

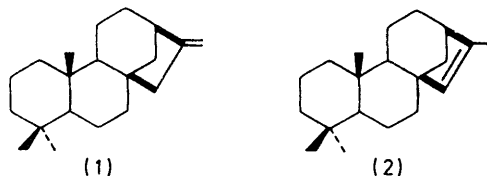
## Reactions of Thallium(I) Carboxylates and Iodine with Alkenes

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Treatment of an alkene with a thallium(I) carboxylate and iodine gives the corresponding *vic*-iodocarboxylate in high yield. The reactions are regiospecific and in conjunction with solvolysis of the products, offer an alternative to the Prévost reaction. Differences in the behaviour of thallium(I) carboxylates and silver carboxylates towards alkenes in the presence of iodine are discussed.

THE classical Prévost reaction<sup>1</sup> for the preparation of *vic*-diol derivatives from alkenes involves the use of silver carboxylates and iodine. In a search for other metal carboxylates which might allow the isolation or detection of initially formed iodine-containing products<sup>2,3</sup> the use of thallium(I) carboxylates has been investigated. Unlike silver carboxylates, which are often unstable and difficult to dry, the less expensive thallium(I) carboxylates are generally stable crystalline solids<sup>4</sup> which are readily prepared in high yield by neutralisation of the appropriate carboxylic acid with thallium(I) ethoxide.<sup>5</sup> In the 'hard and soft acid and base' classification of

Pearson,<sup>6</sup> thallium(I) is a soft acid which is somewhat harder than thallium(III) and might therefore be expected to show properties characteristic of both silver(I), a soft acid, and potassium(I), a hard acid.<sup>4,7</sup> Since initial



experiments using thallium(I) carboxylates and iodine on phyllocladene (1) and isophyllocladene (2) showed promise for the isolation of *vic*-iodocarboxylates<sup>8,9</sup> a

<sup>1</sup> C. V. Wilson, *Org. Reactions*, 1957, **9**, 332; F. D. Gunstone in 'Advances in Organic Chemistry: Methods and Results,' eds. R. A. Raphael, E. C. Taylor, and H. Wynberg, Interscience, New York, 1960, vol. 1, p. 103.

<sup>2</sup> W. Bockemüller and F. W. Hoffmann, *Annalen*, 1935, **519**, 165.

<sup>3</sup> L. H. Briggs, B. F. Cain, R. C. Cambie, B. R. Davis, and P. S. Rutledge, *J. Chem. Soc.*, 1962, 1850; L. Mangoni and V. Dovinola, *Gazzetta*, 1969, **99**, 176, 195.

<sup>4</sup> E. C. Taylor and A. McKillop *Accounts Chem. Res.* 1970, **3**, 338; A. McKillop and E. C. Taylor, *Chem. in Britain*, 1973, **9**, 4.

<sup>5</sup> L. F. Fieser and M. Fieser, 'Reagents for Organic Synthesis,' J. Wiley, New York, 1969, vol. 2, p. 407.

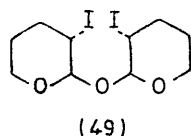
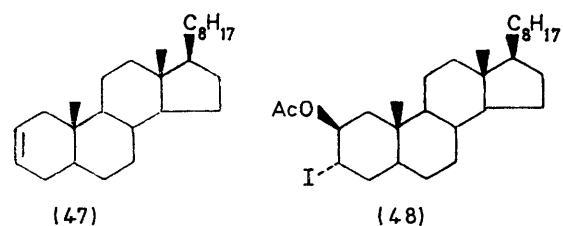
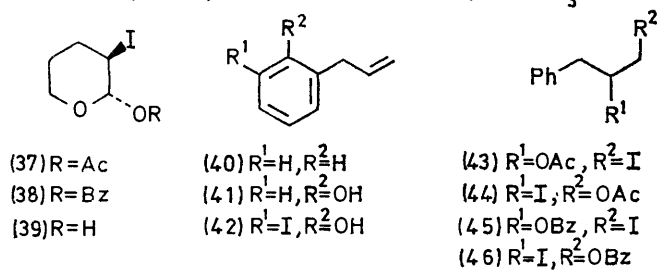
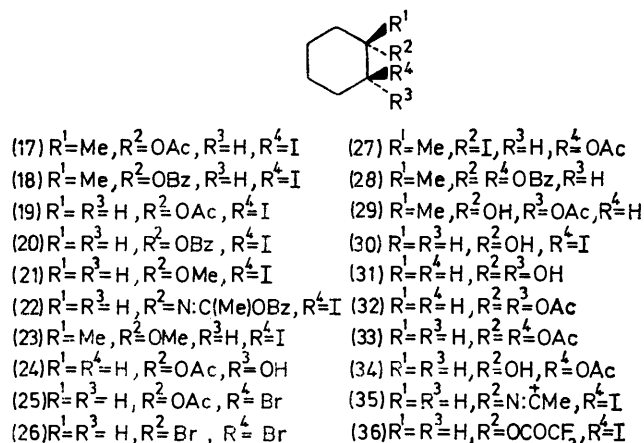
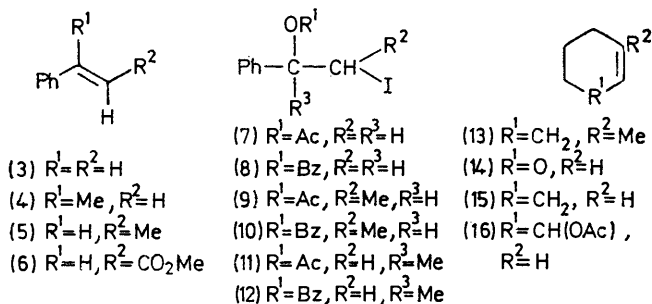
<sup>6</sup> R. G. Pearson, *J. Amer. Chem. Soc.*, 1963, **85**, 3533; *Chem. in Britain*, 1967, **3**, 103.

<sup>7</sup> G. Klopman, *J. Amer. Chem. Soc.*, 1968, **90**, 223.

<sup>8</sup> R. C. Cambie, R. C. Hayward, J. L. Roberts, and P. S. Rutledge, *J.C.S. Chem. Comm.*, 1973, 359.

<sup>9</sup> R. C. Cambie, R. C. Hayward, J. L. Roberts, and P. S. Rutledge, *J.C.S. Perkin I*, 1974, 1120.

more systematic investigation of their use with other alkenes was undertaken.



