J. Org. Chem. **1987**, *52*, 2568–2571

Mechanistic and Kinetic Studies on the Iododediazoniation Reaction

Anil N. Abeywickrema* and Athelstan L. J. Beckwith*

Research School of Chemistry, The Australian National University, Canberra, ACT 2601, Australia

Received October 14, 1986

Treatment of the diazonium salt **1** with sodium iodide in acetone gives a mixture of uncyclized (**4**) and cyclized (**5**) iododediazoniation products, the relative yields of which vary with the amount of added iodine but are independent of iodide concentration. The diazonium salt **6** when similarly treated gives a mixture of the cyclized hydrocarbon **14** and the isomeric vinyl iodides **11** and **13**. The formation of **5**, and of **11** and **13**, involves ring closure of the substituted aryl radicals, **2** and **7**, respectively. The key propagation steps in the iododediazoniation reaction mechanism appear to be reduction of the diazonium ion by single electron transfer from $I_2^{\bullet -}$ and iodine transfer to the aryl radical so formed from I_2 or I_3^-. The iodine transfer step has a rate constant of about 5×10^9 M^{-1} s^{-1} at 20 °C.

The replacement of the diazonium group of arenediazonium salts by a halogen substituent is a well-known and useful procedure for preparing aryl halides. Chloro and bromo dediazoniation reactions are usually carried out under Sandmeyer conditions in which the diazonium compound is treated with the appropriate cupric halide.[1] On the other hand, alkali iodides are usually employed for the iododediazoniation of diazonium salts.[2] No copper halide is required in this case.

Although the synthetic utility of the iododediazoniation reaction has been exploited for a considerable length of time, its mechanism, despite considerable study,[3-9] has not yet been satisfactorily elucidated. It is known that Sandmeyer reactions occur via the reduction of diazonium salts by Cu^I species to give aryl radicals that subsequently abstract halogen from Cu^{II} halides.[1] A number of workers have proposed that iododediazoniation reactions also proceed by a radical mechanism.[4-9] In an early account, Hodgson[4] suggested that *p*-nitrobenzenediazonium salts react with iodide ions by the mechanism shown in Scheme I. Although this mechanism acknowledged the generation of aryl radicals, the formation of the product iodide was said to occur by an ionic reaction between ArN_2^+ and I_3^-. Carey et al.,[3] who found that a number of diazonium triiodides decomposed to give the corresponding aryl iodides upon warming, proposed a completely ionic mechanism for the process. More recently Kumar and Singh[7] studied the reaction between diazonium salts and sodium iodide in methanol solution and reported that iododediazoniation was accompanied by the formation of arenes, biaryls, and iodine and was inhibited by oxygen. They proposed a radical-chain mechanism to account for their observations (Scheme II). The intermediacy of aryl radicals in iododediazoniation reactions has since been supported by other work in this laboratory[8] and by Packer[9] and his co-workers. As pointed out by both Waters[5] and Galli,[6] the redox potential of the I_2/I^- couple is similar to that of the Cu^{II}/Cu^I couple. Hence, by analogy with the Cu^I-initiated Sandmeyer reactions, it is reasonable to expect iododediazoniations to be initiated by electron transfer from I^- to ArN_2^+. A key step in the Kumar and Singh mechanism[7] is the formation of the radical anion $R{-}I^{\bullet -}$ by the attack of an iodide ion on an aryl radical. However, as has been pointed out elsewhere,[6,9] the plausibility of this step remains questionable. For example, it is known that aryl radicals do not react with iodide ions,[10] except possibly when strongly electron withdrawing substituents are present.[11] Furthermore, attempted preparation of iodoarene radical anions by electroreduction[11] or pulse radiolysis[12] of aryl iodides leads immediately to aryl radicals and iodide ions. Such a fragmentation is indeed an intermediate step in the $S_{RN}1$ reaction of aryl iodides.[10a] The dubious nature of this important step in the Kumar and Singh mechanism raises the question of which iodine species does react with aryl radicals. Galli[6] has suggested that I_2 or $I^\bullet$ may be alternatives to I^-. On the other hand, as proposed by Packer,[9] it is possible that I_3^- (which is

