

Figure 1. Alkyl region of the CIDNP spectrum obtained during thermal decomposition of *cis*-1 in benzene at 40°.

for *trans*-1. This difference suggests that AMS as well as benzene and diphenylpropane are formed from radicals which have lived as pairs much longer than the pair which leads to *trans*-1. This interpretation is supported by the small yield of these products and is in agreement with Scheme I which requires the phenyl-diazenyl radical to lose nitrogen before the secondary pair can be formed. Further support for this scheme is derived from scavenging experiments. Addition of BrCCl_3 does not affect the intensity of the emission signal of *trans*-1 but almost completely eliminates the AMS signals. From these observations, one can estimate the rate constant for loss of nitrogen from $\text{Ph-N}_2\cdot$ to fall between 10^7 and 10^9 sec^{-1} .

Even though AMS is a minor product, detailed analysis of its spectrum is most informative. Figure 2 shows the CIDNP spectrum of AMS and the calculated spectrum using the known magnetic parameters of cumyl radical. The best fit is obtained with an apparent Δg of 1.3×10^{-3} and $A_N > 75 \text{ G}$, establishing an upper limit for the g factor of $\text{PhN}_2\cdot$ of 2.0012.¹⁰ Both parameters are consistent with a bent σ radical, a structure expected for $\text{PhN}_2\cdot$ which is isoelectronic with the benzoyl radical.¹¹

Finally, dicumyl and cumene originate from the free radicals which have escaped the pairs. Most of their net A-type polarization is lost through nuclear relaxation in the free-radical state and the AE multiplet in cumene most likely originates from noncorrelated pairs formed by diffusive encounter of the cumyl and phenylcyclohexadienyl radical pair.¹²

It appears worth noting that the photochemical decomposition of *trans*-1 proceeds through *cis*-1 which decomposes thermally under the reaction conditions. The lack of photodecomposition at temperatures where *cis*-1 is stable is also consistent with the notion that the only photochemical act of consequence at room temperature is *trans*-*cis* isomerization.

Results obtained on the decomposition of 1 support the previous claims that suitably substituted azo com-

(10) The apparent Δg is only an upper limit of the Δg in the phenyl-diazenyl-cumyl pair because the cumyl radical spends part of its lifetime with the phenyl radical as its partner whose g factor is close to the free electron value.

(11) P. J. Krusic and T. A. Rettig, *J. Amer. Chem. Soc.*, **92**, 722 (1970).

(12) The participation of phenylcyclohexadienyl radical in the formation of cumene was demonstrated by the lack of cumene signals when the reaction was run in hexadeuteriobenzene.

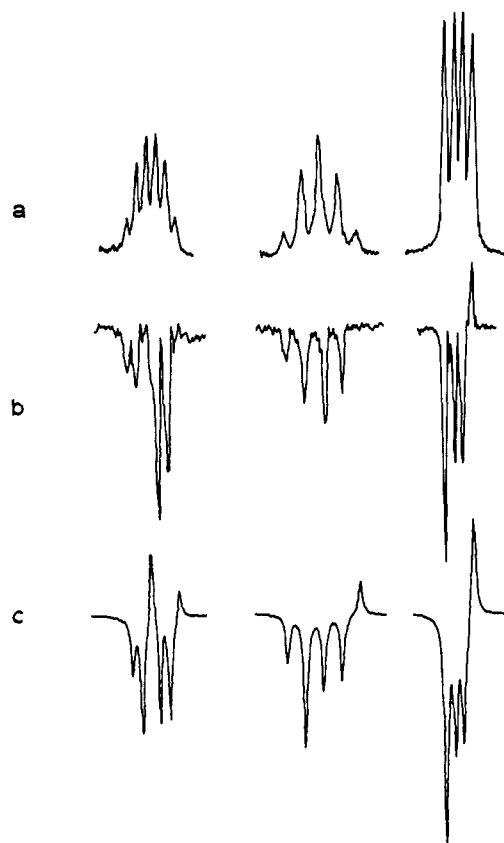


Figure 2. Spectra of AMS: (a) normal spectrum; (b) CIDNP spectrum obtained on photolysis of *trans*-1; (c) calculated spectrum with $A_H = 18$, $A_N = 75 \text{ G}$, $\Delta g = 1.3 \times 10^{-3}$. Discrepancies between b and c must at least in part be attributed to neglect of relaxation in c.