Treatment of a representative series of alkenes with iodine and either a solution of thallium(I) acetate in acetic acid or a suspension of thallium(I) benzoate in dry

\* The epoxide of 2,3-dihydropyran is unstable.<sup>10</sup> Reaction of the iodoacetate (37) with sodium hydrogen carbonate in ether gave products identified as the iodohydrin (39) and the dimer (49).<sup>11</sup>

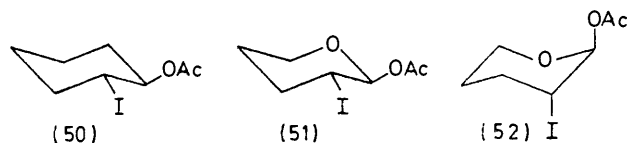
benzene gave high yields (Table) of iodocarboxylates identical with those obtained using the corresponding silver carboxylate. With the exception of that from

Iodocarboxylation products				
Alkene	Thallium(I) carboxylate	Solvent	Product	Yield (%)
(15)	Acetate	HOAc	(19)	85
(15)	Benzoate	PhH	(20)	81
(15)	Acetate	MeOH	(21)	92
(15)	Benzoate	MeCN	(20), (22)	
(15)	Trifluoroacetate	Et <sub>2</sub> O	(36)	95
(3)	Acetate	HOAc	(7)	98
(3)	Benzoate	PhH	(8)	60
(5)	Acetate	HOAc	(9)	97
(5)	Benzoate	PhH	(10)	66
(4)	Acetate	HOAc	(11)	98
(4)	Benzoate	PhH	(12)	64
(13)	Acetate	HOAc	(17)	90 *
(13)	Benzoate	PhH	(18)	80
(13)	Acetate	MeOH	(23)	80
(14)	Acetate	HOAc	(37)	89
(14)	Benzoate	PhH	(38)	84
(40)	Acetate	HOAc	(43), (44)	83
(41)	Benzoate	PhH	(42)	24
(6)	Acetate	HOAc	†	
(6)	Benzoate	PhH	†	
(47)	Acetate	HOAc	(48)	80
(41)	Benzoate	PhH	(42)	24

\* Use of elevated temperatures (ca. 90°) and wet acetic acid as solvent gave the hydroxyacetate (29). † No reaction.

2,3-dihydropyran \* (14) treatment of each iodocarboxylate with potassium carbonate in aqueous methanol afforded an epoxide which was identical with that obtained by epoxidation of the parent alkene thereby confirming the *trans*-relationship of the iodo- and acetoxy-groups. The stereochemistry of the addition product from the action of thallium(I) acetate and iodine on cyclohexene was also confirmed by a detailed examination of its n.m.r. spectrum. The spectrum included a one-proton multiplet at  $\delta$  4.10 ( $J_{1,2}$  10,  $J_{2,3a}$  9.5,  $J_{2,3e}$  5 Hz) assigned to the C-2 proton,<sup>12</sup> and a second, poorly resolved, one-proton multiplet at 4.99 ( $J_{1,2} = J_{1,6a}$  10,  $J_{1,6e}$  5 Hz) assigned to the C-1 proton. This splitting pattern is consistent with a *trans*-diequatorial conformation (50) indicating a stereospecific *trans*-addition. Confirmation of these proton assignments followed from spin decoupling experiments on the fully expanded spectrum after addition of  $Eu(fod)_3$  (Figure).

Application of each of the equations  $J_{H,H'} = (7.8 - 10\cos\phi + 5.6\cos 2\phi)(1 - 0.1\Delta X)$ <sup>13</sup> where  $\Delta X$  is the



sum of the differences in electronegativities of the substituents and hydrogen, and  $J_{obs} = N J_{aa} + (1 - N) J_{ee}$

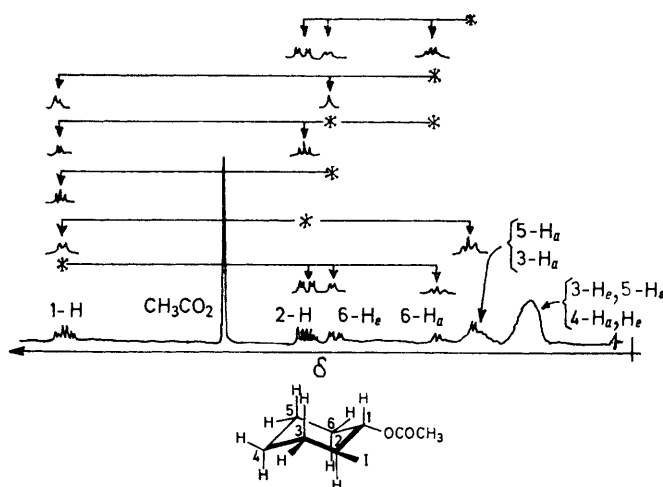
<sup>10</sup> C. Wakselman and L. Wartski, *Bull. Soc. chim. France*, 1967, 2242.

<sup>11</sup> Cf. R. Aguilera and G. Descotes, *Bull. Soc. chim. France*, 1966, 3318, 3323.

<sup>12</sup> U. E. Diner and J. W. Lown, *Canad. J. Chem.*, 1971, 49, 403.

<sup>13</sup> P. L. Durette and D. Horton, *Org. Magn. Resonance*, 1971, 3, 417.

where  $N$  is the fraction of the  ${}^4C_1$  conformer (51),<sup>14</sup> indicated a *ca.* 1:1 conformational equilibrium between the  ${}^4C_1$  (51) and  ${}^1C_4$  (52) conformers for the iodoacetate formed from 2,3-dihydropyran.



Spin decoupling of the expanded n.m.r. spectrum of the iodoacetate (50), after addition of  $\text{Eu}(\text{fod})_3$

No change in the products occurred when the mixture containing the iodo-carboxylates prepared from alkenes such as cyclohexene was heated under reflux for 2 h in the presence of an excess of the thallium(I) carboxylate. In contrast to the reaction with silver acetate which led to the *cis*-hydroxyacetate (24), treatment of cyclohexene with thallium(I) acetate and iodine in wet acetic acid (*cf.* ref. 15) under similar conditions gave only the iodoacetate (19), even at elevated temperatures. Replacement of iodine by bromine in the reaction with cyclohexene gave the bromoacetate (25) and variable amounts of the bromination product (26). As expected, no reaction was detected between the thallium(I) carboxylates and cyclohexene in the absence of iodine, and in contrast to the known reactions of iodine with silver carboxylates,<sup>16</sup> attempts to form a solution of an acyl hypoiodite failed. Subsequent addition of cyclohexene to a mixture of the thallium(I) carboxylate and iodine resulted in the recovery of much of the alkene and indeed, in order to obtain any appreciable reaction it was necessary for cyclohexene, the thallium(I) carboxylate, and iodine all to be present. Replacement of thallium(I) carboxylates by sodium or potassium carboxylates or by other thallium(I) salts, *e.g.* nitrate or sulphate, in acetic acid or benzene, resulted in no reaction. When acetic acid or benzene were replaced by methanol as the solvent high yields of methoxyiodides were formed.