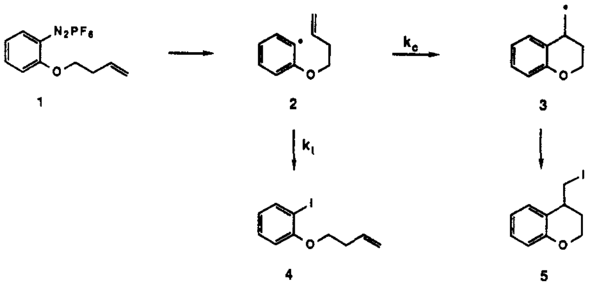
Scheme I

$$ArN_2^+ + I^- \rightarrow Ar^\bullet + N_2 + I^\bullet$$
$$2I^\bullet \rightarrow I_2$$
$$I_2 + I^- \rightarrow I_3^-$$
$$ArN_2^+ + I_3^- \rightarrow ArI \bullet N_2 + I_2$$

Scheme II

$$ArN_2^+ + I^- \rightarrow Ar^\bullet + N_2 + I^\bullet$$
$$Ar^\bullet + I^- \rightarrow ArI^{\bullet -}$$
$$ArI^{\bullet -} + ArN_2^+ \rightarrow ArI + Ar^\bullet + N_2$$

Scheme III



---

[1] Kochi, J. K. *Organometallic Mechanism and Catalysis*; Academic Press: New York, 1978; Chapter 9.

[2] Lucas, H. J.; Kennedy, E. R. *Organic Syntheses*; Wiley: New York, 1948; Collect. Vol. II, p 351.

[3] Carey, J. G.; Jones, G.; Millar, I. T. *Chem. Ind.* (*London*) **1959**, 1018. Carey, J. G.; Millar, I. T. *Chem. Ind.* (*London*) **1960**, 97.

[4] Hodgson, H. H.; Birtwell, S.; Walker, J. *J. Chem. Soc.* **1941**, 770.

[5] Waters, W. A. *J. Chem. Soc.* **1942**, 266.

[6] Galli, C. *J. Chem. Soc., Perkin Trans. 2* **1981**, 1459.

[7] Kumar, R.; Singh, P. R. *Tetrahedron Lett.* **1972**, 613. Singh, P. R.; Kumar, R. *Aust. J. Chem.* **1972**, *25*, 2133.

[8] Beckwith, A. L. J.; Meijs, G. F. *J. Chem. Soc., Chem. Commun.* **1981**, 136. Beckwith, A. L. J.; Meijs, G. F. *J. Org. Chem.*, in press.

[9] Packer, J. E.; Russell Taylor, R. E. *Aust. J. Chem.* **1985**, *38*, 991.

[10] (a) Rossi, R. A.; de Rossi, R. H. *Aromatic Substitution by the $S_{RN}1$ Mechanism*; ACS Monograph 178; American Chemical Society: Washington, D.C., 1983. (b) For a discussion of the factors that determine the reactivity of various nucleophiles with aryl radicals, see ref 10a, Chapter 6.

[11] Lawless, J. G.; Hawley, M. D. *J. Electroanal. Chem.* **1969**, *21*, 365.

[12] Steelhammer, J. C.; Wentworth, W. E. *J. Chem. Phys.* **1969**, *51*, 1802.

Table I. Effect of Various Iodine Species on Iododediazoniation Products[a]

run	$[ArN_2^+]$,[b] M	$[Na^+I^-]$,[b] M	$[I_2]$,[b] M	$[C_2H_5OCS_2K]$,[b] M	yield,[c] %		[4]/[5][c]
					4	5	
1	0.05	0.05			4	80	0.05
2	0.05	0.10			5	84	0.06
3	0.05	0.05	0.025		29	50	0.58
4	0.05	0.05	0.05		32	31	1.03
5	0.05		0.05	0.05	16	35	0.46
6	0.05	0.05		0.05	d	4	

[a] All reaction carried out in acetone solvent at 20 °C. [b] Initial concentrations calculated by assuming no reaction prior to complete mixing of solutions. [c] As determined by GC. [d] Trace only.

