Effect of Pressure on the Rate of Methylation of a Buttressed Pyridine[1]

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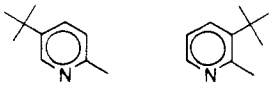
3,5-Di-*tert*-butylpyridine (**3**) and 2,6-dimethyl-3,5-di-*tert*-butylpyridine (**4**) have been synthesized. Compound **3** was obtained by means of acid-catalyzed condensation of *N*-*tert*-butylmethanimine with *N*-(3,3-dimethylbut-1-enyl)piperidine; this reaction also furnished 3,5-di-*neo*-hexylpyridine (**7**). Compound **4** was prepared from Hantzsch's ester **8**, by an application of the Schleyer method for converting ester groups into *tert*-butyl functions. The methylation rates of **3** and **4** in acetonitrile at 45 °C were compared with those of pyridine and 2,6-lutidine. It was deduced that the two *tert*-butyl groups cause a retardation by buttressing by a factor of 57. Comparison with the known rates of 5- and 3-*tert*-butyl-2-methylpyridines (**1** and **2**, respectively) shows that the buttressing effect is minimized in the latter case by bending of the incipient *N*-methyl bond. The rates were also measured under pressure; the activation volumes follow the normal trend expected of directly hindered Menschutkin reactions.

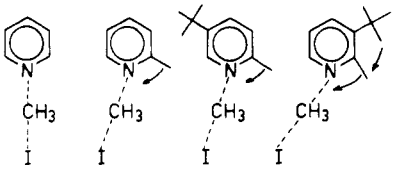
Introduction

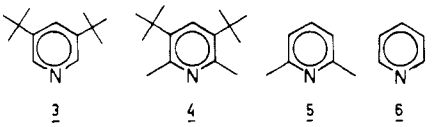
It has long been known that reactions with negative activation volumes are often especially sensitive to pressure if they are sterically hindered.[2] In some instances, the acceleration then is so pronounced that the reaction is essentially possible only at high pressures; thus, pivalones form semicarbazones only at high pressure.[3] A systematic study[4] of the rates of methylation of 2,6-disubstituted pyridines led us to conclude that the more hindered transition states are "later", i.e., they have more fully formed C–N bonds and hence larger dipole moments, and this condition produces the larger volume shrinkage. In other words, the phenomenon is a manifestation of the Hammond postulate,[5] or better,[6] of the Melander corollary[7] of this postulate. Presently, we report a study of the question whether indirectly hindered ("buttressed") reactions are also subject to this phenomenon.

There is one example of a buttressed Menschutkin reaction: Howie and Brown[8] observed that the methylation rate of 5-*tert*-butyl-2-methylpyridine (**1**) is 3.9 times faster than that of 3-*tert*-butyl-2-methylpyridine (**2**). We decided to explore the possibility of a similar study with compounds **3** and **4** for two reasons. One of these was that we simply needed a larger effect to justify the expectation of a correlation with pressure-induced rate enhancement; the other was our curiosity whether the transition state with **2** might have adjusted to buttressing on one side by increased N-methyl bending (in or out-of-plane) on the other. If such bending is important, one could imagine that buttressing in **4** might be much more severe than in **2**. We expected to assess the various substituent effects by comparing the methylation rates of **3**, **4**, 2,6-lutidine (**5**), and pyridine itself (**6**).



1 **2**





3 **4** **5** **6**

Results

Howie and Brown[8] had prepared their compounds by means of initial exhaustive methylation (methyl iodide and sodamide in liquid ammonia) of the methyl group in 3-picoline to give 3-*tert*-butylpyridine followed by the ring methylation in the α-positions via thermal lead tetraacetate decomposition. We repeated these reactions but found that the initial step could not be used to prepare **3**: the 3,5-diisopropyl homologue could be obtained in excellent yield from 3,5-lutidine, but after that the conversion rate became too low to overcome mounting recovery losses. A small amount of **3**, sufficient for characterization, became available in this way, but this route was clearly not a suitable one to **4**.

