**α-Bromocamphor-*3-d* (3).**—A solution of sodium ethoxide in ethanol-*O-d* was prepared by the reaction of 0.020 g (0.008 g-atom) of sodium with 20 ml of ethanol-*O-d*.[13] α-Bromocamphor (2.3 g, 0.001 mol) was added and the mixture was heated for 66 hr on a steam bath. The solvent was removed by evaporation and the residue was sublimed to yield 2.0 g (87%) of crystals, mp 78° (lit.[14] mp 76° for α-bromocamphor). The nmr spectrum revealed the presence of *ca.* 14% of the undeuterated material based on the integrated area of the HCBr doublet at δ 4.84.

**Camphor-*3-endo-d* (4).**—The above material was debrominated by the same procedure as before except that unlabeled acetic acid was used. There was obtained an 89% yield of 4, mp 170–177°: mass spectrum *m/e* (rel intensity, average of five runs) 154 (14.0), 153 (100), and 152 (26.3). The calculated deuterium distribution[15] for these ratios was 21.1% $d_0$, 78.5% $d_1$, and 0.4% $d_2$. Upon correction for the unlabeled starting material, the following distribution of label was calculated: $d_0$, 8.3%; $d_1$, 91%; and $d_2$, 0.5%. The errors in peak height measurement limit the accuracy of these percentages to ±1% (absolute error).

**Registry No.**—1, 1925-58-2; 2, 27808-88-4.

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[13] D. J. Pasto and G. R. Meyer, *J. Org. Chem.*, **33**, 1257 (1968).

[14] T. M. Lowry, V. Steele, and H. Burgess, *J. Chem. Soc.*, **121**, 633 (1922).

[15] K. Bieman, "Mass Spectroscopy, Organic Chemistry Applications," McGraw-Hill, New York, N. Y., 1962, p 223.

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# Epoxidation by Thallium Triacetate[1]

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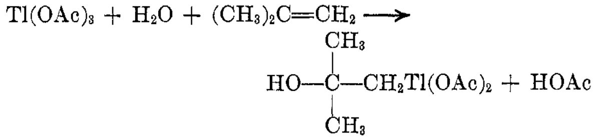
It has been known for several years that the oxidation of olefins with thallium triacetate in aqueous acid medium yields glycols and carbonyl compounds.[2] In acetic acid[3] and methanol,[4] 1,1-and 1,2-acetates and ethers as well as allylic oxidation products are formed. The preparation of σ-bonded oxythallation adducts[4,5] in nonaqueous systems, and kinetic[6] as well as polarographic[7] evidence of their presence in aqueous systems strongly suggest that such adducts are involved in the reaction sequence. Decomposition of these adducts occurs by heterolytic splitting of the metal–carbon bond giving thallous ions and oxidation products which result from neutralization of the incipient carbonium ion by one or more of the following routes: attack of the solvent, hydride shift, or neighboring group participation.[8] In only one favorable case, the oxidation of isobutylene, has neighboring hydroxyl participation been suspected.[6] In that study, conducted in strongly acidic aqueous medium, isobutyraldehyde, which can be formed only by neighboring hydroxyl participation, and isobutylene glycol were the products. Isobutylene oxide, the initial product expected, would decompose under the reaction conditions to the observed products. If hydroxyl participation occurs in aqueous acid, one might expect that in weaker solvating media, which favor this effect, the adducts from other olefins such as propylene may also decompose by this route. Furthermore, in less acidic systems the initial oxide product is more stable and can perhaps be isolated.

This note reports that, indeed, epoxides are obtained in weakly solvating media, not only with isobutylene but also with propylene. Thus, in 50% (v/v) aqueous acetic acid, thallium triacetate oxidized propylene to propylene oxide and acetone in a 1:1 ratio. In addition, by employing a less polar solvent, the ratio of epoxide to carbonyl compound can be changed significantly in favor of the epoxide. For example, in 70% (v/v) tetrahydrofuran, 20% water, and 10% acetic acid, the oxidation products of propylene consisted of 72% propylene oxide, 16% acetone, and 12% 1-acetoxy-2-propanol, giving an epoxide to carbonyl ratio of 4:1. For isobutylene, in the same solvent system, the ratio of isobutylene oxide to isobutyaldehyde was about 25:1, together with 15% 1-acetoxy-2-methyl-2-propanol. The product distribution for isobutylene was less sensitive to solvent composition. Blank experiments for the decomposition of the epoxides under our experimental conditions showed that the glycolic ester, and not the carbonyl compound, was formed from the epoxides. No glycols (<2%) were found under conditions of the experiments. Use of *tert*-butyl alcohol, dioxane, and other weakly solvating cosolvents gave similar results. With ethylene and *cis*- and *trans*-2-butene, only traces of epoxides were detected.

