2.4–2.8 (m, 7, aromatic and NH, one proton exchangeable with D_2O), 5.7–6.2 (pair of overlapping quartets, 4, methylene coupled to phosphorus), 8.77 (t, 6, methyl).

Anal. Calcd for $C_{24}H_{28}NO_3P$: C, 71.5; H, 5.5; N, 3.5; P, 7.7. Found: C, 71.6; H, 5.5; N, 3.5; P, 7.9.

1-Aminoperylene (2b).—Reduction of 1-nitroperylene (**2a**) was performed as described[1] for 3-nitroperylene, except that 1,2-dimethoxyethane proved to be a better solvent. A solution was prepared by heating 1.0 g (0.0034 mol) of 1-nitroperylene in 50 ml of 1,2-dimethoxyethane. About 100 mg of 10% palladium on charcoal was added, followed by 2 ml of 64% hydrazine. After the mixture had been heated for 3 min, the catalyst was removed and the solvent was distilled to leave a yellow solid. Recrystallization from a mixture of benzene (soluble) and ethanol gave 0.75 g (83%) of amine **2b**, mp 195–197°.

Anal. Calcd for $C_{20}H_{13}N$: C, 89.9; H, 4.9; N, 5.2. Found: C, 89.5; H, 4.5; N, 5.0.

The 3-amino compound[1] **1b** was prepared in better yield by using this solvent in place of ethanol.

Registry No.—**1a**, 20589-63-3; **1b**, 20492-13-1; **2a**, 35337-20-3; **2b**, 35337-21-4; **3**, 35337-22-5; **4**, 35337-23-6; perylene, 198-55-0.

Thallium in Organic Synthesis. XXXV. Oxidation of Cyclohexanones to Adipoins Using Thallium(III) Nitrate[1,2]

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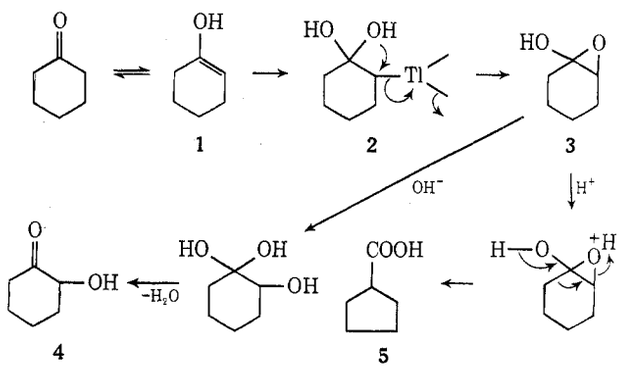
There are only four reports describing the reactions of cyclohexanones with thallium(III) salts. Oxidation with thallium(III) acetate in hot acetic acid has been found to result in α-acetoxylation in low yield,[3,4] but conflicting claims have been made as to the products formed using thallium(III) perchlorate in aqueous acidic media. Littler reported that cyclohexanone was converted first into adipoin and then into cyclohexane-1,2-dione.[5] In a later study, however, Wiberg and Koch found that the major product was cyclopentanecarboxylic acid (75%), and that only 3% of adipoin was obtained. They also showed that adipoin did not serve as the precursor for the ring-contracted product.[6] In view of this apparent duality in reaction pathway we have investigated the reaction of cyclohexanone with thallium(III) nitrate (TTN).[7]

Oxidation of cyclohexanone with TTN in acetic acid at room temperature proceeded rapidly, and precipitation of thallium(I) nitrate was complete in a few minutes. Filtration and neutralization of the filtrate with aqueous sodium bicarbonate solution followed by extraction with ether gave adipoin in 84% yield. This result at first sight confirmed Littler's claim; closer investigation of the reaction, however, revealed that the nature of the product formed on oxidation was temperature dependent. Thus, if oxidation was performed at room temperature, the thallium(I) nitrate was removed by filtration, and the filtrate was heated above about 40° for a few minutes, no adipoin was obtained. The sole product isolated, again in 84% yield, was cyclopentanecarboxylic acid.

That there were indeed two different reaction pathways was readily proved as follows. Oxidation of cyclohexanone was carried out as described above. The filtrate obtained after removal of the thallium(I) nitrate was divided into two equal portions. One of these was treated with aqueous sodium bicarbonate and gave adipoin (**4**). The other was heated for a few minutes and gave cyclopentanecarboxylic acid (**5**). Each product was uncontaminated by the other, thus indicating the intermediacy of a common precursor. Moreover, this precursor cannot be an organothallium derivative, as thallium(I) nitrate had been recovered in almost quantitative yield. It would therefore appear from the above results that both Littler and Wiberg and Koch may have been correct with respect to the products they isolated. There is little doubt, however, that the mechanism postulated by Wiberg for formation of the cyclopentanecarboxylic acid is incorrect, as it involved the intermediacy of an organothallium derivative.

