Pergamon

Tetrahedron, Vol. 53, No. 29, pp. 10009-10018, 1997
© 1997 Elsevier Science Ltd
All rights reserved. Printed in Great Britain
0040-4020/97 $17.00 + 0.00

PII: S0040-4020(97)00343-8

Protodediazoniation of Aryldiazonium Fluoroborates by Dimethylformamide[1]

J. Hodge Markgraf,*[a] Raymond Chang,[a] John R. Cort,[a] Joseph L. Durant, Jr.,[b]
Manuel Finkelstein,[ac] Andrew W. Gross,[a] Michael H. Lavyne,[a] W. Michael Moore,[c]
Raymond C. Petersen,[c] and Sidney D. Ross[c]

[a] Department of Chemistry, Williams College, Williamstown, MA 01267, USA

[b] Combustion Research Facility, Sandia National Laboratories, Livermore, CA 94551, USA

[c] Research Laboratories, Sprague Electric Company, North Adams, MA 01247, USA

Abstract. The protodediazoniation of aryldiazonium fluoroborates can be effected by warm dimethylformamide (DMF). The conversion of 4-nitrobenzenediazonium fluoroborate to nitrobenzene was studied in detail. Products derived from trapping experiments were consistent with a homolytic process. Studies with deuterated DMF established that H atom abstraction occurred from both sites in DMF with a formyl:methyl preference of 3.5:1.0. This mechanism was consistent with bond energies and kinetic isotope effects calculated for the DMF radical cation. © 1997 Elsevier Science Ltd.

The replacement by hydrogen of the diazonium group on an aromatic ring has been studied for well over a century,[2] and new methods continue to be developed.[3,4] While more than two dozen procedures are known, only four involve no other reagent than solvent. The latter group, comprised of cyclic ethers,[5] tetramethylurea,[6] hexamethylphosphoramide (HMPA),[7] and dimethylformamide (DMF),[3,8] effects protodediazoniation of aryldiazonium salts without added acid, base, catalyst, or another hydrogen source. The first systematic study of the use of DMF was by Doyle and coworkers,[9] who reported the aprotic diazotization of arylamines and compared DMF with other hydrogen sources.

RESULTS AND DISCUSSION

We independently observed this reaction some years ago when aryldiazonium salts were used in place of quaternary ammonium salts in electrochemical studies in DMF. We briefly explored the scope of this reaction. In Table 1 are presented some of our results, which supplemented the earlier report of Lahoti, *et al.*[8b] Our primary focus, however, was on the mechanism of this transformation. The dediazoniation process is known to proceed stepwise, and the intermediate may be either an aryl cation or radical.[10] Mechanistic studies are complicated by the fact that the nature of the intermediate is determined both by the solvent and by the substituent. Thus for a given substituent, the solvent controls the pathway. For instance, 4-nitrobenzenediazonium fluoroborate (**1**) generated the aryl radical in dimethylsulfoxide (DMSO),[11] but the aryl cation in acetonitrile.[12] In both solvents benzenediazonium fluoroborate (**2**) gave the phenyl cation.[13] Conversely, for a given solvent, the substituent is determinative. In DMSO or acidic methanol **1** generated the

Table 1. Reaction of $ArN_2^+BF_4^-$ in DMF[a]

$ArN_2^+BF_4^-$	ArH (%)
3-trifluoromethylphenyl	79
4-nitrophenyl	75
4-methoxyphenyl	54
4,4'-biphenyl	25
2-naphthyl	14

[a] Conditions: 95 °C, 2 hours.

