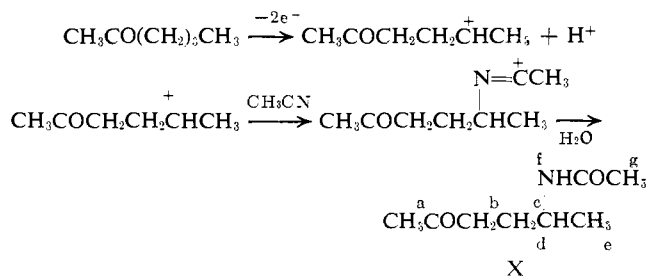data are given in Table II and were definitive with respect to the position of substitution. The nmr spectrum of product X, for example, was analyzed as follows (nmr data in δ): H_a, 2.18; H_b, 2.36–2.77; H_c, 1.57–2.17; H_d, 3.65–3.93; H_e, 1.17; H_f, 6.10; H_g, 1.93.

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.

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

$$CH_3CO CH_2CH_2\overset{+}{C}HCH_3 \xrightarrow{CH_3CN} CH_3COCH_2CH_2\overset{\overset{+}{N}=CCH_3}{\overset{|}{C}HCH_3} \xrightarrow{H_2O}$$

$$\overset{a\quad\quad b\quad c}{CH_3^{}COCH_2CH_2}\overset{\overset{f\quad\quad g}{NHCOCH_3}}{\underset{d\quad\quad e}{CHCH_3}}$$

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
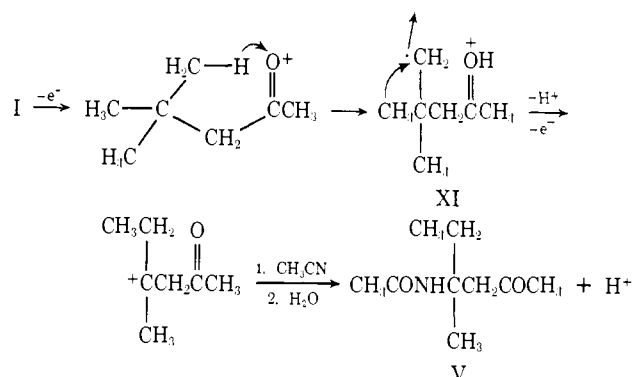
The basic outlines of this mechanism are consistent with the observations made to date. Initial electron transfer from substrate is indicated since background current at 2.3 V is only $\sim2\%$ of that due to added ketone. Also, if the concentration of ketone is increased the initial current increases proportionately. $E_{p/2}$ values (Table 1) 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

(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.

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
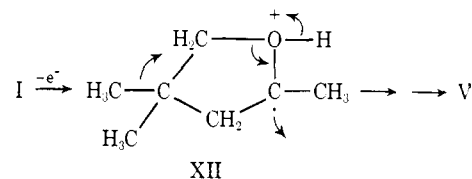
The intermolecular mechanism was tested by oxidizing I in the presence of a tenfold excess of diisopropane and the hydrocarbon did not change the current at 2.3 V. Careful examination of the products did not reveal any dimeric hydrocarbon, e.g., $[(CH_3)_2CHC(CH_3)_2]_2$, or any amide from the hydrocarbon, 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.

(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.
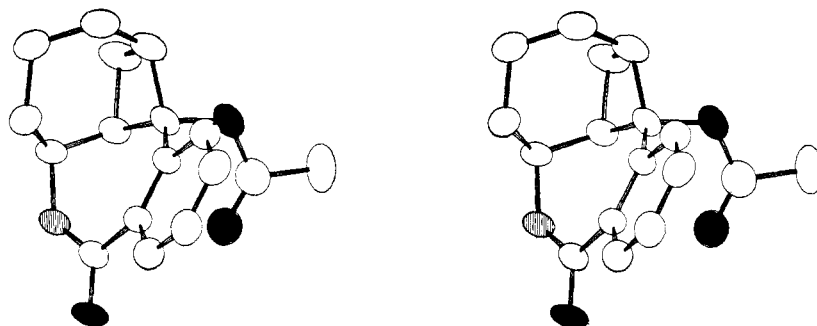
Figure 1. A stereodiagram of the structure of the O-acetyl derivative 6. The shaded atom is N while the blackened atoms represent O. The ellipsoids represent thermal motion at the 50% probability level.

