The basic skeletons of homoadamantane (IX, Y = $(CH_2)_2$) and of bicyclo[3.3.1]nonane (IX, Y = H, H) are very similar (Table VIII). Distortion from the "perfect" adamantane structure is caused in the former by the ethylene bridge and in the latter by repulsions between the two *endo*-hydrogen atoms (Y = H, H in IX). The distance, *d* in IX, is calculated to be almost identical in the two molecules.[72] If the ground-state structures are very similar, it might be anticipated that the bridgehead bromides IX, X = Br (Y = $(CH_2)_2$ and H,H), would solvolyze at similar rates. Our full analysis (Tables IX and X) predicts that this will not be the case. 1-Bicyclo[3.3.1]nonyl bromide (VII, X = Br) should react quite rapidly, only a little less rapidly than *t*-butyl bromide and 10^2 faster than 1-homoadamantyl bromide (VI, X = Br). This is a consequence of the greater flexibility of the bicyclic molecule in absorbing the angular distortion at the bridgehead position in the ion. We plan to study these cases experimentally.

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[72] This distance has been measured experimentally as 3.06 and 3.02 A by X-ray studies of two related molecules.[73,74]

[73] W. A. C. Brown, J. Martin, and G. A. Sim, *J. Chem. Soc.*, 1844 (1965).

[74] M. Dobler and J. D. Dunitz, *Helv. Chim. Acta*, 47, 695 (1964).

The Electrochemical Formation of Carbonium and Iodonium Ions from Alkyl and Aryl Iodides

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Abstract: The electrochemical oxidation of organic iodides at a platinum electrode has been studied in acetonitrile solution containing lithium perchlorate as supporting electrolyte. It has been discovered that alkyl iodides are oxidized and converted *via* alkyl carbonium ions to N-alkylacetamides. Contrastingly, cations resulting from electrooxidation of aryl iodides do not undergo carbon–iodine bond scission but can attack aromatic molecules forming diaryliodonium ions.

Previous work on the electrooxidation of organic halides has been limited to oxidations of aryl halides. In early work,[1] iodobenzene was found on nonpotentiostatic anodization in aqueous sulfuric acid to form benzoquinone and iodine. In contrast, phenyl iodosoacetate and iodoxybenzene were produced in aqueous acetic acid. In nonaqueous media, anodic half-wave potentials at a rotating platinum electrode have been tabulated for bromobenzene[2] and iodobenzene,[3] and iodobenzene has been converted in a silver fluoride–acetonitrile mixture to iodobenzene difluoride.[4] This paper reports some observations on the products and gross mechanistic features of the electrooxidation of both aryl and alkyl halides.

Results

The oxidations reported here were performed potentiostatically in 0.5 *M* lithium perchlorate–acetonitrile solution at a platinum foil anode. Preliminary studies established that under these conditions the halobenzenes as well as simple alkyl iodides could be conveniently oxidized in the potential range limited by the background oxidation of solvent and/or electrolyte at 2.4 v.[5] Alkyl bromides and chlorides, however, could not be oxidized before background.

Alkyl Iodides. Analysis of the products of methyl iodide oxidation at 1.9 v established the presence of iodine (92% yield), N-methylacetamide (75%), acetamide, and traces of methanol.

The buildup of iodine, N-methylacetamide, and acetamide with time is illustrated by some typical data in Table I. Aliquots were removed at various times from the anolyte and analyzed for the above compounds as well as for methyl iodide. The analytical method for the latter, however, was highly irreproducible and gave only qualitative data. These data were sufficient, however, to demonstrate the lack of correlation of current with methyl iodide concentration since, for example, roughly two-thirds of the methyl iodide was consumed when the current had only decreased from 640 to 500 ma. It can be noted that approximately two electrons per molecule of methyl iodide were consumed when the reaction was terminated. In other runs *n* values as large as 3.5 were determined.

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[1] F. Fichter and P. Lotter, *Helv. Chim. Acta*, **8**, 438 (1925).

[2] C. Parkanyi and R. Zahradnik, *Collection Czech. Chem. Commun.*, **30**, 4287 (1965).

[3] W. C. Neikam, G. R. Dimeler, and M. M. Desmond, *J. Electrochem. Soc.*, 111, 1190 (1964).

[4] H. Schmidt and H. Meinert, *Angew. Chem.*, 72, 109 (1960).

