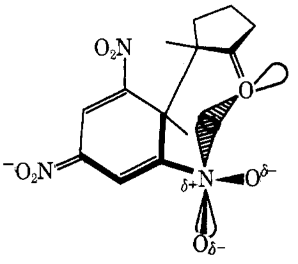
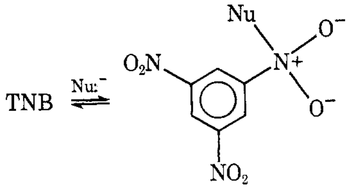
ν_2. It should be noted from the data summarized in Table II that $\Delta_{1,2}$ is the largest for cyclopentanone and appreciable for cyclohexanone. This would be expected if a strong stabilizing dipole attractive force exists between functionalities on the ketonic and anionic rings of the complex so that rotation about the CH^3–CH^4 bond is hindered. This conclusion is exactly the opposite of that offered earlier to explain the large values for $\Delta_{1,2}$ in the cyclic ketone complexes where restricted rotation was attributed to a repulsive interaction.[4] At the time this explanation was advanced no thermodynamic data were available, however.

We propose that the conformation of the cyclopentanone–TNB complex 1 in which steric repulsions of the rings are minimized may be additionally favored because of the stabilizing overlap of a filled nonbonding orbital on carbonyl oxygen with the positively polarized end of the carbon–nitrogen bond of a partially formed ortho nitronate function. Conformations leading to such an interaction are readily attained in Drieding models of the complex. With acyclic ketones the much greater rotational freedom may not favor such an interaction, since other low-energy conformations may be available which minimize nonbonded interactions.[5]



1

Interaction of nucleophiles with nitrogen of an aromatic nitro group is not unusual. Substantial evidence has been obtained for such an interaction with nitrogen nucleophiles and adducts like 2 have been characterized from the reaction of TNB with certain nitrogen bases.[6,7] Since most of the charge on the trinitrocyclohexadienate ring of 1 resides on the para NO_2 group, the ortho NO_2 groups probably contain nitrogen with a considerable positive polarization. Certainly there is sufficient polarization for a dipole interaction such as we propose here.



2

Experimental Section

Materials. Diethyl ketone (Eastman) and cyclohexanone (Mallinkrodt) were each distilled twice and the fractions boiling at 102 and 156°, respectively, were collected and stored in the dark over molecular sieves until use. The preparation and purification of all other materials has been reported previously.[1]

Calorimetry. The apparatus and techniques for this study were identical with those employed earlier.[1] Two types of experiments were conducted and are presented as "Dilution Series" (Table III) and "Reaction Series" (Tables IV and V).[8] The terms "dilution" and "reaction" indicate the absence or presence, respectively, of samples of the aromatic in the DMSO-filled ampoules that were reacted with mixtures of DMSO, triethylamine, and ketone. Values obtained for the "Dilution Series" become the vaporization correction, q', that appears in Tables IV and V. In each experiment the reaction mixture comprised 90 ml of DMSO, 5 ml of triethylamine, and 5 ml of the appropriate ketone. The values of ΔH listed in Tables IV and V may be obtained from the data by $\Delta H = (q - q')/n$, where n is the number of moles of aromatic that have reacted.

Acknowledgment. The authors thank the U.S. Army Research Office at Durham for support of this work.

Supplementary Materials Available. Thermodynamic data in Tables III, IV, and V will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C., 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number JOC-75-1499.

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Correlations of Electron Impact Fragmentations of Pyrimidyl Alkyl Ketones with Photochemical Reactivity