process[4] followed by retrotransannular ring opening to benzazepinones.[5] When the 4-alkyl substituent has γ-hydrogen with respect to the newly formed ketonic carbonyl (position 5), type II photoelimination occurs with 4-dealkylation.[5]

Irradiation of **1a** in 10 mM acetonitrile solution with a 1-kW high-pressure mercury lamp for 2 hr afforded **3a** in 48% yield (mp 210–212°; ir 1695 (CO), 1650 cm⁻¹
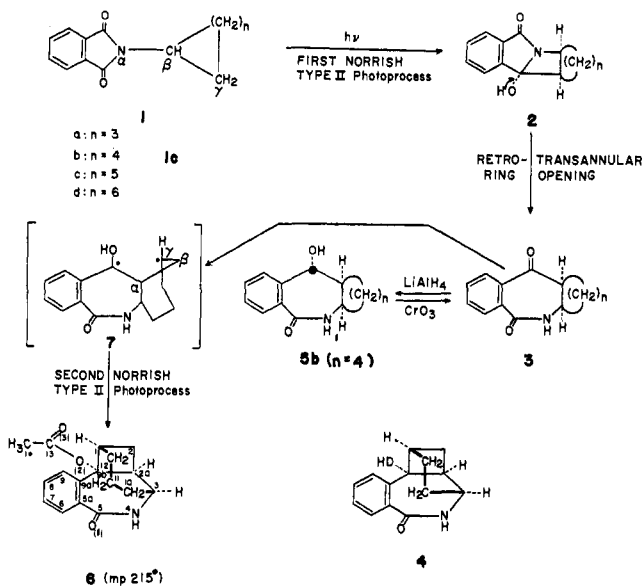
(NHCO); nmr (CDCl₃) 4.00–4.45 (NHCH); mass spectrum m/e 215 (M⁺). Its formation is readily explained by the type II process to give **2** followed by ring opening. The 3,4-cis junction of **3a** was confirmed by independent synthesis from 3-ethoxyisoindolone and cyclopentene, in analogy to the synthesis of the cyclohexene homolog.[6] Likewise, **1b** afforded, as expected, **3b** (mp 230–234°, 10%) whose structure was established by direct comparison with an authentic sample.[6] In addition a new compound, **4** (mp 244–246°, 14%), was isolated. The photolysis of **1a** and **1b** in ethanol produced the reduction products of **3a** and **3b**, viz., the lactam alcohols **5a** and **5b**, respectively, which were obtainable also by LiAlH₄ reduction from **3a** and **3b** and were oxidizable to the ketolactams by CrO₃. Photolysis of **1b** in tert-butyl alcohol increased the yield of the new photoproduct to 23%, while **1c** under the same conditions afforded exclusively another novel product, **6** (un-

(4) P. J. Wagner, Accounts Chem. Res., **4**, 168 (1971).
(5) Y. Kanaoka, Y. Migita, K. Koyama, Y. Sato, H. Nakai, and T. Mizoguchi, Tetrahedron Lett., 1193 (1973).
(6) T. H. Koch and K. H. Howard, Tetrahedron Lett., 4035 (1972).

acetylated), in 55% yield. Conversely, **3d** was the sole product (30%) of the photolysis of **1d**. These results demonstrate the effect of ring size and conformational parameters of **1** on the course of the photocyclizations and on the ratio of photoproducts.

The novel cyclization products **4** and **6** (unacetylated) have the same molecular weights (m/e 229 and 243) as their respective starting materials, **1b** and **1c**; they are both lactams (ir, 1642 cm⁻¹), possess a hydroxyl (3320 cm⁻¹), and form an O-acetate (**6**) and an N,O-diacetate. An X-ray diffraction analysis of a single crystal of the O-acetyl derivative **6** (mp 213–215°) established the complete structure as 1,2,2a,3,4,9b-hexahydro-9b-acetoxy-1,3-propano-5H-cyclobuta[d][2]benzazepin-5-one, with the three hydrogens in **1**, **2a**, and **3** and the oxygen function in **9b** all α or all β (pictured arbitrarily as one antipode).

