distribution of the isotopes of boron, carbon, and hydrogen. In agreement with observation in our laboratory on the 70-V mass spectra of other amine boranes, the positive ion derived by hydrogen loss from the parent molecule is the most abundant species.

The molecular weight obtained in a vapor pressure osmometer with benzene as solvent was 135.

The ^{11}B spectrum gave two 1:2:1 triplets with A_{B-H} = 110 Hz at +12.3 ppm for one triplet and A_{B-H} = 97 Hz at +25.2 ppm for the remaining triplet (trimethyl borate reference).

The triplet at +12.3 ppm is assigned to the boron in position 2 of the ring based on a similar chemical shift to the boron atoms in $[(CH_3)_2NBH_2]_2$. The triplet at +25.2 ppm is assigned to the boron atom in position 4 of the ring based on a similar chemical shift and coupling constant to the boron atoms in compound II.

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A Remote, Anodic Rearrangement–Substitution Reaction of Aliphatic Ketones

Sir:

A conceptually useful analogy between mass spectrometry and anodic chemistry is emerging from studies of the anodic chemistry of aliphatic compounds. Recent studies have, for example, demonstrated that branched alkanes[1] and α-branched ketones[2,3] anodically mimic the fragmentations observed by mass spectrometry. We, therefore, reasoned that ketones without α-branching should anodically give an intramolecular hydrogen abstraction and perhaps β-cleavage in analogy with the McLafferty rearrangement.[4] This paper reports an initial investigation of that hypothesis. To our knowledge, there are no literature reports of the anodic oxidation of such aliphatic ketones in aprotic media. The results obtained reveal a unique and potentially useful reaction which should be general for ketones.

The ketones investigated were 4,4-dimethyl-2-pentanone (I), 4-methyl-2-pentanone (II), 2,6-dimethyl-4-heptanone (III), and 2-hexanone (IV). The reactions were performed potentiostatically, in a three-compartment cell,[5] at room temperature, in acetonitrile at platinum. The reference electrode was Ag|0.1 *N* $AgNO_3$ in acetonitrile. The solvent was twice distilled from phosphorus pentoxide and lithium perchlorate (0.1 *N*) was the supporting electrolyte. Further information on the oxidations and $E_{p/2}$ values for the ketones is shown in Table I.

The oxidations were arbitrarily terminated after passage of ~2 faradays/mol of added ketone. The anolyte was worked up by distillation of the acetonitrile (not to dryness, contains $HClO_4$!). Then, 10% aqueous $NaHCO_3$ was added and the mixture extracted several times into chloroform. The chloroform solution was dried over anhydrous magnesium sulfate, filtered, and evaporated, and the products were isolated by preparative glc on a 10% SE-30 on Chromosorb W column. All the isolated products were ketoamides which were characterized spectrally (Table II).

The ir spectra of V–X gave bands near 3300, 1660, and 1550 cm^{-1} characteristic of *N*-alkylacetamides and a ketone band at 1710 cm^{-1}. Nmr and mass spectral

Table I. Voltammetric Data

Substrate (mmol)	$E_{p/2}$[a]	E[b]	n[c]	i_0,[d] mA	Product (% yield)[e]
I (4.0)	2.45	2.25	2.2	270	V (50)
(2.0)		2.30	3.3	130	V (40)
I (1.0) + $(CH_3)_2$-CHCH$(CH_3)_2$ (10.0)		2.25	2.2	130	V (50)
II (5.3)	2.40	2.20	2.0	120	VI (20) VII (20)
III (3.65)	2.50	2.25	2.0	120	VIII (20) IX (20)
IV (1.65)	2.45, 2.60	2.30	2.2	80	X (40)

[a] Potentials are quoted *vs.* Ag|0.1 *N* $AgNO_3$ reference electrode at a voltammetric sweep rate of 0.5 V/sec. [b] The controlled potential used in preparative experiments. [c] Number of electrons transferred per molecule of added substrate. [d] Initial current. The background current for all experiments was 2–3 mA at 2.3 V. [e] Yields based on isolated products compared to added reactant.