[5] All potentials refer to Ag|0.01 *M* $AgNO_3$ in acetonitrile. The rotating platinum electrode potentials were measured against sce, but were normalized to the Ag|Ag^+ scale by adding −0.30 v.

Table I. Methyl Iodide Oxidation[a]

Q, mfaradays	i, ma	I_2, mmoles	N-Methylacetamide, mmoles	Acetamide, mmole
0	640	0	0	0
2.0	600	0.7	0.9	...
2.9	550	1.2	1.5	...
4.1	550	1.7	1.9	...
7.8	500	3.2	3.0	0
15.0	200	2.5	3.8	0.8

[a] Oxidation of 7.5 mmoles of CH_3I at 1.8 v. Insoluble sodium bicarbonate was included in the anolyte to avoid reactions catalyzed by strong acids. Similar data were obtained in the absence of added base.

Although the other oxidation products proved stable under the experimental conditions, iodine was oxidized at 1.9 v. In separate experiments iodine was found to undergo a four-electron per molecule oxidation at 1.95 v. Although it was consumed during electrolysis, iodine was slowly regenerated in the anolyte after the current was stopped.

Rearrangement, giving rise to a 16–21% yield of *t*-pentylacetamide, occurred in neopentyl iodide oxidations. Iodine, small amounts of several unidentified components of longer vpc retention time, and acetamide were also detected. *t*-Pentyl alcohol, 2-methyl-2-butene (which would be detectable at <15% yield), and N-neopentylacetamide (which would be detectable at <5%) additional products which might have formed were absent. An apparent $n = 4$ was determined coulometrically. A comparison of the above products with those arising from *t*-pentyl iodide oxidation was not possible owing to the rapid solvolysis of *t*-alkyl iodides in acetonitrile–lithium perchlorate solution. It was established, however, that *t*-pentylacetamide was formed in 21% yield from this solvolysis.

In an effort to detect olefin formation, isopropyl iodide was oxidized at 1.95 v. Nitrogen was continuously sparged through the anolyte throughout the run to sweep any product propene into bromine–carbon tetrachloride solution. Dibromopropene was identified after removing the excess bromine with aqueous thiosulfate and the carbon tetrachloride by evaporation.

Representative iodides were also oxidized at the rotating platinum electrode. Well-defined waves were obtained in each case with the only unusual feature (other than the large diffusion current) being a decrease in current at high potentials for *t*-butyl iodide.

Table II. Voltammetry at Rotating Platinum Electrode

Compound	$E_{1/2}$	n
Methyl iodide	2.12	3.5
Neopentyl iodide	2.14	5
Isopropyl iodide	2.04	7.5
t-Butyl iodide[a]	1.87	5

[a] The voltammetric curve was run immediately after addition of the freshly distilled *t*-butyl iodide. The absence of significant decomposition of this labile iodide was indicated by the negligible current passed at potentials corresponding to oxidation of iodide ion.

The n values (number of electrons per molecule) were determined from a comparison of the magnitude of the limiting diffusion current with that from reversible one-electron oxidations.

Cyclic voltammetric studies were carried out at a platinum electrode with both methyl and neopentyl iodide. In each case no metastable intermediates were observed, although the iodide–iodine couple was identified. Sweep rates as high as 336 cps were employed in the neopentyl iodide oxidation; these would have detected a neopentyl iodide cation radical with a lifetime greater than 1 msec.[6]

Aryl Iodides. In contrast to alkyl iodides, aryl iodides do not undergo carbon–iodine bond scission when oxidized, but couple. Thus, the major product of iodobenzene oxidation at 1.65 v is 4-iododiphenyliodonium perchlorate (IIa), isolated in 45% yield and characterized by its infrared, nmr, and ultraviolet spectra. Oxidation of iodobenzene at a rotating platinum microelectrode gave $E_{1/2} = 1.92$, $n = 2$. A cyclic voltammetric study indicated that if a cation radical was formed it must have a lifetime of less than 0.020 sec while the lifetime of the corresponding dication must be less than 0.018 sec, since neither was observed.

The oxidation of iodobenzene at 1.65 v in the presence of 5% (by volume) benzene in acetonitrile changed the major product from IIa to diphenyliodonium perchlorate (IIb). This product obviously results from one molecule of iodobenzene and one of benzene but is a consequence of iodobenzene oxidation since the benzene present was shown not to be oxidized below 1.9 v. Similarly, *p*-iodotoluene oxidized at 1.6 v in the presence of a fourfold excess of benzene led to a 44% yield of *p*-methyldiphenyliodonium perchlorate (IIc).

