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SILVER II COMPLEXES AS OXIDISING AGENTS

J. B. Lee and T. G. Clarke

The University, Loughborough, LEICS.

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An interest in the properties of silver electrodes, and in the possible oxidation of carbohydrates and aralkyl compounds catalytically with silver salts, led us to examine the range and specificity of silver II picolinate as an oxidising agent[1].

Ammonia is readily oxidised by argentic silver[2] and the oxidation of amino groups should thus probably proceed readily, and perhaps selectively.

We examined the oxidation of a range of compounds initially to compare the stability of various functional groups, using as solvents water, dimethylsulphoxide (DMSO), or DMSO - dimethoxyethane mixtures.

We find argentic picolinate to be a powerful oxidising agent, oxidising a wide variety of functional groups, but nevertheless some selectivity of action is apparent.

Thus toluene is oxidised initially to benzyl alcohol, which in turn is oxidised to benzaldehyde, thence to benzoic acid. Surprisingly, this reaction may be carried out in stepwise fashion by control of reagent ratios. Ethyl benzene is converted to acetophenone, as is DL -phenylethanol.

Primary alcohols are readily converted to aldehydes; in this way ethanol, n-propanol, n-butanol, n-pentanol, n-hexanol and 3-methylbutanol-1, for example, gave the corresponding aldehydes in yields greater than sixty percent. Secondary alcohols also are readily oxidised: Thus isoborneol, *cyclo*hexanol, 4-hydroxymethyl-1,3-dioxolane, 2-phenyl-5-hydroxy-1,3-dioxane, and 1-decalol were rapidly converted respectively into camphor, *cyclo*hexanone, 4-formyl-1,3-dioxolane, 2-phenyl-1,3-dioxan-5-one, and 1-decalone.

Aldehydes are rapidly converted into the corresponding acids, although they can be obtained as reaction products under appropriate conditions. Thus butanal, *p*-tolualdehyde and 2-ethyl-hexanal rapidly give the corresponding acid under mild conditions.

Amines are oxidised very rapidly to the corresponding carbonyl compounds. In this case the use of DMSO as solvent produces remarkable increases in the rate of reaction and yields of product. Decreasing the basicity of the amine reduced the reaction rate. Thus, for example, both benzylamine and its *N*-acetate gave benzaldehyde, on oxidation, but the latter reacted considerably less readily.

Olefines reacted readily, but a more complex reaction occurred. Thus oxidation of *cyclo*hexene gave three products, *cyclo*hexanone, *cyclo*hexan-1,2-diol, and a third compound, possibly *cyclo*hexan-1,2-dione. In contrast diphenylacetylene was recovered unchanged under quite severe conditions.

Considerable differences in reactivity were observed between amino and hydroxy compounds. Thus both *cyclo*hexylamine and D-glucosamine (2-amino-2-deoxy-D-glucose) rapidly react at room temperature; *cyclo*hexanol and D-glucose require warming to ensure rapid reaction.

Action upon activated methylenes proceeds readily, but gives mixtures of products. Thus four products were obtained from the oxidation of 5,5-dimethyl-*cyclo*hexa-1,3-dione; the 1,2,3-triketone seemed to be a major product.

Application to carbohydrates indicated considerable potentiality. By the action of the reagent 2,3:5,6-di-O-isopropylidene-D-mannofuranose was converted smoothly into the mannonic acid. Similarly 1,2:3,4-di-O-isopropylidene-α-D-galactose, 2,3:4,5-di-O-isopropylidene D-fructose and 2,3: 4,6-di-O-isopropylidene-L-sorbose were converted into the corresponding acids. The oxidation of the secondary hydroxyl groups in 1,2:5,6-di-O-isopropylidene-3-O-benzoyl-D-mannitol and methyl-2,3-O-isopropylidene-L-rhamnoside proceeded readily to give 1,2:5,6-di-O-isopropylidene-4-O-benzoyl-D-arabo-3-hexulose and methyl-2,3,-O-isopropylidene-L-lyxohexo-5-uloside.

The action upon nitrogen containing compounds other than amines was less clearcut. Thus cyclohexanone oxime formed a stable green complex with the reagent. Benzoin α-oxime underwent scission to give benzoin and only small amounts of benzil, oxidation of the hydroxylamine residue occurring preferentially. Similarly cyclohexanone semicarbazone was split to give cyclohexanone, the nitrogen residue again being oxidised. In contrast, 2-methylcyclohexanone semicarbazone was only oxidised with difficulty.

Phosphites and tertiary phosphines reacted very rapidly, reaction being complete within a few minutes at 50°C.

The detailed mechanism of these oxidations is under investigation. These results are summarised in the appended table. From this initial survey it appears that the reagent is promising as an oxidant for suitably protected sugars as well as other materials, and as a possible selective reagent for multi-functional compounds. Yields are generally above 60% although no attempt to maximise conditions has been made in many cases.

Both the direct and catalytic uses of the reagent are under investigation.

References

(1) Compare e.g: A. J. Berry, "Qual. Inorg. Anal.," Cambridge Univ. Press., Cambridge, England (1938). W. Treibs, Ber., 72, 1194 (1939). N.A. Milas, J. Amer, Chem. Soc., 59, 2342 (1937). R. G. R. Bacon, Chem. Ind., 19 (1962). B. Braumer and B. Kuzma, Ber., 41, 3371 (1907). G.A. Barbieri, Atti Accad. Lincei, 17, 1078 (1953). E. G. Cox, W. Wardlaw, and K. C. Webster. J. Chem. Soc., 775 (1936).

