Oxidations involving silver. II. The oxidation of alcohols and aldehydes with silver(II) picolinate

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The oxidation of alcohols by argentic picolinate has been studied and has been shown to give high yields of aldehyde and ketone. Examination of the oxidation of aldehydes shows that smooth conversion to the acid occurs in most cases, but in some cases, an anomalous reaction occurs, which probably involves attack upon the aromatic ring of substituted benzaldehydes. The oxidation of aldehydes occurs much more slowly than alcohol-oxidation under similar conditions.

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In connection with the use of solid silver anodes (1) for the oxidation of organic compounds, we examined the effect of some complexing agents upon the course of oxidations at these electrodes. Since oxidation may proceed by formation of some species which diffuse into the mass of the electrolyte (2) before reacting, it was important to know the behavior of these species. One such species in our studies was silver(II) picolinate.

The argentic oxides produced at a silver anode, or in persulfate oxidations of silver salts, are stoichiometrically AgO. Study shows them to be in fact lattice compounds of Ag(I) and Ag(III), (3). In contrast, complexing agents such as picolinic acid permit the isolation of definite Ag(II) compounds (4), thus offering the possibility of studying the oxidizing activity of the Ag(II) state[2] uncomplicated by Ag(III); likewise derivatives of Ag(III) may be obtained and studied (5)[3].

One measure of the relative oxidizing power of these compounds is their relative oxidation potential. We measured the electrode potentials of the systems H^+ $pic^-/Ag(I)\ pic_{(s)}/Ag$ and H^+ $pic^-/Ag(II)pic_{2(s)}/Ag$ at 25 °C and pH 5, and found them to be respectively 0.694 and 0.720 V. The corresponding (extrapolated) electrode potentials for the $Ag/Ag_2O/OH^-$ and $Ag/AgO/OH^-$ systems are 0.60 and 0.86 V respectively. Although these figures represent free energy changes for reversible equilibria, and most organic oxidations are not reversible processes in this sense, the figures indicate the approximate oxidizing power of the reagents. We have found one immediate difference between the oxide and picolinate, namely that, while the latter usually (but not always) undergoes the equivalent of a one-electron change giving silver(I) picolinate as product, under similar (neutral) conditions AgO usually undergoes a two-electron change, metallic silver being the main inorganic product in most of the cases we have examined. Differences in selectivity of action and products formed might be expected from this, but, while differences have been noted, they are surprisingly few. Thus, for example, both reagents convert benzylic alcohols to aldehydes (some acid also is obtained using AgO), toluene and *p*-cymene to benzaldehyde and *p*-cumaldehyde respectively, and 2-ethylhexanol to 2-ethylhexanal. With each reagent, alcohols are oxidized more slowly than amines, which oxidize more slowly than phosphines and phosphites. (The oxidation of triphenylphosphite by AgO at room temperature, for instance, is almost explosive.)

Our experiments show, in those cases we have examined, that product-wise there is a close parallel with oxidations at the electrode, under similar conditions[4].

We here discuss the oxidizing action of silver(II) picolinate in isolation from the electrode system. The action of AgO will be discussed separately[4].

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[2] Details of the preparation and reactivity of some new Ag(II) complexes will be presented shortly in Part VI (in preparation).

[3] The oxidation of organic compounds by these reagents proceeds in many ways more parallel to the action of Cu(III) derivatives; J. B. Lee, unpublished results.

[4] For a preliminary survey of the oxidizing actions of Ag(II) picolinate and AgO see ref. 18 and Parts III and IV of this series, which are in preparation.

