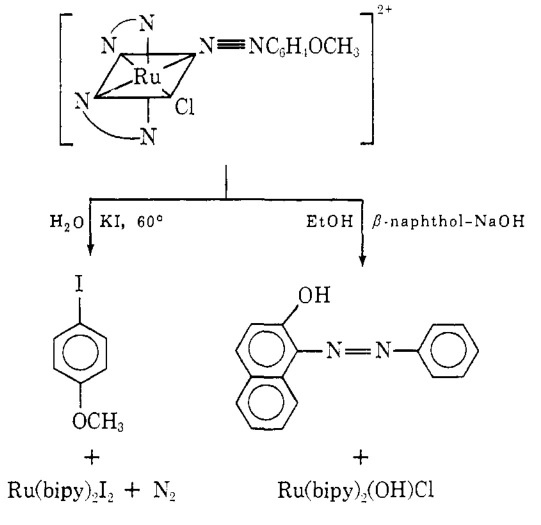
and 2250 cm^{-1},[14] respectively. Compound IIa was shown to be a 2:1 electrolyte by a conductometric titration in acetone, as expected for a diazonium complex of ruthenium(II). Reaction 1 (Ar = p-$CH_3OC_6H_4$–) was also carried out using $Ru(bipy)_2(^{15}NO)Cl^{2+}$, and the diazonium product showed a $\Delta\nu_{NN}$ of *ca.* −30 cm^{-1} (acetonitrile). The observed shift in ν_{NN} shows that the nitrosyl nitrogen is incorporated into the product, probably still bound to the ruthenium. The importance of back-bonding in both the nitrosyl and diazonium complexes is clear from their electronic spectra. The spectra of bis-2,2′-bipyridyl complexes of ruthenium(II) are characterized by intense, low energy $t_{2g} \rightarrow \pi^*$(bipy) transitions (*e.g.*, λ_{max} 555 nm for $Ru(bipy)_2Cl_2$ in dichloromethane).[15,16] For the complexes $Ru(bipy)_2(NO)Cl^{2+}$ and $Ru(bipy)_2(N_2C_6H_4OCH_3)Cl^{2+}$ in acetonitrile, the first transitions are observed at λ_{max} 325 and λ_{max} 353 nm, respectively, indicating considerable stabilization of the t_{2g} levels by π bonding.

Recently, Laing, Robinson, and Uttley have reported the preparations of the complexes $MX_3(N_2Ar)(P(C_6H_5)_3)_2$ (M = Ru, Os; X = Cl, Br) by direct reaction between diazonium tetrafluoroborate salts and $MX_2(P(C_6H_5)_3)_3$ in the presence of LiX.[12] Their reported ν_{NN} values occur in the range 1850–1900 cm^{-1}, and from a preliminary X-ray study[12] the N–N–Ar angle in one of the ruthenium complexes was found to be 137°. This report raises the interesting possibility that a range of cases intermediate between $ArN{=}N^-$ and $ArN{\equiv}N^+$ may exist in which the N–N–Ar bond angle varies from ~120 to ~180° with corresponding changes in ν_{NN} and in chemical reactivity.

In addition to physical properties of bound ArN_2^+, compound IIa showed chemical reactivity characteristic of a diazonium ligand stabilized by complexation. At 60° in aqueous solution N_2 gas is evolved. With excess KI, p-iodoanisole was produced along with $Ru(bipy)_2I_2$ and N_2 (eq 2). Complex IIa also reacts with β-naphthol in alkaline ethanolic solution to produce the known azo coupling product. The reaction of $[Ru(bipy)_2(NO)Cl](PF_6)_2$ with other aryl amines and with aliphatic amines seems to be general and further reactions are currently under investigation.



(2)

Acknowledgment. We gratefully acknowledge the University of North Carolina Research Council and the American Cancer Society for financial assistance on this work.

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(15) G. M. Bryant and J. E. Fergusson, *Aust. J. Chem.*, **24**, 257 (1971); J. E. Fergusson and G. M. Harris, *J. Chem. Soc. A*, 1293 (1966).

(16) S. A. Adeyemi, J. N. Braddock, T. R. Weaver, and R. W. Callahan, unpublished results.

