vinyl ether bands at 1630, 1260, and 1150 cm^{-1}.[10] A long-wavelength absorption at 304 nm (log ϵ 4.51) in the ultraviolet is consistent with the assigned structure and inconsistent with the presence of only styrene type chromophores.

In a few runs, a highly fluorescent polymer $(C_{16}H_{12})_n$ was also found. It melted sharply at ~273° and it was thermally stable to about 225°, but pyrolysis at 285° yielded 1,3,5-triphenylbenzene together with several other unidentified products.

Experimental Section

The nmr spectra were run on a Varian A-60 spectrometer with tetramethylsilane (TMS) as an internal standard. Ultraviolet spectra were determined on a Cary 14 spectrophotometer. Infrared spectra were taken in potassium bromide discs on either a Perkin-Elmer 337 or 521 spectrophotometer. Melting points were taken on a Kofler hot stage apparatus and are uncorrected.

1,2,5,7,8,11-Hexaphenylpentacyclo[8.2.0.0^{2,9}.0^{3,8}.0^{4,7}]dodeca-5,11-diene (V).—The crude product (8.0 g) from the potassium *tert*-butoxide driven elimination reaction of 25.0 g (43.4 mmol) of 1,3-diphenyl-2,4-cyclobutanebis(trimethylammonium) iodide (I)[2,11] was carefully chromatographed on an alumina column using increasing amounts of ether in benzene as the eluent. From the early fractions (0.5–10% ether), 0.369 g (1.3 mmol, 3%) of butadiene VI was isolated; from the middle fractions (15–19% ether), 3.46 g (8.4 mmol, 39.2%) of the cyclooctatetraene formed from II was obtained; and from the fractions with 20–25% ether, 2.55 g (6.3 mmol, 28%) of the cyclooctatetraene derived from III containing some V was obtained. Recrystallization of this material from methylene chloride–ethanol followed by trituration of the solid with cold hexane gave a residue of 0.54 g (0.89 mmol, 2.0%) of compound V as white microcrystals. In other runs, yields of 0–2% were obtained. Crystallization of V from methylene chloride–ethanol gave tiny white plates: mp 220.5° dec; uv λ_{max}^{ether} 263 nm (log ϵ 4.59), 255 sh (4.56), 271 (4.56), 285 sh (4.20), 293 (3.60); nmr, see text.

Anal. Calcd for $C_{48}H_{36}$: C, 94.08; H, 5.92; mol wt, 612.8. Found: C, 94.08; H, 5.81; mol wt, 608 (Signer–Barger).

Pyrolysis of Compound V.—Compound V (38.89 mg, 0.0636 mmol) was sublimed at 200° (15 μ). The total sublimate was then carefully washed from the cold finger of the sublimator and the solvent was removed to give 39.5 mg (0.129 mmol, 101%) of 1,2,4-triphenylbenzene. Ultraviolet and infrared comparisons as well as melting points and mixture melting points proved the identity of the product. Thin layer chromatography (silica gel) using 1:4 benzene–petroleum ether (bp 30–60°) gave a single spot, R_f 0.46.

Small amounts of the trimer V were heated in evacuated capillaries at various temperatures for different time intervals to detect possible intermediates. At 155° for 15 min, no change was found by tlc but at 180°, three compounds were observed: a possible intermediate at R_f 0.22, starting material V, and 1,2,4-triphenylbenzene. At 240° for 30 hr, only 1,2,4-triphenylbenzene was detected.

Hydrogenation of Compound V.—V (25 mg, 0.041 mmol) was hydrogenated in 5 ml of ethyl acetate containing 20 mg of prereduced 10% Pd/C. Uptake of hydrogen (corrected) was 1.6 equiv in 15 min and 1.95 equiv in 1 hr. At the end of 17 hr, no additional hydrogen had been absorbed.

1,3-Diphenyl-4-*tert*-butoxy-1,3-butadiene (VI).—From the earliest fractions of the chromatography above (5–10% ether in hexane), 369 mg (1.3 mmol, 3.0%) of compound VI was isolated after removal of the solvent. Crystallization from isopentane gave colorless needles: mp 101–103°; uv λ_{max}^{MeOH} 230 nm (log ϵ 4.12) and 303 (4.51); ir 3030 (w), 2980 (s), 2940 (w), 1630 (s), 1260 (s), 1150 (vs), and 1105 cm^{-1} (s). A qualitative test for nitrogen was negative.