Oxidation of alcohols proceeds rapidly in neutral conditions at moderate temperatures. The overall reaction may be written

$$2\mathrm{Ag(pic)_2} + \mathrm{R_2CHOH} \rightarrow 2\mathrm{Ag(pic)} + \mathrm{R_2C{=}O} + 2\ \text{pic-H}$$

(pic = picolinate)

While the rate of reaction is influenced by the nature of the solvent, (use of dimethyl sulfoxide (DMSO), for example, generally leads to more rapid reaction) we find that reaction proceeds quite satisfactorily in water, despite the heterogeneous nature of the system, and isolation of products is simplified. Volatile products may be swept out in a nitrogen stream; less volatile products are isolated by extraction with a suitable solvent. Reaction is rapid in the 30–70 °C range.

Secondary alcohols are converted in high yield into ketones. More interestingly, high yields of aldehydes are obtained from primary alcohols with negligible over-oxidation to acids. Table I lists some products and yields obtained. No attempt has been made to maximize these yields. The identity of the products has been confirmed in each case by physical properties, chromatographic comparison, formation of derivatives, and/or examination of infrared (i.r.) and proton magnetic resonance (p.m.r.) spectra, as appropriate.

TABLE I

Reaction of alcohols with silver(II) picolinate

Alcohol	Product	% Yield*
CH_3	Formaldehyde	80
Ethyl	Acetaldehyde	77
n-Propyl	Propionaldehyde	71
iso-Propyl	Acetone	80
n-Butyl	Butyraldehyde	76
iso-Butyl	iso-Butyraldehyde	57
sec-Butyl	Ethylmethyl ketone	68
n-Amyl	*n*-Valeraldehyde	74
iso-Amyl	iso-Valeraldehyde	61
n-Hexyl	*n*-Hexaldehyde	69
2-Ethylhexyl	2-Ethylhexaldehyde	55
n-Heptyl	*n*-Heptaldehyde	54
n-Decyl	*n*-Decaldehyde	68
DL-Phenylethyl	Acetophenone	73
2-Phenylethyl	Phenylacetaldehyde	61
Bornyl	Camphor	66
Cyclohexyl	Cyclohexanone	70
Benzyl	Benzaldehyde	80
p-Nitrobenzyl	*p*-Nitrobenzaldehyde	83
Anisyl	Anisaldehyde	87
Veratryl	Veratraldehyde	83
Piperonyl	Piperonaldehyde	77
Tetrahydrofurfuryl	Tetrahydrofurfuraldehyde	62
2-Ethoxyethyl	2-Ethoxyacetaldehyde	53

*No attempt was made to maximize yields.

These results indicate the wide applicability of the reagent. Many methods are available for the preparation of aldehydes from primary alcohols, but nearly all suffer from limitations in one or other respect, giving low yields, involving severe conditions, or product-isolation difficulties. Recently Syper (6) has described the use of AgO as an oxidant but the conditions he employed (hot concentrated acids) are rather severe. In our experience AgO is a useful oxidant in neutral or mildly alkaline conditions[4].

Chromic acid oxidations (7) may give good yields, but involve acid conditions, and formation of esters etc. often reduces yields, unless the aldehyde can be removed quickly from the mixture (8). *t*-Butyl chromate and chromium trioxide in pyridine are more successful (9), but may occasionally prove hazardous. Manganese dioxide[5] has been often applied for benzylic and allylic alcohols (10) and may in certain cases oxidize saturated systems if a large excess of oxidant is used (11). The strongly basic conditions of the Oppenauer oxidation are conducive to condensation and polymerization of the aldehyde (12). A variety of other reagents including selenium dioxide (13), nickel peroxide (14, 16), nitrogen tetroxide (15), lead(IV), thallium(III), and mercury(II) complexes (16), and *N*-halo-compounds (17), etc. have been used for these conversions, but often usefully only with benzylic alcohols.

The influence of structure on rate of oxidation is illustrated in Tables II–V. Table II lists the approximate rates of oxidation of some aliphatic alcohols under comparable conditions relative to ethanol, as standard. It can be seen that the rate decreases with increasing chain length for primary and secondary alcohols; primary alcohols are oxidized more rapidly than secondary alcohols. Applications of these differences to selective oxidation of single hydroxyl groups in polyhydroxy compounds and sugars will form the subject of a later publication. Benzyl alcohol is oxidized somewhat more readily than ethanol,

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[5] We (J.B.L. and T.G.C.) have used a method for the preparation of highly active MnO_2, sufficiently active to inflame alcohols on contact in some cases, but even in this case a large excess of reagent is required, and losses occur unless excess oxidant is carefully destroyed with SO_2.

