h) anhydrous THF (140 mL) solution of HMDST[7b] (1 mmol; 208 μL) and $LiEt_3BH$ (2 equiv) was added (at 25 °C) dropwise a THF (10 mL) solution of 12-bromododecanoyl chloride (1 mmol; 330 mg). The reaction mixture was then refluxed for 6 h and flash evaporated and the residue taken up in benzene (25 mL), filtered to remove inorganic material, and then concentrated in vacuo. Chromatography of the resulting oily residue on silica gel using hexanes/benzene (1:1) as the eluent gave three mobile components identified as a monomer, a dimer, and a trimer. Monomer (47%): ^1H NMR ($CDCl_3$) δ 2.96 (2 H, t, J = 5 Hz), 2.53 (2 H, t, J = 5 Hz), 1.29–1.77 (18 H, m); IR ($CHCl_3$) 1680 cm^{-1} (C=O); MS, calcd for $C_{12}H_{22}OS$ m/z 214.1389, found m/z 214.1393. Dimer (16%): ^1H NMR ($CDCl_3$) δ 2.89 (2 H, t, J = 7 Hz), 2.54 (2 H, t, J = 6 Hz), 1.26–1.55 (18 H, m); MS, calcd for $C_{24}H_{44}O_2S_2$ m/z 428.2778, found m/z 428.2753. Trimer (9%): ^1H NMR ($CDCl_3$) δ 2.87 (2 H, t, J = 7 Hz), 2.54 (6 H, t, J = 7 Hz), 1.26–1.58 (18 H, m); MS, calcd for $C_{36}H_{72}O_3S_3$ m/z 642.4167, found m/z 642.4119. Carrying out the same reaction using 1.4 L (instead of 140 mL) of solvent gave an 86% isolated yield of the monomer and only trace quantities of the dimer and trimer.

Thiohexanolide. Monomer (73%): ^1H NMR ($CDCl_3$) δ 2.78–3.03 (4 H, m), 1.73–2.11 (6 H, m); IR ($CHCl_3$) 1660 cm^{-1} (C=O); MS, calcd for $C_6H_{10}OS$ m/z 130.0451, found m/z 130.0453.

Thiooctanolide. Dimer (30%): ^1H NMR ($CDCl_3$) δ 2.91 (2 H, t, J = 7 Hz), 2.54 (2 H, t, J = 7 Hz), 1.32–1.62 (12 H, m); IR ($CHCl_3$) 1675 cm^{-1} (C=O); MS, calcd for $C_{16}H_{28}O_2S_2$ m/z 316.1529, found m/z 316.1554.

Thioundecanolide. Monomer (19%): ^1H NMR ($CDCl_3$) δ 3.01 (2 H, t, J = 6 Hz), 2.54 (2 H, t, J = 6 Hz), 1.30–1.89 (16 H, m); IR ($CHCl_3$) 1670 cm^{-1} (C=O); MS, calcd for $C_{11}H_{20}OS$ m/z 200.1234, found m/z 200.1263. Dimer (20%): ^1H NMR ($CDCl_3$) δ 2.91 (2 H, t, J = 7 Hz), 2.55 (2 H, t, J = 7 Hz), 1.28–1.85 (16 H, m). Trimer (12%): ^1H NMR ($CDCl_3$) δ 2.91 (2 H, t, J = 7 Hz) 2.54 (2 H, t, J = 7 Hz), 1.28–1.86 (16 H, m).

Thiohexadecanolide. Monomer (64%): ^1H NMR ($CDCl_3$) δ 2.94 (2 H, t, J = 5 Hz), 2.56 (2 H, t, J = 7 Hz), 1.30–1.58 (26 H, m); IR ($CHCl_3$) 1670 cm^{-1} (C=O); MS, calcd for $C_{16}H_{30}OS$ m/z 270.2016, found m/z 270.2020.

Preparation of the Thiolactones Listed in Table II by the Gladysz Route.[5c] General Procedure: Preparation of Thiododecanolide. To a suspension of elemental sulfur (1 mmol; 32 mg) in anhydrous THF (140 mL) was added $LiEt_3BH$ (2 equiv). After the mixture was stirred for 15 min, a THF (10 mL) solution of 12-bromododecanoyl chloride was added dropwise. The reaction mixture was then refluxed for 6 h and worked up as above to give 53 mg (25%) of monomeric thiododecanolide identical in all respects with the material obtained by the above procedure.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada and the Imperial Oil Company (Canada) Ltd. for financial support. We are also grateful to Professor D. N. Harpp for helpful discussions.