We suggest that the mechanisms of these transformations are best represented as shown in Scheme I, and

SCHEME I



that the common precursor to **4** and to **5** is the epoxy enol **3**. Oxythallation of enols (*cf.* **1** → **2**) is a known process,[8] while Kruse and Bednarski have recently shown that epoxides may be prepared by oxidation of olefins with thallium(III) acetate.[9] Not unexpectedly, all attempts to isolate **3** from the reaction mixture were unsuccessful. One noteworthy feature of the mechanism shown in Scheme I is that water is involved as nucleophile in the oxythallation step; this must be the

(1) Part XXXIV: A. McKillop, O. H. Oldenziel, B. P. Swann, E. C. Taylor, and R. L. Robey, *J. Amer. Chem. Soc.*, in press.

(2) We gratefully acknowledge partial financial support of this work by Eli Lilly and Company, the CIBA Pharmaceutical Company, and G. D. Searle and Company.

(3) H.-J. Kabbe, *Justus Liebigs Ann. Chem.*, **656**, 204 (1962).

(4) S. Uemura, T. Nakano, and K. Ichikawa, *J. Chem. Soc. Jap.*, **88**, 1111 (1967).

(5) J. S. Littler, *J. Chem. Soc.*, 827 (1962).

(6) K. B. Wiberg and W. Koch, *Tetrahedron Lett.*, 1779 (1966); we have confirmed this result.

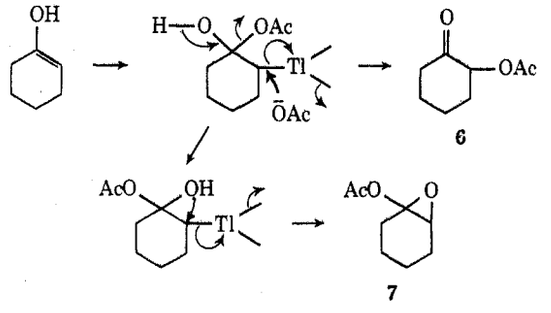
(7) A. McKillop, J. D. Hunt, E. C. Taylor, and F. Kienzle, *ibid.*, 5275 (1970).

(8) A. McKillop, B. P. Swann, and E. C. Taylor, *J. Amer. Chem. Soc.*, **93**, 4919 (1971).

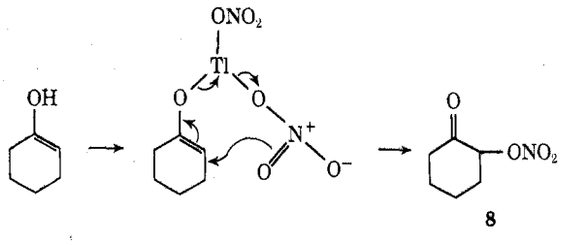
(9) W. Kruse and T. M. Bednarski, *J. Org. Chem.*, **36**, 1154 (1971).

water of crystallization of TTN.[10] The mechanisms outlined in Scheme I are also consistent with the observations that neither 2-acetoxycyclohexanone (**6**),[11] 1-acetoxycyclohexene oxide (**7**),[12] nor 2-oxocyclohexyl nitrate (**8**)[13] is the immediate precursor to **4** and **5**. Plausible mechanisms can be postulated both for formation of these intermediates (Schemes II and III)

SCHEME II



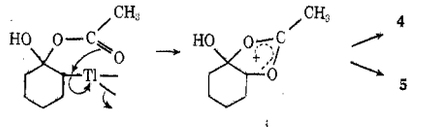
SCHEME III



and for their subsequent conversion into **4** and **5**. Each of these compounds was therefore prepared independently and subjected to the isolation procedures used in the oxidation reaction. Both 2-acetoxycyclohexanone and 2-oxocyclohexyl nitrate were recovered virtually unchanged from both aqueous sodium bicarbonate solution and hot acetic acid.[14] Treatment of 1-acetoxycyclohexene oxide with aqueous sodium bicarbonate solution resulted in quantitative hydrolysis to adipoin, but all attempts to induce ring contraction of **7** to cyclopentanecarboxylic acid were unsuccessful.

