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CLEAVAGE OF CYCLOPROPENE RING BY MEANS OF TRANSITION METAL SALTS

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Abstract—The oxidative ring cleavage of 1,3,3-trimethylcyclopropene (**1**) with $Hg(OAc)_2$ in methylene chloride gives 1,1-diacetoxy-2,3-dimethyl-2-butene (**5**). The reaction of **1** with $Tl(OAc)_3$ or $Pb(OAc)_4$ gives in addition to **5**, 3,3-diacetoxy-2-methylpropene and 2-acetoxy-4-methyl-1,3-pentadiene. These products are explained by assuming the addition of metal acetates onto the double bond of **1** followed by the ring cleavage to give vinylcarbene-metal acetate complexes or inverse ylides. The reaction of benzocyclopropene (**14**) with $Hg(OAc)_2$ affords bis(*o*-acetoxymethylphenyl)mercury as a single product. Cyclopropene ring cleavage of **14** effected by Cu(II) or Ag(I) acetate furnishes 9,10-dihydrophenanthrene and benzyl acetate. These products are ascribed to the intermediary vinylcarbene-metal acetate complexes produced from **14**.

The σ-bonds of highly strained polycyclic compounds such as bicyclobutane are easily cleft by the action of transition metal species to afford carbene-metal complexes as reaction intermediates in a formal retro (carbene addition) manner.[1-4] Little is known on such metal-catalysed reaction of cyclopropenes, but 1,2,3-triphenyl-substituted one has been reported to give indenes *via* 1,3-diradical intermediates.[5,6] The present report describes the ring cleavage of 1,3,3-trimethylcyclopropene (**1**) and benzocyclopropene (**14**) in the presence of transition metal acetates.*

The oxidative ring cleavage of **1** *with transition metal acetates.*[8] The reaction of **1** with $Hg(OAc)_2$ (1:1 or 1:2 molar ratio) in methylene chloride at room temp for 18 hr gave a single product, 1,1-diacetoxy-2,3-dimethyl-2-butene (**5**), in a 65% yield (based on the starting amount of **1**). Treatment of **1** with $Tl(OAc)_3$ (1:1 molar ratio) at room temp for 16 hr afforded **5** (50%) and 3,3-diacetoxy-2-methylpropene (**9**) (20%). When the molar ratio was taken to be 1:2, the reaction products were **5** (20%) and **9** (40%). These products were isolated by GLC separation. The ring cleavage of **1** was effected also by $Pb(OAc)_4$ at room temp to give **5** (40%), **9** (a trace amount) and 2-acetoxy-4-methyl-1,3-pentadiene (**10**) (5%) after 17 hr reaction. The product distribution was not affected by the molar ratio of the components (1:1 or 1:2).

The formation of **5** is ascribed to the ring cleavage of **1** *via* the path *a* in Scheme 1. We suppose that the electrophilic attack of metal acetates onto the double bond of **1** furnishes the adducts **2** and **3**,[9] the latter of which then experiences ring cleavage to give a formal carbene-$M(OAc)_n$ complex **4** (M = Hg, Tl or Pb). This is an inverse ylide and should furnish **5** under liberation of $:M(OAc)_{n-2}$.†‡ The path *b* involves the conversion of the complex **2** into another carbene complex **7**, whose transformation to **10** is explained by assuming the intermediary stage **11**.

Furthermore, the complex **7** possibly gives rise to an intermediate, 4,4-diacetoxy-2-methyl-2-pentene (**8**), whose second acetoxymetallation[11] affords **12** or alternatively **13**. The following cleavage as indicated would account for **9**. The fate of acetoxymethylcarbene is not clear. The absence of such cleavage in **5** is ascribed to the tetrasubstitution of the olefinic bond and to the resulting congestion.