TABLE II

Approximate relative oxidation rates of aliphatic alcohols with silver(II) picolinate

Alcohol	Rate*
Ethanol	100
Propanol-1	83
Propanol-2	71
Butanol-1	45
2-Methyl-propanol-1	43
Butanol-2	32
Pentanol-1	42
3-Methyl-butanol-1	38
Benzyl alcohol	125

*Relative to ethanol as 100.

TABLE III

Approximate relative oxidation rates of benzyl alcohols

Alcohol	Rate*
3,4-(Methylenedioxy)benzyl	950
3,4-Dimethoxybenzyl	1330
p-Nitrobenzyl	43
p-Methoxy benzyl	266
Benzyl	100

*Relative to benzyl alcohol as 100.

TABLE IV

Approximate relative oxidation rates of some β-alkoxy alcohols

Alcohol	Rate*
Ethanol	100
2-Ethoxyethanol	80
2-Butoxyethanol	71
2-Acetoxyethanol	31
Tetrahydropyran-2-carbinol	59
Tetrahydrofuran-2-carbinol	76

*Relative to ethanol as 100.

and Table III illustrates the effect of various substituents upon the rate of oxidation of benzylic alcohols relative to benzyl alcohol itself. It is clear that the reaction is facilitated by electron-releasing groups, retarded by electron-attracting substituents. It is interesting to note that the effect of a β-oxygen function is to markedly increase the rate of oxidation over that which one might expect for a molecule of similar steric size. Table IV lists the approximate oxidation rates of some β-alkoxy alcohols, and one β-acyloxy alcohol, compared with ethanol as standard, and it may be seen that 2-ethoxyethanol, for example, is oxidized considerably more quickly than *n*-amyl alcohol which is approximately equivalent sterically. The influence of substituents in cyclohexanols, on the oxidation rate relative to the rate of oxidation of cyclohexanol itself, is shown in Table V. Since these materials were mixtures of *cis* and *trans* isomers, little more can be concluded beyond noting the obvious reduction in rate with steric crowding of the hydroxyl group.

Although the reagent converts primary alcohols into aldehydes in good yield, the oxidation of aldehydes to acids also proceeds smoothly in most cases. Aliphatic, aromatic, and heterocyclic aldehydes are oxidized rapidly in neutral aqueous solution at 50 °C. Aliphatic aldehydes (e.g. 2-ethylbutanal and 2-ethylhexanal) are oxidized more quickly than for example furfural, which again oxidizes more quickly than benzaldehyde. The rate of oxidation of aromatic aldehydes is increased by electron-releasing substituents, and decreased by electron-attracting substituents, as can be seen by reference to Table VI, which indicates the approximate rates relative to furfuraldehyde (taken as 100).

TABLE V

Approximate relative oxidation rates of some cyclohexanols

Alcohol	Rate*
Cyclohexanol	100
4-Methylcyclohexanol	35
3,5-Dimethylcyclohexanol	33
2,5-Dimethylcyclohexanol	31
2,2-Dimethylbutanol-3†	10

*Relative to cyclohexanol as 100.
†Included for comparison.

TABLE VI

Approximate relative oxidation rates of some aldehydes

Aldehyde	Rate*
Piperonaldehyde	2000
2-Ethylbutyraldehyde	855
2-Ethylhexaldehyde	375
Veratraldehyde	363
Anisaldehyde	125
(Furfuraldehyde	100
p-Tolualdehyde	75
Benzaldehyde	42
Benzyl alcohol†	910
p-Nitrobenzyl alcohol†	384

*Relative to furfuraldehyde as 100.
†Included for comparison.