Our next attempt was based on the reported[9] formation of ethyl 3,5-di-*tert*-butyl-2-picolinate in the aluminum bromide catalyzed low-temperature cyclocongregation of *tert*-butylacetylene with methyl cyanoformate; however, removal of the ester function led to 3,4-di-*tert*-butylpyridine, exposing an error in structure assignment.[10] At this time, Komatsu reported[11] the general approach to the synthesis of 3,5-dialkylpyridines shown in Scheme I; the compounds so formed included **3** although the yield was only 20% (by NMR) and this material was not isolated.

(1) Based in part on the thesis of R.W., State University of New York at Stony Brook, 1984.

(2) For review: Asano, T.; le Noble, W. J. *Chem. Rev.* **1978**, *78*, 407. A sequal to this article, coauthored by R. van Eldik, has been accepted for publication.

(3) A report on this fact has been accepted for publication in *J. Org. Chem.*

(4) (a) le Noble, W. J.; Ogo, Y. *Tetrahedron* **1970**, *26*, 4119. (b) le Noble, W. J.; Asano, T. *J. Am. Chem. Soc.* **1975**, *97*, 1778.

(5) Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334.

(6) Farcasiu, D. *J. Chem. Ed.* **1975**, *52*, 76.

(7) Melander, L. *The Transition State*, Special Publication No. 16; The Chemical Society: London, 1962; p 119.

(8) Howie, M. S. Ph.D. Thesis, Purdue University, 1960. We are indebted to Professor H. C. Brown for making a copy of this thesis available to us and to Dr. B. Haske of Dowling College for preparing a sample of **3** by this route.

(9) Hogeveen, H.; Kingma, R. F.; Kok, D. M. *J. Org. Chem.* **1982**, *47*, 989.

(10) Wedinger, R.; Hogeveen, H.; le Noble, W. J. *J. Org. Chem.* **1984**, *49*, 1338.

(11) Komatsu, M.; Takamatsu, S.; Vesaka, M.; Yamamoto, S.; Oshiro, Y.; Agawa, T. *J. Org. Chem.* **1984**, *49*, 2691.

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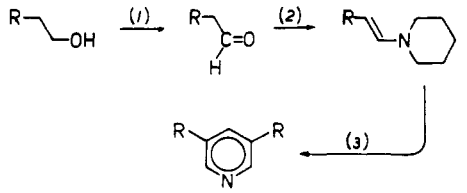
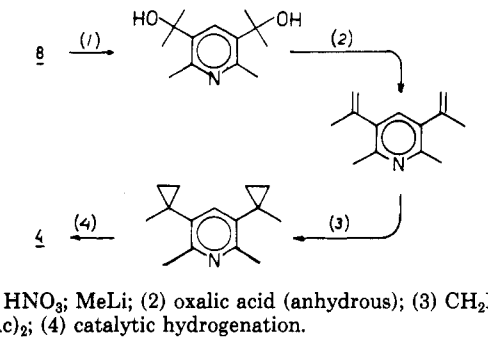
Scheme I[a]



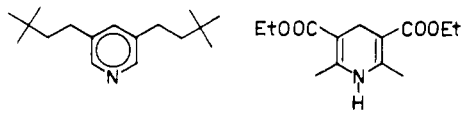
[a] (1) Dicyclohexylcarbodiimide in DMSO–CF_3COOH–pyridine; (2) piperidine, *p*-toluenesulfonic acid; (3) *p*-toluenesulfonic acid, alkyl azomethine, benzene, 200 °C.

Scheme II[a]



[a] (1) HNO_3; MeLi; (2) oxalic acid (anhydrous); (3) CH_2N_2–$Pd(OAc)_2$; (4) catalytic hydrogenation.