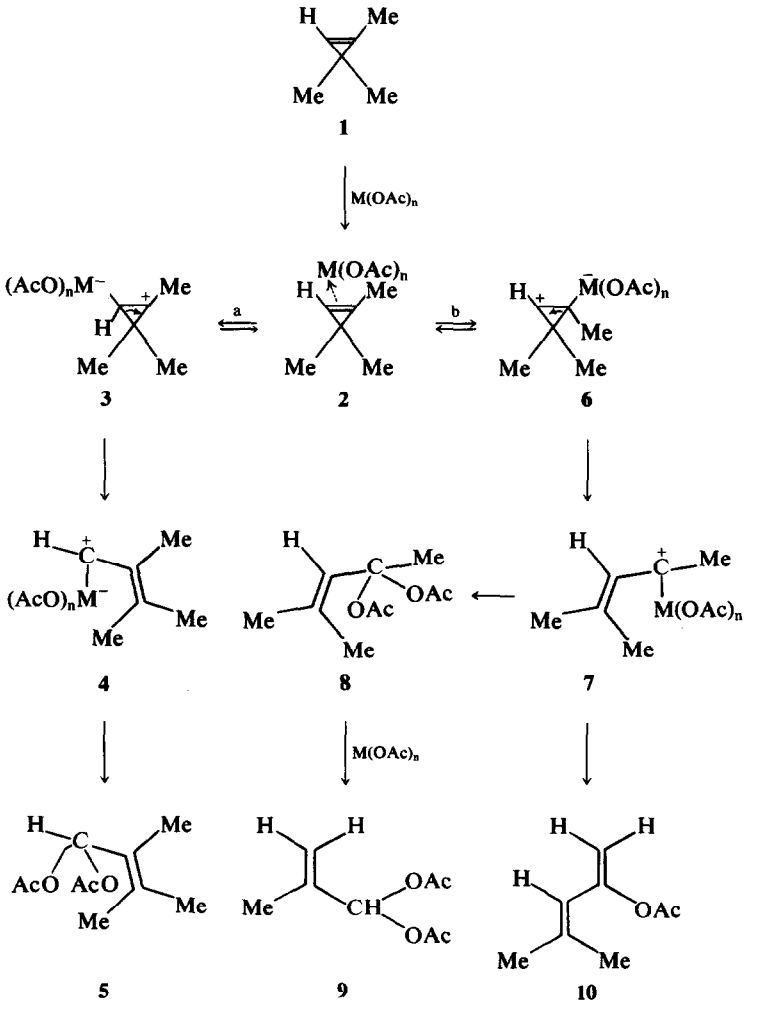
The ring cleavage of benzocyclopropene (**14**) *with transition metal acetates.* Benzocyclopropene derivatives are recorded to undergo iodine-addition, hydrogenation in the presence of PtO_2[12] or thermal ring cleavage *via* 1,3-diradical,[13] but reactions with metal species are unknown.

The reaction of **14** with $Hg(OAc)_2$ in methylene chloride at room temp afforded an acetoxymercurial, bis(*o*-acetoxymethylphenyl)mercury (**19**), in an 80% yield. Compound **19** was identified by spectral and analytical data, and by bromination to give *o*-bromobenzyl acetate and *o*-bromobenzyl bromide. Incidentally, the photolysis of **19** in benzene afforded *o*-phenylbenzyl acetate and benzyl acetate. The reaction of **14** with $Cu(OAc)_2$ in ether at room temp gave 9,10-dihydrophenanthrene (**22**) (40%) and benzyl acetate (15%). The presence of isomeric 9,10-dihydroanthracene

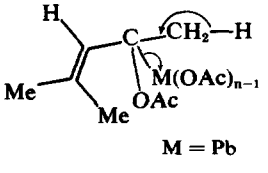
*Part of this paper was published in a preliminary form.[7]

†The reaction of **1** with Cu(I)Cl-acrylonitrile is recorded to afford 2,3,6,7-tetramethylocta-2,4,6-triene *via* vinylcarbene-copper complex. See ref 10.

‡Treatment of **1** with Ag(I)OAc in methylene chloride gave a mixture of four isomers which are probably the tetramethyloctatriene above described. These products could not be characterized.



SCHEME 1

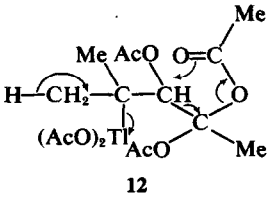


M = Pb

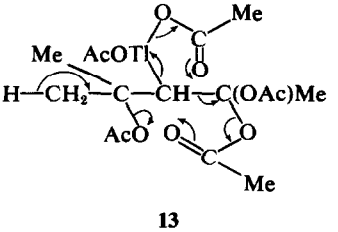
11

(23) was not detected among the products. The similar reaction proceeded in the presence of AgOAc suspended in ether at room temp to give 22 (5%) and benzyl acetate (40%).