The yields of acid obtained were often less satisfactory (*p*-nitrobenzoic acid, for example was isolated in only 31% yield), and in two cases highly anomalous reactions occurred. Thus with piperonal and veratraldehyde very rapid reduction of the silver(II) picolinate occurred, but in neither case could any trace of the corresponding acids be found. Furthermore, the aldehydes were largely (approx. 80%) recovered unchanged. Although no definite product has been isolated, it would appear that the oxidant is consumed, in these two cases, in attack upon the aromatic ring, with cleavage occurring rapidly to the exclusion of the expected mode of action, and with consumption of several moles of oxidant per mole of aldehyde.

Silver in the Ag(I) state is well known to complex with olefines and aromatic rings, and the oxidation of benzene to benzoquinone by AgO (6) may involve a similar (unstable) coordination compound. Our results with a number of other systems are in agreement with the possible formation of (unstable) Ag(II) olefine- and aryl-complexes. In contrast, the successful oxidation of piperonyl alcohol and veratryl alcohol to the corresponding aldehydes without complication must depend upon the more powerful coordination of the alcoholic oxygen to the silver in these two cases. Since the other aromatic aldehydes examined react more normally, we consider that the electron-releasing effect of the substituent groups is sufficient to favor aryl–silver rather than oxygen–silver coordination for piperonal and veratraldehyde.

The successful oxidation of alcohols to aldehydes depends upon the lower reactivity of the latter. Thus benzyl alcohol is oxidized at approximately 20 times the rate for benzaldehyde under similar conditions; the rates for both benzyl alcohol and paranitrobenzyl alcohol have been included in Table VI for comparison.

The oxidation of hydroquinone was examined. 1,4-Benzoquinone was obtained in 89% yield. The use of the reagent with this type of compound is probably restricted by the great instability of the products.

Silver(II) picolinate is a square planar complex isomorphous with the analogous copper(II) derivative and probably having a *trans* planar structure like the latter.

Oxidation could proceed through an outer-sphere mechanism, with electron-transfer via an OH^- or a water ligand, or the relative rates observed for aliphatic alcohols may represent the steric requirements for formation of an Ag—O linked intermediate, before the actual oxidation process. On this basis the effect of changing substituents on the reactivity of benzyl alcohol would reflect the changing nucleophilicity of the alcohol oxygen atom.

Further experiments, including kinetic and labelling studies, are under way to clarify the mechanism.

Experimental

Infrared spectra were recorded using Perkin–Elmer 237 and 257 spectrophotometers. Nuclear magnetic resonance spectra were measured upon a Perkin–Elmer R 10 (60 megacycle) instrument. Ultraviolet (u.v.) spectra were recorded using a Unicam S.P. 800 instrument. Where available, analytical grade materials were used. Otherwise reagent grade materials were suitably purified. Gas–liquid chromatographic (g.l.c.) examination of materials was carried out using Pye 104 Chromatographs, single and dual columned, isothermal, or temperature programed models, and one or more stationary phases including silicone oil, dinonyl phthalate, tricresyl phosphate, PEGA, carbowax, and apiezon L, usually 5% or 10% upon celite. (Nitrogen gas carrier; flame-ionization detector.)

Picolinic Acid

α-Picoline (50 g, 0.54 mole) and potassium permanganate (90 g, 0.57 mole) in water (2.5 l) were heated on a steam bath until no purple coloration remained. A further 90 g portion of potassium permanganate in water (500 ml) was added and heating was continued until again no purple coloration remained. The mixture was cooled slightly and then filtered at the pump through a thin layer of Kieselguhr. The precipitated manganese dioxide was washed with boiling water (1 l). The combined filtrate and washings were concentrated under reduced pressure to give about 200 ml of solution. The solution was acidified to congo red with concentrated hydrochloric acid. Solvent was removed at the pump and the residue was repeatedly extracted with portions (250 ml) of 95% aqueous ethanol. Evaporation of the extract gave α-picolinic acid (40 g, 60% of theoretical yield) m.p., 128–129 °C, raised to 136–138 °C on recrystallization from ethanol. The p.m.r. spectrum showed a multiplet at 1.0–2.0 τ (in D_2O), with no other signals. The i.r. spectrum (KBr discs) showed bands at 3420 (b, s), 3100 (w), 1720 (w), 1654 (m), 1600 (s), 1563 (w), 1516 (w), 1446 (w), 1378 (s), 1388 (w), 1286 (m), 743 (s), and 672 (s) cm^{-1}.