We were able to prepare **3** in reasonable quantities by this route, which gave 3,5-di-*neo*-hexylpyridine **7** as an unexpected byproduct. We later also found that we could



transform the commercially available 3,5-dibromopyridine into **3** by means of Bell's procedure.[12] This involves treatment with excess *tert*-butylmagnesium chloride in THF at −85 °C with cuprous cyanide catalysis. The yield was low, but optimization may improve it. Compound **4** was obtained by elaboration of Hantzsch's ester **8**[13] by the route shown in Scheme II; this is essentially the method advocated by Schleyer[14] for introducing *tert*-butyl groups. The method's success depends on which of the cyclopropyl bonds is most likely to be reduced.[15] Thus, we found that the method could not be applied in the absence of the 2- and 6-methyl groups; the reduction then leads to a highly complex mixture, and we presume that the "wrong" bond is then opening. The ^{13}C signals of C_2, C_3, and C_4 in **3** and **4** appear at 144.4, 145.0, and 129.6, and at 152.2, 139.7, and 132.0 ppm, respectively, in excellent agreement (±1–2 ppm) with the values calculated on the basis of the additivity scheme used previously.[10]

For the rate measurements, we wished to use the conductance method, which is convenient and accurate; it is usually recommended that the medium contain some water since otherwise curved Guggenheim plots[16] may be obtained. Unfortunately, the low solubilities of **3** and **4** and the slow, competing hydrolysis of methyl iodide interfered.

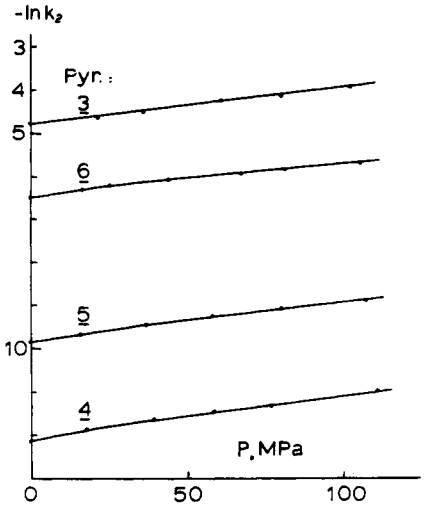


Figure 1. Effect of pressure on the rates of methylation of pyridines **3**–**6** in acetonitrile at 45.0 °C.

Table I. Second-Order Rate Constants and Activation Volumes of Pyridines 3–6 in Acetonitrile–Methyl Iodide at 45.0 °C

compd	10^3k_2, M^{-1} s^{-1}	$\Delta V^{\ddagger}$, cm^3/M
3	8.44	−21.4 ± 0.4
4	0.00528	−32.5 ± 0.5
5	0.0520	−30.8 ± 0.2
6	1.471	−28.5 ± 0.2

Somewhat to our surprise, dry acetonitrile also gave excellent linear plots under conditions of temperature (45.0 °C), pressure (0–100 MPa; 1 MPa = 10 bar), and pyridine concentration (<10^{-3} M) that were convenient to us. A similar finding has been reported recently by Yoh.[17] The methyl iodide concentration was 0.08 M for the faster reactions of **3** and **6** and 1.6 M for the slower ones of **4** and **5**. Infinity resistances could not be measured since methyl iodide does eventually generate a detectible conducting species.

The 1-atm rate constants and volume data are given in Table I. The rate for each compound was measured at six to seven pressures; the results are displayed in Figure 1 and recorded in tabulated form in the supplementary pages. The individual pseudo-first-order rate constants are the results of fits with correlation coefficients that exceed 0.999 99 in most cases and that in no case are below 0.9996. Values of duplicate runs generally agreed to about 1%. Curvature in the pressure dependencies are exceedingly small or absent altogether; it is therefore estimated that the activation volumes are reliable to better than usual precision.

Discussion

The data show that the 3,5-*tert*-butyl groups in **3** accelerate the Menschutkin methylation of **6** by a factor of 5.74 under the conditions chosen. The 2,6-methyl groups of **5** retard the reaction by a factor of 28.3 (comparable to the ratio of 35 we had observed earlier in acetone at 25 °C[4a]). When both factors operate simultaneously, retardation by a factor of 280 is observed. If the electronic and steric effects of the *tert*-butyl and methyl groups had been additive, we should have expected retardation by a factor of 28.3/5.74 = 4.93; hence, an extra factor of 280/4.93 = 57 is operating, which can be attributed to buttressing. On the basis of the data measured by Howie and Brown,[8] one