Table II. Products of Electrooxidation and Spectroscopic Data

Substrate	Product	Nmr[a] and mass spectra
I	4-Acetamido-4-methyl-2-hexanone (V)	Nmr: 0.75 (t, 3 H), 1.27 (s, 3 H), 1.80 (oct, 2 H, J = 2.5 Hz), 1.85 (s, 3 H), 1.91 (s, 3 H), 2.88 (AB quartet, 2 H, J = 16.5 Hz), 5.91 (s,[b] 1 H). Mass spectral: 171.1277 ($M\cdot^+$), 156, 142, 128, 114, 113, 100, 58, 57, 43
II	4-Acetamido-4-methyl-2-pentanone (VI)	Nmr: 1.40 (s, 6 H), 1.95 (s, 3 H), 2.10 (s, 3 H), 2.98 (s, 2 H), 6.20 (s,[b] 1 H). Mass spectral: 157.1090 ($M\cdot^+$), 114, 100, 58, 57, 43
	4-Acetamido-2-hexanone (VII)	Nmr: 0.9 (t, 3 H), 1.5 (m, 2 H), 2.0 (s, 3 H), 2.2 (s, 3 H), 2.65 (d, 2 H), 4.2 (m, 1 H), 6.2 (s,[b] 1 H). Mass spectral: 157.1111 ($M\cdot^+$), 128, 114, 100, 58, 43
III	2-Acetamido-2,6-dimethyl-4-heptanone (VIII)	Nmr: 0.9 (d, 3 H), 1.4 (s, 6 H), 1.95 (s, 3 H), 2.0–2.4 (m, 3 H), 2.9 (s, 2 H), 6.8 (s,[b] 1 H). Mass spectral: 199 ($M\cdot^+$), 184, 157, 142, 114, 100, 58, 43
	6-Acetamido-2-methyl-4-octanone (IX)	Nmr: 0.8–1.1 (m, 9 H), 1.5 (m, 2 H), 1.98 (s, 3 H), 2.3 (3 H), 2.65 (d, 2 H), 4.1 (m, 1 H), 6.2 (s,[b] 1 H). Mass spectral: 199 ($M\cdot^+$), 170, 157, 142, 128, 114, 100, 86, 58, 43
IV	5-Acetamido-2-hexanone (X)	Nmr: 1.17 (d, 3 H), 1.93 (s, 3 H), 2.18 (s, 3 H), 1.57–2.17 (m, 2 H), 2.37–2.77 (m, 2 H), 3.65–3.93 (m, 1 H), 6.10 (s,[b] 1 H). Mass spectral: 157 ($M\cdot^+$), 114, 100, 86, 58, 57, 43

[a] Nmr data are given in ppm. [b] Broad singlet.

(1) T. M. Siegel, L. L. Miller, and J. Y. Becker, *J. Chem. Soc., Chem. Commun.*, in press.
(2) V. Koch and L. L. Miller, *J. Amer. Chem. Soc.*, **95**, 8631 (1973).
(3) Unpublished results of T. M. Siegel and J. Y. Becker.
(4) H. Budzikiewicz, C. Djerassi, and D. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco, Calif., 1967, Chapter 3.
(5) E. A. Mayeda, L. L. Miller, and J. F. Wolf, *J. Amer. Chem. Soc.*, **94**, 6812 (1972).

data are given in Table II and were definitive with respect to the position of substitution. The nmr spectrum of product X, for example, was analyzed as follows (nmr data in δ): H_a, 2.18; H_b, 2.36–2.77; H_c, 1.57–2.17; H_d, 3.65–3.93; H_e, 1.17; H_f, 6.10; H_g, 1.93.

The simplest process we have observed is exemplified by the formation of X from 2-hexanone. X is the major product, and other ketoamides are present in negligible amount. Abstraction of γ-hydrogen[6] and acetamidation of the resulting carbonium ion[3] can account for X.

$$CH_3CO(CH_2)_3CH_3 \xrightarrow{-2e^-} CH_3COCH_2CH_2\overset{+}{C}HCH_3 + H^+$$

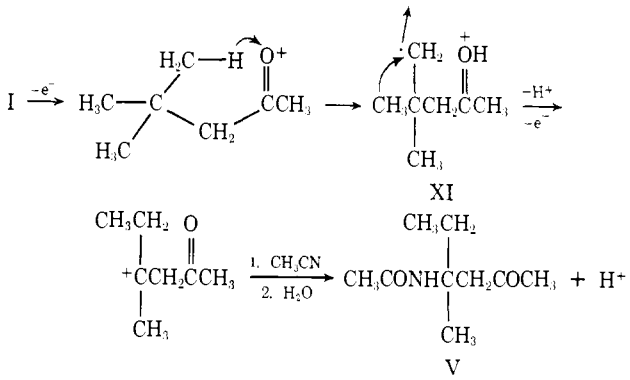
$$CH_3COCH_2CH_2\overset{+}{C}HCH_3 \xrightarrow{CH_3CN} CH_3COCH_2CH_2CH(N{=}\overset{+}{C}CH_3)CH_3 \xrightarrow[H_2O]{}$$

$$CH_3\overset{a}{C}OCH_2\overset{b}{C}H_2\overset{c}{C}H(\overset{f}{N}H\overset{g}{C}OCH_3)\overset{d}{C}H_3\overset{e}{}$$

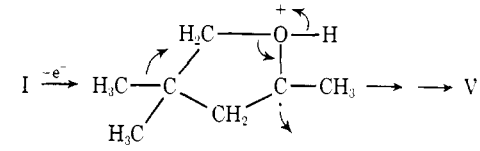
X

Formation of V from I requires loss of an unactivated hydrogen, rearrangement and addition of the acetamide moiety. An intramolecular mechanism which incorporates these steps and explains products VI–X as well is shown in Scheme I.

