of activated alumina, 0.25 mL (2.47 mmol) of pyridine–borane,[18] 10 mL of cyclohexane, and 1.00 mL (8.48 mmol) of *p*-tolualdehyde[18] (added in the sequence described in the Standard Reduction Procedure) was stirred vigorously at room temperature for 12 h. Subsequent dilution with 25 mL of anhydrous ether, followed by filtration of the mixture to remove the alumina and thorough washing of the latter with anhydrous ether, afforded after removal of the ether under reduced pressure 1.00 g (97%) of a mixture shown by NMR analysis (CH_2OH vs. CHO signals) to be a 4:1 mixture of *p*-tolylcarbinol and starting aldehyde, respectively, uncontaminated by any borate compounds or pyridine–borane. These results indicate 92% utilization of the latter's available hydride for this reduction.

Chemoselective Reduction of *p*-Tolualdehyde in the Presence of Acetophenone. To a reaction flask containing 10 mL of activated alumina were added in succession 0.25 mL (2.47 mmol) of pyridine–borane,[18] 10 mL of cyclohexane, 0.75 mL (6.42 mmol) of acetophenone, and 0.75 mL (6.36 mmol) of *p*-tolualdehyde. This mixture was then stirred vigorously at room temperature for 8 h, after which the product was isolated as outlined in the Standard Reduction Procedure. NMR analysis of the crude product (1.536 g) prior to destruction of any residual pyridine–borane indicated the mixture to contain *p*-tolylcarbinol and unreduced aldehyde in a 96:4 ratio, respectively (determined by integration of the CH_2OH vs. CHO signals), whereas <2% of the ketone had been reduced (determined by integration of the $CH_3C{=}O$ vs. CH_3CHOH signals).

Reduction of Ketones Using Pyridine–Borane Adsorbed on Silica Gel. To a 100-mL flask containing a stirring bar and 10 mL of silica gel (Baker analyzed, 40–140 mesh) were added, in succession, 0.25 mL (2.47 mmol) of pyridine–borane,[18] 10 mL of cyclohexane, and 0.75 mL (6.17 mmol) of 2-methylcyclohexanone.[18] This mixture was then stirred vigorously at room temperature for 20 h, after which the product was isolated as outlined in the Standard Reduction Procedure. Since IR analysis indicated a weak carbonyl absorption and only a trace amount of residual pyridine–borane,[22] a successful reduction[23] had been

(15) Reduction of a 1:1 molar mixture of benzaldehyde and acetophenone with pyridine–borane in chloroform afforded a 35:65 mixture of benzyl alcohol and 1-phenylethanol, respectively. See: Andrews, G. C. *Tetrahedron Lett.* **1980**, *21*, 697.

(16) Pyridine–borane has previously been reported[1] to reduce aldehydes, ketones, and carboxylic acids at elevated temperature. However, treatment of a solution of lauric acid in 1:1 (v/v) cyclohexane/benzene with pyridine–borane in the presence of either silica gel or alumina afforded no reduction products after 20 h at room temperature. Even more remarkable was the fact that a substantial amount (>80%) of pyridine borane could be recovered from such a reaction mixture after extraction with ether and removal of the carboxylic acid with aqueous sodium hydroxide washes. An attempt to exploit this observation by reduction of a ketone in the presence of a carboxyl moiety was subsequently carried out. Thus a suspension of β-benzoylpropionic acid[18] (5.6 mmol) in 9 mL of 2:1 (v/v) hexane/ether, mixed with pyridine borane (2.47 mmol) adsorbed on 10 mL of silica gel, was stirred vigorously at room temperature for 15 h. Subsequent dilution of this mixture with 25 mL of 4:1 (v/v) ether/dichloromethane and 20 mL of 9:1 (v/v) saturated brine/2 M aqueous HCl, followed by filtration to remove the silica gel and separation of the organic and aqueous layers, afforded in quantitative yield a 1:1 mixture of starting ketone and the expected reduction product (4-hydroxy-4-phenylbutanoic acid). Although no reduction of the carboxyl moiety had occurred, a slow evolution of hydrogen (with concomitant loss of available active hydride) was observed during the course of this reaction—perhaps reflecting the enhanced reactivity of the alkoxyborane intermediate toward the acid.

(17) This contrasts with results of previous work on the reduction of ketones with tertiary amine–boranes. See: Wolfe, T.; Kelly, H. C. *J. Chem. Soc., Perkin Trans. 2* **1973**, 1948; White, S. S., Jr.; Kelly, H. C. *J. Am. Chem. Soc.* **1970**, *92*, 4203 and references cited therein.