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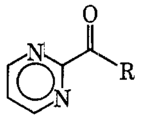
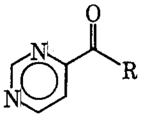
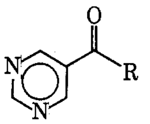
A number of studies designed to correlate the electron-impact fragmentation of organic molecules with their photochemical reactivity have been carried out over the past several years.[1] These studies have dealt primarily with molecules containing a carbonyl functionality and have focused on ketones. In general the studies have shown the behavior of ketones upon electron impact to be similar to that exhibited by them upon photochemical excitation. Thus, simple aromatic and aliphatic ketones having a propensity to undergo type I and type II cleavage reactions when exposed to ultraviolet light have been shown to undergo analogous α cleavage and McLafferty rearrangement reactions in the mass spectrometer. We recently reported[2] on the photochemistry of the propyl 2-, 4-, and 5-pyrimidyl ketones **1**, **2**, and **3**. Ketones **1**, **2**, and **3** were found to exhibit enhanced photochemical reactivity toward intramolecular hydrogen abstraction with respect to butyrophenone, and to the related butyrylpyridines. Moreover, in the case of the propyl 4-pyrimidyl ketone (**2**), intramolecular hydrogen abstraction in polar solvents occurred by way of a ring nitrogen atom and led to cyclopropanol formation. In light of these results we considered it informative to examine the mass spectra of the propyl 2-, 4-, and 5-pyrimidyl ketones **1**, **2**, and **3**, and a number of the homologous methyl, ethyl, and butyl pyrimidyl ketones. It was of interest to us to determine whether any analogy existed between the photochemical reactions of the ketones and their unimolecular framentations induced by electron impact.

Table I
Mass Spectra of Alkyl Pyrimidyl Ketones at 70 eV

m/e	Ketone 1	2	3	4	5	6	7	8	9	10	11
164						27	25	6			
150	35	16	11								
136				62	27						
135	32	17				79	44				
122	12	16	39			100	24	100	53	25	58
108	14	21		23	70	53	45				
107	29	19	100	37	27	32	16	50	13		100
94	15	13			14	42	22		46	20	
85						18	17				
81	36	14		42	23	40	13		14		
80	100	100		100	100	97	100		100	45	
79	58	28	29	93	51	12	25		25	18	49
71	23	25									
57				66	99	40	38				
53	50	26	13	72	51				24	38	29
52	18	39	17	29	99		73			42	31
43	86	78	13						46	100	47


1, R = propyl
4, R = ethyl
6, R = butyl
9, R = methyl


2, R = propyl
5, R = ethyl
7, R = butyl
10, R = methyl

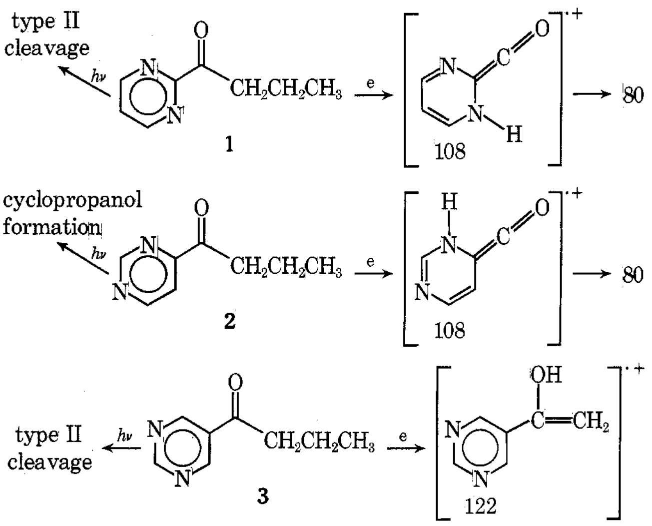

3, R = propyl
8, R = butyl
11, R = methyl

Results

The mass spectra of the propyl 2-, 4-, and 5-pyrimidyl ketones **1**, **2**, and **3**, and the 2- and 4-ethyl, 2-, 4-, and 5-butyl, and 2-, 4-, and 5-methyl pyrimidyl ketones **4–11** were measured at 70 eV. The principal ions (>10%) (Table I) from the fragmentation of the alkyl pyrimidyl ketones **1–11** were found to be very similar to those observed in the mass spectra[3] of the related alkyl pyridyl ketones. For the most part the principal fragments in the pyrimidyl series differed from those of the corresponding pyridyl solely by the additional ring nitrogen substitution.