(12) Bell, T.; Hu, L.-Y.; Patel, S. V.; *J. Org. Chem.* **1987**, *52*, 3847.
(13) Hantzsch, A. *Justus Liebigs Ann.* **1882**, *215*, 1. Blatt, A. H. *Organic Syntheses*; Wiley: New York, 1943; Collect. Vol. II, p 214. We are indebted to Dr. P. Staub for preparing this compound.
(14) Woodworth, C. W.; Buss, V.; Schleyer, P. v. R. *J. Chem. Soc., Chem. Commun.* **1968**, 569.
(15) Majerski, Z.; Schleyer, P. v. R. *Tetrahedron Lett.* **1968**, 6195.
(16) Guggenheim, E. A. *Phil. Mag.* **1926**, *7*(2), 538.
(17) Yoh, S.-D.; Park, J.-H.; Lee, K.-A.; Han, I.-S. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 1149.

should have expected a buttressing factor of 3.9[2] or 15.2; the extra factor of 57/15.2 = 3.8 is attributable to the escape hatch in the form of the bending described above. The effect is obviously small; nevertheless, the accuracy of the data warrants the claim that it has been detected.

The activation volumes are large and negative as is to be expected for reactions in which charge generation goes hand in hand with bond formation,[18] with both features contributing to the shrinkage. The trend among the $\Delta V^{\ddagger}$ values is also normal, with the fastest reaction being accelerated the least, and the slowest the most. The difference between **5** and **6**, 2.3 cm^3/mol, is within the error limits the same as that observed[4a] earlier in acetone (2.5 cm^3/mol). The relatively modest contraction in the case of **3** is somewhat surprising; a value of −25 or −26 cm^3/mol would have seemed more in line with the other values. We can presently not account for this value. Overall, however, the sequence nicely agrees with the interpretation offered earlier,[4b] to the effect that the more negative activation volumes of the slower substrates are a manifestation of the Hammond postulate.

Experimental Section

Melting points, recorded by means of Thomas-Hoover apparatus, are uncorrected. ^{1}H NMR spectra were variously recorded with an HFT-80 (Varian) or a Nicolet NT-300 instrument. 2D NMR spectra were measured with a QE-300, spectrometer; the chemical shifts are given relative to TMS and with $CHCl_3$ as internal standard at δ 7.25 and $CDCl_3$ at δ 77.00. UV spectra were recorded with a Cary-14 spectrometer. GC analysis and separations were carried out with a Varian Aerograph Model-920 gas chromatograph with a 6-ft column, 20% Carbowax on Chromosorb (30–60 mesh). Mass spectra were recorded by means of a Hewlett-Packard 5980-A instrument. Elemental analyses were done by Galbraith Laboratory, Inc.

3,5-Bis[2-(2-hydroxypropyl)]-2,6-lutidine. 3,5-Dicarbethoxy-2,6-dimethylpyridine[13] (13.5 g, 48 mmol) was dissolved in 146 mL of dry ether under nitrogen, and 180 mL of 1.5 M methyllithium was added in 2 h. The resulting orange suspension was stirred at room temperature overnight, cooled to 0 °C, and quenched with 60 mL of saturated aqueous ammonium chloride. The aqueous layer was washed with methylene chloride (3 × 60 mL); the organic layers were combined and dried over anhydrous sodium sulfate. After filtration, the solvent was removed to give the diol in essentially 100% yield. The product was sublimed to give orange needles. ^{1}H NMR: δ 1.64 (s, 12 H), 2.13 (s, 2 H), 2.66 (s, 6 H), 7.85 (s, 1 H).