Although bromobenzene is oxidized at 2.0 v, preliminary efforts to obtain diarylbromonium salts[7] failed. Complex mixtures were obtained which have not been resolved. Hydrolysis of the reaction product from bromobenzene oxidation gave only a trace of *p*-dibromobenzene, an expected decomposition product of *p*-bromodiphenyliodonium perchlorate.[8]

Discussion

Aryl Halides. The major product of iodobenzene oxidation was identified as 4-iododiphenyliodonium perchlorate by its microanalysis, infrared spectrum (characteristic *para* substitution and perchlorate bands), and ultraviolet spectrum, which is characteristic of known diaryliodonium salts.[9a]

The formation of this salt is reasonably explained by the mechanism shown below in which an initially formed iodobenzene cation radical attacks an unreacted molecule of iodobenzene forming the cation radical, I, which decomposes to product by formal loss of a proton and an electron. Although an alternate scheme involving initial two-electron transfer (an EC mechanism) is equally consistent with the available data, the formation of a free iodobenzene dication

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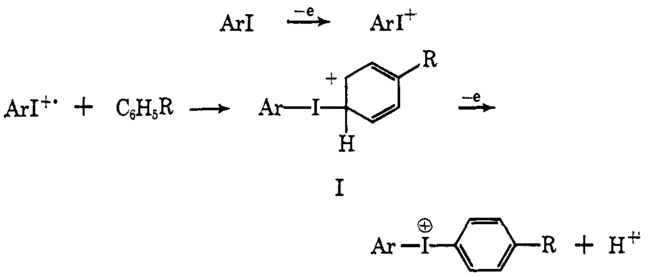
(6) We wish to thank Dr. T. B. Reddy for this cyclic voltammetric study.

(7) Diarylbromonium salts have been reported by: A. N. Nesmeyanov and T. P. Tolstaya, *Dokl. Akad. Nauk SSSR*, **105**, 94 (1955); A. N. Nesmeyanov, T. P. Tolstaya, and L. S. Isaeva, *ibid.*, **104**, 872 (1955); A. N. Nesmeyanov, L. G. Makarova, and T. P. Tolstaya, *Tetrahedron*, **1**, 145 (1957); R. B. Sandin and A. S. Hey, *J. Am. Chem. Soc.*, **74**, 274 (1952).

(8) M. C. Caserio, D. L. Glaser, and J. D. Roberts, *ibid.*, **81**, 336 (1959), have shown that the direction of cleavage of unsymmetrical diaryliodonium salts is not sensitive to the aryl substituent.

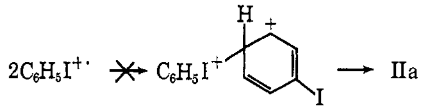
(9) (a) F. M. Beringer and I. Lillien, *ibid.*, **82**, 5135 (1960); (b) F. M. Beringer, M. Drexler, E. M. Gindler, and C. C. Lumpkin, *ibid.*, **75**, 2705 (1953); (c) F. M. Beringer, *et al.*, *ibid.*, **81**, 342 (1959).



IIa, R = I; Ar = C_6H_5
b, R = H; Ar = C_6H_5
c, R = H; Ar = p-$CH_3C_6H_4$

is less attractive than a cation radical on electrostatic grounds. The possibility, however, of a complexed iodobenzene dicationic intermediate (such as the unknown iodobenzene diperchlorate) cannot be ruled out. In agreement with either of these schemes the direct proportionality of the current at 1.6 v to the iodobenzene concentration indicates a rate-determining step that is first order in iodobenzene. Attempts to gain direct evidence for an iodobenzene cation using cyclic voltammetry, however, were unsuccessful and indicated a lifetime of less than 0.02 sec for these species. The possibility exists, however, that these lifetimes are limited by reactions with traces of water (*vide infra*). Since only one-half of the total reaction product has been accounted for and the apparent n will be the weighted average of all electron-transfer reactions occurring at the electrode during the measurement, meaningful interpretation of the n = 1.6 determined coulometrically or n = 2 (rotating platinum electrode) is not possible.