Anal. Calcd for $C_{20}H_{22}O$: C, 86.28; H, 7.97. Found: C, 86.33; H, 8.03.

Miscellaneous Products.—In several runs, a highly fluorescent white solid was isolated in the chromatography fractions immediately following the elution of 1,3,5,7-tetraphenylcyclooctatetraene (derived from II) with yields up to 1.5% (based on a trimeric structure). After crystallization from dichloromethane–ethanol to a constant melting point, white plates were obtained, mp 273.0–273.5°. The ultraviolet spectrum had a single maximum at 267 nm (log ϵ 4.32 based on the molecular weight for a trimer, 612.8).

Anal. Calcd for $(C_{16}H_{12})_n$: C, 94.08; H, 5.92. Found: C, 94.10; H, 6.02; mol wt, 426, 508 (micro Rast).

The compound sublimed unchanged at 225° (15 μ) but at 285° it was converted into at least four different compounds; one was identified as 1,3,5-triphenylbenzene by tlc (color formation and R_f at 0.48; silica gel with 1:4 benzene–petroleum ether).

In later chromatographic fractions using solvent containing more than 25% ether, extremely viscous, highly colored oils remained on evaporation of the solvent. In the infrared, these oils showed strong carbonyl absorption at 1700–1750 cm^{-1}. A random fraction from one run was chosen for analysis (100% ether fraction).

Anal. Found: C, 90.70; H, 6.08; N, 0.00.

Registry No.—IV polymer, 36812-97-2; V, 36789-10-3; VI, 36789-11-4.

Acknowledgment.—We thank the Petroleum Research Fund administered by the American Chemical Society (PRF 328-A) for support of this work and Dr. J. D. Rose (Imperial Chemical Industries Ltd., Manchester, England) for a generous sample of 1,2,4-triphenylbenzene.

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[10] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Wiley, New York, N. Y., 1958, p 115.

[11] R. L. Stern, Ph.D. Thesis, The Johns Hopkins University, 1963; Earl W. Friend, Jr., Ph.D. Thesis, The Johns Hopkins University, 1967.

Thallium in Organic Synthesis. XXXI. Oxidative Cleavage of Glycols by Thallium Salts[1]

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Glycol cleavage reactions are of considerable utility in both synthesis and degradation, and from a practical point of view periodate and lead(IV) acetate are generally the oxidants of choice.[2,3] A wide range of oxidants has been investigated with respect to glycol cleavage and Rigby has defined the efficiency of such reagents as oxidants "which concern elements which (a) can reasonably be envisaged as capable of forming a preliminary cyclic compound with the glycol, and (b) exist in two stable oxidation states which are two valence units apart, the lower representing a substance which is not an oxidizing reagent under ordinary conditions [Pb(II) or Bi(III)] or which no longer fulfills condition a (the IO_3^- ion)."[4] According to this definition, thallium(III) salts, which are isoelectronic with lead(IV) salts, should function as efficient glycol

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[1] Part XXX: E. C. Taylor, R. L. Robey, and A. McKillop, *Angew. Chem.*, **84**, 60 (1972); *Angew. Chem., Int. Ed. Engl.*, **11**, 48 (1972).

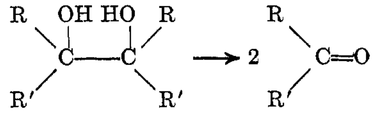
[2] A. S. Perlin in "Oxidation: Techniques and Applications in Organic Synthesis," R. L. Augustine, Ed., Marcel Dekker, New York, N. Y., 1969, pp 189–212.

[3] C. A. Bunton in "Oxidation in Organic Chemistry," K. B. Wiberg, Ed., Academic Press, New York, N. Y., 1965, pp 367–407.

[4] W. Rigby, *J. Chem. Soc.*, 1907 (1950).