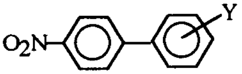
aryl radical, but **2** gave the phenyl cation.[14] There are further subtleties related to atmosphere, complexing agents, and co-solvents. In methanol 3- and 4-halobenzenediazonium fluoroborates generated only aryl radicals under a nitrogen atmosphere, but also some aryl cations under an oxygen-containing atmosphere; **1** gave only radicals under either atmosphere.[14c] Complexing agents have also altered pathways. Whereas **1** gave the aryl cation in acetonitrile,[12] it gave the aryl radical in acetonitrile containing 18-crown-6;[15] the same effect was observed in 1,2-dichloroethane.[16] The decomposition mode of **2** has been changed from heterolytic to homolytic by the addition of pyridine.[17] The pathway was even observed to be magnetic-field dependent.[18]

Given the complexity of the above factors, mechanistic pathways must be established on a case by case basis. We focused on **1** in DMF because the competing pathways were known for other solvents, the product (nitrobenzene, **3**) was conveniently isolated, and the solvent presented a choice of hydrogen abstraction sites. The latter aspect was not applicable to the earlier solvent-only studies involving dioxane,[5] tetramethylurea,[6] and HMPA.[7] We initially sought evidence for a radical intermediate by chemically induced dynamic nuclear polarization (CIDNP) studies. A solution of **1** in DMF-d_7 at 50° exhibited strong CIDNP signals; but the number and complexity of the peaks, consistent with multiple radical species, did not permit identification of either the aryldiazenyl radical or the aryl radical. CIDNP experiments have been helpful with some systems;[17c] but such data were ambiguous in other cases, including spectra of **1** and **2**.[19]

The nature of the intermediate has most often been deduced by adding substituted benzenes (C_6H_5Y) to the reaction mixture and determining the substitution patterns of the derived biphenyls.[11-13,15] That method was applied to the decomposition of **1** in DMF containing anisole or nitrobenzene. The results are presented in Table 2, in which the product ratio of the $C_6H_4NO_2$ substituent *meta* or *para* to Y reflected the nature of the arylating species. The results, very similar to those reported by Kamigata, *et al.*,[12] were consistent only with a 4-nitrophenyl radical intermediate (**4**). Particularly informative was the arylation of nitrobenzene (*m*/*p* 0.17). The data also indicated no temperature or atmospheric effects.[11a,14c]

Another probe for aryl radical intermediates has been transiodination.[3,11b,20] From the decomposition of **1** in DMF containing iodobenzene, 4-nitroiodobenzene was isolated. The product, which could arise only from **4**, was noteworthy despite the minor yield (10%) because the major product (**3**) is known to inhibit transiodination even in small amounts.[21] These results confirm the trapping experiments reported by Wassmundt and Kiesman.[3]

Table 2. Reactions of **1** with C_6H_5Y in DMF

							
Y	Temp., °C	Atmosphere	Yield, %	2-Y	3-Y	4-Y	*m*/*p*
OCH_3	60	air	36	74	10	15	0.67
OCH_3	60	argon	26	76	9	15	0.60
OCH_3	80	argon	31	78	9	13	0.69
NO_2	60	argon	7	66	5	29	0.17

Thus it appeared conclusive that **1** in DMF underwent homolysis to produce aryl radical **4**; but, before charting a pathway, a side product needed to be identified. Analysis of the crude product mixture by GC/MS revealed a minor component (*ca.* 10%) with a molecular ion (*m/z* 194) consistent with N,N-dimethyl-4-nitrobenzamide. However upon isolation the compound, despite its mass and nmr (methyl singlets at δ 3.28 and 3.60 ppm) spectra, was identified as 1-(4-nitrophenyl)-3,3-dimethyltriazene (**5**) by independent synthesis. This minor product implied the intermediacy of the 4-nitrophenyldiazenyl radical (**6**). The ease of the latter's formation was confirmed by voltammetric measurements. Polarographic reduction of **1** occurred readily with $E_{1/2} = +0.04$ v (*vs.* Ag/Ag^+); oxidation of DMF occurred with $E_p = +2.05$ v. Comparable data have been reported for 4-chlorobenzenediazonium fluoroborate and HMPA.[7]