A Chain Photoreaction of Sodium Borohydride with Halogenated Aromatic Hydrocarbons. Evidence for Initiation by Aryl Radicals

Sir:

We wish to report that the photoreduction of the chloro, bromo, and iodo derivatives of aromatic hydrocarbons by sodium borohydride in aqueous acetonitrile solution proceeds *via* a radical chain mechanism to give the hydrocarbon in virtually 100% yield and in a quantum yield often considerably in excess of unity.

Continuing our studies[1] into the photoreduction of aromatics, we irradiated (λ 254 nm) solutions (0.5 *M*) of chloro-, bromo-, and iodobenzene with $NaBH_4$ (1.0 *M*) in 6% v/v aqueous acetonitrile. The sole organic product (glc) in all cases was benzene, formed in quantitative yield. The corresponding quantum yields[2] were 0.5, 5.7, and 7.5, respectively. In addition, (i) a gas was evolved shown to be mainly hydrogen with traces of diborane (m/e 28, 14), (ii) the solution contained halide ion, and (iii) a white solid was precipitated giving a positive test for borate. There was no detectable reaction with fluorobenzene.

To accommodate these results, we propose the mechanism shown in Scheme I.

Scheme I

$$C_6H_5{\cdot}X \xrightarrow{h\nu} [C_6H_5{\cdot}X]^* \longrightarrow C_6H_5{\cdot} + X{\cdot} \qquad \text{initiation}$$

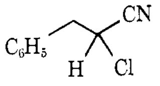
$$X{\cdot} + BH_4^- \longrightarrow BH_3{\cdot}^- + X^- + H^+$$

$$\left.\begin{array}{l} C_6H_5{\cdot} + BH_4^- \longrightarrow BH_3{\cdot}^- + C_6H_5H \\ C_6H_5X + BH_3{\cdot}^- \longrightarrow C_6H_5{\cdot} + BH_3 + X^- \end{array}\right\} \text{propagation}$$

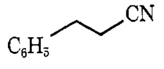
$$2BH_3 \longrightarrow B_2H_6 \xrightarrow{H_2O} \text{borate} + H_2$$

$$C_6H_5{\cdot} + X{\cdot} \longrightarrow C_6H_5X \qquad \text{termination}$$

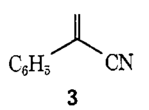
The intervention of phenyl radicals was demonstrated (i) by showing that the photoreduction was totally inhibited by small amounts of acrylonitrile (an efficient trap for phenyl radicals) and (ii) by irradiating a mixture of chlorobenzene (0.5 *M*) and acrylonitrile (0.5 *M*) in acetonitrile, a procedure which gave rise to the products **1**, **2**, and **3**.



1



2



3

It is known[3–5] that phenyl radicals generated by the

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(1) J. A. Barltrop, *Pure Appl. Chem.*, **33**, 179 (1973); J. A. Barltrop and R. J. Owers, *J. Chem. Soc., Chem. Commun.*, 592 (1972).

(2) These are initial values obtained by extrapolating quantum yields back to zero time.

(3) C. F. Koelsch, *J. Amer. Chem. Soc.*, **65**, 57 (1943).

(4) C. F. Koelsch and V. Boekelheide, *J. Amer. Chem. Soc.*, **66**, 412 (1944).

(5) J. K. Kochi, *J. Amer. Chem. Soc.*, **79**, 2942 (1957).

decomposition of benzenediazonium chloride react with acrylonitrile to give **1**. Thus, the formation of **1** in our photochemical experiment is consistent with the hypothesis that excited chlorobenzene dissociates homolytically. The extra photoproducts **2** and **3** have been shown to be derived from **1** by photolysis in acetonitrile.

We therefore suppose that excitation of chlorobenzene gives rise to C_6H_5 and Cl, which react with $NaBH_4$ by the mechanism suggested or with acrylonitrile to give **1**.

Further evidence in support of our proposal is provided by an experiment in which iodobenzene (0.5 *M*) and $NaBH_4$ (1.0 *M*) in liquid ammonia and MeCN was reduced with sodium. Benzene was formed in 675% yield (calculated on Na consumed); replacement of the $NaBH_4$ by NaCl gave benzene in only 51% yield. Sodium is known[6,7] to transfer an electron to iodobenzene yielding $C_6H_5\cdot$ and I^-.