TABLE I

OXIDATIVE CLEAVAGE OF GLYCOLS WITH THALLIUM SALTS



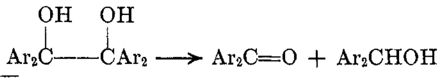
Registry no.	Compd	R	R′	Oxidant[a]	Aldehyde or ketone yield, %[b]
492-70-6	1	H	C_6H_5	A	61
5132-85-4	2	CH_3	C_6H_5	A	63
464-72-2	3	C_6H_5	C_6H_5	A	91
				B	85
2002-32-8	4	C_6H_5	2-$CH_3C_6H_4$	A	83
				B	70
808-12-8	5	C_6H_5	4-$CH_3C_6H_4$	A	86
				B	83
912-17-4	6	C_6H_5	4-ClC_6H_4	A	84
				B	90
3073-51-6	7	Fluorenone pinacol		A	89
				B	95
6272-59-9	8	Xanthone pinacol		A	91
				B	90

[a] A = $Tl(NO_3)_3 \cdot 3H_2O/CH_3COOH$; B = $TlOC_2H_5/C_2H_5OH$. [b] Based on pure redistilled or recrystallized material.

cleavage reagents, since both of the criteria a and b used by Rigby are satisfied. Furthermore, the mechanisms of oxidation postulated for lead(IV) acetate glycol cleavage are, theoretically, equally applicable to thallium(III) salts. There is only one reference in the literature to the reactions of glycols with a thallium(III) salt. Kabbe reported that treatment of glycols with thallium(III) acetate resulted in complete reduction of the inorganic reagent. He was, however, unable to isolate any products of oxidation of the glycols.[5]

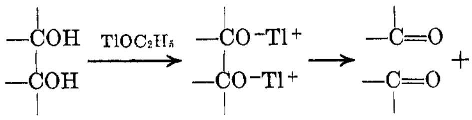
We have examined the reactions of a wide variety of glycols with thallium(III) acetate, trifluoroacetate (TTFA), and nitrate (TTN) under different reaction conditions and have found that certain types of glycols are cleaved smoothly with all three salts. The most efficient reagent system in terms of product yield and rate of reaction was a solution of TTN in acetic acid, but glycol cleavage occurred only with substrates which contained vicinal aromatic substituents. Thus, irrespective of the stereochemistry of the hydroxyl groups, no oxidation was observed with the following compounds: ethylene glycol, pinacol, pinacolone pinacol, diethyl tartrate, 2,3-dihydroxy-2-methyl-3-phenylbutane, bicyclopentyl-1,1′-diol, bicyclohexyl-1,1′-diol, *cis*- and *trans*-1,2-dihydroxycyclohexane, 1,2-dihydroxycyclododecane, and *cis,exo*-2,3-dihydroxycamphane. With substrates which contained at least two aromatic substituents, glycol cleavage took place smoothly. Yield data are summarized in Table I.

It has been known for over 30 years that treatment of certain tetraaryl-substituted glycols with alkali metal alkoxides in ether–benzene solution results in carbon–carbon bond cleavage and formation of equal quantities of the corresponding ketone and secondary alcohol (eq 1).[6] These reactions, which were originally thought to be free radical in nature, have recently been reexamined by Schenck and his coworkers and shown to proceed by both ionic and free-radical pathways.[7] We have found that thallium(I) ethoxide in ethanol reacts smoothly with tetraaryl-substituted glycols, but the reactions are significantly different from those of the alkali metal alkoxides. Thus, bond cleavage occurs virtually instantaneously at 50° in ethanol, thallium(I) ethoxide is reduced quantitatively to thallium metal, and the corresponding diaryl ketones are formed in high yield. Conversion data are summarized in Table I.



$$Ar_2C(OH)-C(OH)Ar_2 \longrightarrow Ar_2C{=}O + Ar_2CHOH \qquad (1)$$

Unlike the reactions with other metal alkoxides, very little (0–14%) of the corresponding benzhydrol was formed in the thallium(I) oxidations. Conversion of the glycol into the ketone represents a two-electron oxidation, while reduction of thallium(I) to thallium(0) is a one-electron process. We suggest that the most probable mechanism is formation of the dithallium salt followed by rapid, concerted radical decomposition to products (eq 2). Attempts to detect radical intermediates, however, were unsuccessful. In none of the reactions were the characteristic red-blue colorations due to ketyl radicals observed,[6] and no evidence for radical species was obtained by esr spectroscopy. Moreover, acrylamide is an efficient radical trap,[8] and addition of this compound to glycol fission reactions known to proceed by free-radical pathways has been shown to result in almost total suppression of oxidation.[8] When acrylamide was added to a mixture of thallium(I) ethoxide and benzopinacol, however, the reduction in yield of benzophenone was only 13%. Consequently, it appears that if radical



$$\begin{array}{l}-\overset{|}{C}OH\\ -\underset{|}{C}OH\end{array} \xrightarrow{TlOC_2H_5} \begin{array}{l}-\overset{|}{C}O^-Tl^+\\ -\underset{|}{C}O^-Tl^+\end{array} \longrightarrow \begin{array}{l}-\overset{|}{C}{=}O\\ -\underset{|}{C}{=}O\end{array} + 2Tl \qquad (2)$$