Since DMF provided two hydrogen donor sites, deuterium labeling experiments were undertaken. Prior studies involving deuteride reagents and deuterated methanol established that homolytic protodediazoniation proceeded by hydrogen abstraction from the methyl group of methanol.[14c,22] For a closely related system, the aprotic diazotization of anilines with alkyl nitrites, Doyle, *et al.*,[9] studied dual reagent mixtures of $PhCD_2ONO/CH_3CN$ and $PhCH_2ONO/CD_3CN$; the arene product derived hydrogens from both sources. In DMF, however, the same authors found that $ArNH_2$ with $PhCD_2ONO$/DMF and $PhCH_2ONO/DMF/D_2O$ gave only ArH. They suggested that hydrogen transfer occurred primarily from the N-methyl group of DMF. That DMF was the sole source of hydrogen was confirmed by Wassmundt and Kiesman for the $FeSO_4$-catalyzed decomposition of 2,4-dinitrobenzenediazonium fluoroborate in DMF-d_7/H_2O.[3] Both sites in DMF must be considered, since hydrogen transfer has been shown to occur from the N-methyl groups of tetramethylurea and N,N-dimethylacetamide[3] and from the formyl group of formamide.[23]

The decomposition of **1** in deuterated DMF gave the results presented in Table 3. The outcome in DMF-d_7 for these uncatalyzed reactions was the same as for $FeSO_4$ catalysis[3] and confirmed the absence of any extraneous source of hydrogen. In the conversion of **1** to **3** hydrogen transfer thus occurred from both sites. Comparable duality for DMF has also been observed with radicals generated from peroxides, although the regioselectivities differed.[24,25] In the present case the product of the kinetic isotope effects, derived from the ratios of **3** and **3**-d_1 from DMF-d_1 and DMF-d_6, was calculated to be 36. Hess and Durant have found that the kinetic isotope effect is dependent on the exothermicity of the reaction.[26] The exothermicities of **4** → **3** via H

Table 3. Product Ratios from **1** in Deuterated DMF[a]

DMF	AR–H **3**	AR–D **3**-4d_1
$\mathrm{H{-}CO{-}N(CH_3)_2}$	100	0
$\mathrm{D{-}CO{-}N(CH_3)_2}$	91	9
$\mathrm{H{-}CO{-}N(CD_3)_2}$	78	22
$\mathrm{D{-}CO{-}N(CD_3)_2}$	0	100

[a] AR = 4-nitrophenyl

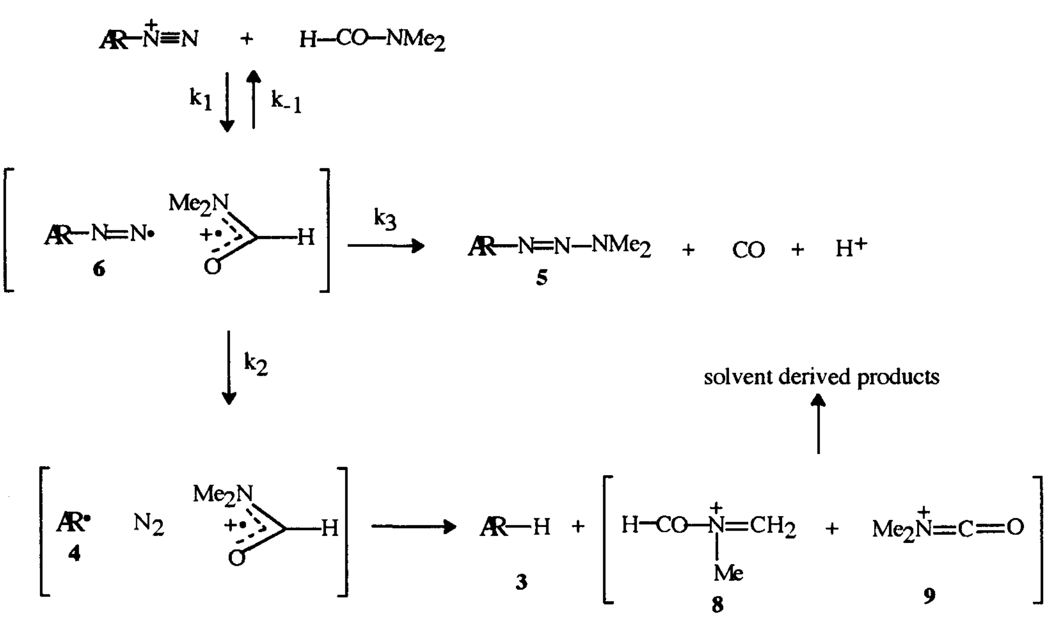
atom abstraction from methyl or formyl were estimated to be 80 and 81 kcal/mole based on bond energies of 112 kcal/mole for AR–H[27] and 31.9 and 30.7 kcal/mole for methyl C–H and formyl C–H, respectively, in the DMF radical cation (Table 4). Given the comparable exothermicity of either pathway, we expect the two kinetic isotope effects (KIE) to be approximately equal and therefore $k_H/k_D \approx 6$ for the homolysis of either the methyl or formyl C–H bond. Our KIE data, in conjunction with the observed regioselectivities normalized on a per hydrogen basis, corresponded to a 3.5:1.0 ratio for formyl:methyl sites. The preference for formyl H abstraction was consistent with our calculated bond energies.