The quantitative photoreduction by $NaBH_4$ of 1- and 2-bromonaphthalene and 9-bromophenanthrene to the corresponding hydrocarbons was also inhibited by acrylonitrile and the hydrocarbons obtained in the presence of $NaBH_4$–D_2O contained no deuterium.

We note a marked similarity between the results of our photochemical experiments and those of Brown and Krishnamurthy,[8] who reduced halogenated benzenes in the dark with $LiAlH_4$ in tetrahydrofuran. It may be that the presence of peroxides in this solvent initiates a chain reaction with the consequences described above.

Acknowledgments. We gratefully acknowledge financial support of this work by Brasenose College, Oxford.

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(6) J. E. Bennett, B. Mile, and A. Thomas, *Proc. Roy. Soc., Ser. A*, **293**, 246 (1966).

(7) A. R. Buick, T. J. Kemp, G. T. Neal, and T. J. Stone, *J. Chem. Soc. A*, 666 (1969).

(8) H. C. Brown and S. Krishnamurthy, *J. Org. Chem.*, **34**, 3918 (1969).

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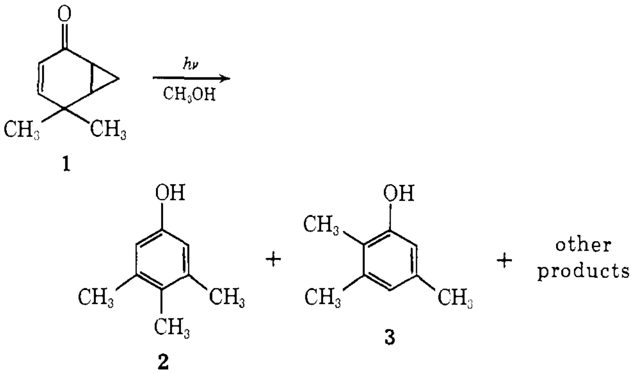
Photoisomerization of 5,5-Dimethylbicyclo[4.1.0]hept-3-en-2-one and 4,6,6-Trimethylbicyclo[3.1.0]hex-3-en-2-one[1]

Sir:



Irradiation of 5,5-dimethylbicyclo[4.1.0]hept-3-en-2-one (**1**) in methanol at room temperature gives among other products two rearranged phenols (**2** and **3**, *ca.* 50%, identified by ir and nmr comparison). These products are formed in a complex series of transformations which culminate in the thermal isomerization of the primary photoproducts of 4,6,6-trimethylbicyclo[3.1.0]hex-3-en-2-one. Deuterium labeling has shown that the cyclopropyl methylene group of **1** becomes the third methyl group found in the phenolic products.[1] This observation and the results of Dauben's studies on the photochemistry of fused-ring cyclopropyl ketones[2] suggest that the first step in the rearrangement might be photoisomerization of **1** to 3,4,4-trimethyl-2,5-cyclohexadienone (**4**). Attempts to detect **4** during the irradiation of **1** were frustrated by the fact that **4** is destroyed photochemically far more efficiently than **1**. Irradiation of **4** in methanol at room temperature gives only **5**.[3] Irradiation of **5** in methanol at room temperature gives phenols **2** and **3** among other products. The sequence **4** → **5** → **2** and **3** is analogous to the rearrangements observed with 4,4-diphenyl-2,5-cyclohexadienone[4] and 4,4-dimethyl-2,5-cycohexadienone.[5] Irradiation of **5** as a neat film at 77°K gives primary product bands at 2107 and 1810 cm^{-1}.[6] Continued irradiation produced carbon monoxide at the expense of the 1810-cm^{-1} band. These observations together with the results of our earlier investigations[7] suggest that the 2107-cm^{-1} band is due to a ketene and the 1810-cm^{-1} band to a cyclopropanone. Irradiation of **4** at −78° in methanol–ether (1:2) gives (*via* **5**) the methanol adducts **6** and **7** and the ester **8**.[8] An analogous ester is observed in the irradiation of 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one.[9] Irradiation of either **4** or **5** in furan–ether (1:4) at −78° gives a furan adduct **9**.[10] Similar irradiation of **10** gives adduct **11** (mp 113–115°). Adduct **11** was selected for X-ray analysis because it gave better crystals.

