D. Radiochemical Experiments. 1. Electrolysis of C_6H_5HgCl–phenylmercuric chloride, radiolabeled with Hg^{203}, was exhaustively electrolyzed (25 ml. of a 2×10^{-3} M solution) to yield quantitatively diphenylmercury, as evidenced by ultraviolet absorption spectra and polarography. As a control, a similar solution was stirred, without electrolysis for a similar time period. The supernatant liquids in both experiments as well as an original sample of the labeled C_6H_5HgCl solution were counted by standard liquid scintillation techniques by Dr. Byron Branson of Taft Sanitary Engineering Center, U. S. Public Health Service. Counting efficiency (geometry) was 16.9%. Chart I indicates counts/min. summed over the seven channels encompassing the photopeak due to Hg^{203}. The figures represent the averages of two to four experiments.

2. Cleavage of $C_6H_5HgC_2H_5$ with $Hg^{203}Cl_2$ to 0.05 mole of C_6H_5-HgC_2H_5 in 25 ml. of glyme, which was 0.1 M in $(C_4H_9)_4NClO_4$, was initiated under a nitrogen blanket. The solution was permitted to rest for 30 min., sufficient for complete disproportionation to occur. The solution then was electrolyzed under controlled potential conditions such that only the C_6H_5HgCl now present was reduced to the subvalent form. After the passage of 4.9 coulombs, polarographic study indicated that approximately 90% of the C_6H_5HgCl had been discharged, and that the diffusion current of the C_2H_5HgCl was that to be expected from the concentration the *in vitro* synthesis should have yielded. Control experiments involving the electrolysis of $C_6H_5Hg^{203}Cl$ alone, and in admixture with C_2H_5HgCl indicated that the electrolysis of C_6H_5HgCl is not interfered with by the presence of other organomercury species. Chart I indicates the results averaged from two to four runs. Counting procedures are described above.

Organometallic Electrochemistry. III. Organometallic Anions Derived from Group V Elements

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Abstract: The electrochemical behavior of organic derivatives of group V elements, with particular reference to compounds of the type Ph_2MX, has been studied. The phosphorus compounds give transient radicals which abstract hydrogen from solvent to give Ph_2PH and $PhPH_2$. The arsenic, antimony, and bismuth derivatives lead to Ph_2MMPh_2 presumably *via* radical coupling. Further reduction of the coupled product, Ph_2MMPh_2, gave rise to novel organometallic anions, $Ph_2M:^-$. Some reactions of these anions are reported. The cyclic voltammetric behavior of the diphenylarsenic system is discussed.

R eports on the polarographic reduction of group V organometallics have involved either studies in aqueous solution[1,2] or investigations of phosphonium salts.[3-6] Wagenknecht also explored the electrolytic reduction of triaryl derivatives of group V elements in dimethylformamide.[6] He concluded, after identification of the products of the large-scale electrolytic reduction of triphenylphosphine, that the anion radical formed initially decomposed to phenyl radical and diphenylphosphide anion.

$$Ph_3P + e \longrightarrow Ph_3P^{\bar{\cdot}} \longrightarrow Ph\cdot + Ph_2P^- \qquad (1)$$

From determinations of i_d, the diffusion current constant, and the slope of the polarographic wave it was thought that eq. 1 involved a reversible one-electron reduction. In contrast, i_d values indicated a two-electron reduction for the triaryl derivatives of arsenic, antimony, and bismuth.

(1) V. F. Toropova and M. K. Saikina, *Chem. Abstr.*, **48**, 12579 (1954).
(2) M. K. Saikina, *ibid.*, **51**, 7191 (1957).
(3) E. L. Colichman, *Anal. Chem.*, **26**, 1204 (1954).
(4) M. Shinagawa, H. Matsuo, and N. Malei, *Japan Analyst*, **5**, 20 (1956).
(5) L. Horner and A. Mentrup, *Ann.*, **646**, 65 (1961).
(6) J. H. Wagenknecht, Ph.D. Dissertation, Feb. 1964, State University of Iowa.