Table 4. Calculated Bond Strengths[a]

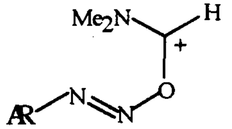
Bond	Method DFT	G2(MP2)
$\mathrm{H{-}CO{-}N(CH_3)CH_2{-}\mathbf{H}}$	89.1	94.1
$\mathrm{\mathbf{H}{-}CO{-}N(CH_3)_2}$	89.7	94.1
$\mathrm{[H{-}CO{-}N(CH_3)CH_2{-}\mathbf{H}]^{\bullet+}}$	41.7	31.9
$\mathrm{[\mathbf{H}{-}CO{-}N(CH_3)_2]^{\bullet+}}$	39.0	30.7

[a] D_0 (0° K) in kcal/mole.

Scheme 1



The pathways in Scheme 1 account for the radical intermediates, isotope effects, and product structures. The first step is considered to be an outer-shell electron transfer[28] to generate aryldiazenyl radical **6** as part of a cation radical pair, which dediazoniates via k_2 to aryl radical **4** and rearranges via k_3 to triazene **5** with concomitant loss of CO and H^+. The abstraction of a H atom from $DMF^{\bullet+}$ by **4** is shown as a single step, but a chain mechanism is also a possibility at this stage. The latter pathway was clearly established for DMF with $FeSO_4$ catalysis and was considered likely as well for the uncatalyzed reaction.[3] The higher yields of triazenes **5** and **5**-d_6 correlated with those solvents (DMF and DMF-d_6) with a formyl protium, while the lower yields of **5** and **5**-d_6 were obtained in DMF-d_1 and DMF-d_7 which possessed a formyl deuterium (Table 5). Because $k_2 \gg k_3$ the **5**:**5**-d_6 ratios, which can be derived from Table 5, should be equal and lead to an estimate of $k_H/k_D = 5 \pm 1$ for k_3. Triazene formation must be concerted to exhibit the observed KIE. The pathway can involve either an outer-shell electron transfer to form a cation radical pair or an inner-shell electron transfer to form diazo ether **7**.



7

Table 5. Yields (%) of Triazenes in Deuterated DMF[a]

DMF	$Ar{-}N{=}N{-}N(CH_3)_2$ **5**	$Ar{-}N{=}N{-}N(CD_3)_2$ **5**-*d*$_6$
$H{-}CO{-}N(CH_3)_2$	10	0
$D{-}CO{-}N(CH_3)_2$	1.9	0
$H{-}CO{-}N(CD_3)_2$	0	11
$D{-}CO{-}N(CD_3)_2$	0	2.6

[a] Ar = 4-nitrophenyl

The latter could undergo homolysis via k_2 to **4** and collapse via k_3 in a four-center reaction to **5**. Such diazo ether intermediates have been considered by others;[3,7,11] but the empirical data of Doyle, *et al.*,[28] support the outer-shell process, and that route is shown in Scheme 1. When **3** is produced by hydrogen atom transfer from the DMF cation radical, species **8** and **9** are generated. These cations are known to give solvent-derived products during electrolysis,[29] but no attempt was made in the present work to detect such products upon work up.