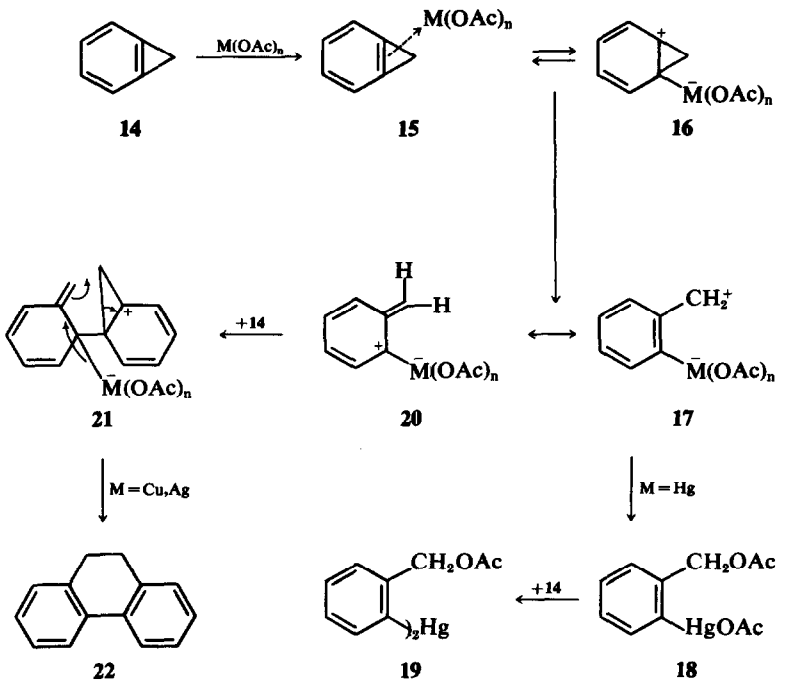
The formation of 19 should presumably involve the addition of $Hg(OAc)_2$ onto the double bond of cyclopropene ring of 14, the subsequent ring cleavage furnishing the complex 17, and the final



12



13



SCHEME 2

acetate transfer as shown in Scheme 2. The compound **18** reacts immediately with **14** to afford the product **19**. The isomeric preference of **22** over **23** is tentatively ascribed to the intermediary zwitterion **21** derived from an inverse ylide form **20**.*

EXPERIMENTAL

All m.ps and b.ps are uncorrected. The microanalyses were performed by Mrs. K. Fujimoto. The NMR spectra were taken in CCl_4 solns at 60 MHz on a JEOL C-60-H spectrometer and chemical shifts were given in ppm from TMS internal standard. Abbreviations *s*, *d*, *t* and *m* refer to singlet, doublet, triplet and multiplet, respectively. The mass spectra were obtained on a Hitachi RMU-6L spectrometer. GLC analyses and separations were performed with columns (1 m) packed with HVSG (30%) on Celite 545 or SE 30 (5%) on Chromosorb.

Materials. 1,3,3-Trimethylcyclopropene was prepared by the thermolysis of mesityl oxide tosylhydrazone sodium salt at 160°,[14] while benzocyclopropene by the treatment of 7,7-dichlorobicyclo[4.1.0]hep-3-ene with t-BuOK in DMSO.[15] 1,2,3-Triphenylcyclopropene and benzocyclobutene were synthesized according to the accepted procedures.[16,17]

The ring cleavage of 1,3,3-trimethylcyclopropene (**1**) *with mercury*(II) *acetate in methylene chloride.* The cyclopropene **1** (0·10 g, 1·2 mmol) was added to a suspension of $Hg(OAc)_2$ (0·39 g, 1·2 mmol) in CH_2Cl_2 (20 ml) at room temp under N_2. Stirring was continued for 18 hr. The mixture was immediately filtered from the precipitated metal salts and the filtrate was distilled to give only **5** (0·16 g, 65%), b.p. 100–110°/2 mm (bath temp) and m.p. 53–54·5°. IR (KBr): 1750, 1672, 1239, 1205, 1172, 1045, 1007, 949, 915 and 765 cm^{-1}. NMR (CCl_4, 20%): δ 7·47 (*s*, 1H, -CH(OAc)$_2$), 2·01 (*s*, 6H, -OAc), 1·87 (*m*, 3H, Me) and 1·70 (*m*, 6H, *gem*-dimethyl). MS (relative abundance): *m/e* 140 (10), 99 (58), 98 (53), 83 (9), 69 (15) and 43 (100). (Found: C, 59·7; H, 8·0%. $C_{10}H_{16}O_4$ requires: C, 60·0; H, 8·1%).