$$Ph_3M + 2e \longrightarrow Ph_2M^- + Ph^- \qquad (2)$$
$$(M = As, Sb, or Bi)$$
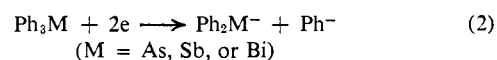
The present study was undertaken to investigate the possible preparation and properties of subvalent organometallics (by electrolytic reduction) derived from systems of the type

$$R_2MX + e \longrightarrow R_2M\cdot + X^- \qquad (3)$$
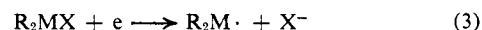
(R = organic radical; X = halide or acetate; M = P, As, Sb, or Bi)

Electrolytic reductions were achieved at a stirred mercury cathode in anhydrous glyme, using tetrabutylammonium perchlorate as supporting electrolyte. Controlled potential coulometry, polarography, ultraviolet spectroscopy, and cyclic voltammetry were employed to elucidate the fate and nature of the subvalent species $R_2M\cdot$. Five possible pathways were available to the $R_2M\cdot$ species in this system: (a) stability, (b) coupling to give R_2MMR_2, (c) abstraction of hydrogen from solvent to give R_2MH, (d) arylation of the mercury pool, and (e) disproportionation.

Examples of coupling and abstraction were observed. When coupling occurred, a further reduction of R_2-MMR_2 to novel organometallic anions took place.

Table I. Half-Wave Potentials of Various Group V Phenyl Derivatives

	P	As	Sb	Bi
		$-E_{1/2}$, v.[a]		
Ph$_3$M	3.5	3.4	3.3	3.1
Ph$_3$MX$_2$	...	0.9,[b] 3.4 (Br)	1.4, 3.3 (Br) / 2.0, 3.3 (Cl)	~1.1,[b] 3.1 (Br)
Ph$_2$MX	3.3 (Cl)	0.9,[b] 2.7 (Br) / 1.0,[b] 2.7 (I) / 1.0,[b] 2.7 (ClO$_4$)	1.0, 2.5 (I) / 1.4, 2.5 (OAc) / 0.9, 2.5 (ClO$_4$)	1.0, 2.3 (Cl)
Ph$_2$MMPh$_2$	...	2.7	2.5	2.3
PhMX$_2$	2.5 (Cl)	0.9,[b] ... (Cl)	...	...
Ph$_4$MX	3.1 (Cl)	3.0 (Cl)	...	3.1 (ClO$_4$)
Ph$_2$MOMPh$_2$	...	2.7	2.5	...

[a] 10^{-3} M Ag|AgClO$_4$ reference. [b] Show polarographic maxima, even at 0.5×10^{-4} M, which cannot be suppressed by methylene blue (gelatin is insoluble in monoglyme).

The cyclic voltammetry and some reactions of these anions were investigated.

Experimental Section

The apparatus and techniques which were involved in the use of the polarographic apparatus, controlled potential coulometry, and cyclic voltammetry have been described previously.[7] Purification of solvent and supporting electrolyte has also been described. Ultraviolet spectra were recorded by performing the electrolysis in the cavity of the spectrometer, using the cell previously described,[7] but with a 1-cm. cell attached to the cathode compartment by means of a standard, ground-glass joint.

Triphenylphosphorus, -arsenic, -antimony, and -bismuth and triphenylphosphorus oxide were purchased from M and T Chemicals Inc., and recrystallized before use.

Tetraphenylphosphonium chloride, tetraphenylarsonium chloride, diphenylphosphorus chloride, and phenylphosphorus dichloride were obtained from K & K Laboratories Inc., and used without further purification.

The following compounds were prepared according to standard procedures available in the literature: biphenylarsenic iodide,[8] tetraphenyldiarsine,[9] triphenylantimony dichloride,[10] trimethylantimony dichloride and dimethylantimony chloride,[11] bis(diphenylantimony) oxide,[12] diphenylantimony acetate,[12] diphenylantimony iodide,[12] tetraphenyldistibine,[12] diphenylbismuth chloride.[13]

Tetraphenyldiarsine and -distibine were prepared under an atmosphere of argon in a Schlenck tube and transferred directly, under argon, to the polarographic cell containing deaerated glyme.

Solutions of diphenylarsenic and diphenylantimony perchlorates were obtained by adding equimolar amounts of silver perchlorate to a glyme solution of the appropriate halide. Precipitated silver halide was removed by filtration.