With the exception of 3-phenylpropene (40), in all

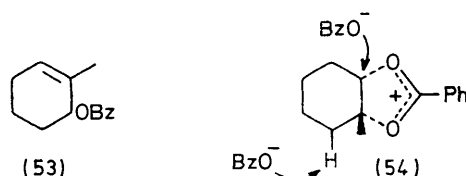
\* Use of silver benzoate gave a similar mixture of the iodo-benzoates (45) and (46).

<sup>14</sup> P. L. Durette, D. Horton, and N. S. Bhacca, *Carbohydrate Res.*, 1969, **10**, 565; F. A. L. Anet, *J. Amer. Chem. Soc.*, 1962, **84**, 1053.

<sup>15</sup> R. B. Woodward and F. V. Brutcher, *J. Amer. Chem. Soc.*, 1958, **80**, 209.

<sup>16</sup> L. Birckenbach, J. Goubeau, and E. Berninger, *Ber.*, 1932, **65**, 1339.

cases formation of iodo-carboxylates from unsymmetrical alkenes (Table) was found to be electronically regio-specific, addition occurring in a Markownikov sense. The only ambiguity which arose in assigning structures to the above iodo-carboxylates was with the highly unstable adducts of 1-methylcyclohexene (13) for which the n.m.r. data were consistent with either Markownikov or anti-Markownikov addition. Initially, the adduct using thallium(I) acetate was assigned the structure (27)<sup>8</sup> since a signal which appeared in the n.m.r. spectrum at  $\delta$  4.86 appeared to be more consistent with this formulation than with the alternative structure (17). However, this may not be the case since the C-1 proton of the iodo-carboxylate (19) was subsequently found to resonate at  $\delta$  4.99. Treatment of 1-methylcyclohexene with thallium(I) benzoate and iodine in benzene at 60° did not give an iodo-benzoate but afforded two other products which presumably arose by decomposition of the iodo-benzoate. The major product was identified as the allylic benzoate (53) and the minor product as the *trans*-dibenzoate (28). Each product probably arises



from a dioxolan-2-ylum cation<sup>17</sup> (54) formed by neighbouring group participation but the cation could arise equally well from the iodo-benzoate of either a Markownikov or anti-Markownikov addition. However, assignment of the structure of the adduct from thallium(I) acetate as (17) would be consistent with the other examples in the Table and with iodine azide and iodine isocyanate additions to 1-methylcyclohexene.<sup>18</sup> When the reaction with 1-methylcyclohexene was carried out at 90° with wet acetic acid as the solvent the *cis*-hydroxyacetate (29) was obtained as the sole product. The *cis*-relationship of the hydroxy- and acetoxy-groups of the latter compound was confirmed by a Serini reaction<sup>19</sup> in which it was converted in high yield into 2-methylcyclohexanone by heating with zinc dust.

With 3-phenylpropene (40) there was a loss of regio-specificity, reaction with thallium(I) acetate giving an inseparable mixture (1:1) of the iodoacetates (43) and (44).<sup>\*</sup> This result was unexpected in the light of a report that iodine azide adds regiospecifically to terminal alkenes such as 3-phenylpropene.<sup>20</sup> A rationalisation for the lack of regiospecificity in the present case is that

<sup>17</sup> J. F. King and A. D. Allbutt, *Canad. J. Chem.*, 1970, **48**, 1754; C. U. Pittman, S. P. McManus, and J. W. Larsen, *Chem. Rev.*, 1972, **72**, 357.

<sup>18</sup> A. Hassner, M. E. Lorber, and C. Heathcock, *J. Org. Chem.*, 1967, **32**, 540; A. Hassner, R. P. Hohlitt, C. Heathcock, J. E. Kropp, and M. Lorber, *J. Amer. Chem. Soc.*, 1970, **92**, 1326; A. Hassner, *Accounts Chem. Res.*, 1971, **4**, 9.

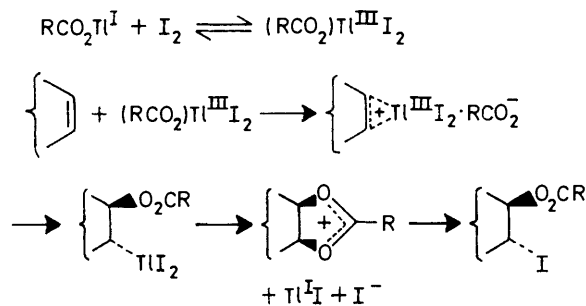
<sup>19</sup> E. Ghera, *J. Org. Chem.*, 1970, **35**, 660.

<sup>20</sup> F. W. Fowler, A. Hassner, and L. A. Levy, *J. Amer. Chem. Soc.*, 1967, **89**, 207; A. Hassner and F. W. Fowler, *J. Org. Chem.*, 1968, **33**, 2686.

an iodonium ion intermediate may be opening by both nucleophilic attack at the incipient carbenium ion and by  $S_N2$  displacement.