Argentic Picolinate

The method of Cox *et al.* (4) proved unsatisfactory in our hands, and the following modification was developed. To a solution of picolinic acid (61.5 g, 0.5 mole) in water (2 l) was added a solution of silver nitrate (42.5 g, 0.25 mole). Aqueous potassium persulfate (33.8 g, 0.125 mole) was added to the vigorously stirred suspension. Stirring was continued for 48 h. The red precipitate was separated, washed with distilled water, and dried in darkness at room temperature in vacuo to constant weight; yield 75 g. This material was stable on storage in the dark at room temperature over several months.

Silver(II) Oxide (AgO)

A solution of sodium hydroxide (36 g) in water (500 ml) was brought to 80 °C, and maintained at this temperature while potassium persulfate (37.5 g) and silver nitrate (25.5 g) were added successively with stirring, the latter substance being added in small portions. Stirring was continued for 5 min, and the solution was maintained at 80 °C for a further 45 min. The cooled solution was filtered at the pump, and the residue was washed successively with sodium hydroxide (5 g) in water (500 ml), and then distilled water (500 ml). The dark brown argentic oxide was dried in vacuo; yield 18.3 g (almost quantitative).

Oxidations with Argentic Picolinate

The following are typical procedures.

Oxidation of Methanol

Methanol (1 ml) was stirred at 40 °C with argentic picolinate (2.1 g) in DMSO (15 ml) and water (15 ml), while a stream of N_2 swept the surface. The N_2 was passed into aqueous 2,4-dinitrophenylhydrazine (19) and the yellow precipitate was separated, washed, dried, and weighed (0.48 g, 80%); m.p. 165–166 °C, (lit. (19) m.p. 166 °C).

Oxidation of C_2–C_{10} Alcohols

Using a similar technique with N_2 blown *through* the solution, the aldehydes (or ketones) up to C_{10} could be swept from the mixture, although it was necessary to raise the temperature, after reaction was complete, to recover all the highest boiling members.

To confirm that no skeletal rearrangement had occurred, the p.m.r. spectra of the 2,4-dinitrophenylhydrazones were routinely examined. All these showed resonances at 0.88 τ (1 proton, doublet, very slightly split further, $J_{H_3H_5} = 2.8$ c.p.s.), $H_{(3)}$: 1.65 τ (1 proton double doublet $J_{H_3H_5} = 2.8$ c.p.s. and $J_{H_5H_6} = 9.8$ c.p.s.), $H_{(5)}$: 2.05 τ (1 proton doublet $J_{H_6H_5} = 9.8$ c.p.s.), $H_{(6)}$: 1.0 τ (broad singlet, NH). The signal due to the $H_{(1')}$ proton (i.e. —CH=N—) in aldehyde 2,4-dinitrophenylhydrazones regularly appeared at 2.4 τ (triplet usually, quartet for acetaldehyde) where no β-branching was present. β-Branched compounds gave doublets centered at 2.45 to 2.55 τ. Remaining signals were as expected in the 7.4–9.1 τ region, and no evidence of any skeletal change was observed.