3,5-Diisopropenyl-2,6-dimethylpyridine. The diol (12.5 g, 56 mmol) was mixed with 9.40 g of anhydrous oxalic acid[19] and heated under nitrogen to 180–190 °C for 1 h. After a half hour, 5.89 g of additional anhydrous acid was employed. The mixture melted to a viscous dark brown liquid. Upon cooling, 300 mL of ether and 300 mL of 5% sodium bicarbonate solution were added; the aqueous solution was separated, neutralized with dilute sodium hydroxide, and extracted with ether (3 × 100 mL). The combined organic layers were washed with saturated salt solution (2 × 200 mL) and dried over anhydrous sodium sulfate. After filtration, the solvent was evaporated to a residue, which was twice distilled under vacuum to give a pale yellow oil (5.93 g, 56%). ^{1}H NMR: δ 2.02 (m, 6 H), 2.48 (s, 6 H), 4.88 (m, 2 H), 5.20 (m, 2 H), 7.11 (s, 1 H).

3,5-Bis(α-methylcyclopropyl)-2,6-dimethylpyridine. The diene (5.2 g, 28 mmol) was dissolved in 20 mL ether and cooled to 0 °C, and 50 mg of palladium acetate[20] was added. With vigorous stirring, 200 mL of an ethereal solution of diazomethane (prepared from 20 g of *N*-nitroso-*N*-methylurea[21] and 60 mL of 40% potassium hydroxide) was added. After gas evolution ceased, the dark solution was stirred for 2 h; 5 mg of fresh palladium acetate was added to ensure complete decomposition of the diazomethane. After a half hour, the solution was filtered and concentrated to small volume. The cyclopropanation is not efficient; it was repeated 15 times before the unconverted and half-converted compounds were no longer detectable by GC (150 °C). The crude product was vacuum distilled to give 1.2 g (20%) of pure product. ^{1}H NMR: δ 0.72 (s, 6 H), 1.27 (s, 8 H), 2.58 (s, 6 H), 7.40 (s, 1 H). ^{13}C NMR: δ 13.97, 19.27, 21.61, 25.67, 136.84, 138.99, 154.92.

3,5-Di-*tert*-butyl-2,6-lutidine (4). A mixture of 0.803 g (3.7 mmol) of 3,5-bis(α-methylcyclopropyl)-2,6-lutidine, 25 mL of acetic acid, and 2.4 g of platinum oxide was subjected to hydrogenation at 80 °C and 60 psi in a Parr apparatus for 72 h. It was cooled to room temperature, filtered, and flash evaporated; 2.5% sodium hydroxide (20 mL) was added to the residue. After extraction with methylene chloride (4 × 50 mL), drying over anhydrous sodium sulfate, and filtration, solvent removal gave 0.733 g (89% yield) of a pale yellow oil. Further purification by GC served to give samples suitable for kinetic studies. ^{1}H NMR: δ 1.39 (s, 18 H), 2.67 (s, 6 H), 7.60 (s, 1 H). ^{13}N NMR: δ 25.46, 30.57, 34.38, 131.96, 139.67, 152.20.

3,3-Dimethylbutanal. 3,3-Dimethylbutanol (1.2 mL, 10 mmol), 30 mL of dry benzene, 33 mL of dry dimethyl sulfoxide, 0.8 mL of dry pyridine, 0.4 mL of trifluoroacetic acid, and 6.6 g of dicyclohexylcarbodiimide[22] were mixed, in that order. After 18 h of stirring under nitrogen, benzene (30 mL) was added, and the white crystalline dicyclohexylurea was filtered and washed with benzene. Upon distillation, the colorless aldehyde was collected from 101–103 °C (504 mg, 50%e. ^{1}H NMR: δ 1.05 (s, 9 H), 2.22 (d, 2 H), 9.75 (t, 1 H).

1-(3,3-Dimethyl-1-butenyl)piperidine. 3,6-Dimethylbutanal (500 mg, 5 mmol), 0.6 mL (6 mmol) of piperidine, 8 mg of *p*-toluenesulfonic acid, and 20 mL of anhydrous benzene were placed in a 50-mL flask fitted with a Dean–Stark trap and refluxed overnight. The product was cooled, poured into 20 mL of water, and extracted with methylene chloride (3 × 20 mL). The extracts were combined, dried, and filtered, the excess solvent was removed, and the yellow oily residue was subjected to bulb-to-bulb distillation to give a pale yellow product (0.67 g, 80%). ^{1}H NMR: δ 1.01 (s, 9 H), 1.50 (br s, 6 H), 2.70 (br s, 4 H), 4.45 (d, J = 14.4 Hz, 1 H), 5.7k (d, J = 14.4 Hz, 1 H).