Convincing support for the proposed mechanism (either the ECE or EC) comes from the isolation of diphenyliodonium perchlorate (IIb) as a product of iodobenzene oxidation in the presence of benzene. The trapping of intermediates by benzene, which has been established to be electroinactive in the potential region employed, demonstrates the reactivity of iodoaryl cations toward aromatic molecules and strongly suggests that IIa does not arise by cation radical dimerization.



Although the proposed pathway seems eminently reasonable, the work of Beringer and co-workers[9] suggests an alternative involving the conjugate acid of iodosobenzene, III. This species, potentially available in the present case from reaction of the iodobenzene cations with traces of water

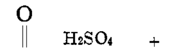
$$\underset{}{ArI + H_2O - 2e \longrightarrow \underset{\text{III}}{Ar\overset{+}{I}OH} + H^+}$$

has been proposed as the reactive intermediate in the condensation reactions of iodosobenzene with aromatics in sulfuric acid.[9b]

$$ArIO + Ar'H \xrightarrow{H_2SO_4} Ar\overset{+}{I}Ar'$$

It does not, however, seem to be involved in the electrochemical formation of iodonium salt. Although iodosobenzene is soluble in acetonitrile acidified with perchloric acid (probably forming III), this mixture does not attack iodobenzene. The reaction of iodobenzene cations with water, in fact, is undoubtedly a competing reaction which does not give iodonium salt product since oxidation of iodobenzene in aqueous (8%) acetonitrile produced no p-iododiphenyliodonium perchlorate. The reaction of iodobenzene cations with water finds parallel in the work of Fichter[1] who found that at a platinum anode in mixed acetic–sulfuric acids or in aqueous acetic acid, iodobenzene was converted to phenyl iodosoacetate in yields as high as 60%.

The unreactivity of III compared to the iodobenzene cation suggests that the latter and not III may be the key intermediate in other diaryliodonium salt syntheses.[10] The reaction cited above between iodosobenzene and aromatics, for example, may involve attack on the aromatic molecule by iodobenzene cation radicals, formed in a reaction related to the conversion of certain aromatic sulfoxides to the corresponding sulfinium salts, IV.[11,12]



$$Ar\overset{\overset{O}{\|}}{S}Ar \xrightarrow{H_2SO_4} \underset{\text{IV}}{Ar\overset{+}{S}Ar\cdot}$$

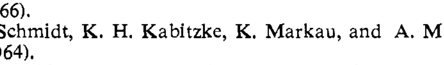
It has been demonstrated[11] that di-p-anisyl sulfoxide, for example, forms a stable sulfinium cation radical (IV, Ar = p-anisyl) in concentrated sulfuric acid. The cation radical can also be formed by chemical oxidation of the corresponding thioether in this medium and will react with anisole to form tri-p-anisylsulfonium ion. The latter reaction can be carried out in inert solvent and is completely analogous to the reaction of iodoaryl cation radicals with aromatics proposed here.

Although the applicability of this coupling reaction has not been fully explored, it should, within the limits of certain obvious oxidation potential and reactivity considerations, have considerable utility for the one-step formation of unsymmetrical diaryliodonium salts. An obvious extension of this reaction is the synthesis of diarylbromonium and -chloronium ions.[7] Although preliminary experiments toward this end have been unsuccessful, further attempts with other aromatic bromides under other conditions are contemplated.

Alkyl Iodides. The oxidation potential of primary, secondary, and tertiary alkyl iodides is also sufficiently low ($E_{1/2}$ = 1.9–2.1 v) to permit oxidation prior to background. Although tertiary iodides solvolyzed much too rapidly in the electrolyte medium to permit controlled potential electrolysis, primary and secondary iodides were found to be stable in this mixture. The formation of N-alkylacetamide in alkyl iodide oxidations is most simply rationalized in terms of the following reactions.

$$RI \xrightarrow{-e} R^+ + 0.5I_2$$

$$R^+ + CH_3CN \longrightarrow \underset{\text{V}}{RN{=}C^+{-}CH_3}$$



$$RN{=}C^+{-}CH_3 + H_2O \longrightarrow \underset{\text{VI}}{CH_3\overset{\overset{O}{\|}}{C}{-}NHR}$$

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(10) For a recent review of such reactions see D. F. Banks, *Chem. Rev.*, **66**, 243 (1966).

(11) U. Schmidt, K. H. Kabitzke, K. Markau, and A. Muller, *Ann*, **672**, 78 (1964).

(12) H. J. Shine and D. R. Thompson, *Tetrahedron Letters*, 1591 (1966), and references cited therien.

