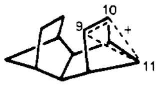
Comparison of **1**-ODNB-d_6 and **4**-ODNB-d_8 isotope effects is instructive. The diametric results are indicative that the reactivities of the diene and monoene differ in origin. In this regard, a k_H/k_D value substantially greater than unity for **4**-ODNB-d_8 is striking. Several observations, taken collectively, lead to a plausible explanation of the effect. First, **4**-ODNB has very high solvolytic reactivity. Comparison of **4**-ODNB with the *anti*-7-norbornenyl and 7-norbornyl systems show a relative rate ratio of $10^{14}:10^{11}:1$, respectively. This and the product results clearly indicate that solvolysis of **4**-ODNB proceeds by anchimeric assistance to give charge delocalized intermediate **8**. Second, an examination of scale molecular models shows that severe steric repulsion occurs between the C_4C_5 inside ϵ hydrogens and the C_9C_{10} π-electron bridge.[12] This indicates that the C_9C_{10} π electrons are forced closer to the C_{11} reaction site in the reactant state and that additional rate enhancement of 10^3 for **4**-ODNB over the *anti*-7-norbornenyl structure is a consequence of the severe sterically congested environment. Finally, it is well known that C-H bonds have greater vibrational amplitudes compared with analogous C-D bonds.[13] These considerations predict $k_H/k_D > 1$.[13] On the basis of information now available the best working hypothesis is that the remote ϵ deuterium isotope effect of $k_H/k_D = 1.13$ is of steric derivation.

All things considered, it is clear that the ϵ-D inverse isotope effect observed with **1**-ODNB-d_6 is neither inductive nor steric in nature. This result is accounted for best in terms of remote C_4C_5 π-electron participation in the rate-determining step by relay through the C_9C_{10} bridge to the C_{11} reacting site to give charge delocalized cation **2**. A net inverse effect is just what is expected for rehybridization going from sp^2 toward sp^3 C.[14] Support for neighboring double-bond participation is found in the k_H/k_D value observed for solvolysis of **9** in 96% EtOH.[15a] Participating π electrons in the rate-determining step for **9** → **10** is well documented. Additional confirmation is afforded by the similar magnitude of the ϵ-D isotope effect observed[15b] for acetolysis of the closely analogous **11** → **12** process.[16]



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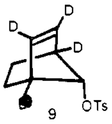
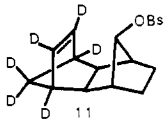


9

$k_H/k_{d_4} = 0.93$

10



11

$k_H/k_{d_6} = 0.93$

12

These new results provide clear-cut evidence that the near identity of solvolytic reactivity found with **1**-ODNB and **4**-ODNB *is not due* to the inability of the remote C_4C_5 π electrons of **1**-ODNB to assist ionization in the rate-determining step as maintained by Paquette and Dunkin.[4] Instead the correspondence in rate acceleration is purely fortuitous and it is due to different reactivity factors operating with each system. For **4**-ODNB the rate enhancement is a consequence of severe steric strain. In the case of **1**-ODNB the remote π electrons are a part of the driving force for anchimerically assisted ionization.

Acknowledgment. This work is supported by the National Science Foundation with Grant CHE-76-01129.

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Received December 1, 1978

Photochemical Cyanation of Acetophenones. Acetyl Displacement

Sir:

In a previous communication Letsinger and Colb reported that a variety of methyl- and methoxy-substituted acetophenones underwent nucleophilic attack by cyanide upon irradiation.[1] From structure elucidation studies of the principal isolable products, three reaction modes were documented: rearrangement by acetyl migration, cyanation by methoxy-group displacement, and phthalide formation by cyanide incorporation and hydrogen transfer. This communication reports preliminary details of a fourth reaction type, the net displacement of acetyl by cyanide, a transformation which was discovered while investigating solvent effects upon the reported photochemical reactions. Acetyl displacement from acetophenones through either a photochemical or thermal process appears to be without prior precedent in the chemical literature. Indeed, Snyder[2] has reported that carbonyl compounds such as benzophenone and benzaldehyde are thermally unreactive toward cyanide in DMF, a potent cyanation medium.