The monoacetyl derivative **6** crystallizes in the monoclinic space group $P2_1/n$ with $a = 12.480$ (8) Å, $b = 13.614$ (10) Å, $c = 8.871$ (4) Å, and $\beta = 103.5$ (1)°. There are four molecules per unit cell corresponding to a calculated crystal density of 1.29 g/cm³. There were 2379 independent reflections collected from a colorless crystal (∼0.55 × 0.70 × 0.48 mm) on an automatic computer-controlled diffractometer with Cu Kα radiation (λ 1.54178 Å). The structure was solved by the symbolic addition procedure for centrosymmetric crystals,[7] and the molecular geometry for one antipode of the racemate is pictured in Figure 1. The atomic coordinates, which are listed in Table I, and thermal parameters were refined by the full-matrix least-squares method. All the hydrogen atoms were located in a difference map. Bond distances and angles lie within normal limits. Average distances are C_{sp^2}—C_{sp^2} = 1.402, C_{sp^2}—C_{sp^3} = 1.515, and C_{sp^3}—C_{sp^3} = 1.550 Å except for the cyclobutyl ring where the average C—C bond is 1.571 Å and C=O = 1.214 Å. The C—N and C—O bond lengths show the effects of conjugation with the adjacent C=O groups, thus N—C_{sp^2} = 1.361 Å, while N—C_{sp^3} = 1.475 Å and O—C_{sp^2} = 1.348 Å and O—C_{sp^3} = 1.479 Å in the acetyl moiety. The average C–C–C angle in the four-membered ring is 88.2°. The molecular packing is influenced by the presence of a pair of NH···O hydrogen bonds, N···O = 2.87 Å, which link the molecules into dimeric pairs across a center of symmetry. The hydrogen to oxygen distance is 1.90 Å and the N–H–O angle is 173.5°. There are no other intermolecular approaches less than van der Waals separations.

(7) J. Karle and I. L. Karle, Acta Crystallogr., **21**, 849 (1966).

Table I. Fractional Coordinates for
1α,2,2aα,3α,4,9bα-Hexahydro-9b-acetoxy-1,3-propano-5H-
cyclobuta[d][2]benzazapin-5-ne, One Arbitrary Antipode of 6.

Atom	x	y	z
C(1)	0.7053	0.1016	0.3829
C(2)	0.8203	0.0636	0.3651
C(2a)	0.8654	0.0800	0.5446
C(3)	0.8600	−.0100	0.6449
N(4)	0.9056	0.0175	0.8084
C(5)	0.8658	0.0862	0.8911
C(5a)	0.7586	0.1393	0.8261
C(6)	0.7022	0.1653	0.9411
C(7)	0.6004	0.2119	0.9027
C(8)	0.5531	0.2362	0.7485
C(9)	0.6101	0.2128	0.6337
C(9a)	0.7131	0.1646	0.6726
C(9b)	0.7678	0.1510	0.5382
C(10)	0.7471	−.0631	0.6345
C(11)	0.6753	−.0781	0.4680
C(12)	0.6238	0.0187	0.3952
C(13)	0.8666	0.3057	0.5828
C(14)	0.8702	0.4075	0.5147
O(1)	0.9137	0.1006	0.0279
O(2)	0.7928	0.2495	0.4860
O(3)	0.9225	0.2792	0.7049
Std dev[a] (average)	0.0005	0.0004	0.0006

[a] Standard deviations are based solely on least-squares parameters.

Crystal structure analysis of the O-acetyl derivative of 5b (n = 4) confirmed the structural formula and established the relative stereoconfiguration at the point of attachment of the OH group. The details of the structure will be published elsewhere.[8]

By analogy with unacetylated 6, 4 must be the lower homolog formed by photolysis of 1b. The formation of 4 and 6 (unacetylated) is perfectly consistent with our previous observations; at the benzazepinone stage, 3 or 5, it is again the γ-hydrogen which is abstracted, and the cyclobutanols 6 and 4 are formed presumably via biradical intermediates of type 7.[9] This novel approach to the synthesis of other polycyclic benzazepines containing bridged cyclobutane systems as well as more detailed mechanistic studies are now under investigation.