Table II. Variation of Product Ratio with I^- and I_2[a]

$[ArN_2^+]$,[b] M	$[I_2]$,[b] M	$[I^-]$,[b] M	[4]/[5][c]
0.01	0.1	0.025	1.82
0.01	0.1	0.05	1.72
0.01	0.1	0.1	1.85
0.01	0.1	0.2	1.76

[a] All reactions carried out in acetone solution at 20 °C. [b] Initial concentrations calculated by assuming no reaction prior to complete mixing of solutions. [c] As determined by GC.

always present in mixtures of I_2 and I^-)[13] may also be involved. To shed further light on these questions, we decided to study the dediazoniation of *o*-(but-3-enyloxy)benzenediazonium salts (1, Scheme III) in the presence of several possible iodine species. It was expected that the intermediate *o*-(but-3-enyloxy)phenyl radical (2), the rate of ring-closure of which has been recently determined,[14] would act as a mechanistic and kinetic probe for the reaction leading to the new C–I bond.

Preliminary studies showed that the treatment of 1 with sodium iodide in acetone solution gave a mixture of compounds 4 and 5 in good yield. The formation of the cyclized iodide 5 via the diagnostic ring-closure[14] $2 \rightarrow 3$ confirmed the involvement of aryl radical intermediates. Significant amounts of the corresponding reduction products, (but-3-enyloxy)benzene and 4-methyl-3,4-dihydro-2*H*-1-benzopyran were not observed, indicating that a carbanionic pathway was not important. Furthermore, since radical anions of the type $R{-}I^{\bullet -}$ are even more likely to fragment when R is alkyl rather than aryl,[15] the formation of the cyclized iodide 5 in good yield provides further evidence against a mechanism involving such radical anions. Careful observation of the reaction mixture, particularly at low temperature (<0 °C), showed that when I^- was added to a solution of the diazonium salt a deep red rapidly appeared. This was immediately discharged and was accompanied by the evolution of gaseous nitrogen.

In order to investigate the relative importance of the reactions of various iodine species with aryl radicals, we carried out a series of experiments in which the unimolecular ring-closure of aryl radical 2 was allowed to compete with possible bimolecular reactions leading to the aryl iodide 4 (Table I). When interpreting the results in the various tables, one must bear in mind that the dediazoniation reaction commences instantaneously upon mixing of the diazonium salt with iodide ions. Hence the listed concentrations (which are calculated on the assumption that no reactions occur prior to complete mixing) are only approximate values.

Nevertheless, it can be seen from runs 1 and 2 that there is virtually no increase in the [4]/[5] ratio although the concentration of I^- is doubled. Hence it appears that the iodide ion is not directly involved in the reaction step leading to the C–I bond. On the other hand, in reactions where added iodine is present (runs 3 and 4), there is a very large increase in the amount of the uncyclized iodide (4) at the expense of the cyclized iodide (5). Furthermore, the [4]/[5] ratio is approximately proportional to the concentration of the added iodine. We conclude that the formation of the C–I bond occurs by the attack of aryl radicals on I_2 (or I_3^- which is present) and not I^- as proposed by Kumar and Singh.[7] Such an iodine atom transfer is analogous to the abstraction of halogen ligands from Cu^{II} halides in the Sandmeyer reaction.[1] To investigate further the role played by I^- in the dediazoniation process, we treated (run 5) a solution of the diazonium salt 1 and iodine (which show no noticeable reaction with each other) with a solution of potassium ethyl xanthate which is a known reagent for reducing diazonium salts to aryl radicals.[16] The results in Table I show that the products 4 and 5 were indeed formed in this case as well, although in lower yield. This suggests that in normal iododediazoniation reactions, I^- merely acts as an electron donor for the reduction of diazonium salts to aryl radicals. The diminished [4]/[5] ratio in run 5 compared to run 4 may be due to the lowering of $[I_2]$ by reduction of I_2 itself to I^- by the xanthate.