An independent synthesis of **5** was performed according to the method reported.[18] IR, NMR, MS and GLC retention time were identical with those of the original sample (mixed m.p. 53–54°).

The reaction of **1** *with thallium*(III) *triacetate in methylene chloride.* The cyclopropene **1** (0·25 g, 3·1 mmol) was treated with $Tl(OAc)_3$ (1·15 g, 3·1 mmol) in CH_2Cl_2 (20 ml) at room temp for 16 hr under N_2. Work-up followed by GLC separation gave **5** (0·30 g, 50%) and **9** (0·10 g, 20%). Compound **9** was identified by the comparison with the authentic sample (IR, NMR, MS and GLC retention time).[18]

The reaction of **1** *with lead*(IV) *tetraacetate in methylene chloride.* The cyclopropene **1** (0·10 g, 1·2 mmol) was treated with $Pb(OAc)_4$ (0·53 g, 1·2 mmol) in CH_2Cl_2 (20 ml) at room temp for 17 hr under N_2. Work-up followed by GLC separation gave **5** (0·10 g, 40%), **9** (trace) and **10** (0·009 g, 5%). Compound **10** was identified by the comparison with the authentic sample (IR, NMR, MS and GLC retention time).[19]

The ring cleavage of benzocyclopropene (**14**) *with mercury*(II) *acetate in methylene chloride.* The cyclopropene **14** (0·20 g, 2·2 mmol) was added to the suspension of $Hg(OAc)_2$ (0·35 g, 1·1 mmol) in CH_2Cl_2 (20 ml) at room temp under N_2. Stirring was continued for 21 hr and the mixture was treated with water and extracted with benzene. The extract was washed with water, dried

*Attempted ring cleavage of 1,2,3-triphenylcyclopropene or benzocyclobutene under similar conditions failed to give any products, but resulted in the complete recovery of the starting materials.

(Na_2SO_4) and concentrated *in vacuo*. The residue formed a crystalline product, m.p. 82–85° (0·50 g, 90%). Recrystallization from dry ether gave **19** (0·45 g, 80%), m.p. 86–88°; IR (Nujol): 1722, 1253, 1226, 1022, 991, 945, 760 and 732 cm^{-1}; NMR (CCl_4, 15%): δ 7·5–7·0 (*m*, 8H, aromatic), 5·10 (*s*, 4H, methylenes) and 1·97 (*s*, 6H, acetate). MS (relative abundance): *m/e* 150 (36), 149 (25), 108 (100), 107 (50), 91 (89), 90 (50), 79 (39), 78 (36), 77 (39) and 43 (100). (Found: C, 42·8; H, 3·7%. $C_{18}H_{18}HgO_4$ requires: C, 43·3; H, 3·6%).

The bromination of acetoxymercurial **19**. Br_2 (0·09 g, 0·56 mmol) was added to the soln of **19** (0·11 g, 0·22 mmol) in glacial AcOH (5 ml). The mixture was heated at 80–90° for 5 hr until the red colour had disappeared. The mixture was cooled and then neutralized with $NaHCO_3$aq. The soln was extracted with benzene. GLC separation gave *o*-bromobenzyl acetate (0·06 g, 59%) and *o*-bromobenzyl bromide (0·04 g, 36%). Both products were identified by the comparison with the authentic samples (IR, MS and GLC retention times).[20,21]

The photolysis of acetoxymercurial **19** *in benzene*. A benzene soln (10 ml) of **19** (0·20 g, 0·40 mmol) was irradiated by means of a 200 W high pressure mercury lamp (quartz jacket) for 45 hr at room temp under N_2. The mixture was treated with water and extracted with benzene. The extract was washed with water, dried (Na_2SO_4) and concentrated *in vacuo*. GLC separation gave benzyl acetate (0·08 g, 66%) and *o*-phenylbenzyl acetate (0·04 g, 22%). The latter compound was identified by the comparison with the authentic sample (IR, MS and GLC retention time).[22]