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

[6] W. E. Bachmann, *J. Amer. Chem. Soc.*, **55**, 355 (1933).

[7] G. O. Schenck, G. Matthias, M. Pape, M. Cziesla, G. von Bunau, E. Roselius, and G. Koltzenburg, *Justus Liebigs Ann. Chem.*, **719**, 80 (1968).

[8] W. S. Trahanovsky, L. H. Young, and M. H. Bierman, *J. Org. Chem.*, **34**, 869 (1969).

intermediates are involved they must be extremely short lived, and in no sense "free" radicals.

Experimental Section[9]

Starting Materials.—Compounds **1** and **3** (Table I) were commercial samples and were purified prior to use. Compounds **2** and **4–8** were prepared by bimolecular coupling of the appropriate ketones with anhydrous magnesium iodide according to the procedure described by Gomberg and Bachmann.[10]

General Procedure for Glycol Cleavage with TTN.—A mixture of 2.74 mmol of the glycol and 2.74 mmol of TTN in 25 ml of acetic acid was stirred and heated at 75° for 30 min. The reaction mixture was then cooled, diluted with 50 ml of water, and extracted with chloroform, and the extracts were washed with saturated aqueous sodium bicarbonate solution. Evaporation of the dried chloroform extract gave the crude product, which was freed from traces of inorganic thallium salts by passage through a short column of alumina using chloroform as eluent. The pure ketone was then obtained by crystallization or distillation of the concentrated eluent.

General Procedure for Glycol Cleavage Using Thallium(I) Ethoxide.—Thallium(I) ethoxide (2.74 mmol) was added to a suspension of 2.74 mmol of the glycol in 25 ml of ethanol and the mixture was gently heated to about 50°. After a few seconds thallium metal was deposited. After 5 min excess powdered potassium iodide was added to remove traces of thallium(I) salts as thallium(I) iodide. The reaction mixture was filtered, concentrated, and passed through a short column of alumina using chloroform as eluent. Concentration of the eluate gave the crude product, which was purified as described above.

Direct nmr examination of the crude reaction product obtained after chromatography showed in some cases a small peak at *ca.* τ 4.5 due to the methine proton of the corresponding benzhydrol. The amount of this by-product was easily determined from the relative integrations of the aromatic and methine proton areas. Standard control experiments established that benzhydrols are oxidized to benzophenones only very slowly by thallium(I) ethoxide; the alcohol did not therefore serve as precursor to the ketone.

Registry No.—$Tl(NO_3)_3$, 13746-98-0; $TlOC_2H_5$, 20398-06-5.

[9] Melting points were determined on a Kofler hot-stage melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model PE 237 grating infrared spectrophotometer using the normal liquid film and Nujol mull techniques. Nuclear magnetic resonance spectra were recorded in carbon tetrachloride solution, using tetramethylsilane as internal standard, on a Perkin-Elmer R12 60-MHz spectrometer.

[10] M. Gomberg and W. E. Bachmann, *J. Amer. Chem. Soc.*, **49**, 236 (1927).