The importance of I_2 was further illustrated by run 6 in which a solution of the diazonium salt was treated with a solution of iodide ions and potassium ethyl xanthate. In this case only trace amounts of iodocarbons were found, accompanied by other unidentified products. Since the xanthate reduces any I_2 formed in the reaction back to I^-, the very low steady-state concentration of iodine must be inadequate for effective iododediazoniation to occur. In the present context it must be borne in mind that the equilibrium constant for the reaction between I_2 and I^- in acetone solution is very large.[13] Hence, in the presence of excess I^-, any I_2 that is formed in the reaction will be converted to I_3^-. Therefore, in normal iododediazoniation reactions where there is no added I_2, it is possible that I_3^- could well be the kinetically significant species.[9]

To investigate this possibility, we carried out a number of dediazoniation reactions in which the amount of initially added iodine was kept constant while the amount of iodide was gradually increased (Table II). Thus, for runs 1–3 the equilibrium concentration of I_2 decreases while that of I_3^- increases such that the total concentration $[I_2 + I_3^-]$ is effectively constant. The results in Table II show that the ratio [4]/[5] is essentially invariant for the series of reactions. This suggests that the aryl radicals react with both I_2 and I_3^- at almost identical rates. In the case of aryl radical 2, the unimolecular ring-closure must compete with the bimolecular reactions with I_2 and I_3^-. Application of the usual steady-state approximation shows that when I_2/I_3^- are in large excess, $k_I/k_c = [4]/[I_2 + I_3^-][5]$ where

---

[13] Nelson, I. V.; Iwamoto, R. T. *J. Electroanal. Chem.* **1964**, *7*, 218.

[14] Abeywickrema, A. N.; Beckwith, A. L. J. *J. Chem. Soc., Chem. Commun.* **1986**, 464.

[15] Wentworth, W. E.; Becker, R. S.; Tung, R. *J. Phys. Chem.* **1967**, *71*, 1652.

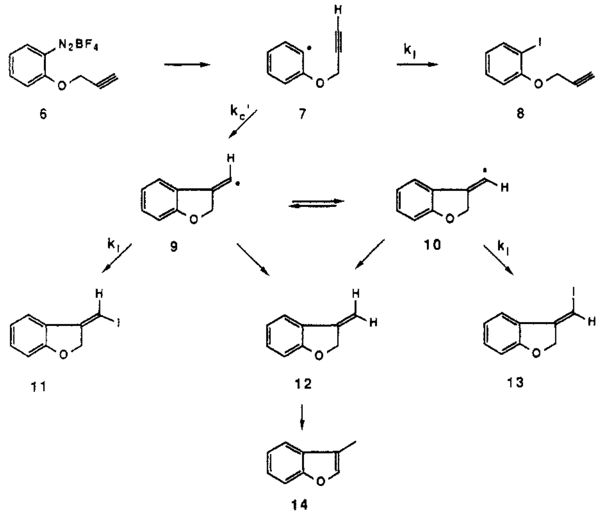
[16] Meijs, G. F.; Beckwith, A. L. J. *J. Am. Chem. Soc.* **1986**, *108*, 5890.

Table III. Effect of Reactant Concentration on the Iododediazoniation of 6[a]

run	$[ArN_2^+]$,[b] M	$[Na^+I^-]$,[b] M	$[I_2]$,[b] M	yield,[c] % 11	13	12	14	[11 + 13]/ [12 + 14]
1	0.1	0.1		34	31	6		10.8
2	0.025	0.025		40	31	13	1	5.1
3	0.01	0.01		38	28	8	9	3.9
4	0.025	0.1		42	41	10	1	7.5
5	0.025	0.025	0.005	33	29	2		31.0

[a] All reactions carried out in acetone solvent at 20 °C. [b] Initial concentrations calculated by assuming no reaction prior to complete mixing of solutions. [c] As determined by GC.