Although the fate of the iodine fragment (*vide infra*) is not as simple as this scheme suggests, the intermediacy of alkyl carbonium ions is the most reasonable explanation for N-alkylacetamide formation. Attack on nitriles by carbonium ions has ample analogy in the literature[13] and, indeed, the formation of only rearranged N-*t*-pentylacetamide from oxidation of neopentyl iodide requires a mechanism involving carbonium ions. Although the poor nucleophilicity of acetonitrile and perchlorate ion make the formation of N-neopentylacetonitrilium ion (V, R = neopentyl) or neopentyl perchlorate unlikely, their formation and subsequent rearrangement cannot be eliminated since their stability to the reaction environment was not ascertained. N-Neopentylacetamide was, however, stable to these conditions and absent from the products.

The partitioning of a *t*-pentyl carbonium ion in acetonitrile solution is expected to produce about 80% trimethylethylene and 20% N-*t*-pentylacetamide. This ratio is anticipated on the basis of recent literature reports of silver ion catalyzed alkyl halide solvolyses[14] as well as deaminations in acetonitrile[15] and the 21% yield of *t*-pentylacetamide resulting from solvolysis of *t*-pentyl iodide, which was independently carried out in our electrolyte solution. On this basis the 20% yield of *t*-pentylacetamide indicates almost complete rearrangement of the neopentyl system to the *t*-pentyl carbonium ion. Large yields of the other expected product, trimethylethylene, were not detected. Its absence, however, is not unexpected since this olefin has been found to oxidize at the potential employed. Although the products of this oxidation have not been fully elucidated, significant amounts of *t*-pentylacetamide are not produced. Olefin addition reactions involving iodine monocations (*vide infra*) may provide an additional path for the consumption of trimethylethylene. Such reactions may lead to iodoamides similar to those reported by Hassner and co-workers.[16] Under the vigorous oxidizing conditions employed here, moreover, such organic iodides should be subject to further oxidation.

Even though high yields of iodine were obtained in each alkyl iodide oxidation, it is expected from the work of Popov and Geske[17] on iodide oxidations in acetonitrile at a platinum electrode that iodine atoms and molecules will be oxidized at these potentials. Indeed, it has been confirmed that iodine is oxidized under the macroscale conditions (potentials > 1.9 v) in a many-electron oxidation. At 1.95 v an apparent $n = 4$ was determined for iodine oxidation. For this oxidation, coulometric n values undoubtedly depend on the potential, *i.e.*, the oxidation rate, since iodine was slowly reformed in a nonelectrochemical reaction. It seems likely that in both iodine and alkyl iodide oxidations, as proposed by Popov and Geske for the former,[17] monopositive iodine species are formed which react with solvent acetonitrile. Such a reaction seems to be responsible for the formation of acetamide in alkyl iodide oxidations since this product was also generated by oxidizing molecular iodine under the same conditions. Furthermore, it is clear that the coulometric and rotating platinum n values should be treated as the sum of electron transfers from alkyl iodide, zero-valent iodine, and other products of the initial alkyl iodide oxidation.

Although the detailed mechanism of carbonium ion formation has not been elucidated, it most reasonably arises from a fleeting initially generated iodoalkyl cation radical. In fact, all of the data presented here for both alkyl and aryl iodide oxidations can be rationalized in terms of an initial one-electron transfer from the highest filled molecular orbital of the organic iodide to the electrode. In subsequent steps, iodoalkyl cations undergo scission of the carbon–iodine bond to form carbonium ions and oxidizable iodine while the iodoaryl cations, retaining the carbon–iodine bond intact, behave as strong electrophiles. This change in mechanism undoubtedly reflects the difference in stability of alkyl and aryl carbonium ions and bears a striking resemblance to changes documented for the reactions of aryl- and alkyldiazonium ions.[18] The latter are highly unstable and decompose to alkyl carbonium ions while aryldiazonium salts are relatively stable with respect to carbon–nitrogen bond cleavage and undergo electrophilic coupling reactions with reactive aromatic molecules.