pounds decompose *via* one-bond scission leading to diazenyl radicals.²⁻⁴ However, a previous CIDNP study of 2 failed to produce any evidence for a radical pair with a finite Δg (only pure multiplet effect spectra were observed) indicating either a concerted mechanism or a lifetime of the diazenyl radical of less than 10^{-10} sec .¹³

(13) G. L. Closs and A. D. Trifunac, *J. Amer. Chem. Soc.*, **91**, 4554 (1969); **92**, 2186 (1970).

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Photoinduced Aromatic Substitution, Addition, and Rearrangement Reactions of Aromatic Ketones¹

Sir:

The extensive studies on the photochemistry of aromatic ketones have revealed a variety of reactions at the carbonyl function, such as photoreduction, the Paterno-Büchi reaction, and the Norrish type I and II cleavages.² We describe in this communication

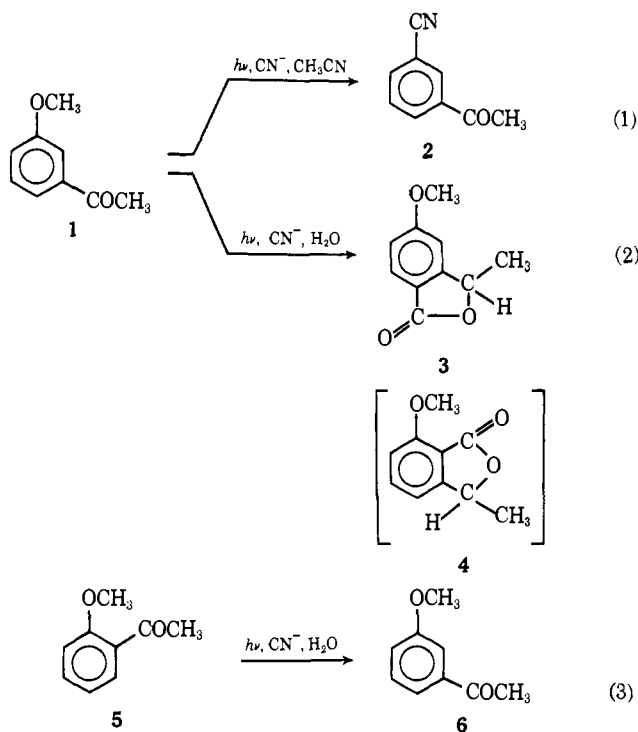
(1) Photoinduced Substitution. XI. This research was supported by the National Science Foundation (GP-5715). Part X: W. C. Petersen and R. L. Letsinger, *Tetrahedron Lett.*, 2197 (1971).

Table I. Photoreactions of Substituted Acetophenones with Cyanide

Expt	ArCOCH ₃	mg	NaCN, g	Solvent, ml of CH ₃ CN-H ₂ O	Min irradiat	Recovered ketone, ^a mg	Isolated product ^b	mg
1	3-CH ₃ O	400	2	1000:200	15	322	3-CN	39
2	3-CH ₃ O	450	8	1000:200	72	6	3-CN	90
3	3-CH ₃ O	400	8	10:1190	210	180 ^c	Lactones 3 + 4	157 ^d
4	2-CH ₃ O	200	4	150:1500	45	54	3-CH ₃ O	19
5	2-CH ₃ O	200	4	150:1500	10	146	3-CH ₃ O	11
6	2-CH ₃ O	125	1.8	5:200 (D ₂ O)	20	60	3-CH ₃ O	6
7	3,5-Di(CH ₃)	150	1	1100:100	23	38	2,4-Di(CH ₃)	13
8	3,5-Di(CH ₃)	150	1	1100:100 (D ₂ O)	7	28	2,4-Di(CH ₃)	6
9	3,5-Di(CH ₃)	300	1	1000:200 (D ₂ O)	17	150	2,4-Di(CH ₃)	8