Registry No. **2**, 2471-92-3; HMDST, 3385-94-2; $Br(CH_2)_6Br$, 629-03-8; $Br(CH_2)_7Br$, 4549-31-9; $Br(CH_2)_8Br$, 4549-32-0; $Br(CH_2)_9Br$, 4549-33-1; $Br(CH_2)_{10}Br$, 4101-68-2; $Br(CH_2)_{12}Br$, 3344-70-5; $CH_2(CH_2)_5S(CH_2)_6S$, 295-32-9; $CH_2(CH_2)_6S(CH_2)_7S$, 295-80-7; $CH_2(CH_2)_{11}S(CH_2)_{12}S$, 98268-21-4; $Br(CH_2)_5COCl$, 22809-37-6; $Br(CH_2)_7COCl$, 73674-09-6; $Br(CH_2)_{10}COCl$, 15949-84-5; $Br(CH_2)_{11}COCl$, 61658-00-2; $Br(CH_2)_{15}COCl$, 73782-15-7; $CH_2(CH_2)_4COS$, 17689-16-6; $CH_2(CH_2)_6COS(CH_2)_7COS$, 98268-22-5; $CH_2(CH_2)_9COS$, 98268-23-6; $CH_2(CH_2)_9COS(CH_2)_{10}COS$, 98268-24-7; $CH_2(CH_2)_{10}COS$, 98268-25-8; $CH_2(CH_2)_{10}COS(CH_2)_{11}COS$, 98268-26-9; $CH_2(CH_2)_{14}COS$, 98268-27-0; Li_2S, 12136-58-2; MeLi, 917-54-4; $CH_2(CH_2)_{11}S(CH_2)_{12}S(CH_2)_{12}S$, 98303-54-9; $LiEt_3BH$, 89556-21-8; $CH_2(CH_2)_{10}COS(CH_2)_{11}COS(CH_2)_{11}COS$, 98268-28-1; $CH_2(CH_2)_9COS(CH_2)_{10}COS(CH_2)_{10}COS$, 98268-29-2; thiepane, 4753-80-4; thiocane, 6572-99-2; thionane, 6007-54-1; thiecane, 6048-83-5; thiacycloundecane, 408-32-2; 1,12-dithiacyclodocosane, 296-90-2; thiacyclotridecane, 295-05-6; α,α′-dibromo-o-xylene, 91-13-4; bis(triphenyltin) sulfide, 77-80-5.

(11) In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

Synthesis of Aldehydes and Ketones from Nitro Paraffins[1]

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Received April 17, 1985

In connection with recent studies in this laboratory on the total synthesis of epimeric bicyclo[2.1.0]pentane derivatives **1a** and **1b** as potential thromboxane (TXA_2) inhibitors, and as synthetic precursors to prostaglandin endoperoxide PGH_2 (Scheme I), aldehyde **3a** figured prominently in our synthetic scheme.[3]

Several attempts to prepare this aldehyde by meticulously following the published procedure[4] for the ethyl carbamate analogue **3b** (Scheme II), in our hands, ended in complete and frustrating failure for both derivatives. With these examples, the Nef procedure's success is inhibited by the extreme lability of potassium salt derivatives **5**.[4] Since nitro paraffins are readily available[5] and since the Nef[6a] reaction presents one of the more attractive ways of converting nitro functionalities into carbonyl units,[6] we have developed, and describe herein, experimental modifications to this reaction that overcome the need to isolate labile intermediates such as **5**.

Ever since Nef[6a] first reported that primary and secondary nitro paraffins could upon treatment with mineral acids be respectively transformed into aldehydes and ketones, several variations of this reaction have appeared in the chemical literature.[6b-f] However, even recent experimental improvements as the most promising one of Kornblum,[6b] based on earlier work,[6c] failed to give appreciable yields for such functionally endowed structures such as our **3**. We have found that treatment of primary or secondary nitro paraffins with methanolic potassium hydroxide, in methanol at 0 °C, produces a stable, soluble form of the corresponding potassium salt. Oxidation, in situ, into its corresponding carbonyl derivative is then readily achieved and in high yield (see Table I) by addition

(1) Reagents for Organic Synthesis. 5. For the previous paper in this series, see: Steliou, K., Salama, P.; Corriveau, J. *J. Org. Chem.*, in press.