Since the Prévost reaction with silver carboxylates provides a method for obtaining *cis*- or *trans*-*vic*-diols without recourse to reagents such as osmium tetroxide or performic acid, methods for the conversion of the *trans*-iodocarboxylates into dioxygenated derivatives were examined. Solvolysis of the cyclohexane iodoacetate (19) in wet acetic acid afforded high yields of the corresponding *cis*-hydroxyacetate while solvolysis in dry acetic acid with added sodium acetate afforded the *trans*-diacetate (33). Conversion of the alkene (15) into the *cis*-hydroxyacetate (24) could be effected in high yield without isolation of the intermediate iodoacetate in a 'one-pot' reaction.\* However, if during reactions with unsymmetrical alkenes the precipitated thallium(I) iodide was filtered off and wet acetic acid was removed under reduced pressure, the formation of minor solvolysis products was minimised. Selective hydrolysis of the iodoacetate (19) with aqueous sodium hydrogen carbonate-ether gave the iodohydrin (30) while hydrolysis of the *cis*-hydroxyacetate (24) gave the known *cis*-diol (31).<sup>21</sup>

From the above and earlier<sup>9</sup> results it is clear that marked differences exist between the reactions of thallium(I) carboxylates and silver carboxylates in iodocarboxylations. Since thallium(I) carboxylates and iodine do not give acyl hypoiodites directly an alternative mechanism must be operating which results in the formal



SCHEME 1

addition of the elements of  $\text{RCO}_2\text{I}$  to an alkene. Since there is precedent<sup>22</sup> for the formation of a thallium(III) species from a thallium(I) carboxylate and bromine it is possible to envisage a route to an iodocarboxylate which

\* Since publication of our preliminary communication,<sup>8</sup> L. Mangoni, M. Adinolfi, G. Barone, and M. Parrilli (*Tetrahedron Letters*, 1973, 4485) have shown that the use of silver acetate is also not necessary in the Woodward-Prévost reaction for formation of the iodoacetate.

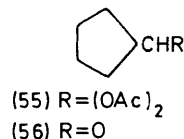
† A third alternative involving interaction between thallium(I) and an alkene is unlikely since thallium(I) is a weak soft acid<sup>6</sup> and is known not to complex with alkenes.<sup>31</sup>

<sup>21</sup> S. Winstein, *J. Amer. Chem. Soc.*, 1942, **64**, 2792; S. Winstein and R. E. Buckles, *ibid.*, p. 2780; S. Winstein, H. V. Hess, and R. E. Buckles, *ibid.*, p. 2796.

<sup>22</sup> B. Cocton and A. Crastes de Paulet, *Bull. Soc. chim. France*, 1966, 2947; E. Goldschmidt, *Diss. Berlin*, 1903, S.45, quoted in 'Gmelin's Handbuch der Anorganischen Chemie, Vol. 38, Thallium,' Verlag Chemie, Berlin, 1940.

invokes oxythallation of an alkene by a thallium(III) species (Scheme 1).

However, such a sequence would be remarkable both for its regioselectivity and the oxidation of  $\text{Tl}^{\text{I}}$  to  $\text{Tl}^{\text{III}}$  by iodine. Although the specificity might well be a consequence of the reagent, it has been found<sup>23</sup> that oxidation of cyclohexene with thallium(III) acetate in dry acetic acid gives a mixture of the *cis*- and *trans*-diacetates (32) and (33), a ring contracted diacetate (55), an aldehyde (56), and the allylic acetate (16). In wet acetic



acid the diol monoacetates (34) and (24) were also obtained. Although a report has appeared<sup>24</sup> apparently showing the oxidation of a thallium(I) to a thallium(III) pseudohalide, such a result would not be expected from a consideration of electrochemical data. The standard potential of the  $\text{Tl}^{\text{I}}/\text{Tl}^{\text{III}}$  and  $\text{I}^-/\text{I}_2$  couples are +1.25<sup>4</sup> and +0.53 V<sup>25</sup> and hence  $\text{Tl}^{\text{III}}$  will oxidise iodide to iodine. Moreover, the calculated value<sup>26</sup> for the equilibrium constant of the reaction:



is *ca.*  $10^{-24}$  so that iodine would not be expected to oxidise  $\text{Tl}^{\text{I}}$ . It has also been shown<sup>27</sup> that the solid tri-iodide  $\text{TlI}_3$ , formed from iodine and thallium(I) iodide is a thallium(I) compound although its solution in methanol does not show normal  $\text{I}_3^-$  absorption in the u.v.,<sup>26,28</sup> a fact attributed to formation of a complex.<sup>26</sup> Most evidence suggests that complexes between thallium(I) salts and iodine contain  $\text{I}_3^-$  or higher polyiodides<sup>29</sup> and hence it seems unlikely that thallium(III) is involved in the present work. Moreover, an attempt to trap any thallium(III) species present as a stable adduct with *o*-allylphenol (41)<sup>30</sup> was unsuccessful. Only the 2-allyl-6-iodophenol (42) was formed which implies the presence of an  $\text{I}^+$  or potential  $\text{I}^+$  donor.

For a mechanism involving thallium(I) two extremes may be proposed, one initiated by iodine-thallium(I) interaction and the other initiated by iodine-alkene interaction.† The first is shown in Scheme 2, with thallium retaining an oxidation state of +1. Although thallium(I) is a weak soft acid, precedent for thallium(I)-iodine interaction exists.<sup>24</sup> Thus the initial step in

<sup>23</sup> C. B. Anderson and S. Winstein, *J. Org. Chem.*, 1963, **28**, 605.

<sup>24</sup> S. S. Batsanov and N. R. Serebryanaya, *Izvest. Vysshikh Ucheb. Zavedenii, Khim. i Khim. Tekhnol.*, 1960, **3**, 980 (*Chem. Abs.*, 1961, **55**, 12,126).

<sup>25</sup> G. H. Aylward and T. J. V. Findlay, 'S.I. Chemical Data,' John Wiley, Sydney, 1971.

<sup>26</sup> A. G. Sharpe, *J. Chem. Soc.*, 1952, 2165.

<sup>27</sup> A. C. Hazell, *Acta Cryst.*, 1963, **16**, 71.

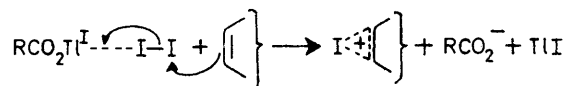
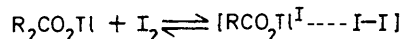
<sup>28</sup> A. J. Berry, T. M. Lowry, and R. R. Goldstein, *J. Chem. Soc.*, 1928, 1748.

<sup>29</sup> M. B. Robins and P. Day, *Adv. Inorg. Chem. Radiochem.*, 1967, **10**, 371.

<sup>30</sup> H.-J. Kabbe, *Annalen*, 1962, **656**, 204.

<sup>31</sup> B. T. Guran and L. B. Rogers, *J. Gas Chromatog.*, 1965, **3**, 269 (*Chem. Abs.*, 1966, **64**, 1326).