(8) J. L. Flippen, Acta Crystallogr., to be submitted for publication.
(9) Photochemical formation of bicyclobutanols from cycloalkyl and bicycloalkyl phenyl ketones has recently been reported: F. D. Lewis, R. W. Johns, and R. A. Ruden, J. Amer. Chem. Soc., 94, 4292 (1972); F. D. Lewis and R. W. Johnson, ibid., 94, 8914 (1972).

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## Hydroacylation. The Synthesis of Ketones from Olefins Using Metal Hydride Reagents

Sir:

Hydroformylation, an extensively employed and well-studied synthetic sequence, proceeds via olefin insertion into a metal hydride bond followed by CO insertion into the resulting metal carbon bond to yield metal acyl which then undergoes C–H reductive elimination of aldehyde (olefin → alkyl → acyl → aldehyde).[1] Or, more simply, hydroformylation can be considered to be the stepwise addition of H– and –C(O)H to an olefin. We now wish to report that ketones, too, can be synthesized through a stoichiometric procedure mechanistically analogous to hydroformylation in which, formally, H– and –C(O)R are added, stepwise, to olefins. Hydroacylation as described herein provides a facile route to ketones from terminal olefins rapidly, under neutral reaction conditions, at room temperature, and with inexpensive reagents.

Several organometallic-based ketone syntheses have recently been reported in which metal alkyls are formed under necessarily strongly basic conditions by reaction of an alkyllithium reagent with a metal halide at low temperature[2] or of a metalloanion with an alkyl halide.[3] In both procedures acyl halide is oxidatively added to the metal alkyl; reductive elimination gives the ketone. The scope of the former is limited by the availability of the alkyllithium reagent, that of the latter by susceptibility of the alkyl halide to nucleophilic attack by the metalloanion. In contrast to these routes, hydroacylation involves formation of the metal alkyl under neutral reaction conditions through insertion of olefin into a metal–hydride bond. We have demonstrated that hydroacylation succeeds even in cases where the position of the equilibrium for reversible M–H β-insertion into the olefin overwhelmingly disfavors the metal alkyl.[4] In this scheme, too, oxidative addition of acyl halide is followed by reductive elimination of ketone.

The results of hydroacylation involving either cobalt or rhodium hydrides are summarized in Tables I and II. These procedures are briefly described below. In a typical experiment, $HRh(CO)L_3$ (1)[4] (75 mg, 0.082 mmol) was stirred in 15 ml of benzene under 40 psi of ethylene for 20 min at room temperature. The reaction mixture was depressurized, a slight molar excess of benzoyl chloride was added, and the mixture was stirred for 12 hr at 20° (again under 40 psi of ethylene). Depressurization followed by evaporative distillation of volatiles yielded propiophenone (76%). The residue of distillation, $L_2Rh(CO)Cl$, could be recycled to 1 almost quantitatively (see reaction 1).

L = PPh$_3$
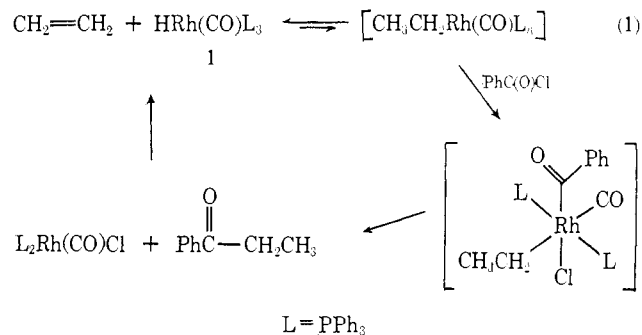
(1) See, for example, C. W. Bird, "Transition Metal Intermediates in Organic Synthesis," Academic Press, New York, N. Y., 1966.
(2) L. S. Hegedus, S. M. Lo, and D. E. Bloss, J. Amer. Chem. Soc., 95, 3040 (1973).
(3) J. P. Collman, S. R. Winter, and D. R. Clark, J. Amer. Chem. Soc., 94, 1788 (1972).
(4) G. Yagupsky, C. K. Brown, and G. Wilkinson, J. Chem. Soc. A, 1392 (1970).