In the transformations outlined below, the acetyl group of certain acetophenones (**1a–d**) was displaced by cyanide ion[3] to form the corresponding benzonitriles (**2a–d**). On a preparative scale, the yields of methoxybenzonitriles were modest, the highest being ~41% overall of 2′-methoxybenzonitrile, equivalent to 64% yield at 65% conversion.[4] In other prepar-

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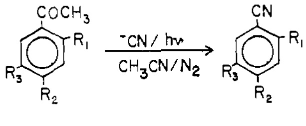

Ia-d 2a-d

Ia, 2a: R$_1$ = R$_2$ = R$_3$ = H
Ib, 2b: R$_1$ = OCH$_3$; R$_2$ = R$_3$ = H
Ic, 2c: R$_1$ = OCH$_3$; R$_2$ = CH$_3$; R$_3$ = H
Id, 2d: R$_1$ = OCH$_3$; R$_2$ = H; R$_3$ = CH$_3$

ative-scale reactions run to ~50% conversion, the isolated yield of 2′-methoxy-4′-methylbenzonitrile was 32%, that of the 5-methyl isomer 28%, and that of benzonitrile only 3–4%. These novel reactions appeared to proceed efficiently[5] in dried acetonitrile solution, were inhibited by added water, and were not observed in the absence of light. Prior to irradiation, no shift in the wavelength maxima or minima was observed in the UV spectrum of the ketone upon addition of cyanide. In general, the reaction course contrasts specifically with the photoinduced rearrangement of 2′-methoxyacetophenone found in aqueous solutuon.[1]

For a typical experiment, the ketone (2.0 mmol) and a tenfold molar excess of cyanide were dissolved in purified acetonitrile[1] contained in a 1-L Hanovia photochemical reactor (450-W lamp, Pyrex well). The solution was irradiated under nitrogen purge until about one-half of the starting material had been consumed as determined by GC analysis. After routine workup, the base-insoluble products were isolated by preparative GC (FFAP stationary phase) either with or without prior column chromatography on silica gel to remove nonvolatile material. Products were identified by ^{1}H NMR and IR analysis and by comparison of spectra with those of authentic samples, independently synthesized by routine methods.

A superficial analogy can be drawn between these acetyl displacement reactions and the reported photoinduced cyanations in which hydride[7,9] or nitrite[8,9] served as the leaving group. In the present study, as in nitrite displacement by cyanide,[8c] absence of spectral changes prior to irradiation provided evidence that the reaction course was not mediated by a ground-state complex between nucleophile and aromatic. Displacement of hydride, in at least one case,[7a] apparently depended upon the presence of oxygen, water, and an electron-acceptor molecule such as *p*-dicyanobenzene. None of these compounds was requisite for acetyl displacement which was inhibited both by added water and by oxygen.

A comparison of the photoreactivity of other aryl methyl ethers with that of methoxyacetophenones suggests obvious similarities. Anisole,[10] 1,2-dimethoxybenzene,[9b] and 1,3-dimethoxybenzene[9b] undergo photosubstitution by cyanide to form products where cyanide is incorporated ortho and/or para to a methoxy group. Similarly, Letsinger and McCain[8c] have shown that photoinduced cyanation of *o*-nitroanisole results in the formation of 4-cyano-2-nitroanisole (29%) and 6-cyano-2-nitroanisole (26%). Based on these and a number of other reactions, Cornelisse and Havinga[9] have proposed that methoxy groups are ortho/para directing in photosubstitution reactions. The formation of methoxy benzonitriles can thus be accounted for by the displacement of an acetyl group positioned ortho to a methoxy group. The low-yield reaction to form benzonitrile obviously cannot be discussed in terms of ortho directing effects. If acetyl is positioned meta to methoxy, photocyanation results not in acetyl displacement but in methoxy displacement with the formation of 3-cyanoacetophenone in a70–80% overall yield.