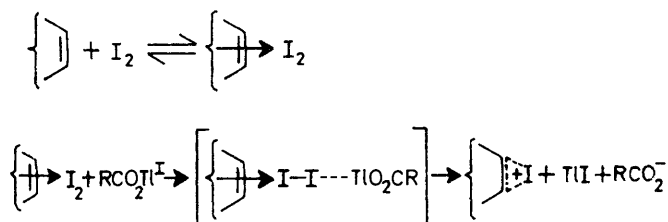
'oxidative addition' of halogens to thallium(I) azide and thallium(I) thiocyanate has been considered to be an increase in the valency of thallium(I) prior to oxidation of the anion. Reaction of an alkene with a complex



SCHEME 2

such as  $[RCO_2Tl^I \cdots I-I]$  via the polarised halogen molecule could give rise to an iodonium ion and thence the observed products. Although such a scheme is consistent with experimental observations it remains speculative especially in the light of inconsistencies in the reported reactions of halogens with thallium(I) compounds.

In a mechanism involving initial complexing between iodine and the alkene<sup>32</sup> the extreme polarisability of iodine<sup>33</sup> could assist in the interaction of a  $\pi$ -complex with the thallium(I) carboxylate to give an iodonium ion (Scheme 3). 'Outer' or  $\pi$ -complexes<sup>34</sup> of iodine



SCHEME 3

with alkenes are only weakly polarised and unlike the  $\sigma$  (or 'inner') complexes of chlorine or bromine are usually incapable of adding an anion or anionic group.<sup>35</sup> The role of the thallium(I) species could be to assist the charge separation in the formation of an iodonium ion from the initial  $\pi$ -complex. The nett effect would be to produce a loose iodonium-carboxylate ion pair. Support for the existence of a loose ion pair was obtained when it was found that the action of thallium(I) benzoate-iodine on cyclohexene in the polar solvent acetonitrile gave an unstable product (22) arising from solvent incorporation. The compound (22) is presumably formed from a nitrilium ion intermediate (35).<sup>36</sup> Under identical conditions silver benzoate-iodine gave only a trace of the compound (22), affording the *trans*-iodobenzoate (20) as the major product, presumably from a tighter iodonium-carboxylate ion pair. Although formation of the adduct (22) could also be rationalised as arising by a more concerted process, the effect of solvent polarity on both the rate and products of the reaction of thallium(I)

<sup>32</sup> J. E. Dubois and F. Garnier, *Tetrahedron Letters*, 1965, 3961; 1966, 3047; *J. Chim. Phys.*, 1966, **63**, 351; G. B. Sergeev and Yu. A. Serguehev, *Teor. i ekspr. Khim.*, 1968, **4**, 406 (*Chem. Abs.*, 1968, **69**, 70,794).

<sup>33</sup> R. M. Noyes and E. Kőrös, *Accounts Chem. Res.*, 1971, **4**, 233.

<sup>34</sup> R. S. Mulliken, *J. Phys. Chem.*, 1952, **56**, 801.

acetate and iodine with phyllocladene<sup>9</sup> would seem to imply involvement of an ionic intermediate in these reactions. Establishment of a mechanism or mechanisms for alkene iodocarboxylation must await further work but evidence to date would appear to favour the involvement of a thallium(I) species, an iodine-alkene  $\pi$ -complex, and an iodonium ion type intermediate.

#### EXPERIMENTAL

Unless otherwise indicated i.r. spectra were recorded for  $CHCl_3$  solutions with Perkin-Elmer 237 or 337 spectrophotometers and u.v. spectra were recorded with a Unicam SP 800A spectrophotometer. N.m.r. spectra were measured in  $CDCl_3$  on Varian A60 or T60 spectrometers with tetramethylsilane as internal reference. Alumina for chromatography was Spence type H material deactivated with 5% (v/v) of aqueous 10% acetic acid, and silica gel for chromatography was kieselgel S (Riedel de Haen) deactivated with 10% (v/v) of water. Thin layer chromatography (t.l.c.) was carried out on plates of kieselgel DG (Riedel de Haen) while preparative t.l.c. (p.l.c.) was carried out on 1 mm thick plates of kieselgel PF<sub>254</sub> + 366 (Merck). Thallium(I) ethoxide and thallium(I) carboxylates were prepared as described previously.<sup>5,9</sup>

*General Procedures for Iodocarboxylations.*—(a) *Iodoacetoxylations.* A solution of iodine (1 equiv.) in acetic acid was added dropwise to a stirred solution of the alkene (1 equiv.) and thallium(I) acetate (1.2 equiv.) in acetic acid at 20°. The mixture was stirred at 20° for 48 h, or at 20° for 2 h and then warmed to 90° in order to complete the reaction. Thallium(I) iodide was removed and washed with ether. The filtrate and washings were concentrated *in vacuo* to give a product which was taken up in ether and washed successively with 5% aqueous sodium thiosulphate, saturated aqueous sodium hydrogen carbonate, and water. Removal of solvent from the dried solution gave the iodo-carboxylates as unstable oils which were examined by n.m.r. as soon as possible after preparation.

(b) *Iodobenzoylations.* A solution of iodine (1 equiv.) in dry benzene was added dropwise to a stirred suspension of thallium(I) benzoate (2 equiv.) in a solution of the alkene (1 equiv.) in dry benzene. The mixture was stirred for 48 h and worked up as in (a).

The results are summarised in the Table, and the products are described below.

*trans*-2-Iodocyclohexyl acetate (19),  $\nu_{max}$  1730  $cm^{-1}$  (CO),  $\delta$  2.10 (s, OAc), 4.10 (oct,  $J_{1,2}$  10,  $J_{2,3a}$  9.5,  $J_{2,3e}$  5 Hz, 2-H), and 4.99 (sext,  $J_{1,2} = J_{1,6a}$  10,  $J_{1,6e}$  5 Hz, 1-H). Solvolysis of the iodoacetate (19) in refluxing wet acetic acid gave *cis*-2-hydroxycyclohexyl acetate (24) as an oil (80%),  $\nu_{max}$  3620, 3450 (OH), and 1720  $cm^{-1}$  (CO),  $\delta$  2.06 (s, OAc), 2.38 (s, OH, exchanged with  $D_2O$ ), 3.84 (m, 2-H), and 4.88 (m, 1-H). Solvolysis in dry acetic acid in the presence of sodium acetate under reflux gave the *trans*-diacetate (33). Hydrolysis of the acetate (24) in ethanol with aqueous sodium hydroxide under reflux for 3 h gave *cis*-cyclohexane-1,2-diol (31) which crystallised from carbon tetrachloride as needles,

<sup>35</sup> V. I. Staninets, E. A. Shilov, and E. B. Koryak, *Doklady Acad. Nauk. S.S.S.R.*, 1970, **192**, 817.