(2) W. G. Palmer, "Experimental Inorganic Chemistry," Cambridge Univ. Press, Cambridge, England, 1954.

Some oxidations with silver II picolinate

Compound	Solvent	Temp. (°C)	Time (min)	Product
Benzylamine	DMSO	40	5	Benzaldehyde
	H_2O	70	60	Benzaldehyde
N-Acetyl-Benzylamine	DMSO	50	20	Benzaldehyde
	H_2O	70	20 hour	Benzaldehyde
DL-phenylethanol	DMSO	40	10	Acetophenone
Isoborneol	DMSO	40	15	Camphor
Cyclohexanol	DMSO	40	10	Cyclohexanone
Toluene	DMSO	65	60	Benzyl alcohol
4-Hydroxymethyl-1,3-dioxolane	DMSO	50	20	4-Formyl-1,3-dioxolane
2-Phenyl-5-hydroxy-1,3-dioxane	DMSO	70	20	2-Phenyl-1,3-dioxan-5-one
1-Decalol	DMSO	70	30	1-Decalone
Benzyl alcohol	DMSO	65	15	Benzaldehyde
Butanal	DMSO	40	20	Butyric acid
p-Tolualdehyde	DMSO	40	15	p-Toluic acid
2-Ethylhexanal	DMSO	40	25	2-Ethyl-hexanoic acid
Diphenyl acetylene	DMSO	80	60	Recovered unchanged
2,3:5,6-Di-O-isopropylideneα-D-mannofuranose	DMSO	50	15	2,3,:5,6-Di-O-isopropylidine mannonic acid
1,2:3,4-Di-O-isopropylideneα-D-galactopyranose	DMSO	90	10	1,2:3,4-Di-O-isopropylidineα-D-galacturonic acid

Some oxidations with silver II picolinate (cont'd.)

Compound	Solvent	Temp. (°C)	Time (min)	Product
2,3:4,5-Di-O-isopropylidene-D-fructopyranose	DMSO	85	10	2,3:4,5-Di-O-isopropylidene-D-arabinohexulos-2-onic acid
2,3:4,6-Di-O-isopropylidene-L-sorbose	DMSO	95	35	2,3:4,6-Di-O-isopropylidene-L-xylohexulos-2-onic acid
1,2:5,6-Di-O-isopropylidene-3-O-benzoyl-D-mannitol	DMSO	90	60	1,2:5,6-Di-O-isopropylidene-4-O-benzoyl-D-arabo-3-hexulose
Methyl-2,3-O-isopropylidene-L-rhamnoside	DMSO	90	50	Methyl-2,3-O-isopropylidene-L-lyxohexo-5-uloside
Benzaldehyde	DMSO	65	45	Benzoic acid

Relative ease of oxidation of some groups of compounds

Approximate reaction time in hours under comparable conditions.

A. OLEFINES - 50°C.

*cis*Pentene-2	0.25	*Cyclo*pentene	1.25
*Cyclo*hexene	1.5	4-Methyl *cyclo*hexene	2
Indene	2.5	Hexene-2	3
*Cyclo*heptene	3	Methylene *cyclo*hexane	3.25
*Cyclo*dodecene	3.5	Heptene-3	4
α-Methylstyrene	4	2-Ethylhexene-1	5
Styrene	11	*trans*-Stilbene	17
Cyclo octene	19.5	Octene-1	20.5
Di isobutylene	23	2,4,4-Trimethylpentene-2	24
2-Methylbutene-1	27	Maleic acid	99
2-Methylbutene-2	100	Fumaric acid	100

B. ALCOHOLS - 40°C.

(a)

*Cyclo*hexanol	8	Ethanol	16.5
4-Methyl *cyclo*hexanol	22.5	3,5-Dimethyl *cyclo*hexanol	24
2,5-Dimethyl *cyclo*hexanol	25.5	2,3-Dimethyl butanol-2	50
3-Methyl *cyclo*hexanol	50	2,3-Dimethyl *cyclo*hexanol	96
3-Methyl butanol-1	96	2,2-Dimethyl butanol-3	96

(b)

Benzyl	8	Ethanol	10
Propanol-1	12	Isopropanol	14
2-Butoxyethanol	14	Butanol-1	22

Isobutanol	23	Pentanol-1	24
Isopentanol	26	Butanol-2	30.5
tert Butanol	No reaction		

C. ALDEHYDES - 50°C.

4-Dimethylamino-benzaldehyde		Instant*	
2-Ethylbutanal	0.3	2-Ethyl hexanal	0.8
Furfuraldehyde	3	*p*-Tolualdehyde	4
Benzaldehyde	7		

*Attack on the amino group.

D. PHOSPHITES, PHOSPHINES - 50°C (Time in min.)

Tri-isopropyl phosphite	Instant	Tri-amyl phosphite	Instant
Tri-butyl phosphite	"	Tri-hexyl phosphite	"
Tri-(2-Ethylhexyl) phosphite	5	Triphenyl phosphite	5
Tri-phenyl phosphine	10	Tridecyl phosphite	10
Dibenzyl phosphite	10	Trilauryl phosphite	35