Results and Discussion

The polarographic half-wave potentials of all the compounds studied are reported in Table I. In most cases well-defined, irreversible, diffusion-controlled polarographic waves were observed. For convenience, the results for each group V element will be discussed in turn.

Phosphorus. Diphenylphosphine was obtained in quantitative yield, as determined by ultraviolet spectroscopy, from the controlled potential coulometric electrolysis of diphenylphosphorus chloride at −3.4 v. The reduction involved one electron, and diphenylphosphine most probably resulted from abstraction of hydrogen from solvent by diphenylphosphorus

radical (cf. Ph$_3$SiCl).[7] Cyclic voltammetry at a sheared

$$Ph_2PCl + e \longrightarrow Ph_2P\cdot + Cl^- \quad (4)$$
$$\downarrow solvent$$
$$Ph_2PH$$

mercury electrode using sweep rates of 100 v./sec. showed no evidence of reversible charge transfer, indicating that the preabstraction lifetime of diphenylphosphorus radical in this system is less than 10 msec.

Phenylphosphorus dichloride was reduced in a two-electron step to give phenylphosphine by a similar pathway. Once again, no evidence for reversible charge

$$PhPCl_2 + 2e \longrightarrow PhP: + 2Cl^- \quad (5)$$
$$\downarrow solvent$$
$$PhPH_2$$
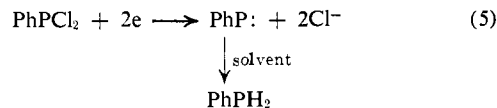
transfer was furnished by cyclic voltammetry studies.

Arsenic. Electrolytic reduction of diphenylarsenic bromide provided a novel source of diphenylarsenic anion[14] with which the tetrabutylammonium counter-ion precluded any covalent interaction. Two one-electron reductions were involved.

$$Ph_2AsBr + e \longrightarrow 0.5Ph_2AsAsPh_2 + Br^- \quad (6)$$
$$0.5Ph_2AsAsPh_2 + e \longrightarrow Ph_2As^- \quad (7)$$
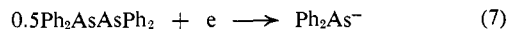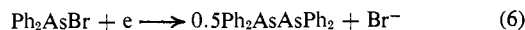
The identity of tetraphenyldiarsine as an intermediate was established by comparison of the polarographic half-wave potential of the solution after first-wave electrolysis of diphenylarsenic bromide with that of a solution of an authentic sample of tetraphenyldiarsine. Additional evidence for the sameness of such solutions was gained from cyclic voltammetric studies (see below). The formation of tetraphenyldiarsine, if it arises from coupling of diphenylarsenic radicals (cf. Ph$_3$-SnSnPh$_3$ formation from electrolysis of Ph$_3$SnCl),[7] indicates the greater stability of diphenylarsenic radical in this system compared to diphenylphosphorus radical.

Addition of an equimolar solution of diphenylarsenic bromide to the yellow solution of diphenylarsenic anion gives a colorless solution of tetraphenyldiarsine, identified by its polarographic half-wave potential and ultraviolet spectrum. This process may involve nu-

$$Ph_2AsBr + Ph_2As^- \longrightarrow Ph_2AsAsPh_2 + Br^- \quad (8)$$

cleophilic attack by, or electron transfer from, diphenylarsenic anion.

(7) Part I of this series: R. E. Dessy, W. Kitching, and T. Chivers, *J. Am. Chem. Soc.*, **88**, 453 (1966).

(8) W. J. Pope and E. E. Turner, *J. Chem. Soc.*, 1447 (1920).

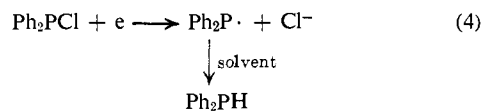(9) F. F. Blicke and F. D. Smith, *J. Am. Chem. Soc.*, **51**, 2272 (1929).

(10) G. E. Coates, "Organometallic Compounds," Methuen and Co., Ltd., London, 1960, p. 219.

(11) G. T. Morgan and G. R. Davies, *Proc. Royal Soc.* (London), 110, 523 (1926).

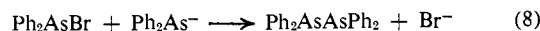(12) F. F. Blicke and V. O. Oakdale, *J. Am. Chem. Soc.*, **53**, 1025 (1931).