Although the existence of hydroxythallation adducts had been previously demonstrated,[5] by working at low temperatures we have now been able to isolate the hydroxythallation adduct I from thallium(III) triacetate and isobutylene in 80% (v/v) THF, 10% $H_2O$, and 10% acetic acid according to eq 1. The structure of I has been assigned on the basis of its nuclear magnetic resonance spectra reported in the Experimental Section.



$$\mathrm{Tl(OAc)_3 + H_2O + (CH_3)_2C{=}CH_2 \longrightarrow HO{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}{-}CH_2Tl(OAc)_2 + HOAc} \qquad (1)$$

I

The rate of decomposition of I and the corresponding propylene adduct in aqueous solution was followed by polarographically monitoring the Tl(I), Tl(III), and thallium adduct concentrations as a function of time.

The decomposition of the thallium(III)–isobutylene adduct followed first-order kinetics in aqueous perchlorate solutions. The rate was found to increase with increasing acidity at 25°; for example, the half-life for its decomposition was 23 min at pH 6.4, 15 min at pH 3.0, and much less than 1 min at pH 1. At pH 10.5, an aqueous perchlorate solution containing $10^{-3}$ *M* I became yellow in color and decomposed at a rate corresponding to a half-life of approximately 2 hr. At

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[2] R. R. Grinstead, *J. Org. Chem.*, **26**, 238 (1961).

[3] C. B. Anderson and S. Winstein, *ibid.*, **28**, 605 (1963).

[4] R. Criegee, *Angew. Chem.*, **70**, 173 (1958); H. J. Kabbe, *Justus Liebigs Ann. Chem.*, **656**, 204 (1962).

[5] K. C. Pande and S. Winstein, *Tetrahedron Lett.*, 3393 (1964).

[6] P. M. Henry, *J. Amer. Chem. Soc.*, **87**, 990, 4423 (1965); **88**, 1597 (1966).

[7] P. M. Henry, personal communication.

[8] P. M. Henry, *Advan. Chem. Ser.*, **70**, 126 (1968).

higher hydroxide ion concentrations, a brown precipitate of $Tl(OH)_3$ was formed.

The reaction described by eq 1 was found to be reversible in 50% aqueous acetic acid containing 1.0 $M$ sodium acetate. The Tl(III)–isobutylene adduct decomposed at approximately equal rates to Tl(III) and Tl(I) ($t_{1/2}$ ~18 min).

Since the Tl(III)–propylene adduct could not be isolated, it was prepared *in situ* at a concentration of about 1 $M$ in a solvent consisting of 10% water, 10% acetic acid, and 80% THF. This solution (1 ml) was dissolved in 100 ml of 0.1 $M$ aqueous $LiClO_4$ solution (pH 7.18). Under these conditions the decomposition of the propylene adduct was several times slower than for I, $t_{1/2}$ was 93 min.

The results of our kinetic experiments show that with increasing $H^+$ concentration, Tl(I) becomes a better leaving group, presumably because of increased positive charge on the Tl(III) due to protonation or exchange of anions in the labile first coordination sphere. A similar dependence on acid concentration was obtained by Jensen and Ouellette[9] for solvolysis reactions of alkylmercuric ions. This mode of adduct decomposition must even outweigh intramolecular displacement of Tl(III) by the adduct alkoxide ion as observed in the conversion of chlorohydrin to epoxides. Such a pathway might have been expected because of the increased acidity of the adduct hydroxyl group.

The slower rate of decomposition and the formation of acetone from the propylene adduct show the sensitivity of this reaction to methyl substitution on the $\beta$ carbon, similar to the chlorohydrin case.[10] The acetone could arise from the $\beta$ hydrogen participating as a neighboring group. However, under strongly acidic conditions where substantial formation of glycolic products does occur, this reaction may proceed exclusively through an epoxide intermediate. This possibility could only be tested by $H_2{}^{18}O$ tracer experiments, similar to the ones Long and Pritchard[11] performed in their study on the hydrolysis of substituted ethylene oxides.

## Experimental Section

The nmr data were obtained with a Varian Associates HR-60 spectrometer, ir spectra with a Perkin-Elmer 237B grating spectrophotometer, and polarographic data with a modular Heath polarograph. The olefins were Phillips CP grade reagents. Thallium triacetate was prepared according to the literature.[12]

**Epoxidation of Isobutylene and Propylene.**—A 0.65 $M$ slurry of thallic acetate (6 ml) in a solvent consisting of 70% (v/v) tetrahydrofuran, 20% water, and 10% acetic acid were placed in a capped pressure tube.[13] The slurry was stirred and isobutylene was introduced under a pressure of about 1.8 atm at room temperature. After the solids dissolved, the reactor tube was placed in a water bath at 70° and connected by means of 2-mm diameter stainless steel tubing to cooled traps made of capped pressure tubes. The reaction mixture was then sparged with isobutylene at a rate of about 40 ml/min. Most of the solvent, isobutylene oxide, and isobutyraldehyde were collected in the first trap held at 0°, and unreacted isobutylene in the second one held at −78°. Within 30 min, 90% of the thallic acetate was reduced to thallous acetate as determined by iodometric titration. The distillates and reaction mixture were quantitatively analyzed by glc (F & M Model 700, 12-ft column, Carbowax 20M). The oxidation products consisted of isobutylene oxide (82%), 1-acetoxy-2-methyl-2-propanol (15%) (left in reactor), and isobutyraldehyde (3%).