Scheme IV



Scheme V

$$ArN_2^+ + I^- \rightarrow Ar\cdot + N_2 + I\cdot$$
$$ArN_2^+ + I_2^{\cdot-} \rightarrow Ar\cdot + N_2 + I_2$$
$$Ar\cdot + I_2 \rightarrow ArI + I\cdot$$
$$Ar\cdot + I_3^- \rightarrow ArI + I_2^{\cdot-}$$
$$I\cdot + I^- \rightarrow I_2^{\cdot-}$$
$$I\cdot + I\cdot \rightarrow I_2$$
$$I_2 + I^- \rightarrow I_3^-$$

K_c is the rate constant for ring-closure and k_I the rate constant for reaction between aryl radicals and I_2/I_3^-. Thus, from the results in Table II the relative rate constant can be evaluated as $k_I/k_c \sim 18$ M at 20 °C. Substitution of the known[14,17] value of k_c gives the absolute rate constant k_I as 5×10^9 M^{-1} s^{-1} at 20 °C. Since the very rapid rate of reaction upon mixing of the reagents probably causes a depletion of the local concentration of I_2/I_3^-, the estimated rate constant must be considered a lower limit. Thus, it can be concluded that aryl radicals react with I_2 and I_3^- essentially at diffusion-controlled rates.[17]

In view of the extremely rapid rate of attack by aryl radicals on I_2/I_3^-, we decided to investigate the use of this reaction as a means of estimating rate constants of unimolecular rearrangements that are too rapid to be calibrated by means of the more conventional atom donor reagents such as the organotin hydrides. We chose *o*-(prop-2-ynyloxy)benzenediazonium tetrafluoroborate (**6**, Scheme IV), as the substrate since preliminary experiments[8] had indicated that one isomer (**11**) of the cyclized product was formed in preference to the other (**12**). A simple rationalization of this observation was that the ring closure of **7** gives initially only one isomer (**9**) of the vinyl radical product (Scheme IV) and that this can be trapped by I_2/I_3^- before it undergoes inversion to give an equilibrium mixture of **9** and **10**. If this were the case, one would be able to obtain an estimate of the rate constant for inversion of vinyl radicals on the assumption that such radicals react with I_2/I_3^- at the same rate as aryl radicals. Also, it was thought possible that the bimolecular reaction between I_2/I_3^- and the initially formed *o*-(prop-2-ynyloxy)phenyl radical (**7**) would compete effectively with the rapid unimolecular ring-closure **7** → **9**, enabling the rate constant (k_c') for the latter process to be estimated.

In the event, the iododediazoniation of **6** in acetone solution in the absence of added iodine gave two cyclized iodides **11** and **13** with the former isomer in slight excess but changes in the iodine concentration did not appear to have a systematic effect on the **11**/**13** ratio. There are three possible explanations for this observation: (i) ring closure of **7** does not initially afford exclusively the isomer **9** but rather gives directly a mixture of **9** and **10**; (ii) the trapping of vinyl radicals is too slow to compete with the rapid inversion process;[19] or (iii) the observed **11**/**13** ratio results from the reversible addition of iodine to the exocyclic olefinic bonds. Further work is required to distinguish between these possibilities.