Ethyl 3-Oxo-2,2-dimethylcyclobutanecarboxylate

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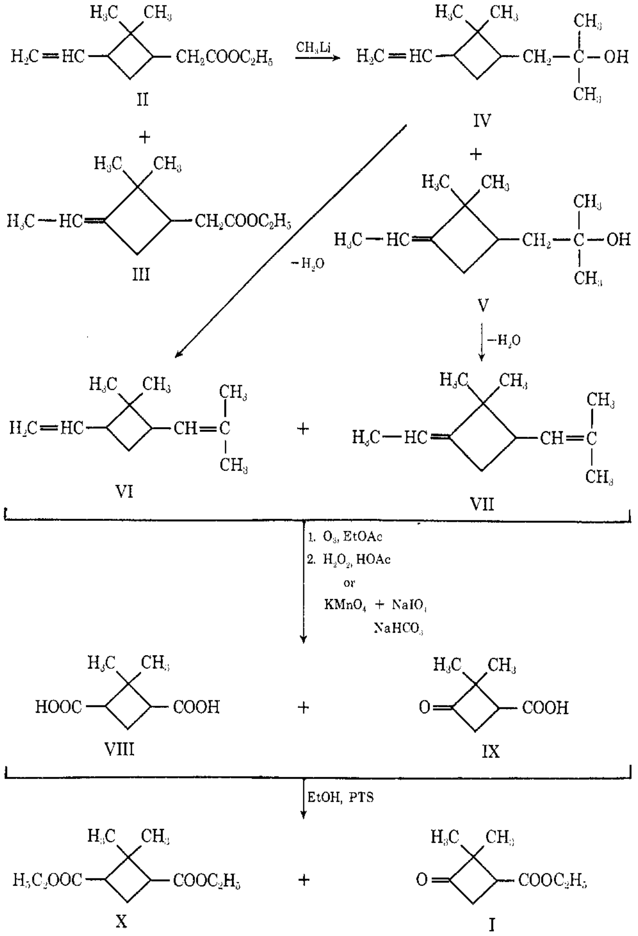
In connection with work toward the synthesis of bridgehead-substituted bicyclobutanes[1] as monomers for polymers containing cyclobutane rings, the synthesis of ethyl 3-oxo-2,2-dimethylcyclobutanecarboxylate (I) from readily accessible α-pinene and its degradation products was investigated.

A mixture of ethyl pinenates [ethyl 2,2-dimethyl-3-vinylcyclobutaneacetate (II) and ethyl 2,2-dimethyl-3-ethylidene cyclobutaneacetate (III)] described by Park, *et al.*,[2] formed the starting material for the synthesis of ethyl 3-oxo-2,2-dimethylcyclobutanecarboxylate. Reaction of a 60:40 mixture of ethyl pinenates with methyllithium afforded a mixture of 1-(2-methyl-2-hydroxypropyl)-3-vinyl-2,2-dimethylcyclobutene (IV) and 1-(2-methyl-2-hydroxypropyl)-3-ethylidene-2,2-dimethylcyclobutane (V). The mixture of alcohols was dehydrated using anhydrous oxalic acid to give a mixture of 1-(2,2-dimethylvinyl)-3-vinyl-2,2-dimethylcyclobutane (VI) and 1-(2,2-dimethylvinyl)-3-ethylidene-2,2-dimethylcyclobutane (VII). Oxidation of this mixture with sodium periodate–potassium permanganate[3] as well as by ozonolysis followed by cleavage of the ozonide with hydrogen peroxide and acetic acid afforded a mixture of norpinic acid (VIII) and 3-oxo-2,2-dimethylcyclobutanecarboxylic acid (IX), which was esterified with ethanol and p-toluenesulfonic acid to give a mixture of diethyl norpinate (X) and ethyl 3-oxo-2,2-dimethylcyclobutanecarboxylate (I). Separation was effected by fractional distillation and the keto ester was characterized as its 2,4-dinitrophenylhydrazone derivative.



Experimental Section

Mixture of 1-(2-Methyl-2-hydroxypropyl)-3-vinyl-2,2-dimethylcyclobutane (IV) and 1-(2-Methyl-2-hydroxypropyl)-3-ethylidene-2,2-dimethylcyclobutane (V).—Methyllithium was prepared by the addition of methyl iodide (42.6 g, 0.3 mol) in anhydrous ether (75 ml) to lithium wire (4.2 g, 0.6 g-atom) in anhydrous ether (150 ml). The lithium was contained in a three-necked

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[1] H. K. Hall, Jr., C. D. Smith, E. P. Blanchard, Jr., S. C. Cherkofsky, and J. B. Sieja, *J. Amer. Chem. Soc.*, **93**, 121 (1971).

[2] J. D. Park, R. L. Settine, and G. W. Hedrick, *J. Org. Chem.*, **27**, 902 (1962).

[3] R. V. Lemiux and E. Von Rudloff, *Can. J. Chem.*, **33**, 1701 (1955).