Oxidation of Isoborneol

A mixture of isoborneol (0.01 mole, 1.54 g) and argentic picolinate (0.02 mole, 7.0 g) in DMSO (10 ml, containing a little water) was warmed to 40 °C for 15 min with gentle stirring, by which time the red coloration had disappeared. The mixture was poured into water (250 ml), filtered, and the residue and filtrate extracted with chloroform. The chloroform layers were combined and washed several times with water, dried over magnesium sulfate, filtered, and evaporated. Camphor (66% yield) was obtained, identical in i.r. spectrum with authentic material (m.p. 170–171 °C), on precipitation as 2,4-dinitrophenylhydrazone. It was identical in retention time on g.l.c. with authentic camphor, and had the expected p.m.r. spectrum.

Oxidation of DL-*Phenylethanol*

Phenylethanol (0.01 mole, 1.2 g) and argentic picolinate (0.02 mole, 7.0 g) were warmed together in DMSO (10 ml) for 10 min at 40 °C. The mixture was poured into water (300 ml) and extracted with petroleum–ether (60–80°). The petrol extract was washed, dried, and evaporated to give acetophenone (73%) identical in i.r. spectrum with authentic material m.p., 246–247 °C (lit. 250 °C) (2,4-dinitrophenylhydrazone). It was identical in retention time on g.l.c. with authentic material.

Oxidation of Hydroquinone

A mixture of hydroquinone (0.31 g) and argentic picolinate (2.0 g) in water (10 ml) was heated using a magnetic stirrer at 50 °C until the red coloration was discharged. The mixture was extracted with ether (2 × 50 ml) and the extract filtered and evaporated to give 1,4-benzoquinone (89%) as a yellow powder which gradually darkened on storage. This material was identical in i.r. spectrum, and in retention time on g.l.c. with authentic material.

Oxidation of Anisyl Alcohol

Anisyl alcohol (0.79 g) and argentic picolinate (4.0 g) were heated with stirring in water (50 ml) at 70 °C. After 25 min the mixture was cooled and extracted with ether. The dried ether layer was examined by g.l.c. (S.E. 30 on Celite: 210°), which showed only ether and anisaldehyde to be present. Evaporation of the extract gave anisaldehyde (0.7 g; 87%, identical in i.r. spectrum with authentic material).

Oxidation of Anisaldehyde

Anisaldehyde (0.4 g) and argentic picolinate (2.0 g) were heated with stirring in water (30 ml) at 70 °C. Stirring was continued until the reaction was complete (9.6 h). The mixture was acidified with dilute HCl and extracted with ether and chloroform. Evaporation of the extracts gave anisic acid.

Measurement of Relative Rates of Oxidation

Approximate measurements of relative reaction rates were made by taking appropriate quantities of materials at a selected thermostat temperature and measuring *either* the decrease in absorbance with time at 325 mμ *or* the disappearance of the red coloration against time. Whilst not suitable for accurate determination of absolute rates, the relative order of rates was found to be reasonably reproducible.

Oxidation of p-Nitrobenzaldehyde

A mixture of *p*-nitrobenzaldehyde (0.43 g) and argentic picolinate (2.0 g) was stirred vigorously in water (10 ml) at 70 °C. After 26 h the reaction was complete. The mixture was acidified with slightly more than the calculated amount of dilute hydrochloric acid, extracted, and the solution was examined by thin-layer chromatography (silica, eluted with ether). The major component corresponded in R_f (0.74) to authentic *p*-nitrobenzoic acid. After isolation, the acid was obtained (0.15 g, 31%) identical in physical constants (m.p., 240–241 °C, i.r. spectrum) with authentic material.

Oxidation of Piperonaldehyde

Piperonaldehyde (0.43 g) and argentic picolinate (2.0 g) were stirred in water (10 ml) at 70 °C. After 25 min no argentic picolinate remained. The mixture was acidified (dilute HCl, calculated quantity) and extracted with ether and chloroform. From the extracts, piperonaldehyde (0.3 g) was recovered but no acid was found. Repetition of the reaction several times led in each case to rapid reduction of argentic picolinate, but in no case was the expected acid found, and in each case a good recovery of aldehyde was obtained.