<sup>36</sup> A. Hassner, L. A. Levy, and R. Gault, *Tetrahedron Letters*, 1966, 3119; H. C. Brown and J. T. Kurek *J. Amer. Chem. Soc.*, 1969, **91**, 5647; V. I. Soikolov and D. A. Reutov, *Izvest. Acad. Nauk. S.S.S.R., Ser. khim.*, 1968, 225; A. B. Suttie, *Tetrahedron Letters*, 1969, 953.

m.p. 96–97° (lit.,<sup>21</sup> 98°),  $\nu_{\max}$  3600–3100 (H-bonded OH) and 1050  $\text{cm}^{-1}$  (OH),  $\delta$  2.85 (s, OH, exchanged with  $\text{D}_2\text{O}$ ) and 3.72 (m, 1- and 2-H).

Hydrolysis of the idoacetate (19) with sodium hydrogen carbonate-ether at 20° gave the iodohydrin (30) as an unstable oil,  $\nu_{\max}$  ( $\text{CCl}_4$ ) 3550–3200  $\text{cm}^{-1}$  (OH),  $\delta$  3.84 and 4.00 (overlapping m, 1- and 2-H).

*trans*-2-Iodocyclohexyl benzoate (20),  $\nu_{\max}$  1735  $\text{cm}^{-1}$  (CO),  $\delta$  4.19 (sext,  $J_{1,2} = J_{2,3a} 10$ ,  $J_{2,3e} 5$  Hz, 2-H), 5.05 (m, 1-H), and 7.25–8.10 (m, ArH).

*trans*-1-Iodo-2-methoxycyclohexane (21),  $\nu_{\max}$  1170–1050  $\text{cm}^{-1}$  (C–O),  $\delta$  3.21 (m, 1-H), 3.34 (s, OMe), and 4.03 (oct,  $J_{1,2a} 10$ ,  $J_{2,3a} 9.5$ ,  $J_{2,3e} 5$  Hz, 2-H).

*trans*-*N*-(1-Benzoyloxyethylidene)-2-iodocyclohexylamine (22), isolated by p.l.c. (chloroform-hexane, 1 : 1),  $\nu_{\max}$  1690 (C=N) and 1735  $\text{cm}^{-1}$  (CO),  $\delta$  1.95 (s, Me), 4.49 (sext,  $J_{1,2} 11$ ,  $J_{1,6e} 4.5$  Hz, 1-H), 5.05 (sext,  $J_{1,2} = J_{2,3a} 11$  Hz,  $J_{2,3e} 4.5$  Hz, 2-H), and 7.23–7.81 (m, ArH).

*trans*-2-Iodocyclohexyl trifluoroacetate (36),  $\nu_{\max}$  1780  $\text{cm}^{-1}$  (CO),  $\delta$  4.09 (sext,  $J_{1,2} = J_{2,3a} 10$ ,  $J_{2,3e} 5$  Hz, 2-H), and 5.00 (sext,  $J_{1,2} = J_{1,6a} 10$ ,  $J_{1,6e} 5$  Hz, 1-H).

*r*-2-Iodo-*c*-1-methylcyclohexyl acetate (17),  $\nu_{\max}$  1730  $\text{cm}^{-1}$  (CO),  $\delta$  1.62 (s, Me), 2.00 (s, OAc), and 4.86 (q,  $J_{2,3a} 7$ ,  $J_{2,3e} 5$  Hz, 2-H). Treatment of 1-methylcyclohexene with thallium(i) acetate and iodine in wet acetic acid at ca. 90° gave the *cis*-hydroxyacetate (29) (100%),  $\nu_{\max}$  ( $\text{CCl}_4$ ) 3620–3100 (H-bonded OH) and 1720  $\text{cm}^{-1}$  (CO),  $\delta$  1.18 (s, Me), 2.08 (s, OAc), 2.29 (s, OH, exchanged with  $\text{D}_2\text{O}$ ), and 4.68 (t,  $J$  6 Hz, 2-H). Reduction of the hydroxyacetate (29) with lithium aluminium hydride gave 1-methylcyclohexane-*r*-1,*c*-2-diol which crystallised from carbon tetrachloride as needles, m.p. 67° (lit.,<sup>37</sup> 67°),  $\nu_{\max}$  3700–3100 (H-bonded OH) and 1050  $\text{cm}^{-1}$  (OH),  $\delta$  1.26 (s, Me), 2.24 (s, OH, exchanged with  $\text{D}_2\text{O}$ ), and 3.40 (t,  $J$  3 Hz, 2-H). Treatment of the hydroxyacetate (29) with zinc dust by the method of Ghera<sup>19</sup> gave 2-methylcyclohexanone (85%), identical (i.r., g.l.c., n.m.r.) with an authentic sample.

*r*-2-Iodo-*c*-1-methylcyclohexyl benzoate (18),  $\nu_{\max}$  1735  $\text{cm}^{-1}$  (CO),  $\delta$  1.80 (s, Me), 4.79 (q,  $J_{2,3a} 7.5$ ,  $J_{2,3e} 5$  Hz, 2-H), and 7.25–7.84 (m, ArH). Treatment of 1-methylcyclohexene with thallium(i) benzoate and iodine in benzene at 60° gave a 4 : 1 mixture of 2-methylcyclohex-2-enyl benzoate (53),  $\nu_{\max}$  ( $\text{CCl}_4$ ) 1725  $\text{cm}^{-1}$  (CO),  $\delta$  1.78br (s,  $W_{\frac{1}{2}} 10$  Hz, 1-H), 5.78 (m,  $W_{\frac{1}{2}} 7$  Hz, 3-H), and 7.38 and 8.20 (2m, ArH), and 1-methylcyclohexane-*r*-1,*t*-diyl dibenzoate (28),  $\nu_{\max}$  1725  $\text{cm}^{-1}$  (CO),  $\delta$  2.74 (s, Me), 5.52 (q,  $J_{2,3a} 7$ ,  $J_{2,3e} 5$  Hz, 2-H), and 7.27–8.15 (m, ArH).

*r*-2-Iodo-*t*-1-methoxy-1-methylcyclohexane (23),  $\nu_{\max}$  1170–1050  $\text{cm}^{-1}$  (C–O),  $\delta$  1.33 (s, Me), 3.20 (s, OMe), and 4.32 (q,  $J_{2,3a} 7.5$ ,  $J_{2,3e} 5$  Hz, 2-H).