Discussion

In the case of the propyl pyrimidyl ketones **1–3**, the mass spectral behavior of the 5 isomer (**3**) is found to be analogous to that reported[3] for butyrophenone and the related propyl 3- and 4-pyridyl ketones. Ketone **3** undergoes two principal modes of fragmentation, α cleavage (150 → 107) and McLafferty rearrangement (150 → 122). In comparison to the 5-propyl ketone **3** the 2- and 4-propyl ketones **1** and **2** show mass spectral behavior similar to that reported[3] for 2-propyl pyridyl ketone, their major mode of framentation being a McLafferty-type rearrangement via a ring nitrogen atom (150 → 108). The respective photochemical behaviors[2] of the propyl 4- and 5-ketones **2** and **3** parallel their principal modes of mass spectral fragmentation. In ketone **2** photochemical cyclopropanol formation requires intramolecular hydrogen abstraction by a ring nitrogen atom, and in ketone **3** the type II cleavage reaction occurs by way of the excited carbonyl. In marked contrast to the propyl pyrimidyl ketones **2** and **3**, propyl 2-pyrimidyl ketone (**1**) shows much less similarity in its principal mode of photochemical vs. mass spectral decomposition. The McLafferty-type rearrangement of ketone **1** involves a ring nitrogen atom, while its type II cleavage reaction involves the excited carbonyl.



In the homologous 2- and 4-ethyl pyrimidyl ketones **4** and **5**, where the nature of the carbonyl side chain allows for hydrogen abstraction by a ring nitrogen atom only, the anomalous behavior of the 2 isomer is maintained. The 2-ethyl pyrimidyl ketone (**4**) shows no detectable photochemical reaction;[4a] yet it undergoes a McLafferty-type rearrangement to nitrogen (136 → 108). This is in contrast to the 4-ethyl pyrimidyl ketone (**5**), which undergoes intramolecular hydrogen abstraction both photochemically[4a] and in the mass spectrometer via a ring nitrogen atom.

When the length of the carbonyl side chain is increased to four carbons, McLafferty rearrangement to oxygen can compete with the McLafferty-type rearrangement to nitrogen.[3] Such a competitive rearrangement process is observed in the mass spectra of the butyl 2- and 4-pyrimidyl ketones (**6** and **7**) (164 → 122, vs. 164 → 108). A similar process however, is not observed photochemically for ketones **6** and **7**. Upon electronic excitation both butyl ketones **6** and **7** undergo hydrogen abstraction by way of the carbonyl oxygen exclusively.[4a,b]

The mass spectra of the methyl 2-, 4-, and 5-pyrimidyl ketones **9**, **10**, and **11** show that loss of ketene (122 → 80) is an important mode of fragmentation in the 2 and 4 isomers **9** and **10** but not in the 5 isomer **11**, where α cleavage (122 → 107) predominates. This suggests that the loss of ketene involves a McLafferty-type rearrangement via a ring nitrogen atom and that the rearrangement can occur by way of a five-membered transition state. Since neither loss of ketene nor type I cleavage is observed photochemically in ketones **9** and **10**,[4a] there appears to be little analogy existing between the mass spectral and photochemical behavior of the methyl pyrimidyl ketones **9–11**.

From the above discussion it is clear that the best correlation of photochemical and mass spectral decomposition of alkyl pyrimidyl ketones exists in the 5-alkyl systems. While the 4-alkyl pyrimidyl ketones show good correlation when the alkyl substituent is ethyl and propyl, they show poorer correlation when it is methyl or butyl. This is in contrast to the 2-alkyl pyrimidyl ketones, which show virtually no correlation at all. The good correlation observed in the 5-alkyl pyrimidyl ketones in comparison to the isomeric 2- and 4-alkyl ketones can best be explained in terms of stereochemical and stereoelectronic factors. In the 5-alkyl ketone systems the geometrical features of the ketones ensure little to no involvement of a ring nitrogen atom in both photochemical and electron impact induced reactions. This leads to behavior in these ketones which is similar to that reported[3,5] for butyrophenone, valerophenone, and the 3- and 4-butyryl and valeryl pyridines. In the case of the 2- and 4-alkyl pyrimidyl ketones the close proximity of a ring nitrogen atom to the reaction center necessitates its involvement. The degree of involvement, however, will depend to a great extent on the relative electron densities of the nitrogen atoms in the excited ketones. When the nature of the electron densities of these atoms in the electronically excited state differ substantially from their relative charge densities in the corresponding ionized state, the photochemical and mass spectral behavior of the ketones will show poor correlation. This appears to be the case for the 4-butyl pyrimidyl ketone **7**, where exclusive type II reaction occurs photochemically and competitive nitrogen and oxygen hydrogen atom abstraction occurs in the mass spectrometer. This is also apparently true of the 2-propyl and 2-butyl pyrimidyl ketones **1** and **6** and of the 2-butyryl and 2-valeryl pyridines,[3,5] where exclusive type II cleavage occurs photochemically and a McLafferty-type rearrangement via a ring nitrogen atom predominates upon electron impact.