Electrode Potentials

The electrode potentials of the systems Ag(pic)/Ag and $Ag(pic)_2/Ag$ were measured (at pH 5 and 25 ± 0.1 °C) against a calomel reference electrode (saturated) using a potentiometer (Tinsley Type 4363E). Solution junctions were made at an asbestos wick, the junction potential being eliminated using saturated KCl. Full details of results will be communicated later.

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1. N. A. Hampson, D. Larkin, and J. R. Morley. J. Electrochem. Soc. **114**, 817 (1967). N. A. Hampson, P. C. Jones, and R. F. Phillips. Can. J. Chem. **45**, 2039 (1967). T. G. Clarke, N. A. Hampson, J. B. Lee, J. R. Morley, and B. Scanlon. Can. J. Chem. **46**, 3437 (1968); Tetrahedron Letters, to be published.
2. H. S. Isbell. Bur. Stds. J. Res. **6**, 1145 (1931); **14**, 359 (1935); **17**, 331 (1936). U.S. Patent 1 976 731 (1934); Chem. Abstr. **28**, 7263 (1934); Ind. Eng. Chem. **24**, 1 (1932).
3. V. Scatturin and P. Bellon. J. Electrochem. Soc. **108**, 819 (1961).
4. G. A. Barbieri. Atti Acad. Lincei, **17**, 1708 (1933). E. G. Cox, W. Wardlaw, and K. C. Webster. J. Chem. Soc. 775 (1936).
5. G. L. Cohen and G. Atkinson. Inorg. Chem. **3**, 1741 (1964).
6. L. Syper. Tetrahedron Letters, 4193 (1967); J. Org. Chem. **32**, 3865 (1967).
7. W. A. Waters. Quart. Rev. London, **12**, 277 (1958).
8. E. Wertheim. J. Am. Chem. Soc. **44**, 2658 (1922). A. L. Henne. J. Am. Chem. Soc. **72**, 3370 (1950).
9. G. L. Poos, L. H. Sarett, G. E. Arth, and R. E. Beyler. J. Am. Chem. Soc. **75**, 422, 427 (1953). L. H. Herzog. J. Am. Chem. Soc. **75**, 5751 (1953). R. M. Lukes, G. L. Poos, R. E. Beyler, W. F. Jones, and L. H. Sarett. J. Am. Chem. Soc. **75**, 1710, 2116 (1953). W. J. Hickinbottom, D. R. Hogg, D. Peters, and D. G. M. Wood. J. Chem. Soc. 4402 (1954). H. W. Bersch and A. V. Mletzko. Arch. Pharm. **291**, 91 (1958). T. Suga, K. Kihara, and T. Matsuru. Bull. Chem. Soc. Japan, **38**, 893 (1965); **38**, 1503 (1965).
10. R. M. Evans. Quart. Rev. London, **13**, 61 (1959).
11. L. T. Harrison. Proc. Chem. Soc. London, 110 (1964). R. J. Gritter and T. J. Wallace. J. Org. Chem. **24**, 1051 (1959).
12. C. Djerassi. Org. Reactions, **6**, 207 (1961).
13. H. P. Kaufmann and D. B. Spannuth. Chem. Ber. **91**, 2127 (1958).
14. K. Nakagawa, R. Konaka, and T. Nakata. J. Org. Chem. **27**, 1597 (1962).
15. B. O. Field and J. Grundy. J. Chem. Soc. 1110 (1955). P. Gray and A. Williams. Chem. Rev. **59**, 283 (1959).
16. J. B. Lee and J. M. Pryce. Unpublished results.
17. J. Blair, W. R. Logan, and G. T. Newbold. J. Chem. Soc. 2443 (1956).
18. T. G. Clarke and J. B. Lee. Tetrahedron Letters, **5**, 415 (1967).
19. F. Wild. Estimation of organic compounds. The University Press, Cambridge, England. 1953. p. 142.