(2) Holder of a Merck (Canada) Predoctoral Fellowship.

(3) For reviews, see: "New Synthetic Routes to Prostaglandin and Thromboxanes"; Roberts, S., Scheinmann, F., Eds.; Academic Press: New York, 1982. Bindra, J. S.; Bindra, R. "Prostaglandin Synthesis"; Academic Press: New York, 1977. "Biochemical Aspects of Prostaglandins and Thromboxanes"; Kharasch, N., Fried, J., Eds.; Academic Press: New York, 1977. Mitra, A. "The Synthesis of Prostaglandins"; Wiley-Interscience: New York, 1977. "Prostaglandin Research"; Crabbé, P. Ed.; Academic Press: New York, 1977; Vol 36.

(4) Corey, E. J.; Narasaka, K.; Shibasaki, M. *J. Am. Chem. Soc.* **1976**, *98*, 6417.

(5) Corey, E. J.; Samuelsson, B.; Luzzio, F. A. *J. Am. Chem. Soc.* **1984**, *106*, 3682.

(6) (a) Nef, J. U. *Justus Liebigs Ann. Chem.* **1894**, *280*, 264. (b) Kornblum, N.; Erickson, A. S.; Kelly, W. J.; Henggeler, B. *J. Org. Chem.* **1982**, *47*, 4534 and references cited therein. (c) Shechter, H.; Williams, F. T., Jr. *J. Org. Chem.* **1962**, *27*, 3699. (d) Noland, W. E. *Chem. Rev.* **1955**, *55*, 137. (e) Keinan, E.; Mazur, Y. *J. Am. Chem. Soc.* **1977**, *99*, 3861. (f) McMurry, J. E.; Melton, J.; Padgett, H. *J. Org. Chem.* **1974**, *39*, 259 and references cited therein.

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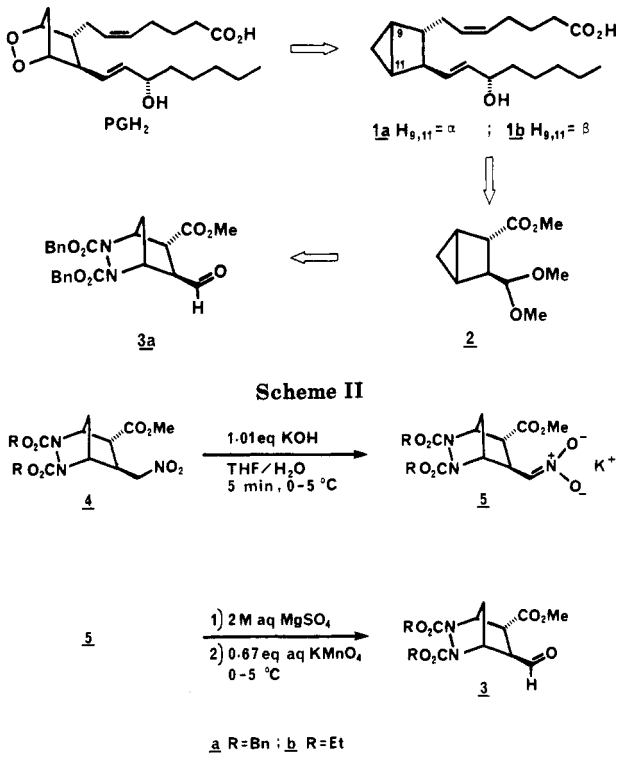
Scheme I



Scheme II

of a concentrated aqueous solution of $KMnO_4$ and $MgSO_4$. For example, by using this method, a nearly quantitative yield of desired aldehyde **3a** and an equally impressive yield (85%) of the ethyl carbamate analogue **3b** (entry 7, Table I) were readily obtained.