In a similar experiment, the reaction mixture was kept under 2 atm of propylene for 30 min at room temperature and then sparged 15 min at 70°; 60% of the thallium triacetate was reduced. The oxidation product consisted of 72% propylene oxide and 16% acetone; the remainder was 1-acetoxy-2-propanol.

**Preparation of Hydroxythallation Adduct.**—In the case of isobutylene, I was isolated at 0° in 40% yield from a solvent mixture of 80% THF, 10% acetic acid, and 10% water and excess isobutylene as a white crystalline product which could be recrystallized from methanol. The experimental details are the same as in the previous paragraph. I melted and decomposed slowly at 70° to isobutylene and isobutylene oxide in about equal amounts. The elemental analysis indicated one water of crystallization. *Anal.* Calcd for $C_8H_{17}O_6Tl$: C, 23.22; H, 4.11; Tl, 49.44. Found: C, 23.16; H, 3.72; Tl, 49.87.

The infrared spectrum of a mineral oil mull of I showed a broad OH band at 3250 $cm^{-1}$ which is an indication of internal hydrogen bonding. In dry, deuterated dimethyl sulfoxide the peak shifted to 3450 $cm^{-1}$, indicating the displacement of complexed water by dimethyl sulfoxide. The characteristic absorption bands assignable to $\nu_{sym}$ (COO) in the solid state were observed at 1608 (vs) and 1555 $cm^{-1}$ (vs); the $\nu_{sym}$ (COO) bands were found at 1375 (vs) and 1337 $cm^{-1}$ (vs) indicating that the acetate was coordinated in two different ways, one probably a bridged structure.[14] The bands at 500 (m) and 455 $cm^{-1}$ (m) were probably due to the $\rho_r$ (COO) modes. Although the origin of the poorly resolved band at 505 $cm^{-1}$ (w) is uncertain, it may be associated with the Tl–C stretching vibrations. The remaining bands at 412 (m) and 350 $cm^{-1}$ (w) have not been assigned. The spectra were obtained in either Nujol (700–4000 $cm^{-1}$) or in hexachlorobutadienes (250–700 $cm^{-1}$) mulls.

In the proton nmr spectrum of I in deuterated dimethyl sulfoxide, a doublet with the expected large spin–spin coupling constant for the geminal protons appeared.[15] Each of the peaks in this doublet had in itself a doublet character. This character is due to the slightly different coupling of the $^{203}Tl$ and $^{205}Tl$ isotopes to the methylene protons ($J_{^{203}Tl-CH_2}$ = 864 Hz, $J_{^{205}Tl-CH_2}$ = 871.5 Hz). The isotopic difference in the long range $Tl-CH_3$ coupling is not resolved although the peaks show broadening ($J_{Tl-CH_3}$ = 101 Hz). The chemical shifts of the protons are $\delta$ 2.70 and 1.38 ppm, respectively.

**Registry No.**—I, 27621-79-0; thallium triacetate, 2570-63-0; isobutylene, 115-11-7; propylene, 115-07-1.

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[9] F. R. Jensen and R. J. Ouellette, *J. Amer. Chem. Soc.*, **83**, 4478 (1961).

[10] A. A. Frost and R. G. Pearson, "Kinetic and Mechanism," Wiley, New York, N. Y., 1961, p 350.

[11] F. L. Long and J. G. Pritchard, *J. Amer. Chem. Soc.*, **78**, 2663 (1956).

[12] L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Vol. I, Wiley, New York, N. Y., 1967, p 1150.

[13] D. F. Shriver, "The Manipulation of Air-sensitive Compounds," McGraw-Hill, New York, N. Y., 1969, p 157.

[14] N. Kurosawa and R. Okawasa, *J. Organometal. Chem.*, **19**, 253 (1969).

[15] F. A. L. Anet, *Tetrahedron Lett.*, 3399 (1964); J. P. Maher and D. F. Evans, *J. Chem. Soc.*, 637 (1965).

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# Amidrazones. I. The Methylation of Some Amidrazones and Hydrazide Imides

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The inner salt 1 has been jointly proposed by Professor M. S. Gibson and us[2] as an intermediate to ac-

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[1] American Chemical Society Petroleum Research Fund Scholar.

[2] M. S. Gibson, R. F. Smith, P. D. Callaghan, A. C. Bates, J. R. Davidson, and A. J. Battisti, *J. Chem. Soc. C*, 2577 (1967).