3,5-Di-*tert*-butylpyridine (3). The enamine (334 mg, 2 mmol), *N*-*tert*-butylmethanimine (85 mg, 1 mmol), 5.2 mg of *p*-toluenesulfonic acid, and 3.0 mL of benzene were put together into a stainless steel tube. The tube was flushed with argon, sealed, and placed in a 200 °C oven for 18 h; the dark brown liquid was recovered with methylene chloride and washed with 50 mL of 2.5% sodium hydroxide and saturated sodium chloride solutions. After drying and filtration, the solution was eluted with methylene chloride through a short column of silica gel. The excess solvent was removed, and the brown liquid was loaded on UV-sensitive preparative TLC plates and developed with 30% (v/v) ethyl acetate/hexane. Two major bands visible under UV light were cut from the plates, with R_f = 0.57 for **3** and 0.80 for **7**. Compound **3** was further purified by preparative GC; 25 mg (13%) was isolated as a white solid, mp 41–43 °C. MS: m/z 191. ^{1}H NMR: δ 1.34 (s, 18 H), 7.65 (t, J = 2 Hz, 1 H), 8.47 (d, J = 2 Hz, 2 H). ^{13}C NMR: δ 31.09, 33.63, 129.64, 144.42, 144.95. Anal. Calcd.: C, 81.60; H, 11.07. Found: C, 81.22; H, 10.91.

Compound **7** was purified by vacuum sublimation; white needles, mp 68–70 °C. MS: m/z 247. UV (chloroform) λ_{max} (nm) 265, 270, 277. ^{1}H NMR: δ 0.96 (s, 18 H), 1.49–1.43 (m, 4 H), 2.56–2.50 (m, 4 H), 7.28 (t, J = 2 Hz, 1 H), 8.24 (d, J = 2 Hz, 2 H). ^{13}C NMR: δ 28.30, 29.29, 30.60, 46.09, 135.43, 138.06, 147.12. Anal. Calcd: N, 5.66. Found: N, 5.76.

Kinetics. Pyridine and 2,6-lutidine were obtained from commercial sources and distilled from activated 4-Å molecular sieves. Methyl iodide was purified by distillation from anhydrous calcium chloride.

The reactions were carried out in a conductance cell containing an acetonitrile solution of the appropriate concentration of methyl iodide and pyridine; the cell was suspended in a high-pressure

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(19) Carlin, R. B.; Constantine, D. A. *J. Am. Chem. Soc.* **1947**, *69*, 50.
(20) Suda, M. *Synth. Commun.* **1981**, 714.
(21) Blatt, A. H. *Organic Syntheses*; Wiley: New York, 1943; Collect. Vol. II, p 165.
(22) Baumgarten, H. E. *Organic Syntheses*; Wiley: New York, 1973; Collect. Vol. V, p 242.

vessel thermostatted at 45.0 ± 0.1 °C. The resistance of the cell, measurable to ±1 Ω by means of a conductance system consisting of an oscilloscope and a AC Wheatstone bridge apparatus, was read every 2 min for fast reactions and every 15–30 min for slower ones for about 1 half-life; the second set of readings was taken at least 1 half-life later. Each rate constant is based on two to three sets of 10 or more resistance measurements. All were calculated by means of Guggenheim's method;[16] further details made be found in an earlier report from this laboratory.[23] The rate constants were fitted by means of the expression $\ln k = a + bP + cP^2$; b is then the slope $(\partial \ln k/\partial P)_T$ at $P = 0$, and ΔV_0^* follows as $\Delta V_0\sigma = -bRT$.[24] To assess interference from possible side reactions, control experiments were done with a 1.6 M solution of methyl iodide in acetonitrile alone. A conducting species does eventually form as indicated by a resistance drop into the measurable range (100 000 Ω); however, the interference had a negligible effect on the rate measurements.