Finally, under these reaction conditions, preferential oxidation of the nitro enolate occurs even in the presence of free hydroxy or other olefinic (see entries 5 and 6, Table I) functionalities. In addition, overoxidation of the nitro paraffin into its corresponding carboxylic acid derivative (a persistent problem with other methods)[6] did not occur with the examples tried. Thus, this version of the Nef reaction provides a direct, general, and synthetically simple procedure for converting nitro functionalities into carbonyl units.

Experimental Section

All reactions were carried out under an atmosphere of argon. Reagents were obtained from commercial sources and used directly. 1-Nitrooctane,[6b] phenylnitromethane,[7a] and ω-nitroundecylene[6b] were prepared by literature methods and nitro derivatives **4a** and **4b** by a modification of the Corey, Narasaka, and Shibasaki procedure.[4] Microanalyses were provided by the Guelph Chemical Laboratories Ltd. (Guelph, Ontario, Canada). Proton nuclear magnetic resonance spectra were recorded on a Bruker Model WH-90 90-MHz instrument and ^{13}C on a Bruker WH-80. All chemical shifts are reported as δ values (ppm) relative to internal tetramethylsilane. Significant ^1H NMR data are tabulated in order: chemical shift; number of protons; multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad); coupling constant(s) in hertz. Infrared spectra were recorded on a Perkin-Elmer 710B grating spectrophotometer, calibrated with the 1602 band of a polystyrene film. Mass spectra were obtained with Micromass-1212 (chemical ionization (CI); low resolution) and Kratos MS-902 (electron impact; high resolution) mass spectrometers. Analytical and preparative thin-layer chromatography (TLC) were carried out with E. Merck F-254 silica gel plates.

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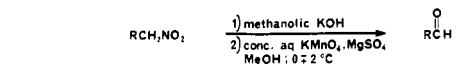
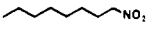
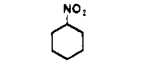
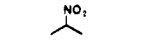
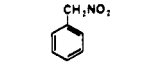
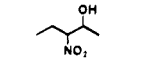
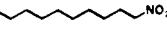
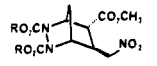
Table I



entry		% isolated yield
1		83
2		93
3		85
4		83
5		73
6		50
7		95, R=Bn 85, R=Et

Preparation of the Aldehydes and Ketones Listed in Table I. General Procedure: Preparation of Aldehyde 3a. To a mechanically stirred solution of **4a**[4] (4.83 g, 10 mmol) in methanol (70 mL) kept at 0 ± 2 °C under an atmosphere of argon was added dropwise over a period of 45 min a freshly prepared methanolic (100 mL) solution of KOH (85 %) (0.67 g, 10.1 mmol). After stirring for an additional 15 min, a freshly prepared aqueous (150 mL) solution of $KMnO_4$ (1.06 g, 6.71 mmol) and $MgSO_4$ (0.89 g, 7.39 mmol) was added dropwise, with vigorous stirring, at a rate that maintained the reaction temperature at 0 ± 2 °C. Upon complete addition, the reaction mixture was stirred for an additional 1 h at 0 °C and then filtered over a layer of Celite. The collected material was washed with benzene (3 × 25 mL), triturated with an additional 100 mL of benzene, and refiltered over a new layer of Celite. The filtrates and washings were combined, diluted with brine (100 mL), and then transferred to a separatory funnel. The aqueous layer was separated from the organic phase and reextracted with benzene (4 × 100 mL). The organic phase and benzene extracts were combined, dried ($MgSO_4$), and concentrated under reduced pressure by rotary evaporation (bath temperature not permitted to exceed 35 °C). The resulting oily residue was then carefully placed under high vacuum which caused a solid voluminous foam to form. The foam was crushed to afford 4.3 g (95% yield) of aldehyde **3a** (pure by ^1H NMR) as a white powder of limited shelf stability. R_f (EtOAc/C_6H_6 3:7) 0.31; IR ($CHCl_3$) 1730 (CO_2CH_3), 1710 cm^{-1} (CHO); ^1H NMR ($CDCl_3$) δ 1.72–1.74 (2 H, m), 3.62 (5 H, s), 4.79 (1 H, br s), 5.04 (1 H, m), 5.15 (2 H, s), 5.21 (2 H, s), 7.26–7.36 (10 H, m), 9.69 (1 H, s); ^{13}C NMR ($CDCl_3$) δ 36.5, 43.8, 52.2, 54.6, 60.3, 62.7, 68.0, 127.5, 127.9, 128.2, 135.4, 156.4, 157.5, 170.0, 197.5; MS (CI), m/z 409 (M^+ + 1). Anal. Calcd for $C_{10}H_{16}O_4$ (derivative **2**): C, 59.98; H, 8.05. Found: C, 59.99; H, 8.01.