COMPUTATIONS

All calculations were performed using the Gaussian 92 or Gaussian 94 program suite.[30] Density Functional Theory (DFT) calculations were performed using the Gaussian implementations for the Becke half-and-half/Lee, Yang and Parr (BH&HLYP) functional.[31,32] The 6-311G(d,p) basis set was used, which has been shown to give accurate energetics with BH&HLYP functionals for transition states. The performance of Gaussian's implementation of the BH&HLYP functional for stable species is less well documented.[33] We have calculated optimized structures, vibrational frequencies, and energies for $H{-}CO{-}N(CH_3)_2$, $H{-}CO{-}N(CH_3)CH_2^{\bullet}$, and $\bullet CO{-}N(CH_3)_2$ and for the cation radicals using DFT with the BH&HLYP functional. The derived bond strengths are listed in Table 4. As a check on the accuracy of the DFT calculations a number of G2(MP2) calculations were carried out by standard methodology.[34] The latter method utilizes perturbation theory to refine Hartree-Fock self consistent-field results and represents an independent route for electonic structure calculations. G2(MP2) has been extensively tested and found to have an absolute average deviation of 1.6 kcal/mole for heats of atomization of 125 diatomic, triatomic, and tetratomic species. The relative bond strengths calculated by the two approaches were in good agreement, although the overall strengths of the bonds were 5-10 kcal/mole higher in the DFT calculations. This difference appears to result largely from differences in the treatment of the DMF and $DMF^{\bullet +}$ species, which had markedly different geometries for the two methods. In contrast, the geometries of the other species were relatively constant between the two approaches. The bond strengths for the methyl and formyl C–H bonds in DMF were virtually identical. For the same bonds in the DMF radical cation, however, the *formyl C–H bond was 1.2 kcal/mole less than the methyl C–H* and both were much lower than the corresponding values for DMF. The geometries allowed considerable charge delocalization. In cation **8** all the heavy atoms were coplanar, as were the formyl and methylene hydrogens. In cation **9** all the heavy atoms were again coplanar, with the OCN moiety being linear.

EXPERIMENTAL SECTION

Methods. NMR ^1H were obtained in $CDCl_3$ on a Brucker WP-200SY spectrometer; chemical shifts are reported in ppm downfield relative to tetramethylsilane. Products reported in Table 1 were identified by GC comparison with authentic samples on a Perkin-Elmer 154 B instrument with a 20% Carbowax 1500 on 60/80 Chromosorb W column (1/4-inch x 6-ft s.s.) Analyses reported in Tables 2, 3, and 5 were performed on a Hewlett-Packard 5890II gas chromatograph with a HP-1 crosslinked methyl silicone gum column (12 m x 200 µm with 33 µm film) and a Hewlett-Packard 5971A mass spectrometer (EI, 70 eV); yields were quantified by an internal standard and were corrected for detector response with authentic samples. Polarographic and linear sweep voltammetric measurements were carried out as previously described.[35]

Materials. Aryl amines were distilled *in vacuo* or recrystallized immediately prior to use. Aryldiazonium fluoroborates were prepared and purified by published procedures.[14c,36] Authentic samples of methoxynitrobiphenyls (Table 2) were obtained from N. Kamigata and M. Kobayashi.[12] Authentic samples of dinitrobiphenyls (Table 2), and triazene **5** were prepared by literature methods.[37,38] DMF was distilled *in vacuo* and stored under nitrogen over 4A molecular sieves; GC/MS analysis indicated the absence of dimethylamine. Deuterated DMF compounds were obtained from Merck, Sharp & Dohme (Canada) and were 98-99.5% isotopically-enriched.

Preparative-Scale Dediazoniations. A solution of aryldiazonium fluoroborate (0.050 mol) in DMF (100 mL) was warmed from room temperature to 100 °C over 2 h, cooled, diluted with water, and the product was isolated by extraction or suction filtration. Results are presented in Table 1.