Experimental Section

The recorded mass spectra were obtained with an LKB 9000 mass spectrometer at a nominal ionizing voltage of 70 eV.

The alkyl pyrimidyl ketones were prepared as previously described[2] and were purified by gas chromatography.

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Registry No.—**1**, 53342-24-8; **2**, 53342-25-9; **3**, 53342-26-0; **4**, 54643-09-3; **5**, 54643-10-6; **6**, 54643-11-7; **7**, 54643-12-8; **8**, 54643-13-9; **9**, 53342-27-1; **10**, 39870-05-8; **11**, 10325-70-9.

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A Method for Cleaving 2,4-Dinitrophenylhydrazones to Ketones

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2,4-Dinitrophenylhydrazone (2,4-DNP) derivatives of ketones and aldehydes are important, both because of their use in purifying and characterizing the parent compounds, and because of their occasional use in synthesis.[1] Regeneration of the parent carbonyl compound from a 2,4-DNP can present severe problems, however. The major difficulty is that 2,4-DNP's are stable to acid hydrolysis. A variety of methods have been devised to overcome this problem.

The most common method of cleaving a 2,4-DNP is to effect an exchange reaction with another carbonyl compound such as pyruvic acid[2,3] or levulinic acid.[4] Yields are often unacceptable in these reactions, however. A second method is to ozonize the C=N double bond at low temperatures.[1,5] The reaction works moderately well, but is clearly *incompatible with the presence of unsaturation within the* molecule. A third general method is to activate the 2,4-DNP toward hydrolysis. This is usually done by reducing the nitro groups to amines with either stannous ion,[6,7] lithium aluminum hydride,[8] or chromous ion.[9] The resulting 2,4-diaminophenylhydrazone then hydrolyzes. Yields are generally acceptable if there are no other reactive functional groups present, but acidic conditions are necessary.

We have had several occasions in our own laboratory to regenerate the parent carbonyl compounds from their 2,4-DNP's, and we have found aqueous titanous ion to be an excellent and convenient new reagent for effecting this transformation.[10] Some of our results are given in Chart I.

We believe that this method has several advantages over presently known ones. The reaction works for a variety of cases, both saturated and unsaturated, and has given high yields of carbonyl products in all examples tested. Further, titanous ion is inexpensive and commercially available as a stable 20% aqueous solution.[11] It thus does not have to be prepared freshly before use as does chromous ion. Most important, however, is the fact that the reaction can be carried out under neutral conditions whereas other methods require acidic conditions.

Mechanistically, there are two obvious possibilities for the course of the cleavage reaction. The simplest possibility is to assume that titanous ion acts by reducing the nitro groups to amino groups in a manner similar to that of stannous or chromous ion, and that the resulting 2,4-diaminophenylhydrazone then undergoes hydrolysis.

It is well known that titanous ion can rapidly reduce nitroarenes to aminoarenes,[12] and thus we cannot completely rule out this mechanism. We nevertheless feel that it is unlikely because, as we have demonstrated, the cleavage reaction works equally well under buffered conditions, and we consider it surprising that a 2,4-diaminophenylhydrazone would hydrolyze so readily at neutral pH.