^a Starting ketone. ^b Substituted acetophenones, except experiment 3. ^c The reaction mixture was stirred for 48 hr in the dark after irradiation. ^d A mixture of two parts 3 and one part 4, as shown by nmr; the pure compounds were subsequently separated by chromatography on silica gel. A small amount of 2 (~10 mg) was also isolated.

three new reactions that involve transformations at the ring carbons of aromatic ketones: (1) photoinduced nucleophilic substitution, (2) photoinduced nucleophilic addition, and (3) photoinduced, cyanide-catalyzed 1,2 migration of an acyl group.



This investigation was stimulated by the observation that aromatic nitro compounds not only undergo photoreduction at the nitro group,^{1,3} analogous to ketones, but exhibit a variety of photoinduced nucleophilic substitution reactions as well.^{1,4} The latter are favored when the nitroaromatic has a substituent, such as methoxyl, that lowers the energy of the π, π^* excited state relative to an n, π^* excited state. In search-

ing for photoinduced nucleophilic reactions of aromatic ketones, therefore, we focused attention initially on 3-methoxyacetophenone since it possesses a potential departing group (methoxide) and also has a low-lying π, π^* excited state, as indicated by spectral data and the inefficiency of photoreduction by isopropyl alcohol.⁵

Irradiations were carried out in a nitrogen atmosphere with a 450-W Hanovia mercury lamp in a cylindrical Vycor vessel. A 1.8-mm Pyrex filter sleeve was used for reactions of the methoxyacetophenones. Neutral products were extracted from aqueous reaction mixtures with ether or methylene chloride and were separated by chromatography on silica gel plates or by vapor phase chromatography. Alkali-soluble products (lactones 3 and 4) were isolated by acidifying the aqueous layer (caution: HCN liberated) and extracting with ether. Products which are known compounds were characterized by nmr spectra in conjunction with mixture melting points, if solids, or vpc retention times, if liquids. In control experiments it was found that none of the new reactions proceeds in detectable amounts under the reaction conditions in the absence of light or on irradiation in the absence of the specified nucleophile (cyanide or hydroxide ion).

As indicated by experiment 1, Table I, replacement of methoxyl by cyanide is the primary reaction when 3-methoxyacetophenone is irradiated in a solution of sodium cyanide (0.025 M) in 5:1 acetonitrile⁶-water. When the solvent is preponderantly water (experiment 3), 3-methyl-5-methoxyphthalide [3, mp 48-50°; λ_{max} (EtOH) 284 nm ($\log \epsilon$ 3.58), 253 ($\log \epsilon$ 4.19); ir, carbonyl at 5.70 μ ; nmr^{7a} 1.5 (d, 3 H, J = 6.5 Hz), 3.87 (s, 3 H), 5.43 (q, 1 H), 6.8-7.2 (d and s, 2 H), 7.7 (d, 1 H). *Anal.* Calcd for C₁₀H₁₀O₃: C, 67.41; H, 5.66. Found: C, 67.32; H, 5.65] and its isomer 4 [isolated as an oil and assigned the lactone structure on the basis of the similarity of the nmr and ir spectra to the spectra of 3] are obtained. Formation of the phthalides can be rationalized on the basis of addition of cyanide to the aromatic ring ortho to the carbonyl group followed by protonation at oxygen, aromatization by

(2) For reviews see R. O. Kan, "Organic Photochemistry," McGraw-Hill, New York, N. Y., 1966; N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1965.

(3) R. Hurley and A. C. Testa, *J. Amer. Chem. Soc.*, **88**, 4330 (1966).

(4) R. L. Letsinger and R. R. Hautala, *Tetrahedron Lett.*, 4205 (1969); R. L. Letsinger and J. H. McCain, *J. Amer. Chem. Soc.*, **91**, 6425 (1969); E. Havinga and M. E. Kronenberg, *Pure Appl. Chem.*, **16**, 137 (1968).

