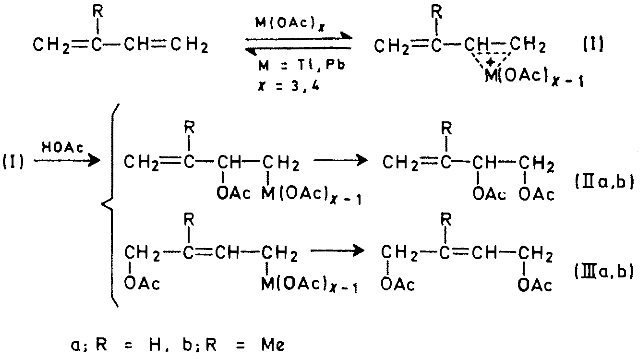
1,2- and 1,4-Diacetoxylation of Conjugated Dienes with Thallium(III) and Lead(IV) Acetates

By SAKAE UEMURA,* AKIRA TABATA, and MASAYA OKANO
(*Institute for Chemical Research, Kyoto University, Uji, Kyoto, Japan*)
and KATSUHIKO ICHIKAWA
(*Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Kyoto, Japan*)

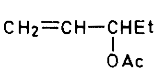
Summary The first example of 1,4-addition of acetoxy-groups to conjugate dienes occurred during oxidation with $\mathrm{Tl^{III}}$ and $\mathrm{Pb^{IV}}$ acetates.

ALTHOUGH much work on oxymetallation reactions of olefins has been published,[1] little is known of these reactions with conjugated dienes. Conjugated dienes such as buta-1,3-diene,[2] isoprene,[3] and 1-phenylbuta-1,3-diene[4] react with mercury(II) acetate to give only a 1,2-addition compound and lead(IV) acetate reacts with 2,3-dimethyl- and 1,4-dimethyl-buta-1,3-diene, cyclopenta-1,3-diene, and cyclohexa-1,3-diene to give only the esters of the 1,2-diols.[5]

Since oxymetallation is electrophilic in nature,[1] both 1,4- and 1,2-addition products would be expected. A recent report on the oxymercuration–demercuration of cyclohexa-1,3-diene cited the possibility of the formation of a 1,4-addition-type oxymercurial as intermediate.[6]

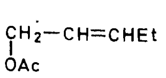


(IV)



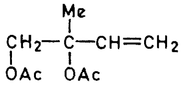
$\mathrm{CH_2{=}CH{-}}\underset{\mathrm{OAc}}{\mathrm{CHEt}}$

(V)

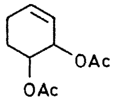


$\underset{\mathrm{OAc}}{\mathrm{CH_2}}\mathrm{{-}CH{=}CHEt}$

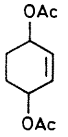
(VI)



$\underset{\mathrm{OAc}}{\mathrm{CH_2}}{-}\overset{\mathrm{Me}}{\underset{\mathrm{OAc}}{\mathrm{C}}}\mathrm{{-}CH{=}CH_2}$



(VII)



(VIII)

We now report preliminary results on the oxidation of several conjugated dienes with thallium(III) and lead(IV) acetates. Cyclohexa-1,3-diene, isoprene, and buta-1,3-diene (the reactivity decreased in this order) were treated with these metal acetates in acetic acid containing 3% (by weight) acetic anhydride at 20—70° for 0·1—2 h. 3,4- and 1,4-Diacetoxyolefins were isolated as main products except in the lead(IV) acetate–butadiene system, where, as in the reaction of styrene and 1,1-diphenylstyrene with lead(IV) acetate in benzene,[7] the addition of methyl and acetoxy-groups was the main reaction. Lead(IV) acetate reacted readily at room temperature, and was in all cases more reactive than thallium(III) acetate. Data are summarized in the Table. All products were separated by preparative g.c. and identified by i.r., n.m.r., and u.v. spectra and elemental analyses. Blank experiments showed that the reaction conditions used did not cause the interconversion of 3,4- and 1,4-diacetoxy-compounds. In view of the reported oxidation mechanism of mono-olefins with mercury(II) and

TABLE

Solvent; HOAc + 3%(*wt*) $\mathrm{Ac_2O}$

Diene (0·10 mol)	$\mathrm{M(OAc)}_x$ (0·05 mol)	Reaction temp. (°)	Reaction Time (h)	Products (diacetoxyolefins) Yield (%)[a]	Isomer	ratio
Buta-1,3-diene	$\mathrm{Tl(OAc)_3}$	60	2	22	(IIa)	66[b]
					(IIIa)	34
	$\mathrm{Tl(OAc)_3}$ + NaOAc	60	2	17	(IIa)	23[b]
					(IIIa)	77
	$\mathrm{Pb(OAc)_4}$	60	1	8	(IIa)	100[c]
					(IIIa)	0
Isoprene	$\mathrm{Tl(OAc)_3}$	60	2	39	(VI)	13[d]
					(IIb)	53
					(IIIb)	34
	$\mathrm{Pb(OAc)_4}$	20	2	28	(IIb)	79[e]
					(IIIb)	21
Cyclohexa-1,3-diene ..	$\mathrm{Tl(OAc)_3}$	70	0·5	46	(VII)	69[b]
					(VIII)	31
	$\mathrm{Pb(OAc)_4}$	70	0·1	42	(VII)	76[b]
					(VIII)	24

[a] Based on $\mathrm{M(OAc)}_x$.
[b] No other products were detected.
[c] Other major products: (IV) (6%) and (V) (16%).
[d] Identification of (VI) is not yet complete.
[e] Other product: acetic acid–isoprene (1 : 1) adduct.

thallium(III) acetate,[1] it is probable that both diacetoxy-compounds are formed through oxymetallation and demetallation steps, and that the former step, involving an electrophilic attack of the metal salt to dienes, proceeds in two modes, *i.e.*, by 1,2- and 1,4-addition. In the thallium(III) acetate oxidation of buta-1,3-diene, the addition of one equivalent of sodium or potassium acetate (to the Tl^{III} salt) resulted predominantly in the formation of 1,4-diacetoxybut-2-ene, (IIIa).

(*Received, October 5th*, 1970; *Com.* 1704.)

---

[1] J. Chatt, *Chem. Rev.*, 1951, **48**, 7; K. Ichikawa, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 1963, **66**, 1037; W. Kitching, *Organometallic Chem. Rev.*, 1968, **3**, 61.

[2] K. H. McNelly and G. F. Wright, *J. Amer. Chem. Soc.*, 1955, **77**, 2553.

[3] L. G. Makarova and A. N. Nesmeyanov in "Methods of Elemento-Organic Chemistry," vol. 4, "The Organic Compounds of Mercury," eds. A. N. Nesmeyanov and K. A. Kocheskov, North-Holland Publishing Co., Amsterdam, 1967, p. 172.

[4] G. F. Wright, *J. Amer. Chem. Soc.*, 1935, **57**, 1993.

[5] R. Criegee, *Annalen*, 1930, **481**, 263.

[6] S. Moon, J. M. Takakis, and B. H. Waxman, *J. Org. Chem.*, 1969, **34**, 2951.

[7] "Oxidation in Organic Chemistry," ed. K. B. Wiberg, Academic Press, New York, 1965, p. 348; R. O. C. Norman and C. B. Thomas, *J. Chem. Soc.* (*B*), 1967, 771.