Octanal: yield 83%; mp [(2,4-dinitrophenyl)hydrazone derivative] 106 °C (lit.[7b] 106 °C).

Cyclohexanone: yield 93%; mp [(2,4-dinitrophenyl)hydrazone derivative] 158 - 160 °C (lit.[7b] 160 °C).

Acetone: yield 85%; mp [(2,4-dinitrophenyl)hydrazone derivative] 125 °C (lit.[7b] 126 °C).

Benzaldehyde: yield 83%; mp [(2,4-dinitrophenyl)hydrazone derivative] 236 °C (lit.[7b] 237 °C).

2-Hydroxy-3-pentanone: For this example, 1.0 mmol of the nitro derivative, 1.5 mmol of KOH, 0.8 mmol of $KMnO_4$, and 1.16 mmol of $MgSO_4$ were used. Yield 73%; mp [(2,4-dinitrophenyl)hydrazone derivative] 145 °C; IR ($CHCl_3$) 3310 (NH, OH), 1620 (C=N), 1595 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.22 (3 H, t, J = 7.3 Hz), 2.14 (4 H, d, J = 5.6 Hz), 2.43 (2 H, m), 2.53 (2 H, m), 8.12 (2 H, q AB, J_1 = 9.7, J_2 = 2.6 Hz), 9.11 (1 H, d, J = 2.4 Hz) and 11.03 (1 H, br s).

ω-Undecenyl aldehyde: For this example, 1.0 mmol of the nitro derivative, 2.0 mmol of KOH, and 2.2 mmol of $MgSO_4$ were used. After workup, the residue was flash chromatographed (petroleum ether (bp 35–60 °C)/CH_2Cl_2 1:1) to afford starting

material (8%) and 84.1 mg (50%) of the aldehyde (identical with an authentic sample): ^{1}H NMR ($CDCl_3$) δ 1.30 (10 H, br s), 1.70 (2 H, m), 2.00 (2 H, m), 2.40 (2 H, br t), 5.00 (2 H, m), 5.81 (1 H, m), 9.78 (1 H, t); IR ($CHCl_3$) 2695 (CH=O), 1715 (C=O) cm^{-1}.

Aldehyde 3b:[4] yield 85%; mp 187–190 °C; ^{1}H NMR (CCl_4) δ 1.4 (6 H, t, J = 7 Hz), 1.65–1.85 (2 H, m), 3.45 (1 H, br t), 3.5–3.68 (1 H, m), 3.85 (3 H, s), 4.4 (4 H, q, J = 7 Hz), 4.8 (1 H, br s), 5.2 (1 H, br s), 9.7 (1 H, s); MS, m/z 328 (M^+).

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada, le Ministère de l'Education du Gouvernement du Québec, and The Upjohn Co. for financial assistance.

Registry No. 3 (R = Bn), 98652-05-2; 3 (R = Et), 98757-08-5; 4 (R = Bn), 98652-04-1; 4 (R = Et), 98717-43-2; $CH_3(CH_2)_7NO_2$, 629-37-8; $CH_3CH_2CH(NO_2)CH(OH)CH_3$, 5447-99-4; CH_2=C-H$(CH_2)_9NO_2$, 40244-98-2; octanal (2,4-dinitrophenylhydrazone derivative), 1726-77-8; cyclohexanone (2,4-dinitrophenylhydrazone derivative), 1589-62-4; acetone (2,4-dinitrophenylhydrazone derivative), 1567-89-1; benzaldehyde (2,4-dinitrophenylhydrazone derivative), 1157-84-2; 2-hydroxy-3-pentanone (2,4-dinitrophenylhydrazone deriv), 98652-06-3; octanal, 124-13-0; nitrocyclohexane, 1122-60-7; cyclohexanone, 108-94-1; 2-nitropropane, 79-46-9; acetone, 67-64-1; nitrophenylmethane, 622-42-4; benzaldehyde, 100-52-7; 2-hydroxy-3-pentanone, 5704-20-1; 10-undecenyl aldehyde, 112-45-8.