As expected, an increase in the concentration of iodine resulted in the formation of significant amounts of the uncyclized iodide **8**. For example at 20 °C when $[I_2 + I_3^-] = 0.2$ M (10-fold excess), the product ratio [**8**]/[**11** + **13**] was found to be 0.23. Using the steady-state expression $k_c'/k_I = [I_2 + I_3^-][11 + 13]/[8]$ and the value of k_I previously evaluated, it was possible to estimate that $k_c' \sim 4 \times 10^9$ s^{-1} at 20 °C. Interestingly, this rate constant is of the same order of magnitude as that previously determined for the cyclization of the *o*-(prop-2-enyloxy)phenyl radical, another extremely rapid reaction.[14]

An interesting corollary to this work is the effect of dilution on product distribution (Table III). It is seen that a decrease in the overall concentration of the reactants leads to a significant increase in the reduction products **12** and **14** at the expense of the usual iodinated compounds **11** and **13** (runs 1–3). Thus it appears that at high dilution, the trapping of highly reactive vinyl radicals by the acetone solvent competes effectively with their reaction with the iodinating species. It is seen that an increase in the concentration of I^- alone has only a small effect on the reduced/iodinated product ratio (cf. runs 2 and 4). On the other hand, the addition of iodine to the reaction mixture (run 5) restores the balance strongly in favor of iodinated products. These observations are in complete agreement with our previous conclusions that I_2 or I_3^- and not I^- acts

---

[17] Dr K. U. Ingold in a private communication has indicated that the value of k_H, the rate constant for the reaction of aryl radicals with Bu_3SnH, and upon which the value of k_c rests, may be in error. However, an independent determination of k_c by a new radical trapping technique[18] has shown that the rate constants derived in the present work are approximately correct.

[18] Beckwith, A. L. J.; Bowry, V. W., unpublished observations.

[19] Fessenden, R. W.; Schuller, R. H. *J. Chem. Phys.* **1963**, *39*, 2147.

as the iodinating species in dediazoniation reactions.

In principle it should be possible to calculate the rate constant, k_H, for hydrogen atom abstraction from acetone by **9** or **10** on the assumption that the rate constant for the competing iodine coupling reaction is the same as that, k_I, for aryl radicals. In practice the large difference between the magnitudes of k_H and k_I made the outcome subject to very large errors. Our results suggest that k_H at 20 °C is probably in the range 10^4–10^5 M^{-1} s^{-1}.

In view of the findings discussed above, it is now possible to define an alternative radical-chain mechanism that is completely consistent with both present and previous experimental observations (Scheme V).

The salient features of the above mechanism are (i) initiation occurs by single electron transfer from iodide ion to the diazonium ion; (ii) the aryl iodine bond is formed by iodine transfer to aryl radical from I_2 and/or I_3^- at diffusion controlled rates; and (iii) $I_2^{\bullet -}$, a key chain transfer reagent, is formed by coupling of $I^\bullet$ with I^- and/or iodine atom transfer from I_3^-.

Experimental Section

General. Analytical grade acetone was distilled from anhydrous potassium carbonate and stored over 4-Å molecular seives under a nitrogen atmosphere. Sodium iodide was oven dried at 110 °C and stored in a vacuum dessicator. Resublimed iodine (May & Baker) was used without further purification. Potassium ethyl xanthate was prepared by a standard procedure[20] and stored under a nitrogen atmosphere. The preparation of *o*-(but-3-enyloxy)benzenediazonium hexafluorophosphate (**1**) has been described elsewhere.[21] *o*-(But-3-enyloxy)iodobenzene (**4**), 4-(iodomethyl)-3,4-dihydro-2*H*-1-benzopyran (**5**), *o*-(prop-2-ynyloxy)benzenediazonium tetrafluoroborate (**6**), *o*-(prop-2-ynyloxy)iodobenzene (**8**), (*E*/*Z*)-3-(iodomethylene)-2,3-dihydrobenzofuran (**11** and **13**), 3-methylene-2,3-dihydrobenzofuran (**12**), and 3-methylbenzofuran (**14**) were either available from previous studies[8] or were prepared according to procedures previously described.[8]

Gas chromatographic analyses were performed on Varian 3400 and 6000 chromatographs equipped with flame ionization detectors and coupled to Hewlett-Packard 3390A recorder/integrators; 6-ft glass columns packed with either 3% SE-30 on 100/120 mesh Chromosorb W or 2% OV-17 on 60–80-mesh Gaschrom Q, or a 25-m vitreous silica capilliary column (BP1, purchased from SGE Australia), were employed with helium as the carrier gas. GC/MS analyses were carried out on a Varian 1440 gas chromatograph coupled to a VG Micromass 7070F mass spectrometer. Thermostated baths accurate to ±0.3 °C were used for temperature control.