(5) N. C. Yang, D. S. McClure, S. L. Murov, J. J. Houser, and R. Dusenbery, *J. Amer. Chem. Soc.*, **89**, 5466 (1967).

(6) The acetonitrile was purified by successive distillation from Na₂CO₃-KMnO₄, NaH, and H₂SO₄.

(7) Expressed in ppm relative to TMS; solvent, CDCl₃; (a) 60 MHz; (b) 90 MHz.

tautomerization, hydrolysis of the nitrile group, and lactonization on acidification.

When the study was extended to 2-methoxyacetophenone, an unexpected rearrangement was observed: some 2-methoxyacetophenone isomerized to 3-methoxyacetophenone (experiments 4 and 5; reaction 3). Special care was taken to ensure the purity of the starting ketone and the product was isolated as a pure substance: nmr^{7b} 2.60 (s, 3 H, acetyl), 3.85 (s, 3 H, methoxyl), 7.0–7.6 (4 H, aromatic). To gain information on the pathway for the rearrangement, 2-methoxyacetophenone was photolyzed in the presence of cyanide in deuterium oxide (experiment 6). Integration of the nmr spectrum of the 3-methoxyacetophenone isolated from this reaction showed that one deuterium had been introduced in the aromatic ring, and the splitting pattern in the aromatic region showed that the deuterium was in the 2 position (see Figure 1).⁸ No deuterium was found in the aromatic portion of the recovered 2-methoxyacetophenone, and a control experiment showed that 3-methoxyacetophenone did not undergo hydrogen–deuterium exchange at the ring under these conditions. Accordingly, we conclude that the H–D exchange accompanies the rearrangement. These results rule out a mechanism in which hydrogen and a neighboring acetyl or methoxyl group simply exchange positions and render unlikely a rearrangement proceeding by a benzvalene-type intermediate.⁹

It was then found that photoexcited 3,5-dimethylacetophenone reacts similarly with cyanide ion (experiment 7); the ketone fraction isolated (34%) after irradiation for 23 min in 0.17 M sodium cyanide in 11:1 acetonitrile–water was 75% 3,5-dimethylacetophenone and 25% 2,4-dimethylacetophenone: nmr^{7b} 2.33 (s, 3 H, methyl), 2.46 (s, 6 H, methyl and acetyl), 6.97 (broad peak with shoulder at 6.91, 2 H, aromatic protons meta to acetyl), and 7.50–7.5 (doublet for 1 H ortho to acetyl). No rearrangement occurred in the absence of cyanide ion. Formation of 2,4-dimethylacetophenone corresponds to migration of acetyl (rather than methyl) in the rearrangement. In support of this pathway, the 2,4-dimethylacetophenone isolated from a reaction conducted in acetonitrile–deuterium oxide had a deuterium atom ortho to the acetyl group.¹⁰ The nmr spectrum of the 3,5-dimethylacetophenone recovered from this experiment showed no incorporation of deuterium in the aromatic nucleus. These results can be accommodated by a mechanism involving attack by cyanide ortho to the acetyl group; however, further data are needed to define the actual pathway.

Only limited work has as yet been done with other nucleophiles. Hydroxide, though less reactive than cyanide, attacks photoexcited 3-methoxyacetophenone