Scheme I



The basic outlines of this mechanism are consistent with the observations made to date. Initial electron transfer from substrate is indicated since background current at 2.3 V is only ~2% of that due to added ketone. Also, if the concentration of ketone is increased the initial current increases proportionately. $E_{p/2}$ values (Table I) fit the crude correlation between $E_{p/2}$ and IP.[7,8] A real or incipient primary carbonium resulting from hydrogen transfer to the oxygen and loss of a second electron seems the requisite intermediate to account for rearrangement.[9] The tertiary carbonium ion so produced would then lead to acetamide in the conventional manner. The γ-hydrogen abstraction is analogous to mass spectrometry[4] and photochemistry.[10] β-Cleavage, however, clearly does not occur. An explanation of this difference between mass spectrometry and the anodic reaction will be deferred, since the presence of excess oxidant and nucleophilic solvent and the absence of excess energy in the anodic process must be considered. Alternative mechanisms to that in Scheme I involve intermolecular reactions or insertion to form XII.



XII

The intermolecular mechanism was tested by oxidizing I in the presence of a tenfold excess of diisopropane and the hydrocarbon did not change the current at 2.3 V. Careful examination of the products did not reveal any dimeric hydrocarbon, *e.g.*, $[(CH_3)_2CHC(CH_3)_2]_2$, or any amide from the hydrocarbon, *e.g.*, $(CH_3)_2CHC(CH_3)_2NHCOCH_3$. The only product detected was ketoamide V. This result indicates that intramolecular abstraction of hydrogen is more likely than an intermolecular reaction, with a molecule expected to be a good hydrogen donor. Furthermore, we have not observed succinonitrile as a product (due to dimerization of acetonitrile).

Products VII and IX can also be explained by the intramolecular mechanism with a methyl migration as in Scheme I. In competition with this γ-abstraction methyl shift, we suspect there is a γ-abstraction hydride shift[9] and/or β-hydrogen abstraction leading to VI and VIII.

In conclusion, a consideration of mass spectrometry mimicry has led to the discovery of a unique reaction which produces carbonium ions from unactivated alkyl groups.[11] Application to geometrically constrained ketones should prove especially profitable from a synthetic viewpoint.

Acknowledgment. This work was supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

(6) It may be noted that abstraction of a δ (primary) hydrogen followed by 1,2 hydride shift produces the same product. We will test this by a deuterium labeling study.

(7) L. L. Miller, D. G. Nordblom, and E. A. Mayeda, *J. Org. Chem.*, 37, 916 (1972).

(8) It was noted that all α-substituted ketones oxidize more easily than their nonbranched counterparts. A corresponding difference is seen in gas phase ionization potentials.

(9) 1,2-Migration of methyl to a primary carbonium ion is a very facile process. On the other hand, methyl migrations of this type are not known for radicals. Literature analogies suggest that isobutyl type carbonium ions (available from II and III) should rearrange by competing hydride and methyl shifts: P. deMayo, "Molecular Rearrangement," Vol. I, Interscience, New York, N. Y., 1963.

(10) R. O. Kan, "Organic Photochemistry," McGraw-Hill, New York, N. Y., 1966.

(11) L. L. Miller and V. Ramachandran, *J. Org. Chem.*, **39**, 369 (1974).

(12) A. P. Sloan Fellow, 1972–1974.

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Photocyclization of N-Alicyclic Phthalimides.[1] Synthesis of Multicyclic Benzazepine Systems[2,3]

Sir:

N-Alkylated phthalimides generally undergo photocyclization to cyclobutanols in a Norrish type II photo-

(1) Photochemistry of the Phthalimide System. VI. Part V: Y. Sato, H. Nakai, H. Ogiwara, T. Mizoguchi, Y. Migita, and Y. Kanaoka, *Tetrahedron Lett.*, 4565 (1973).

(2) Photoinduced Reactions. XV. Part XIV: K. Itoh and Y. Kanaoka, in preparation.

(3) All new compounds gave satisfactory analyses, and their structures were supported by spectral (uv, ir, nmr, mass) data.