Mechanistic Studies. For runs 1–4, Table I, solutions of the diazonium salt (0.1 mmol) in acetone (250 μL) were added to rapidly stirred solutions of NaI/I_2 (in the required amounts) in acetone (1.75 mL) with the aid of a microsyringe, the needle-tip of which was held below the surface of the liquid. A darkening of the color and the evolution of gas was usually observed almost instantaneously on mixing of the two solutions. After further stirring under a nitrogen atmosphere for 10–15 min at 20 °C, the solvent was quickly evaporated under vacuum, and a measured amount of hydrocarbon standard was added. The mixture was extracted with ether, washed with 5% sodium thiosulfate solution, dried (Na_2SO_4), and analyzed by GC. For run 5, Table I, a solution of potassium ethyl xanthate (0.1 mmol) in acetone (1.0 mL) was added to a solution of the diazonium salt 1 (0.1 mmol) and iodine (0.1 mmol) in acetone (1.0 mL), while for run 6 a solution of sodium iodide (0.1 mmol) and potassium ethyl xanthate (0.1 mmol) in acetone (1.0 mL) was added to a solution of **1** (0.1 mmol) in acetone (1.0 mL).

The results in Table II were obtained by adding 0.1 M solutions (100 μL) of the diazonium salt **1** to solutions (900 μL) of I_2/I^- to achieve the desired concentrations. For each of the runs 1–3, Table III, a solution of the diazonium salt **6** (0.1 mmol) in acetone (250 μL) was added to a solutions of NaI (0.1 mmol) in acetone (0.75, 3.75, and 9.75 mL, respectively), while for run 4 it was added to NaI (0.4 mmol) in acetone (3.75 mL) and for run 5 to a mixture of NaI (0.1 mmol) and I_2 (0.02 mmol) in acetone (3.75 mL). Workup and product analyses were carried out as described above.

---

[20] Vogel, A. I. *Textbook of Practical Organic Chemistry*, 4th ed.; Longmans: London, 1978; p 588.

[21] Abeywickrema, A. N.; Beckwith, A. L. J. *J. Am. Chem. Soc.* **1986**, *108*, 8227.

Di-, Tri-, Tetra-, and Pentacationic Alkylammonium Salts. Ligands Designed To Prevent the Nonspecific Electrostatic Precipitation of Polyanionic, Functionalized Cyclopentadienyltitanium-Substituted Heteropolytungstate Electron Microscopy Labels with Cationic Biomolecules

John F. W. Keana,* Yexin Wu, and Guanli Wu[1]

Department of Chemistry, University of Oregon, Eugene, Oregon 97403

Received November 24, 1986

This work relates to the use of organic functionalized heteropolytungstates (HPTs) as protein-specific electron microscopy labels. The objective is the development of a polycationic ligand that prevents the nonspecific precipitation reaction observed between certain polycationic biomolecules and polyanionic heteropolytungstates. Simple tetra- and pentaammonium salts between Keggin HPT **1b** or Dawson HPT **2b** and amines **3–6** or quaternary ammonium compounds **8** and **9** were all of low aqueous solubility as were salts derived from the oxygenated partners **7**, **11**, **12**, and **15–18**. However, tetrakis quaternary salt **23a**, which is made up of several highly oxygenated alkyl groups, effectively prevents precipitation between Dawson HPT **2b** and the exemplary basic proteins lysozyme and poly-L-lysine as well as the lectin concanavalin A.

Keggin-type and Dawson-type heteropolytungstate (HPT) ions[2] are of interest as possible soluble models for industrially important metal oxide supported catalysts[3] and as small, highly electron dense labels for the study of

0022-3263/87/1952-2571$01.50/0 © 1987 American Chemical Society