(18) Available from Aldrich Chemical Co., Inc., Milwaukee, WI.

(19) Due to its low solubility in cyclohexane, the reduction of *m*-nitrobenzaldehyde was conducted in 10 mL of 1:1 (v/v) benzene/cyclohexane. For the reduction of highly polar organic substrates such as β-benzoylpropionic acid, 2:1 (v/v) hexane/ether proved to be a satisfactory solvent mixture.[16]

(20) For the reactions involving citral and cinnamaldehyde, only 4.1 and 4.8 mmol, respectively, of starting aldehyde was used since conjugate reduction in these systems consumed additional hydride.

(21) Prior to destroying the pyridine–borane, the crude product was subjected to NMR analysis to ascertain if any starting aldehyde was present since we had previously demonstrated[2] that attempts to destroy this reducing agent in the presence of an aldehyde with strongly acidic quenches led to rapid reduction of the carbonyl compound.

(22) This compound is readily characterized by a strong infrared absorbtion band at 2360 cm^{-1}.

(23) In a related experiment using 1.00 mL (6.66 mmol) of 4-phenyl-2-butanone[18] and a reaction time of 22 h, NMR analysis (CH_3CHOH vs. $CH_3C{=}O$ signals) of the crude product indicated a 2:1 mixture of 4-phenyl-2-butanol and unreduced ketone, respectively. Since a previous experiment under identical conditions demonstrated that approximately 40% of this ketone had been reduced after only 2 h at room temperature, a slow hydrolysis of pyridine–borane may be simultaneously occurring in the presence of silica gel.

effected, albeit slowly. After destruction of the latter using 1:1 (v/v) tetrahydrofuran/4 M aqueous hydrochloric acid (vide ante), 595 mg (84%) of a mixture was obtained and shown by VPC analysis (6 ft × 0.125 in. Carbowax 20M column; oven temperature 138 °C; retention times: ketone, 2.0 min; alcohol, 2.4 min) to consist of 2-methylcyclohexanol and the corresponding ketone in an 85:15 ratio. The alcohol and ketone were further identified by coinjection with known samples of each compound. Subsequent NMR analysis (CHOH signals) indicated that the alcohol product was a 1:1 mixture of cis:trans stereoisomers.

Registry No. Benzaldehyde, 100-52-7; *p*-tolualdehyde, 104-87-0; *o*-chlorobenzaldehyde, 89-98-5; *m*-nitrobenzaldehyde, 99-61-6; cinnamaldehyde, 104-55-2; decanal, 112-31-2; (*E*)-citral, 141-27-5; (*Z*)-citral, 106-26-3; 4-phenyl-2-butanone, 2550-26-7; acetophenone, 98-86-2; cycloheptanone, 502-42-1; 2-methylcyclohexanone, 583-60-8; phenylcarbinol, 100-51-6; *p*-tolylcarbinol, 589-18-4; *o*-chlorophenylcarbinol, 17849-38-6; *m*-nitrophenylcarbinol, 619-25-0; cinnamyl alcohol, 104-54-1; 1-decanol, 112-30-1; (*E*)-3,7-dimethyl-2,6-octadien-1-ol, 106-24-1; (*Z*)-3,7-dimethyl-2,6-octadien-1-ol, 106-25-2; citronellol, 106-22-9; *cis*-2-methylcyclohexanol, 7443-70-1; *trans*-2-methylcyclohexanol, 7443-52-9; pyridine, 110-86-1; borane, 13283-31-3.

Synthesis and Diels–Alder Reactions of Anthra[2,3-*b*]thiophene

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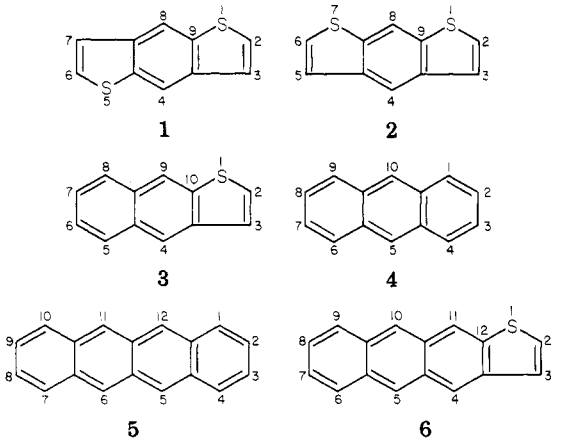
In 1970 Wynberg and co-workers reported studies directed toward the synthesis of heterotriptycenes.[1a-c] Following the findings of Dewar[2] and Brown[3] that a correlation exists between paralocalization energies and Diels–Alder reactivities, they calculated the paralocalization energies for different positions of addition in the linearly fused aromatic and heteroaromatic compounds **1–6**. The most reactive positions in **1–5** were those of the