Gas-Phase Basicity of Ring-Substituted Phenylacetylenes

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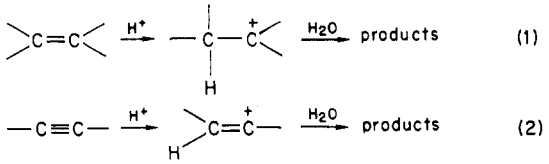
The reactivity of carbon–carbon double and triple bonds toward electrophiles has been the subject of numerous investigations and discussions.[1-3] A particularly interesting feature of these reactions concerns the relative reactivity of double vs. triple bonds bearing equal substituents, which varies greatly (over the 10^{-2}–10^8 range) depending mainly on the electrophile and, to minor extents, on the substituents and solvent.[4,5] In particular, the acid-catalyzed hydration of alkenes and alkynes has been studied in great detail. The reaction proceeds according to the $A_{SE}2$ mechanism, which involves as first and rate-limiting step the protonation of the π-system to give carbenium ion intermediates; these are rapidly trapped by a water molecule (eq 1 and 2). Interestingly, in contrast



to the still widespread, and somewhat erroneous, notion that vinyl cations are intermediates of much higher energy than the corresponding saturated ions, analogously substituted alkynes and alkenes have comparable reactivities toward the proton.[5] This behavior is in contrast with that of other electrophiles, such as Br_2, which are orders of magnitude more reactive toward the double bond relative to the triple bond. In reactions with the proton, it has also been observed that the reactivity of alkynes is somewhat more sensitive to ring-substitution than that of alkenes.[6,7] Thus, arylacetylenes give slightly more negative slope parameters, ρ^+, than the corresponding styrene derivatives in correlations of the rates of protonation in aqueous sulfuric acid solutions with σ^+ constants. The magnitude of these ρs depends on the acid concentration,[6] their absolute values becoming larger as the acidity of the medium is increased. Finally, analysis of these reactions according to the Bunnett and Olsen treatment[8] has indicated the absence of major differential solvent effects in the protonation of triple and double bonds in the acidity range accessible for kinetic determinations.[6]

An extension of the study of the protonation behavior of double and triple bonds to the gas phase is obviously of extreme interest because gas-phase data, free of solvent and counterion effects, are a "clean" measure of the intrinsic properties of the species involved. A recent article reporting on the gas-phase basicities (GB) of ring-substituted styrenes[9] has prompted us to determine the GBs of a series of analogously substituted phenylacetylene derivatives. These data provide a direct comparison of the energetics involved in the protonation of the double and triple bonds in the gas phase at low pressure in the absence of any intramolecular interaction. A brief discussion of the substituent effects, assessed from the ρ^+ parameter, on the thermodynamic gas-phase basicity as well as on the kinetics of protonation in aqueous solutions is also presented.

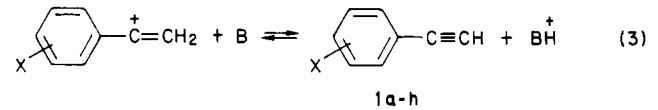
Table I. Gas-Phase Basicities (GB) of Phenylacetylenes 1

compd	GB,[a] kcal mol^{-1}	compd	GB,[a] kcal mol^{-1}
1a	192.2	**1e**	190.8
1b	202.3	**1f**	186.6
1c	196.8	**1g**	187.4
1d	192.5	**1h**	184.2

[a] Data calculated relative to GB(NH_3) = 196.4 kcal mol^{-1}.

Results

The gas-phase basicities (GB) of ring-substituted phenylacetylenes 1 have been determined by measuring, in an FTICR spectrometer, equilibrium constants for reaction 3, where B are suitable reference bases of known basicity. The data are reported in Table I.



1a-h

1a, X = H; **1b**, X = 4-OCH_3; **1c**, X = 4-CH_3; **1d**, X = 4-F; **1e**, X = 4-Cl; **1f**, X = 3-F; **1g**, X = 3-Cl; **1h**, X = 3-CF_3

Plots of GB data against the Brown–Hammett σ^+ substituent constants for substituted phenylacetylenes 1,

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