Dediazoniations in the Presence of Added Arenes. A solution of **1** (0.0237 g, 0.100 mmol) and arene (5.00 mmol) in DMF (1.3 mL) was thermostatted at 60 °C under an atmosphere of air or argon for 40 min., cooled, diluted with water, and extracted with CH_2Cl_2. The combined CH_2Cl_2 extract was washed, dried, concentrated at reduced pressure, and analyzed by quantitative GC with butyl benzoate as an internal standard. Results are presented in Table 2; the data represent triplicate runs (yields ± 2.6%; product ratios ± 0.7%).

In duplicate runs on the same scale the reaction of **1** (0.021 g, 0.089 mmol) and iodobenzene (0.904 g, 0.443 mmol) in DMF (1.3 mL) at 60 °C under argon for 40 min. gave 1-iodo-4-nitrobenzene (10.4 ± 0.2%). A third run with **1** (0.089 mmol) and iodobenzene (1.772 mmol) gave the same product (10.1%).

Dediazoniations in Deuterated DMF. In a similar manner a solution of **1** (0.016 g, 0.067 mmol) in DMF-d_1 (1.0 mL) was thermostatted at 60 °C under argon for 40 min. Identical runs were conducted in DMF-d_6 and DMF-d_7. Standard work-up and analysis gave the results in Tables 3 and 5; the data represent duplicate runs (± 0.3%).

ACKNOWLEDGMENTS

We are grateful to Professor J. F. Bunnett (Santa Cruz) for advice and encouragement. We are indebted to Professors N. Kamigata and M. Kobayashi (Tokyo) for samples of methoxynitrobiphenyls. This work was supported in part by the Williams College Faculty Research Fund and by the Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences.