Experimental Section[19]

With the exception of the compounds described below the materials employed were reagent grade or Eastman White Label. Acetonitrile was purified by distillation from potassium permanganate and sodium bicarbonate, neutralization with sulfuric acid, and redistillation under nitrogen.[20] A Karl Fischer titration assayed 0.15% water in the purified solvent. Although Mallinckrodt Nanograde acetonitrile proved useful for aryl iodide oxidations, it, as well as unpurified reagent grade (<0.1% water), acetonitrile was not suitable for alkyl iodide electrolyses. Lithium perchlorate was G. F. Smith Anhydrous Grade dried over phosphorus pentoxide *in vacuo*.

Neopentyl Iodide. Prepared by the method of Landauer and Rydon[21] from triphenyl phosphite, methyl iodide, and neopentyl alcohol, it was pure by vpc and nmr. The nmr spectrum (CCl_4) had singlets at δ 1.09 (9 H) and 3.13 (2 H).

***t*-Pentyl Iodide.** This iodide was prepared from *t*-pentyl alcohol by the method described in "Organic Syntheses"[22] and was treated with mercury and distilled *in vacuo* immediately before use. The infrared spectrum (Nujol) showed bands at 1130 and 790 cm^{-1}.

N-*t*-Pentylacetamide was made from *t*-pentyl alcohol (0.1 mole), H_2SO_4 (0.18 mole), and acetonitrile (0.3 mole), mp 76–79° (lit.[13a] mp 78–79°). Its nmr spectrum (CCl_4) had singlets at δ 1.84 (3 H) and 1.24 (6 H), a pair of multiplets owing to an ethyl group centered at 1.70 and 0.80, and a broad singlet at 7.2.

Neopentylacetamide. Reduction of pivalonitrile (8.3 g, 0.1 mole) with lithium aluminum hydride (3.8 g, 0.1 mole) in 200 ml of anhydrous ether gave neopentylamine, characterized by its nmr spectrum (D_2O, CF_3CO_2H) which had peaks at δ 1.0 (9 H) and 2.65 (2 H). Reaction of neopentylamine with acetic anhydride was

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[13] (a) J. J. Ritter and P. P. Minieri, *J. Am. Chem. Soc.*, 70, 4045 (1948); (b) H. Meerwin, P. Laasch, R. Mersch, and J. Spille, *Ber.*, **89**, 207 (1956); (c) L. Eberson and K. Nyberg, *Acta Chem. Scand.*, 18, 1567 (1964).

[14] Y. Pocker and D. N. Kevill, *J. Am. Chem. Soc.*, 87, 4771 (1965).

[15] Unpublished work of A. T. Jurewicz quoted by A. T. Jurewicz, J. H. Bayless, and L. Friedman, *ibid.*, 87, 5789 (1965).

[16] A. Hassner, L. A. Levy, and R. Gault, *Tetrahedron Letters*, 3119 (1966).

[17] A. I. Popov and D. H. Geske, *J. Am. Chem. Soc.*, 80, 1340 (1958).

[18] H. Zollinger, "Azo and Diazo Chemistry," Interscience Publishers, Inc., New York, N. Y., 1961.

[19] All melting points are corrected. Microanalyses were performed by Mrs. P. Stehman and associates. Infrared spectra were obtained with a Perkin-Elmer Infracord spectrometer. Nmr spectra were obtained by Dr. J. Lancaster and Mrs. M. Neglia with a Varian Model A-60 instrument. Ultraviolet spectra were measured with a Cary Model 15 spectrophotometer. The rotating platinum electrode voltammograms were executed by Mr. W. Jura.

[20] J. F. O'Donnell, J. T. Ayers, and C. K. Mann, *Anal. Chem.*, **37**, 1161 (1965).

[21] S. R. Landauer and H. N. Rydon, *J. Chem. Soc.*, 2224 (1953).

[22] H. Stone and H. Shechter, "Organic Syntheses," Coll. Vol. IV, John Wiley and Sons, New York, N. Y., 1962, p 323.

carried out in water. Separation by ether extraction and recrystallization from heptane gave colorless flakes, mp 66–67°. The nmr spectrum of this compound showed singlets at δ 0.90 (9 H) and 2.05 (3 H), a doublet at 3.05 (2 H), and a broad peak at 7.0 (1 H). The infrared spectrum had the expected bands near 3300, 3100, 1640, and 1550 cm^{-1}.

Anal. Calcd for $C_7H_{15}NO$: C, 65.0; H, 11.6; N, 10.9. Found: C, 65.0; H, 11.7; N, 11.1.

Iodosobenzene. Prepared from iodobenzene by way of iodobenzene dichloride,[23] it titrated for 99% purity.