Evidence that the nitrile function was actually incorporated at the acetyl-bearing carbon was drawn from the reaction of 2′-methoxy-4′-methylacetophenone (**1c**). The major isolable product from the cyanation of that compound was 2′-methoxy-4′-methylbenzonitrile (**2c**) rather than a position isomer. It is important to note, however, that the position of *initial* cyanide attack is not explicitly resolved by product studies and might involve another carbon. The proposal of a mechanistic hypothesis is reserved until experiments to determine the fate of the acetyl fragment and to elaborate further the reaction pathway are completed.

The dramatic solvent-dependent change in the reaction pathway might be accounted for by either of two recognized solvent effects: a reordering of the electron distribution associated with the reactive excited state[11] or an enhancement in the nucleophilicity and/or basicity of anions in polar, aprotic solvents.[12]

That the added water acted as a competitive quencher has not been specifically tested through quantum yield studies. However, Letsinger[8c] has shown that water competes only ineffectively with cyanide for the short-lived excited states of nitroaromatics, even in overwhelmingly aqueous systems.

The results obtained from parallel, small-scale irradiations on compound **1b** at different concentrations of added water in the range of 0.5–2 M help support the following hypothesis. The reaction pathway depends more on the chemical properties of cyanide in a polar, aprotic solvent than on solvent-dependent, photophysical properties of the ketone. The data from those experiments showed that in the absence of added water almost no ketone remained after an irradiation period of 60 min and that the nitrile was the major volatile product. In the presence of only 2% added water (1.1 M) under otherwise identical conditions, the reaction was strongly inhibited. Less than 1% of the ketone reacted, and a correspondingly small conversion to nitrile was detected. With smaller amounts of added water, more ketone was consumed and more nitrile was formed.

Water concentrations up to the 1.5 M range do not appreciably alter the bulk physical properties of acetonitrile such as viscosity or conductivities of added ions.[13] These facts suggest that a polarity-dependent inversion of the lowest excited state cannot easily account for the observed decrease in photoreactivity, although that phenomenon may account for the completely different pathway (i.e., rearrangement) found in aqueous solution or for the solvent-dependent reactions of 3-methoxyacetophenone.[11] It is well documented[12a] that anions are more basic and more nucleophilic in dipolar, aprotic solvents such as acetonitrile than in water, although published models addressing specifically the solvation of cyanide in aprotic media are sparse. Studies of anion solvation in the presence of added water by Kolthoff,[13] Kuntz,[14] Parker,[15] and Benoit[16] provide evidence that hydration processes become important at 0.5 M water. Since the observed inhibition of the photochemical substitution reaction was nearly complete in this range, a reasonable explanation might lie in the exchange of water for acetonitrile in the solvent shell of cyanide with a concomitant decrease in nucleophilicity. Whatever the mechanistic model, the observed photochemical reaction appears to offer a convenient probe for solvation effects at low water concentration.

Acknowledgments. Wellesley College Faculty Awards Committee and the Huber Foundation are thanked for providing funding for this research.

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Received May 1, 1978

*Book Reviews**

Catalysis in Coal Conversion. By J. A. CUSUMANO, R. A. DELLA BETTA, and R. B. LEVY (Catalytica Associates, Inc.). Academic Press, New York. 1978. xiii + 272 pp. $21.00.

The conversion of coal to synthetic fuels, generally by liquefaction, has become a subject of major importance in the last decade, as the fact that petroleum is nearing its end as a cheap source of energy becomes recognized. The present book is a survey of methods for such conversion, and is based on a report prepared for ERDA (U.S. Energy Research and Development Administration). It is divided into three sections: Survey of Advances in Catalysis; Advances in Supporting Disciplines; and Specific Coal Conversion Processes.

A large amount of information is presented concisely, although rather often it is given in general terms, with references to sources of further details. A great value of the book lies in these references, which are abundant, and are drawn from a wide range of sources, including industrial and government contract reports. Each chapter ends in a "Summary and Conclusions" section, in which needs and recommendations for future research are given; this feature, susceptible to rapid obsolescence, is clearly an inheritance from government report status.

The level of presentation is to the initiated, and newcomers to the field may have to work to achieve full comprehension of the material, but the authors have made a helpful concession by including in the index the many acronyms that have become a part of the jargon of the subject (example: HDN for hydrodenitrogenation). Both chemists and engineers should find this book useful if they are in any way concerned with coal chemistry.