*trans*-2-Acetoxy-3-iodotetrahydropyran (37),  $\nu_{\max}$  1740  $\text{cm}^{-1}$  (CO),  $\delta$  2.05 (s, OAc), 3.85 (m, 3-H), and 5.70 (d,  $J$  5 Hz, 2-H). If the mixture was shaken excessively with sodium hydrogen carbonate during work-up, hydrolysis occurred to give *trans*-2-hydroxy-3-iodotetrahydropyran (39),  $\nu_{\max}$  ( $\text{CCl}_4$ ) 3500–3200 (OH) and 1740  $\text{cm}^{-1}$  (CO),  $\delta$  3.24–4.27 (m, 3- and 6-H) and 4.78 (d,  $J$  5 Hz, 2-H), and *bis*-(*t*-3-iodotetrahydropyran-*r*-2-yl) ether (49), which crystallised from hexane-pentane as needles, m.p. 91–93°, *m/e* 438 ( $M^{++}$ ,  $\text{C}_{10}\text{H}_{16}\text{I}_2\text{O}_3$ ),  $\nu_{\max}$  1130–900  $\text{cm}^{-1}$  (C–O),  $\delta$  3.59 (m, 3-H), 4.00 (m, 6-H), and 4.86 (d,  $J$  4.5 Hz, 2-H).

*trans*-2-Benzoyloxy-3-iodotetrahydropyran (38),  $\nu_{\max}$  1740  $\text{cm}^{-1}$  (CO),  $\delta$  4.40 (m, 2-H), 6.17 (d,  $J$  5 Hz, 1-H), and 7.30–8.15 (m, ArH).

2-Iodo-1-phenylethyl acetate (7),  $\nu_{\max}$  1730  $\text{cm}^{-1}$  (CO),  $\delta$

2.10 (s, OAc), 3.47 (d,  $J$  7 Hz, 2- $\text{H}_2$ ), 5.90 (t,  $J$  7 Hz, 1-H), and 7.34 (s, ArH).

2-Iodo-1-phenylethyl benzoate (8), needles, m.p. 70–71°, from hexane-pentane (Found: C, 51.2; H, 3.7; I, 36.0.  $\text{C}_{15}\text{H}_{13}\text{IO}_2$  requires C, 51.2; H, 3.7; I, 36.1%),  $\nu_{\max}$  1725  $\text{cm}^{-1}$  (CO),  $\delta$  3.50 (d,  $J$  7 Hz, 2- $\text{H}_2$ ), 6.06 (t,  $J$  7 Hz, 1-H), and 7.10–8.00 (m, ArH).

2-Iodo-1-phenylpropyl acetate (9),  $\nu_{\max}$  1740  $\text{cm}^{-1}$  (CO),  $\delta$  1.83 (d,  $J$  6.8 Hz, Me), 2.13 (s, OAc), 4.43 (oct,  $J_{2,3} 6.8$ ,  $J_{1,2} 5.6$  Hz, 2-H), 5.85 (d,  $J_{1,2} 5.6$  Hz, 1-H), and 7.30 (s, ArH).

2-Iodo-1-phenylpropyl benzoate (10),  $\nu_{\max}$  1725  $\text{cm}^{-1}$  (CO),  $\delta$  1.85 (d,  $J$  7 Hz, Me), 4.53 (m, 2-H), 6.11 (d,  $J$  5 Hz, 1-H), and 7.22–8.03 (m, ArH).

2-Iodo-1-methyl-1-phenylethyl acetate (11),  $\nu_{\max}$  1735  $\text{cm}^{-1}$  (CO),  $\delta$  1.94 (s, Me), 2.10 (s, OAc), 3.80 (s, 2- $\text{H}_2$ ), and 7.30 (s, ArH).

2-Iodo-1-methyl-1-phenylethyl benzoate (12),  $\nu_{\max}$  1725  $\text{cm}^{-1}$  (CO),  $\delta$  2.09 (s, Me), 3.64, 3.90 (2d,  $J$  11.5 Hz, 2- $\text{H}_2$ ), 3.66, 4.33 (2d,  $J$  13 Hz, 2- $\text{H}_2$ , unequal conformer populations), and 7.18–7.87 (m, ArH).

$\alpha$ -Iodomethylphenethyl acetate (43),  $\nu_{\max}$  1728  $\text{cm}^{-1}$  (CO),  $\delta$  1.99 (s, OAc), 3.23 (m,  $\text{CH}_2\text{I}$ ), 4.83 (m,  $\alpha$ -H), and 7.30 (s, ArH).

2-Iodo-3-phenylpropyl acetate (44),  $\nu_{\max}$  1728  $\text{cm}^{-1}$  (CO),  $\delta$  2.02 (s, OAc), 4.29 (m, 2-H), 4.40 (m, 1- $\text{H}_2$ ), and 7.30 (m, ArH).

3 $\alpha$ -Iodo-5 $\alpha$ -cholestan-2 $\beta$ -yl acetate (48),  $\nu_{\max}$  1730  $\text{cm}^{-1}$  (CO),  $\delta$  0.65 (s, 18-Me), 0.91 (s, 19-Me), 2.01 (s, OAc), 4.50 (m,  $W_{\frac{1}{2}} 7$  Hz, 2 $\beta$ -H), and 5.14 (m,  $W_{\frac{1}{2}} 8$  Hz, 3 $\alpha$ -H). Treatment of the idoacetate (48) with lithium aluminium hydride gave 5 $\alpha$ -cholestan-2 $\beta$ -ol (100%) which crystallised from chloroform-ethanol as plates, m.p. 151–154° (lit.,<sup>38</sup> 152–154°).

2-Allyl-6-iodophenol (42),  $\nu_{\max}$  3650, 3250 (OH), and 1630  $\text{cm}^{-1}$  (C=C),  $\delta$  6.52 (t,  $J_{3,4} = J_{4,5} 7$  Hz, 4-H), 7.01 (q,  $J_{3,4} 7$ ,  $J_{5,6} 2.5$  Hz, 3-H), and 8.42 (q,  $J_{4,5} 7$ ,  $J_{5,6} 2.5$  Hz, 5-H). The iodophenol (42) was also prepared (21%) using silver benzoate and iodine.