Diffractometer measured cell constants are $a = 15.24$ (2), $b = 6.47$ (1), and $c = 11.15$ (1) Å and $\beta = 115.2$ (2)° for the uniquely determined space group $P2_1/c$. A total of 2476 unique reflections with $\theta \leq 30°$ for Mo Kα radiation were measured and 2476 were judged observed.

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(1) Photochemical Transformations. LI. Abstracted in part from the Ph.D. Thesis of T. A. McDowell, Iowa State University, Ames, Iowa, 1971.

(2) W. G. Dauben, G. W. Shaffer, and E. J. Deving, *J. Amer. Chem. Soc.*, **92**, 6273 (1970); W. G. Dauben and G. W. Shaffer, *Tetrahedron Lett.*, 4415 (1967).

(3) Compound **5**: ν (neat) 1687, 1606 cm^{-1}; uv λ_{max}^{EtOH} 228 (ϵ 4770), 253 (ϵ 3790), 315 nm (ϵ 241); nmr δ (CCl_4) 1.1 (m, 1 H), 1.15 (s, 3 H), 1.23 (s, 3 H), 1.85 (m, 1 H), 2.05 (d, 3 H), 5.50 (m, 1 H). *Anal.* Found: C, 79.32; H, 8.89.

(4) H. E. Zimmerman and D. I. Schuster, *J. Amer. Chem. Soc.*, **84**, 4527 (1962).

(5) J. S. Swenton, E. Saurborn, R. Srinivasan, and F. I. Sonntag, *ibid.*, **90**, 2990 (1968).

(6) Irradiation of 6,6-dimethylbicyclo[3.1.0]hex-3-en-2-one (10) as a neat film at 77°K gives similar bands (2109, 1815 cm^{-1}).[1]

(7) O. L. Chapman, L. L. Barber, and J. D. Lassila, *J. Amer. Chem. Soc.*, **91**, 3664 (1969); O. L. Chapman, *Int. Union Pure Appl. Chem. Congr., XXIIIrd, Spec. Lect.*, 1, 311 (1971).

(8) Compound **6**; ir ν (neat) 1732, 1678 cm^{-1}; nmr δ (CCl_4) 1.02 (s, 3 H), 1.08 (s, 3 H), 1.75 (d, 3 H), 2.19 and 2.47 (q, J_{AB} = 12 Hz, 2 H), 3.32 (s, 3 H), 3.51 (m, 1 H), 5.45 (m, 1 H); parent ion *m/e* 168 (35%). Compound **7**: ir ν (neat) 1680, 1640 cm^{-1}; uv λ_{max}^{EtOH} 247 nm (ϵ 9620); nmr δ (CCl_4) 1.03 (s, 6 H), 1.82 (d, 3 H), 2.19 (s, 4 H), 3.60 (s, 3 H); parent ion *m/e* 168 (66%). *Anal.* Found: C, 71.13; H, 9.63. Compound **8**: ir ν (neat) 1742 cm^{-1}; uv λ_{max}^{EtOH} 244 nm (ϵ 21,500); nmr δ (CCl_4) 1.73 (s, 3 H), 1.82 (m, 6 H), 3.06 (s, 2 H), 3.62 (s, 3 H), 5.97 (m, 2 H). *Anal.* Found: C, 71.25; H, 9.37.

(9) H. E. Zimmerman, R. Keese, J. Nasielski, and J. S. Swenton, *J. Amer. Chem. Soc.*, **88**, 4895 (1966).

(10) Compound **9**: mp 68–70°; ir ν (CCl_4) 1737, 1720 cm^{-1}; λ_{max}^{EtOH} 284 nm (ϵ 128); nmr δ (CCl_4) 0.98 (s, 3 H), 1.24 (s, 3 H), 1.74 (d, 3 H), 1.96 (m, 1 H), 2.43 (m, 1 H), 4.61 (m 1 H), 4.83 (m, 1 H), 5.26 (m, 1 H), 6.25 (m, 2 H); parent ion *m/e* 204 (100)%. *Anal.* Found: C, 76.28; H, 7.78.