Rodd's Chemistry of Carbon Compounds. Second Edition. Volume IV. Part H: Heterocyclic Compounds. Edited by S. COFFEY. Elsevier Scientific Publishing Co., Amsterdam and New York. 1978. xx + 576 pp. $106.95.

Six-membered rings of various sorts dominate this volume, which continues from the previous part with Chapter 36 (Isoquinoline Alkaloids). The remaining five chapters cover rings with a nitrogen atom common to two or more fused rings or with one heteroatom in each of two fused rings (such as furoquinolines), and those six-membered rings that contain two heteroatoms from groups VIB, or VB and VIB, of the periodic table, plus a chapter on lupinane and quinolizidine alkaloids.

Some of these are large subjects indeed, and the contributors have had to compress a formidable amount of literature into their concise chapters. Nevertheless, this has not prevented them from making the text readable, nor from detailing the development of a subject through the correction of errors, such as seen in the revision of the structure of gigantine in 1970 from a phenolic to an alcoholic system. Attention is also given to such important facts as the extraordinary toxicity of certain polychlorodibenzodioxins which may occur as contaminants of polychlorophenols.

The index is of the usual elaborate form, and is preceded by a helpful two-page guide. This is an excellent work and it is a pity that no indication is given as to the termination date of the coverage of the literature.

Advances in Heterocyclic Chemistry. Volume 22. Edited by A. R. KATRITZKY and A. J. BOULTON (University of East Anglia). Academic Press, New York. 1978. ix + 437 pp. $39.50/£25.65.

The practice of bringing older reviews up to date is continued in this volume. It was 15 years and 20 volumes ago that the original chapter in this series on quinoxalines appeared; developments in 1963–1975 are now covered. Quaternization of heteroaromatic compounds is a subject whose original review is only one year younger; the new supplementary review reflects the increased role of kinetics in understanding this class of reaction.

Chapters on phenanthrolines and on isatogens and indolones supplement earlier reviews written in the 1950s. There was still room for two previously unreviewed subjects: aromatic azapentalenes and cyclazines (including related N-bridged annulenes).

The problem of nomenclature and ring numbering is dealt with felicitously by the contributors, who have recognized that names used in *Chemical Abstracts* indexes, which are designed for handling by computers rather than warm-blooded chemists, are often far from satisfactory for quick comprehension. Thus, it is, for example, that Boekelheide's cyclazine nomenclature is used instead of the ring-fusion names of CA. The basic word cyclazine is used to denote a conjugated, unsaturated ring of carbon atoms that is held planar by three bonds to a central nitrogen atom. Whatever one's preference, however, an abundance of clearly drawn and numbered structures makes the text easy to follow.

As in earlier volumes, a highly detailed table of contents substitutes for an index, but there is a cumulative index of chapter titles for the complete run of 22 volumes at the end.

Saturated Heterocyclic Chemistry. Volumes 4 and 5. Edited by M. F. ANSELL and G. PATTENDEN (Vol. 4) and by M. F. ANSELL (Vol. 5). The Chemical Society, London. Vol. 4: 1977. x + 362 pp. $60.00. Vol. 5: 1978. ix + 314 pp. $52.00.

Volume 5 is the swan song of this section of the Specialist Periodical Reports. The Editors foreword explains that it "has ceased to remain viable economically". However, some of the material will be included in the Report on "General and Synthetic Methods". Presumably, rising costs have priced these books out of the personal purchase market, and library purchases alone are not enough to sustain the series.

The volumes follow the established pattern and consist of five tightly written contributions: Three-membered Rings; Four-membered Rings; Five- and Six-membered Rings and Related Fused Systems; Medium-sized Rings, and Bridged Heterocyclics. Volume 4 reviews the literature published in 1974 (1973 as well for medium-sized rings), and Volume 5 covers 1975.

These volumes will remain useful for many years, because of the well-organized way in which widely scattered material is presented, although their primary purpose has been to promote "recent awareness". There is an author index, which is valuable in such works, and

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* Unsigned book reviews are by the Book Review Editor.