(13) See ref. 10, p. 231.

(14) Ph$_2$AsLi has been obtained as a dark red solution by cleavage of triphenylarsenic with lithium metal in tetrahydrofuran: D. Wittenberg and H. Gilman, *J. Org. Chem.*, 23, 1063 (1958).

In order to elucidate the mechanism of this process and related reactions of electrochemically generated organometallic anions in this environment, commutation experiments involving (a) Ph_2As^- and Ph_3SnCl and (b) Ph_3Sn^- and Ph_2AsBr were conducted.

The commutation experiments a and b do not result in the same product. Using the *same* cell geometry and reference electrode, $Ph_3SnSnPh_3$ has $E_{1/2} = -2.86$, $Ph_2AsAsPh_2$, $E_{1/2} = -2.65$. An equimolar mixture exhibits what appears to be a single wave at -2.72. Commutation experiment a yields a solution, $E_{1/2} = -2.74$, which shows augmentation of i_d upon addition of $Ph_3SnSnPh_3$, just as a mixture of the ditin and arsine does. Commutation experiment b yields a solution, $E_{1/2} = -2.80$. This solution shows no sensitivity of i_d to added $Ph_3SnSnPh_3$ in large amounts. Ultraviolet spectral data indicated that (b) yields a product having a λ_{max} at 300 mμ. Synthesis of $Ph_2AsSnPh_3$ *via* the method of Fowles, *et al.*,[15] yields a solution having an absorption at 300 mμ, which is eliminated by oxygen bubbling; the As–Sn compounds are quite susceptible to oxidation. $Ph_3SnSnPh_3$ and/or $Ph_2AsAsPh_2$ do not absorb in this region.

From these data it appears that experiment a yields predominantly a mixture of $Ph_3SnSnPh_3$ and $Ph_2AsAsPh_2$, while (b) yields predominantly $Ph_3SnAsPh_2$. Isolation of the latter was impossible in preparative runs because of its physical characteristics and the supporting electrolyte required for this potential, tetrabutylammonium perchlorate. Although the identity of products from (a) has not been definitively established, the consequences are apparent—the two approaches which appear equally sound, do not, in mathematical language, commute.

Addition of an equimolar solution of silver perchlorate to a yellow solution of diphenylarsenic anion (generated from diphenylarsenic perchlorate to avoid presence of halide ions) gave a clear, golden brown solution, indicating the formation of (diphenylarsenic)silver. No silver ion remained in solution after reaction. Electrochemical degradation of the solution, which regenerated yellow diphenylarsenic anion and deposited metallic silver, provided further evidence for the identity of the product as (diphenylarsenic)silver.

Cyclic voltammetry on solutions of Ph_2AsBr, Ph_2As^-, $Ph_2As^+ClO_4^-$, and $Ph_2AsAsPh_2$ led to the assignments shown in Figure 1. These assignments were based on the following observations.

(1) A was only present in the oscillopolarogram of $Ph_2As^+ClO_4^-$, and must involve the step $Ph_2As^+ \rightarrow Ph_2As\cdot$.

(2) B was present in the oscillopolarograms of all the species studied and involves reduction of $Ph_2As\cdot$ or $Ph_2AsAsPh_2$ to Ph_2As^-.

(3) With cathodic holds, step A was not observed in the oscillopolarogram of a solution of Ph_2As^-. This can be explained by rapid reaction of Ph_2As^+ produced at D with Ph_2As^- in bulk of solution to give $Ph_2AsAsPh_2$.

(4) Conversely, with anodic holds, steps C and D were not observed in the oscillopolarogram of Ph_2As^+-ClO_4^- solutions. Rapid reaction of Ph_2As^- produced