Potentiostatic Oxidations. All oxidations were performed in 0.5 *M* lithium perchlorate–acetonitrile solutions at a 2-in.^{2}, geometric area platinum foil, spot-welded to platinum wire, sealed through glass electrode. The anode compartment of the three-compartment cell was equipped with a thermometer, gas inlet and outlet, and a magnetic stirring bar. The anolyte (95 ml) and catholyte (30 ml) were separated by a 1-in. diameter "fine" glass frit, the reference and anode compartment by a 1-cm "very fine" frit. The reference electrode was a clean silver wire inserted through a serum cap and submerged in 0.5 *M* $LiClO_4$–0.01 *M* $AgNO_3$ in acetonitrile. Prior to use the anode was cleaned with dichromate cleaning solution, rinsed with water and acetone, and dried.

The anolyte was purged before each electrolysis with prepurified nitrogen for at least 10 min and a background polarization curve was determined out to 2.4 v. Background current was invariably insignificant at potentials less than 2.2 v and generally was about 10 ma at 2.3 v. A known quantity, 5–10 mmoles, of the compound to be oxidized was then syringed into the anolyte, and a partial polarization curve was run out to the potential at which the potentiostatic oxidation was performed. The potential was controlled with a potentiostat designed and built by Electronics and Communications, Inc., Wilton, Conn., used in conjunction with a Model QR 60-6 New Jersey Electronics Corp. power supply. Although the potentiostat controlled the anode potential to ±0.05 v, it was also monitored with an RCA Voltohmyst. Coulometry was performed by integrating the current with an Acromag low-inertia, motor counting device. The range of accurately integrable currents was adjusted by the use of various resistors which were placed in parallel with the motor. Each resistor was calibrated with a Sargeant constant-current, coulometric power supply prior to use.

Alkyl Iodide Stability. Methyl, isopropyl, and freshly distilled *t*-butyl iodide were syringed into 0.5 *M* lithium perchlorate–acetonitrile to prepare ~1 m*M* solutions. Although the ultraviolet spectra of the former two solutions were unchanged after 2 hr, the *t*-butyl iodide spectrum was distorted quite rapidly. New absorption at wavelengths below the original symmetrical peak ($\lambda_{\max}$ 266 mμ) was observed within 5 min. This eventually gave a peak with $\lambda_{\max}$ 246 mμ, as did solutions of tetrabutylammonium iodide in the electrolyte solution.

Oxidation of methyl iodide was performed in 50 ml of anolyte solution at 1.9 v. During the oxidation aliquots were removed from the anolyte with a syringe. These mixtures were analyzed by vpc on a 5-ft Carbowax column at 65°, a 5-ft Qf-1 column at 180°, and a 1-m column of 6% NaOH, 24% Ucon No. 24 at 145°. The iodine concentration was assayed from the visible spectrum at 500 mμ from 0.10-ml samples diluted to 10.0 ml with acetonitrile. In the early samples there was some overlap of another absorption on the short wavelength side (<460 mμ) of the iodine band. Data from a typical experiment are compiled in Table I.

The reaction mixture was worked up by evaporating the acetonitrile, adding chloroform and water, neutralizing the acid with sodium bicarbonate, reducing the iodine with sodium thiosulfate, and then separating the chloroform solution. It was analyzed by vpc and mass spectroscopy and was shown to contain 1 mmole of N-methylacetamide. The aqueous phase was continuously extracted with ether for 3 days. Vpc analysis showed a small amount of acetamide and 3 mmoles of N-methylacetamide. This was confirmed by a quantitative nmr analysis using trioxane as a standard. Coulometric *n* values in macroscale oxidations ranged from 2.5 to 3.7.

Oxidation of Neopentyl Iodide. The oxidation of 0.5 ml (3.8 mmoles) of this iodide was performed at 1.9 v. The iodine concentration, shown by the visible spectrum of aliquots removed during the run, built up during the run to give roughly quantitative conversion. Vpc analysis of the oxidized mixture showed no *t*-pentyl alcohol (<3%), but established the presence of *t*-pentylacetamide. The products were worked up by evaporation of the acetonitrile, addition of water and ether, and reduction of the iodine with sodium thiosulfate. Concentration of the ether extracts gave an oil that was analyzed by vpc on a 5-ft Qf-1 column at 210°. A peak area comparison indicated a 16% yield of N-*t*-pentylacetamide. Acetamide was also present, as were numerous components with longer retention times, but neopentylacetamide was absent (<5%). A similar experiment utilizing chloroform extraction confirmed the above vpc results and further identified the *t*-pentylacetamide (21% yield) by nmr and mass spectral comparisons with authentic material. The stability of N-neopentylacetamide and the instability of trimethylethylene to the reaction conditions was confirmed by adding these materials at the start of a neopentyl iodide oxidation and assaying for them at the end by vpc.