Examination of the reactions of a wide variety of ketones with TTN in acetic acid revealed a remarkable specificity with respect to ketone structure. Thus, oxidation of 4-methyl- and 4-*tert*-butylcyclohexanone gave the corresponding adipoins in 98 and 97% yield, respectively. On the other hand, complex mixtures of products were obtained with 2- and 3-substituted cyclohexanones, with 5-, 7- and 12-membered cycloalkanones, and with aliphatic ketones.

(10) TTN is a trihydrate, and participation of the water of crystallization in oxythallation has been noted previously: A. McKillop, J. D. Hunt, R. D. Naylor, and E. C. Taylor, *J. Amer. Chem. Soc.*, **93**, 4918 (1971). It has been suggested by a referee that the nucleophile could alternatively be acetic acid rather than water. This would lead to the acetoxonium ion (i) which could serve as the precursor to **4** and **5**.



i

(11) G. W. K. Cavill and D. H. Solomon, *J. Chem. Soc.*, 4426 (1955).

(12) M. Mousseron and R. Jacquier, *Bull Soc. Chim. Fr.*, 698 (1950).

(13) J. E. Franz, J. F. Herber, and W. S. Knowles, *J. Org. Chem.*, **30**, 1488 (1965).

(14) 2-Oxocyclohexyl nitrate hydrolyzed to the extent of about 10% on treatment with aqueous sodium bicarbonate solution.

Experimental Section[15]

Preparation of Adipoin.—TTN (18 g, 0.04 mol) was added to a solution of 4 g (0.04 mol) of cyclohexanone in 40 ml of acetic acid. Thallium(I) nitrate precipitated almost immediately. The inorganic salt was removed by filtration, the filtrate was neutralized with sodium bicarbonate, and the solution was allowed to stand overnight. It was then extracted with chloroform, and the extracts were washed with 2 *N* sulfuric acid and water and dried (Na_2SO_4). Evaporation of the solvent gave a colorless liquid which slowly solidified on standing. Crystallization of the solid from ethanol gave 3.83 g (84%) of adipoin dimer[16] as beautiful, colorless needles, mp 112.5–113.5° (lit.[17] mp 113°), identical in all respects with a genuine sample prepared by hydrolysis of 2-chlorocyclohexanone.[17]

4-Methyl-2-hydroxycyclohexanone dimer was obtained in 98% yield in exactly the same way from 4-methylcyclohexanone as colorless needles from ethanol, mp 163°.

Anal. Calcd for $C_{14}H_{24}O_4$: C, 65.60; H, 9.44. Found: C, 65.46; H, 9.54.

4-*tert*-Butyl-2-hydroxycyclohexanone dimer was prepared similarly in 97% yield from 4-*tert*-butylcyclohexanone as colorless needles from ethanol, mp 116–118°.

Anal. Calcd for $C_{20}H_{36}O_4$: C, 70.55; H, 10.66. Found: C, 70.33; H, 10.45.

Ring Contraction of Cyclohexanone to Cyclopentanecarboxylic Acid.—Oxidation of cyclohexanone was conducted as described above, and the filtrate obtained after removal of the thallium(I) nitrate was heated gently under reflux for 30 min. Most of the acetic acid was then removed by distillation under reduced pressure, and the residue was neutralized with a solution of sodium bicarbonate. The resulting solution was washed with ether, reacidified with concentrated hydrochloric acid, and extracted with chloroform and the extracts were dried (Na_2SO_4). Removal of the solvent left a pale yellow liquid which on distillation gave 3.84 g (84%) of pure cyclopentanecarboxylic acid, bp 83–85° (5 mm) [lit.[18] bp 102° (14 mm)]. Identity of the acid was confirmed by conversion to the methyl ester and subsequent comparison of ir, nmr, and glpc data with those of a genuine sample.

Registry No.—TTN, 13746-98-0; 4-methyl-2-hydroxycyclohexanone dimer, 35326-28-4; 4-*tert*-butyl-2-hydroxycyclohexanone dimer, 35326-29-5.

(15) Melting points were determined using a Kofler hot-stage microscope melting point apparatus and are uncorrected. Where appropriate, identity of compounds was confirmed by comparison of ir spectra, determined on a Perkin-Elmer Model 257 grating infrared spectrophotometer using the normal Nujol mull or liquid film techniques.

(16) Dimerization of acyloins to 1,4-dioxanes is a general phenomenon: R. Jacquier, *Bull. Soc. Chim. Fr.*, 83 (1950). The acyloins may be regenerated from the dimers by treatment with dilute acid.

(17) P. D. Bartlett and G. F. Woods, *J. Amer. Chem. Soc.*, **62**, 2933 (1940).

(18) H. Rupe and W. Lotz, *Justus Liebigs Ann. Chem.*, **327**, 184 (1903).