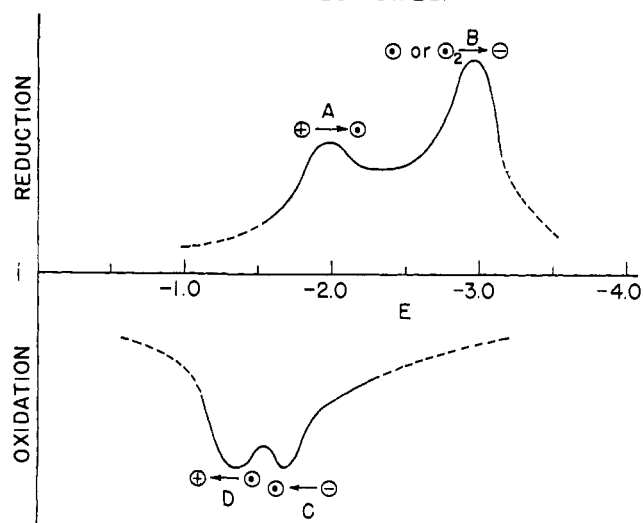(15) I. G. M. Cambell, G. W. A. Fowles, and L. A. Nixon, *J. Chem. Soc.*, 3026 (1964).

Figure 1.

at B with Ph_2As^+ in the bulk solution to give $Ph_2AsAsPh_2$ is consistent with this observation.

(5) That processes A and D, and B and C are "linked"[7] was shown by appropriate alterations of cathodic and anodic sweep limits.

It is interesting to compare the electrode behavior of Ph_2As with that previously discussed for Ph_3Sn. In the Ph_3Sn case, a wave corresponding to the reduction $\cdot \rightarrow -$ is observed, which only appears after reoxidation of Ph_3Sn^-, and which is easily distinguishable from the wave corresponding to the reduction $Ph_3Sn\cdot SnPh_3 \rightarrow Ph_3Sn^-$. In the Ph_2As case, only one wave corresponding to the production of Ph_2As^- is observed, and this may be due to the reduction of either $Ph_2As\cdot$ or $Ph_2As\cdot AsPh_2$. Hence it may be concluded, that either coupling of diphenylarsenic radicals occurs very rapidly and thus the reduction of $Ph_2As\cdot \rightarrow Ph_2As^-$ is not observed, or that the reductions of $Ph_2As\cdot \rightarrow Ph_2As^-$ and $Ph_2As\cdot AsPh_2 \rightarrow Ph_2As^-$ are indistinguishable oscillopolarographically.

A blue solution of $(\sigma\text{-naphthyl})_2As^-$ was obtained from the electrolytic reduction of di(σ-naphthyl)arsenic chloride in two one-electron steps. This species, which was readily oxidized on exposure to air giving a green solution, showed an additional polarographic wave which probably involves transfer of an electron into a π^* orbital of the naphthalene ring system. The $-E_{1/2}$ values for the steps are 1.1, 2.7, and 2.9. It has been well established that naphthalene undergoes more facile reduction at a dropping mercury electrode[16] and by alkali metals[10] than benzene as a result of the lower energy of the available antibonding orbitals. Presumably the same considerations will be pertinent in a comparison of the ease of reduction of naphthyl and phenyl derivatives of arsenic.

Bis(diphenylarsenic) oxide undergoes a two-electron reduction ($E_{1/2} = -2.8$ v.) to give a yellow solution. The reductive process may be represented as

$$Ph_2AsOAsPh_2 + 2e \longrightarrow Ph_2As^- + Ph_2AsO^- \qquad (9)$$
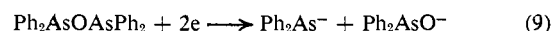
(16) A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1962, p. 178.

since addition of two equivalent amounts of diphenylarsenic bromide causes the color of the solution to disappear and regenerates the polarographic wave at -2.7 v. with wave height now double its original value. Since the polarographic waves of tetraphenylarsine ($E_{1/2} = -2.7$ v.) and diphenylarsenic oxide ($E_{1/2} = -2.7$ v.) are in very close proximity, a solution containing a mixture of these two compounds would show only one polarographic wave whose height would be proportional to the total concentration of electroactive species. Hence, these observations are consistent with the formulation

$$Ph_2As^- + Ph_2AsO^- + 2Ph_2AsBr \longrightarrow Ph_2AsAsPh_2 +$$
$$Ph_2AsOAsPh_2 \quad (10)$$
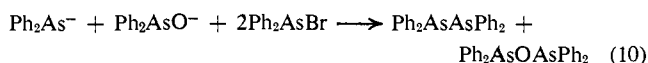
The reduction of $PhAsCl_2$ involves a two-electron step. The product is currently being studied.