Oxidation of Iodobenzene. The oxidation of 9 mmoles of iodobenzene in 100 ml of anolyte solution was terminated after the consumption of 16 mfaradays at 1.65 v. At this point the current had dropped from 500 to 15 ma. Evaporation of most of the acetonitrile followed by the addition of water and ether extraction of the mixture gave an aqueous solution which deposited a crystallizable oil (940 mg). The same product was found on concentrating the ether extract (130 mg). Recrystallization from aqueous methanol gave pure 4-iododiphenyliodonium perchlorate with an unchanged infrared spectrum, mp 149° dec. The ultraviolet spectrum had $\lambda_{\max}^{\mathrm{H_2O}}$ 257 mμ (ϵ 2.7 × 10^4) and rising absorption below 220 mμ. Infrared bands (Nujol) were located at 680, 740, 990, and 1080 (broad) cm^{-1}.

Anal. Calcd for $C_{12}H_9ClI_2O_4$: C, 28.46; H, 1.78, I, 50.01. Found: C, 28.52; H, 2.00; I, 49.81.

Oxidation of Iodobenzene in the Presence of Benzene. Iodobenzene (9 mmoles) was oxidized as above except that the solvent was 5% benzene in acetonitrile. This solvent mixture did not oxidize below 1.9 v. In this case the reaction was terminated somewhat sooner, and the ether-soluble products (570 mg) obtained after concentrating the acetonitrile solution and adding water consisted primarily of unreacted iodobenzene (450 mg analyzed by vpc and infrared). After brief stirring, 900 mg of colorless crystals, mp 170° dec, precipitated from the aqueous solution. Cooling gave a second crop (200 mg). The infrared spectra (Nujol) of these materials had strong bands at 680, 740, 990 (doublet), and 1070 (broad) cm^{-1}. Recrystallization gave constant melting diphenyliodonium perchlorate, mp 170–171° (lit.[24] 173–174°).

Oxidation of *p*-Iodotoluene in the Presence of Benzene. The oxidation of *p*-iodotoluene (2.0 g, 9 mmoles) at 1.60 v in 5% benzene–acetonitrile was effected as with iodobenzene. The product crystallized similarly (1.75 g, second crop 0.25 g, 45% yield). Careful recrystallization from aqueous methanol (some decomposition occured at high temperatures) gave *p*-methyldiphenyliodonium perchlorate, mp 129–132° (in at 110°), $\lambda_{\max}^{\mathrm{H_2O}}$ 238 mμ (ϵ 1.3 × 10^4), tailing below 220 mμ. The infrared spectrum (Nujol) had maxima at 680, 750 (doublet), 810, 980, and 1080 (broad) cm^{-1}. The nmr spectrum (DMSO-d_6) had peaks at δ 2.33 (3 H), 8.2 (4 H), and 7.45 (5 H).

Anal. Calcd for $C_{13}H_{12}ClIO_4$: C, 39.55; H, 3.04; I, 32.18. Found: C, 39.82; H, 3.17; I, 32.33.

Oxidation of Bromobenzene. At the start of the electrolysis at 2.0 v the current dropped off rather rapidly. If, however, the voltage was reduced for a few minutes the current could be restored. Eventually a constant current level of 90 ma was achieved, and the electrolysis was then carried out for 7 hr. The products were worked up by evaporation of most of the acetonitrile, addition of water, and ether extraction. The ether-soluble material contained five major volatile components by vpc on a 5-ft dinonyl phthalate column at 185°. A peak with retention time equal to that of *p*-dibromobenzene had an area equivalent to a 1% yield. The aqueous mixture, which contained a quantity of black insoluble tar, was refluxed overnight and extracted with ether. The ether-soluble products were analyzed similarly and contained a 0.1% yield of a component with *p*-dibromobenzene retention time.

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(24) E. R. Kline and C. A. Kraus, *J. Am. Chem. Soc.*, **69**, 814 (1947).