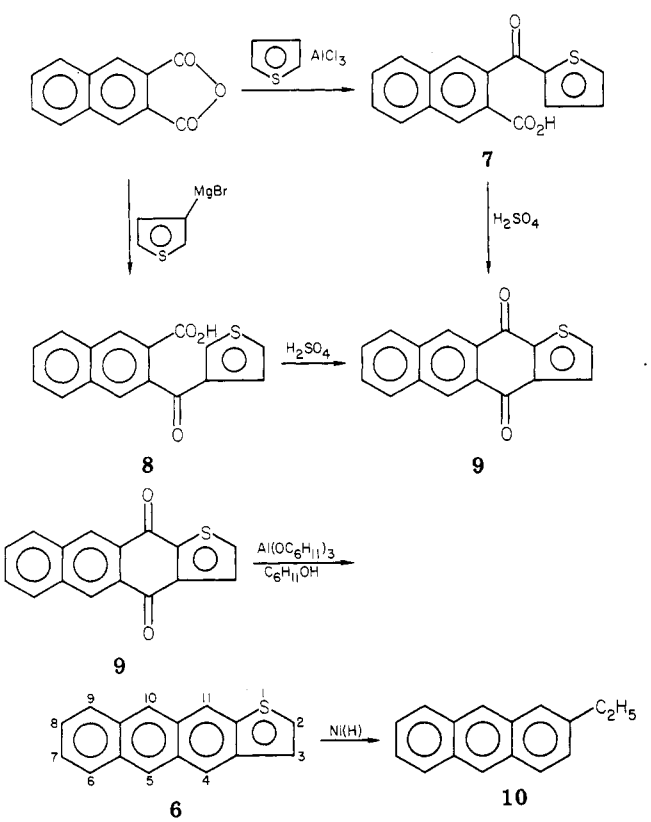
central ring in conformance to the known Diels–Alder reactions of **3**,[1a,4a] **4**, and **5**.[4b] For **6**, the lowest delocalization energy and highest predicted reactivity was at the 5,10-positions.

The present work describes a synthesis of anthra[2,3-*b*]thiophene (**6**) and a study of its reaction with three dienophiles.

The first reference to the synthesis of anthra[2,3-*b*]-thiophene was by Faller[5] who reported that Elbs reaction of 5-*o*-toluoylbenzo[*b*]thiophene afforded a mixture of products from which he isolated a high-melting yellow solid to which he assigned the structure **6**. Recently the synthesis of anthra[2,3-*b*]thiophene was reported by Castle and co-workers[6] who synthesized it in a five-step sequence by an unambiguous route.

The alternative synthesis described below (Scheme I) involves the same starting materials and accomplishes its goal in three steps.

Scheme I



Interaction of naphthalene-2,3-dicarboxylic anhydride with thiophene and succinic anhydride[7] produced **7** (88%). Interaction of the anhydride with 3-thienylmagnesium bromide[8] afforded the isomeric keto acid **8** (50%). Cyclization of either **7** or **8** by means of concentrated H_2SO_4 (steam bath) afforded the quinone **9** in 70% yield in each case. The quinone was reduced to anthra[2,3-*b*]thiophene (**6**) by means of aluminum cyclohexyl oxide in 59% yield.[9] The authenticity of the product was verified by desulfurization with Raney nickel to give 2-ethylanthracene (**10**),

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(2) M. J. S. Dewar, *J. Am. Chem. Soc.*, **74**, 3357 (1952).
(3) R. D. Brown, *J. Chem. Soc.*, 691 (1950).
(4) (a) W. Carruthers, *J. Chem. Soc.*, 4477 (1963); (b) J. S. Meek, F. M. Dewey, and M. W. Hanna, *J. Org. Chem.*, **32**, 69 (1967).
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(7) W. A. Lindley and D. W. H. MacDowell, *J. Org. Chem.*, **47**, 705 (1982).
(8) S. Gronowitz and K. Pettersson, *J. Heterocycl. Chem.*, **13**, 1099 (1976).
(9) J. Vodehnal and V. Stephen, *Collect. Czech. Chem. Commun.*, **36**, 3980 (1971); N. G. Gaylord and V. Stephen, *ibid.*, **39**, 1700 (1974); F. U. Ahmed, T. Rangarajan, and E. J. Eisenbraun, *Org. Prep. Proced. Int.*, **7**, 267 (1975).

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