REFERENCES AND NOTES

1. (a) Based in part on the senior projects and Honors Theses, Williams College, of J.R.C. (1991), A.W.G. (1978), and M.H.L. (1968). (b) Presented in part on the ECTOC-1, www., 12 June-7 July 1995.
2. (a) Griess, P. *Ann. Chem. Pharm.* **1860**, *113*, 201-217. (b) Griess, P. *Phil. Trans. Royal Soc. London* **1864**, *164*, 667-731. (c) Kornblum, N. *Org. React.* **1944**, *2*, 262-340. (d) Zollinger, H. *Azo and Diazo Chemistry*; Interscience Publishers Inc.: New York, 1961; p. 168. (e) Wulfman, D. S. in *The Chemistry of Diazonium and Diazo Groups* Part I, Patai, S. ed.; J. Wiley & Sons: New York, 1978; pp. 286-287. (f) Zollinger, H. in *Supplement C. The Chemistry of Triple-Bonded Functional Groups* Part I, Patai, S.; Rappoport, Z. ed.; J. Wiley & Sons: New York, 1983; Chap. 15. (g) Saunders, K. H.; Allen, R. L. M. *Aromatic Diazo Compounds* 3rd ed.; Edward Larkin: London, 1985; Chap. 10. (h) Galli, G. *Chem. Rev.* **1988**, *88*, 765-792.
3. Wassmundt, F. W.; Kiesman, W. F. *J. Org. Chem.* **1995**, *60*, 1713-1719.
4. Park, K. H.; Cho, Y. H. *Synth. Commun.* **1996**, *26*, 1569-1574.
5. Meerwein, H.; Allendörfer, H.; Beekman, P.; Kunert, F.; Morschel, H.; Pawellek, F.; Wunderlich, K. *Angew. Chem.* **1958**, *70*, 211-215.
6. Rutherford, K. G.; Redmond, W. A. *J. Org. Chem.* **1963**, *28*, 568-570.
7. Tröndlin, F.; Rüchardt, C. *Chem. Ber.* **1977**, *110*, 2494-2505.
8. (a) Zerweck, W.; Schubert, M.; Fleischhauer, R. German Patent 901,175 (7 Jan. 1954). (b) Lahoti, R. J.; Parameswaran, V.; Wagle, D. R. *Indian J. Chem.* **1981**, *20B*, 767-769.
9. Doyle, M. P.; Dellaria, Jr., J. F.; Siegfried, B.; Bishop, S. W. *J. Org. Chem.* **1977**, *42*, 3494-3498.
10. (a) Zollinger, H. *Acc. Chem. Res.* **1973**, *6*, 335-341. (b) Zollinger, H. *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 141-150. (c) Szele, I.; Zollinger, H. *Helv. Chim. Acta* **1978**, *61*, 1721-1729. (d) Broxton, T. J.; Bunnett, J. F. *Nouv. J. Chim.* **1979**, *3*, 133-138.
11. (a) Gloor, B.; Kaul, B. L.; Zollinger, H. *Helv. Chim. Acta* **1972**, *55*, 1596-1610. (b) Hirose, Y.; Wahl, Jr., G. H.; Zollinger, H. *Helv. Chim. Acta* **1976**, *59*, 1427-1437.
12. Kamigata, N.; Kobayashi, M.; Minato, H. *Bull. Chem. Soc. Japan* **1972**, *45*, 2047-2050.
13. (a) Kaul, B. L.; Zollinger, H. *Helv. Chim. Acta* **1968**, *51*, 2132-2134. (b) Kobayashi, M.; Minato, H.; Yamada, E.; Kobori, N. *Bull. Chem. Soc. Japan* **1970**, *43*, 215-219. (c) Ishida, K.; Kobori, N.; Kobayashi, M.; Minato, H. *Bull. Chem. Soc. Japan* **1970**, *43*, 285-286. (d) Kamagita, N.; Hisada, R.; Minato, H.; Kobayashi, M. *Bull. Chem. Soc. Japan* **1973**, *46*, 1016-1018.
14. (a) DeTar, D. F.; Kosuge, T. *J. Am. Chem. Soc.* **1958**, *80*, 6072-6077. (b) Bunnett, J. F.; Yijima, C. *J. Org. Chem.* **1977**, *42*, 639-643. (c) Broxton, T. J.; Bunnett, J. F.; Paik, C. H. *J. Org. Chem.* **1977**, *42*, 643-649.
15. Eustathopoulos, H.; Court, J.; Lambeaux, C.; Bonnier, J.-M. *Nouv. J. Chim.* **1985**, *9*, 737-742.
16. (a) Nakazumi, H.; Szele, I.; Yoshida, K., Zollinger, H. *Helv. Chim. Acta* **1983**, *66*, 1721-1736. (b) Nakazumi, H.; Kitao, T.; Zollinger, H. *J. Org. Chem.* **1987**, *52*, 2825-2830. (c) See also Fukunishi, K.; Hira, J.; Yamanaka, H.; Nomura, M.; Kojo, S. *J. Chem. Soc., Perkin Trans. 1* **1985**, 991-995.
17. (a) Abramovitch, R. A.; Saha, J. G. *Tetrahedron* **1965**, *21*, 3297-3303. (b) Burri, P.; Loewenschuss, H.; Zollinger, H.; Zwolinski, G. K. *Helv. Chim. Acta* **1974**, *57*, 395-402. (c) Loewenschuss, H.; Wahl, Jr., G. H.; Zollinger, H. *Helv. Chim. Acta* **1976**, *59*, 1438-1448.

18. Laali, K. K.; Gao, H. *Helv. Chim. Acta* **1991**, *74*, 304-308.

19. (a) Berger, S.; Hauff, S.; Niederer, P.; Rieker, A. *Tetrahedron Lett.* **1972**, 2581-2584. (b) Bargon, J.; Seifert, K.-G. *Tetrahedron Lett.* **1974**, 2265-2268.

20. (a) Bunnett, J. F.; Wamser, C. C. *J. Am. Chem. Soc.* **1966**, *88*, 5534-5537. (b) Boyle, Jr., W. J.; Bunnett, J. F. *J. Am. Chem. Soc.* **1974**, *96*, 1418-1422.