Antimony. The electrolytic reduction of compounds of the type Ph_2SbX (X = halogen or acetate) in our system was of especial interest in view of the report by Gilman and Woods[17] of the formation of a transitory green color in the reaction between diphenylantimony iodide and sodium in liquid ammonia. It was thought that this coloration might be due to the formation of diphenylantimony radical. However, we find that electrolysis of diphenylantimony acetate at -1.9 v. gives a colorless solution of tetraphenyldistibine, presumably as a result of rapid coupling of diphenylantimony radicals.

$$Ph_2SbOAc + e \longrightarrow OAc^- + Ph_2Sb\cdot \xrightarrow{\text{fast}} Ph_2SbSbPh_2 \quad (11)$$
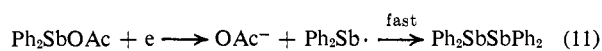
Tetraphenyldistibine undergoes a further reduction at -2.45 v. which involves the uptake of two electrons per mole to give an orange solution of diphenylantimony anion.

$$Ph_2SbSbPh_2 + 2e \longrightarrow 2Ph_2Sb^- \quad (12)$$
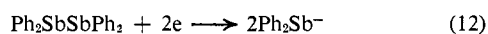
This solution is stable for several hours at room temperature under an atmosphere of argon. Addition of diphenylantimony acetate to the orange solution immediately dissipates the color to give tetraphenyldistibine. Diphenylantimony iodide also gives an orange

$$Ph_2Sb^- + Ph_2SbOAc \longrightarrow Ph_2SbSbPh_2 \quad (13)$$
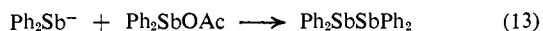
solution of diphenylantimony anion by a similar route. Confirmatory evidence for the proposed pathway for the electrolytic reduction of diphenyl antimony acetate was obtained by performing the operations in the ultraviolet cell. Identical spectra were obtained at stages (11) and (13).

(17) H. Gilman and L. A. Woods, *Chem. Abstr.*, **39**, 693 (1945).

The pentacovalent species, triphenylantimony dichloride and trimethylantimony chloride, both show one-step, two-electron reductions which involve loss of chlorine as chloride ion and production of a triorganoantimony compound.

$$R_3SbCl_2 + 2e \longrightarrow R_3Sb + 2Cl^- \quad (14)$$
$$(R = Me, Ph)$$
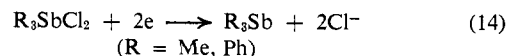
Identical results are found for Ph_3AsBr_2 and Ph_3BiBr_2.

Bismuth. No compounds containing Bi–Bi bonds have been well characterized.[18] When only 1 g.-atom of sodium is added to diphenylbismuth iodide in liquid ammonia, a deep green color results, which changes to red when a second g.-atom is added. It has been suggested that the green color is probably due to the formation of the diphenylbismuth radical,[19] although Coates[20] has indicated the possibility that it is tetraphenyldibismuth. When diphenylbismuth chloride is electrolyzed at -1.2 v., one electron is involved in the reduction and a pale yellow solution results. By analogy with compounds of arsenic and antimony, we take this to indicate the formation of tetraphenyldibismuth by rapid coupling of diphenylbismuth radicals. No arylation of the mercury pool was observed, and in this respect diphenylbismuth radical differs from triphenyllead radical, which rapidly arylates the mercury cathode to give diphenylmercury.[7] As with antimony,

$$Ph_2BiCl + e \longrightarrow Ph_2Bi\cdot + Cl^- \longrightarrow Ph_2BiBiPh_2 \quad (15)$$
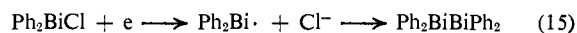
further reduction of tetraphenyldibismuth involves two electrons per mole and gives rise to a green solution. However, unlike antimony, the diphenylbismuth anion is unstable and deposits bismuth metal.

With a simple pathway to these anions available, their chemistry is being explored in detail.

(18) $Me_2Bi\cdot BiMe_2$ has almost certainly been prepared by the reaction between methyl radicals and a heated bismuth mirror, but not enough was obtained for analysis: F. A. Paneth and M. Loleit, *J. Chem. Soc.*, 366 (1935).

(19) H. Gilman and M. L. Yablunky, *J. Am. Chem. Soc.*, **63**, 212 (1941).

(20) See ref. 10, p. 232.