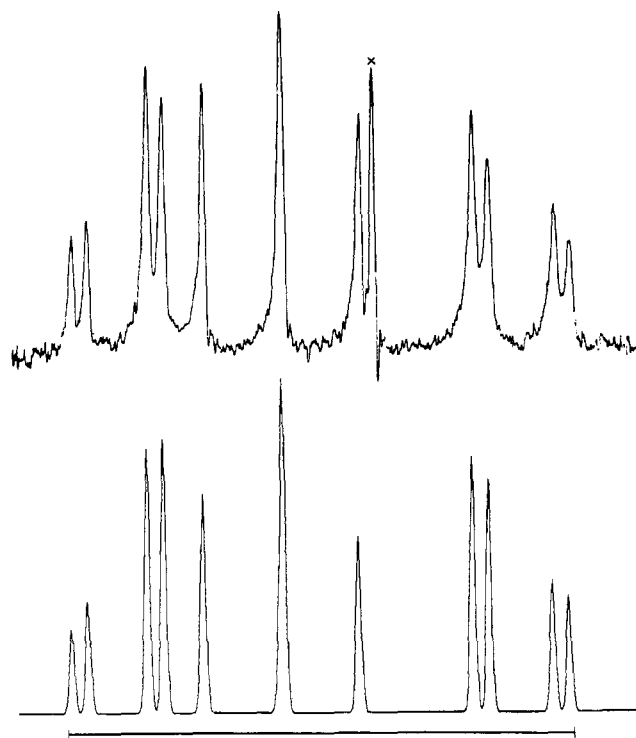


Figure 1. Aromatic hydrogen region of 90-MHz nmr spectrum of 2-deuterio-3-methoxyacetophenone from experiment 6; observed spectrum above, calculated spectrum below.⁸ The calibration bar represents 50 Hz. The peak marked X corresponds to CHCl_3 .

in aqueous solution to give a good yield of 3-hydroxyacetophenone (isolated in 66% yield; on the basis of unrecovered 3-methoxyacetophenone the yield is 90%).

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Stable Carbocations. CXXXIX.¹ Nitro- and Chlorohexamethylbenzenium Ions and 1-Nitro- and 1-Chloro-2,4,6-trifluoromesitylenium Ions

Sir:

A series of long-lived benzenium ions or σ complexes, considered to be intermediates of electrophilic aromatic substitution reactions, has been directly observed.² Some stable long-lived σ complexes have even been isolated as crystalline salts.³ However, these ions until now were all limited to protonated (generally with superacids) or alkylated benzenium ions, such as the heptamethylbenzenium ion.⁴ Long-lived σ -complex intermediates of nitration^{5a} or chlorination^{5b}

(1) Part CXXXVIII: G. A. Olah, *Angew. Chem.*, in press.

(2) (a) For a review, see D. M. Brouwer, E. L. Mackor, and C. MacLean in "Carbonium Ions," Vol. II, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N. Y., 1970; (b) G. A. Olah, R. H. Schlosberg, R. D. Porter, Y. K. Mo, D. P. Kelly, and Gh. D. Mateescu, *J. Amer. Chem. Soc.*, **94**, 2034 (1972).

(3) G. A. Olah, *ibid.*, **87**, 1103 (1965).

(4) W. v. E. Doering, M. Saunders, H. G. Boyton, H. W. Earhart, E. F. Wadley, W. R. Edwards, and G. Laber, *Tetrahedron*, **4**, 178 (1958).

(5) (a) G. A. Olah, *Accounts Chem. Res.*, **4**, 240 (1971). (b) For a review, see H. P. Braendlin and E. T. McBee in "Friedel-Crafts and Related Reactions," Vol. III, Part II, G. A. Olah, Ed., Wiley-Interscience, New York, N. Y., 1963.

(8) The integrated intensity observed for resonance of the aromatic protons relative to the methoxyl protons (3.00) is 3.1, and the intensities for the individual protons are 1.03, 1.07, and 1.01 for H_4 , H_5 , and H_6 , respectively. The chemical shifts and coupling constants for the calculated spectrum (Figure 1) are: H_4 , 7.11 ppm; H_5 , 7.37; H_6 , 7.53; J_{4-5} , 8.25 Hz; J_{4-6} , 1.03; J_{5-6} , 7.61. We are grateful to Dr. J. B. Lambert for helpful discussions concerning the spectra.

(9) I. E. Den Besten, L. Kaplan, and K. Wilzbach, *J. Amer. Chem. Soc.*, **90**, 5868 (1968).

(10) The resonance characteristic of the H_6 proton was absent, and a single peak in the aromatic region was found (6.99 ppm, for $\text{H}_3 + \text{H}_5$). The intensity of this peak relative to that for the 4-methyl group was somewhat low (1.71/3.00 rather than 2/3), suggesting that some deuterium was also incorporated at the 3 and/or 5 positions.