21. Bunnett, J. F. personal communication.

22. (a) Bunnett, J. F.; Takayama, H. *J. Am. Chem. Soc.* **1968**, *90*, 5173-5178. (b) Bloch, M.; Musso, H.; Záhorszky, U.-I. *Angew. Chem. Int. Ed. Engl.* **1969**, *8*, 370. (c) König, E.; Musso, H.; Záhorszky, U.-I. *Angew. Chem. Int. Ed. Engl.* **1972**, *11*, 45-46. (d) Yasui, S.; Nakamura, K.; Ohno, A. *J. Org. Chem.* **1984**, *49*, 878-882.

23. Threadgill, M. D.; Gledhill, A. P. *J. Chem. Soc., Perkin Trans. 1* **1986**, 873-876.

24. Schwetlick, K. *Angew. Chem.* **1960**, *72*, 208.

25. (a) Gardini, G. P.; Minisci, F.; Palla, G.; Arnone, A.; Galli, R. *Tetrahedron Lett.* **1971**, 59-62. (b) Rawlinson, D. J.; Humke, B. M. *Tetrahedron Lett.* **1972**, 4395-4398.

26. Hess, W. P.; Durant, J. L., Jr.; Tully, F. P. *J. Phys. Chem.* **1989**, *93*, 6402-6407.

27. Davico, G. E.; Bierbaum, V. M.; DePuy, C. H.; Ellison, G. B.; Squires, R. R. *J. Am. Chem. Soc.* **1995**, *117*, 2590-2599.

28. (a) Doyle, M. P.; Guy, J. K.; Brown, K. C.; Mahapatro, S. N.; VanZyl, C. M.; Pladziewicz, J. R. *J. Am. Chem. Soc.* **1987**, *109*, 1536-1540. (b) Brown, K. C.; Doyle, M. P. *J. Org. Chem.* **1988**, *53*, 3255-3261.

29. (a) Rudd, E. J.; Finkelstein, M.; Ross, S. D. *J. Org. Chem.* **1972**, 37, 1763-1767. (b) Finkelstein, M.; Nyberg, K.; Ross, S. D.; Servin, R. *Acta Chem. Scand.* **1978**, *B32*, 182-186. (c) Ross, S. D.; Finkelstein, M.; Rudd, E. J. *Anodic Oxidation*; Academic Press Inc.: New York, 1975; Chap. 9.

30. (a) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P.M.W.; Johnson, B. G.; Wong, M. W.; Foresman, J. B.; Robb, M. A.; Head-Gordon, M.; Repogle, E. S.; Gomperts; R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J., Defrees, D. J.; Baker, J.; Stewart, J. P.; Pople, J. A. GAUSSIAN 92/DFT, Revision F.4, Gaussian, Inc.: Pittsburgh, 1993.
(b) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P.M.W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Kieth, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Oritz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M.W.; Andres, J. L.; Repogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. GAUSSIAN 94, Revision B.1, Gaussian, Inc.: Pittsburgh, 1995.

31. Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648-5652.

32. Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev.* **1988**, *B37*, 785-789.

33. Durant, J. L. *Chem. Phys. Lett.* **1996**, *256*, 595-602.

34. Curtiss, L. A.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **1993**, *98*, 1293-1298.

35. Barry, J. E.; Finkelstein, M.; Moore, W. M.; Ross, S. D.; Eberson, L. *J. Org. Chem.* **1985**, *50*, 528-531.

36. (a) Starkey, E. B. *Org. Synth.* **1943**, *Coll. Vol. 2*, 225-227. (b) Roe, A. *Org. React.* **1949**, *5*, 193-228.
37. (a) Blakey, W.; Scarborough, H. A. *J. Chem. Soc.* **1927**, 3000-3009. (b) Gull, H. C.; Turner, E. E. *J. Chem. Soc.* **1929**, 491-500.
38. Vernin, G.; Julliard, M.; Siv, C.; Metzger, J. ; Garcia Lopez, M. T. *An. Quim., Ser. C* **1981**, *77*, 75-81.

(*Received* 4 *November* 1996)