*trans*-2-Bromocyclohexyl acetate (25) was prepared in 45% yield by replacing iodine with bromine,  $\nu_{\max}$  ( $\text{CCl}_4$ ) 1730  $\text{cm}^{-1}$  (CO),  $\delta$  2.07 (s, OAc), 3.94 (oct,  $J_{1,2} 10$ ,  $J_{2,3a} 9.5$ ,  $J_{2,3e} 5$  Hz, 2-H), and 4.88 (sext,  $J_{1,2} = J_{2,3a} 9.5$ ,  $J_{2,3e} 5$  Hz, 1-H).

1-Phenylethylene Dibenzoate.—The iodobenzoate (8) was heated under reflux with silver benzoate in dry benzene for 0.5 h. Work-up gave the *dibenzoate* which crystallised from chloroform-pentane as needles, m.p. 94–95° (Found: C, 76.1; H, 5.2.  $\text{C}_{22}\text{H}_{18}\text{O}_4$  requires C, 76.3; H, 5.2%),  $\nu_{\max}$  1730  $\text{cm}^{-1}$  (CO),  $\delta$  3.56 (d,  $J$  7 Hz, 2- $\text{H}_2$ ), 6.09 (t,  $J$  7 Hz, 1-H), and 7.20–8.20 (m, ArH).

1-Phenylpropylene Dibenzoate.—The iodobenzoate (10) was treated with silver benzoate as above to give the *dibenzoate* which crystallised from chloroform-pentane as needles, m.p. 101–102° (Found: C, 76.5; H, 5.65.  $\text{C}_{23}\text{H}_{20}\text{O}_4$  requires C, 76.65; H, 5.6%),  $\nu_{\max}$  1730  $\text{cm}^{-1}$  (CO),  $\delta$  1.40 (d,  $J$  6.5 Hz, Me), 5.60 (m, 2-H), 6.28 (d,  $J$  4.5 Hz, 1-H), and 7.20–7.90 (m, ArH).

Iodobenzoates (45) and (46).—3-Phenylpropene was treated with silver benzoate and iodine in dry ether as for iodocarboxylation. Work-up gave a ca. 1 : 1 mixture of the iodobenzoates (45) and (46) as an oil (60%),  $\nu_{\max}$  1725  $\text{cm}^{-1}$  (CO),  $\delta$  [for (45)] 3.30 (m,  $\text{CH}_2\text{I}$ ) and 5.06 (m,  $\text{CHOBz}$ ),

<sup>37</sup> C. A. Bunton and M. D. Carr, *J. Chem. Soc.*, 1963, 770.

<sup>38</sup> A. Fürst and P. A. Plattner, *Helv. Chim. Acta*, 1949, **32**, 275.

[for (46)] 4.47 (m, CHI) and 4.50 (m, CH<sub>2</sub>OBz). Treatment of the mixture with silver benzoate in dry benzene under reflux gave 3-phenylpropylene dibenzoate<sup>39</sup> as an oil,  $\nu_{\max}$  1725 cm<sup>-1</sup> (CO),  $\delta$  3.09 (d,  $J$  6.5 Hz, 3-H<sub>2</sub>), 4.40 (sext of AB part of ABM system, 1-H<sub>2</sub>), 5.50 (m, 2-H), and 7.10—7.90 (m, ArH).

*General Procedure for Epoxide Formation.*—A suspension of potassium carbonate (2 equiv.) in 50% aqueous methanol containing the iodocarboxylate (1 equiv.) was stirred at 20° for 12 h and poured into water. The mixture was extracted with ether and the extract was washed successively with water, 5% aqueous sodium thiosulphate, and brine. Removal of solvent from the dried solution gave the epoxide as an oil.

1,2-Epoxy-cyclohexane,<sup>40</sup> prepared from (19) (81%) or (20) (90%), was identical (i.r. and n.m.r. spectra) with a sample prepared by epoxidation of cyclohexene with *m*-chloroperbenzoic acid in dichloromethane,  $\delta$  2.98br (s,  $W_{\frac{1}{2}}$  4 Hz, 1- and 2-H).

2-Phenyloxiran, prepared from (7) (90%) or (8) (90%), was identical (i.r. and n.m.r. spectra) with a sample prepared by epoxidation of (3),  $\delta$  2.71 (dd,  $J_{gem}$  5.8,  $J_{2,3-cis}$  2.6 Hz, 3-H *cis* to 2-H), 3.03 (dd,  $J_{gem}$  5.8,  $J_{2,3-trans}$  4.1 Hz, 3-H

*trans* to 2-H), 3.80 (dd,  $J_{2,3-trans}$  4.1,  $J_{2,3-cis}$  2.6 Hz, 2-H), and 7.30 (s, ArH).

2-Methyl-3-phenyloxiran, prepared from (9) (91%) or (10) (90%), was identical (i.r. and n.m.r. spectra) with a sample prepared by epoxidation of (5),  $\delta$  1.47 (d,  $J$  5.2 Hz, Me), 3.03 (oct,  $J$  5.2,  $J_{2,3}$  2.0 Hz, 2-H), 3.57 (d,  $J_{2,3}$  2.0 Hz, 3-H), and 7.30 (s, ArH).

2-Methyl-2-phenyloxiran,<sup>41</sup> b.p. 74—75° at 10 mmHg, prepared from (11) (90%) or (12) (90%), was identical (i.r. and n.m.r. spectra) with a sample prepared by epoxidation of (4),  $\delta$  1.67 (d,  $J$  0.6 Hz, Me, coupled to *trans* 3-H), 2.73 (oct,  $J_{gem}$  5.6,  $J$  0.6 Hz, 3-H *trans* to Me), 2.89 (d,  $J_{gem}$  5.6 Hz, 3-H *cis* to Me), and 7.33 (s, ArH).

1,2-Epoxy-3-phenylpropane, prepared from (43) and (44) (87%), was identical (i.r. and n.m.r. spectra) with a sample prepared by epoxidation of (40),  $\delta$  2.50 (1H, dd,  $J$  5.2 and 2.2 Hz), 2.63—2.93 (3H, overlapping m), and 2.97—3.33 (m, 2-H).

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<sup>39</sup> E. B. Hershberg, *Helv. Chim. Acta*, 1934, **17**, 351.

<sup>40</sup> M. S. Newman and C. A. VanderWerf, *J. Amer. Chem. Soc.*, 1945, **67**, 233.

<sup>41</sup> V. Danilov and E. V. Danilova, *Ber.*, 1927, **60**, 1050.