(23) le Noble, W. J.; Shurpik, A. *J. Org. Chem.* **1970**, *35*, 3588.
(24) For an improved procedure, see: Asano T.; Okada, T. *J. Phys. Chem.* **1984**, *88*, 238. In the present case, the curvature is too faint to affect the calculations.

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Registry No. **3**, 90554-37-3; **4**, 117860-46-5; **5**, 108-48-5; **6**, 110-86-1; **7**, 117860-47-6; **8**, 1149-23-1; 3,5-dibromopyridine, 625-92-3; 3,5-bis[2-(2-hydroxypropyl)]-2,6-lutidine, 117860-48-7; 3,5-diisopropenyl-2,6-dimethylpyridine, 117860-49-8; 3,5-bis(α-methylcyclopropyl)-2,6-dimethylpyridine, 117860-50-1; 3,3-dimethylbutanol, 624-95-3; 3,3-dimethylbutanal, 2987-16-8; 1-(3,3-dimethyl-1-butenyl)piperidine, 90554-29-3; *N-tert*-butylmethanimine, 13987-61-6; methyl iodide, 74-88-4; 3,5-di-*tert*-butylpyridine methiodide, 117860-51-2; 3,5-di-*tert*-butyl-2,6-dimethylpyridine methiodide, 117860-52-3; 2,6-lutidine methiodide, 2525-19-1; pyridine methiodide, 930-73-4.

Supplementary Material Available: Four tables of the rate constants referred to in this article (4 pages). Ordering information is given on any current masthead page.

A Theoretical Study on the Mechanism of the Thermal and the Acid-Catalyzed Decarboxylation of 2-Oxetanones (β-Lactones)

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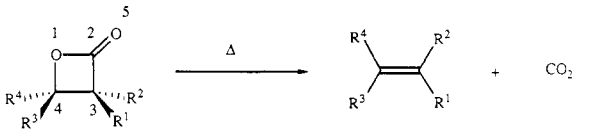
The thermolysis of 2-oxetanones (β-lactones) leading to carbon dioxide and olefins has been studied for the first time from the theoretical point of view by means of the semiempirical SCF-MO methods AM1, MNDO, and MINDO/3 at the RHF level. The reaction of the parent 2-oxetanone is predicted by all three methods to be concerted but highly asynchronous, taking place through a transition state with high zwitterionic character where all ring atoms lie in the same plane. An AM1-HE-CI study of the same process shows the absence of diradical character along the reaction path. The AM1 calculated enthalpy of activation and enthalpy of reaction are the closest to the experimental ones. The process has also been examined on a set of 25 diversely substituted 2-oxetanones by the AM1 method, the experimentally observed substituent effects being well reproduced by the calculations. The decarboxylation of 2-oxetanone protonated at the carbonyl oxygen atom has been studied as a model for the acid-catalyzed thermolysis of 2-oxetanones, finding that in this case the reaction takes place stepwise, through a carbocationic intermediate whose preferred conformation allows an interpretation of the observed stereochemical outcome of the reaction under acid catalysis. A reaction analysis by correlation of localized molecular orbitals has been performed on both the purely thermal and the acid-catalyzed processes, allowing the visualization of the electronic changes that take place along the reaction coordinate. Some simple ways of using the bond index concept for the study of chemical reactions are proposed. Application of these ideas to the thermolysis of 2-oxetanones reveals the existence of significant correlations between the parameters derived from bond index analysis and calculated enthalpies of activation.

Introduction

The thermal decarboxylation of β-lactones (2-oxetanones) is a well-established methodology for the stereospecific synthesis of subtituted olefins.[1] The reaction is also interesting from the mechanistic point of view, since it is one of the very few examples of a [2 + 2]-cycloreversion process taking place with retention of configuration (Scheme I).

Scheme I



On the other hand, the kinetics of the gas-phase thermal decomposition of the parent 2-oxetanone was studied several years ago,[2] and the process was found to be first order, the intermediacy of radicals being excluded by the fact that nitric oxide had no effect on the reaction rate.

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(2) James, T. L.; Wellington, C. A. *J. Am. Chem. Soc.* **1969**, *91*, 7743.

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