The reaction of **14** *with copper*(II) *acetate in ether*. The cyclopropene **14** (0·10 g, 1·1 mmol) was treated with $Cu(OAc)_2 \cdot H_2O$ (0·22 g, 1·1 mmol) in ether (10 ml) at room temp for 20 hr under N_2. Work-up followed by GLC separation gave **22** (0·04 g, 40%) and benzyl acetate (0·025 g, 15%). Compound **22** was identified by the comparison with the authentic sample (IR, MS and GLC retention time).[23]

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REFERENCES

[1a]P. G. Gassman and T. Nakai, *J. Am. Chem. Soc.* **93**, 5897 (1971); [b]P. G. Gassman and F. J. Williams, *Chem. Commun.* 80 (1972).

[2]P. G. Gassman and F. J. Williams, *Tetrahedron Letters* 1409 (1971).

[3a]L. A. Paquette and S. E. Wilson, *J. Am. Chem. Soc.* **93**, 5934 (1971); [b]M. Sakai, H. H. Westberg, H. Yamaguchi and S. Masamune, *Ibid.* **93**, 4611 (1971).

[4]R. Noyori, T. Suzuki and H. Takaya, *Ibid.* **93**, 5896 (1971).

[5a]A. S. Monahan, J. D. Freilich and J.-J. Fong, *Tetrahedron Letters* 1865 (1970); [b]J. A. Walker and M. Orchin, *Chem. Commun.* 1239 (1968).

[6]For the hydrogenation of cyclopropenes in the presence of palladium, see P. A. Waitkus, E. B. Sanders, L. I. Peterson and G. W. Griffin, *J. Am. Chem. Soc.* **89**, 6318 (1967).

[7]T. Shirafuji, Y. Yamamoto and H. Nozaki, *Tetrahedron Letters* 4713 (1971).

[8]For the oxidation of cyclopropenes with peracids, see L. E. Friedrich and R. A. Cormier, *Ibid.* 4761 (1971) and refs cited.

[9]For the reaction of cyclobutenes with Tl^{3+} ion, see J. E. Byrd, L. Cassar, P. E. Eaton and J. Halpern, *Chem. Commun.* 40 (1971).

[10]H. H. Stechl, *Chem. Ber.* **97**, 2681 (1964).

[11a]J. B. Lee and M. J. Price, *Tetrahedron* **20**, 1017 (1964); [b]S. Wolfe and P. G. C. Campbell, *Tetrahedron Letters* 4203 (1966); [c]S. Uemura, R. Kitoh and K. Ichikawa, *Nippon Kagaku Zasshi* **87**, 987 (1966).

[12]E. Vogel, W. Grimme and S. Korte, *Tetrahedron Letters* 3625 (1965).

[13a]G. L. Closs, *Advances in Alicyclic Chemistry* Vol. 1, p. 69. Academic Press, New York and London (1966); [b]G. L. Closs and L. R. Kaplan, *J. Am. Chem. Soc.* **91**, 2168 (1969).

[14]G. L. Closs, L. E. Closs and W. A. Böll, *Ibid.* **85**, 3796 (1963).

[15]W. E. Billups, A. J. Blakeney and W. Y. Chow, *Chem. Commun.* 1461 (1971); See also ref. 12.

[16a]R. Breslow and P. Dowd, *J. Am. Chem. Soc.* **85**, 2729 (1963); [b]R. Breslow and H. W. Chang, *Ibid.* **83**, 2374 (1961).

[17]M. P. Cava and A. A. Deana, *Ibid.* **81**, 4266 (1959).

[18]I. Scriabine, *Bull. Soc. Chim. Fr.* 1194 (1961); *Chem. Abstr.* **55**, 25833 (1961).

[19]B. H. Gwynn and Ed. F. Degering, *J. Am. Chem. Soc.* **64**, 2216 (1942).

[20]J. Kenner and J. Wilson, *J. Chem. Soc.* 1111 (1927).

[21]C. L. Jackson, *J. Am. Chem. Soc.* **2**, 315 (1880).

[22]D. I. Davis and C. Waring, *J. Chem. Soc.* (C) 2332 (1968).

[23]G. Schröter, H. Müller, J. Y. S. Huang, *Ber. Dtsch. chem. Ges.* **62**, 645, 649, 651 (1929).