

SOME Ag(I)-PROMOTED REACTIONS OF TETRACYCLO [3.2.0.0.<sup>2,7</sup>0<sup>4,6</sup>] HEPTANE (QUADRICYCLENE), 1-METHYLTETRACYCLO [3.2.0.0.<sup>2,7</sup>0<sup>4,6</sup>] HEPTANE CARBOXYLATE (2-CARBOMETHOXYQUADRICYCLENE) AND 1,2-DIMETHYLTETRACYCLO [3.2.0.0.<sup>2,7</sup>0<sup>4,6</sup>] HEPTANE DICARBOXYLATE (2,3-BIS(CARBOMETHOXY)QUADRICYCLENE).

Gerald F. Koser\*, Penelope R. Pappas, and Shwn-Meei Yu

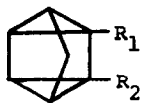
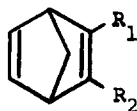
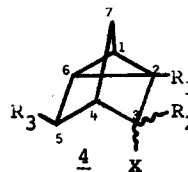
Department of Chemistry, The University of Akron

Akron, Ohio 44325

(Received in USA 27 November 1973; received in UK for publication 29 October 1973)

The ability of Ag(I) salts to initiate skeletal transpositions in and alcoholyses of saturated, strained carbocycles is of synthetic<sup>1a-d</sup> and mechanistic interest.<sup>2a-h</sup> Even so, the highly strained quadricyclene system has been little studied. AgNO<sub>3</sub>-catalyzed isomerization of the parent hydrocarbon 1a to norbornadiene (2a) has been noted, but no quantitative information is available.<sup>3</sup> We know of only one related study and that describes the Ag(I)-promoted methanolysis and rearrangement of diester 3.<sup>4</sup> We detail herein the first systematic investigation of quadricyclene-Ag(I) salt chemistry and have chosen quadricyclenes 1a, 1b, and 1c for initial study. The objective of this preliminary report is to describe general product studies, and, accordingly, consideration of the complex questions regarding mechanism will be largely deferred.

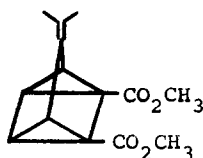
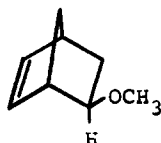
When 1c (1M) was allowed to react with AgOCCF<sub>3</sub> (1M) in CH<sub>3</sub>OH, there was negligible (<3%) conversion of 1c to diene 2c and 15% reduction of Ag(I) to Ag<sup>0</sup>. Distillation of the crude product gave a 71% yield of nortricycyl ether 4c as an equimolar mixture of C-3 epimers. Similar treatment of 1c with AgOCCF<sub>3</sub> in CH<sub>3</sub>OD afforded the C-3 deuterioether 4d in 64% yield. Preliminary nmr rate studies on 1M solutions of 1c in CD<sub>3</sub>OD have shown silver ion to be an active electrophilic catalyst for alcoholysis of the 3-5 bond. Thus, in the presence of 1M AgOCCF<sub>3</sub>, addition of CD<sub>3</sub>OD to 1c was complete within one hr at room temperature and gave ether 4e in apparently quantitative yield. However, when 0.98M CF<sub>3</sub>COOH was the catalyst, the same reaction was ca 58% complete after 38 hr. Hence, if Ag(I)

124

	<u>R<sub>1</sub></u>
<u>a</u> ;	H
<u>b</u> ;	H
<u>c</u> ;	CO <sub>2</sub> CH <sub>3</sub>

<u>R<sub>2</sub></u>
H
CO <sub>2</sub> CH <sub>3</sub>
CO <sub>2</sub> CH <sub>3</sub>

	<u>R<sub>1</sub></u>	<u>R<sub>2</sub></u>	<u>R<sub>3</sub></u>	<u>X</u>
<u>a</u> ;	H	H	CH <sub>3</sub> O	H
<u>b</u> ;	H	CO <sub>2</sub> CH <sub>3</sub>	CH <sub>3</sub> O	H
<u>c</u> ;	CO <sub>2</sub> CH <sub>3</sub>	CO <sub>2</sub> CH <sub>3</sub>	CH <sub>3</sub> O	H
<u>d</u> ;	CO <sub>2</sub> CH <sub>3</sub>	CO <sub>2</sub> CH <sub>3</sub>	CH <sub>3</sub> O	D
<u>e</u> ;	CO <sub>2</sub> CH <sub>3</sub>	CO <sub>2</sub> CH <sub>3</sub>	CD <sub>3</sub> O	D
<u>f</u> ;	CO <sub>2</sub> CH <sub>3</sub>	CO <sub>2</sub> CH <sub>3</sub>	CF <sub>3</sub> COO	H
<u>g</u> ;	CO <sub>2</sub> CH <sub>3</sub>	CO <sub>2</sub> CH <sub>3</sub>	HO	H

35

reduction is accompanied with stoichiometric formation of CF<sub>3</sub>COOH, the acid-catalyzed methanolysis of 1c is not likely to be a competitive process.

When 1c (1.3M) was allowed to react with AgOCCF<sub>3</sub> (1.3M) in acetone, a solvent of low nucleophilicity, there was 53% reduction of Ag(I) to Ag<sup>0</sup>. Distillation of the crude product gave epimeric nortricyclyl trifluoroacetate 4f (17%) and epimeric nortricyclyl alcohol 4g (53%). The isolation of 4g as the major organic product was unexpected, but the reaction mixtures do become appreciably acidic, and it seems likely that acid-catalyzed dehydration of acetone may provide the water necessary for alcohol formation. As before, there was low (~3%) conversion of 1c to 2c.

Treatment of 1c (1M) with anhydrous AgBF<sub>4</sub> (1M) in ClCH<sub>2</sub>CH<sub>2</sub>Cl gave Ag<sup>0</sup> (25%) and diene diester 2c (42%, 31% by isolation); no other organic products were identified.

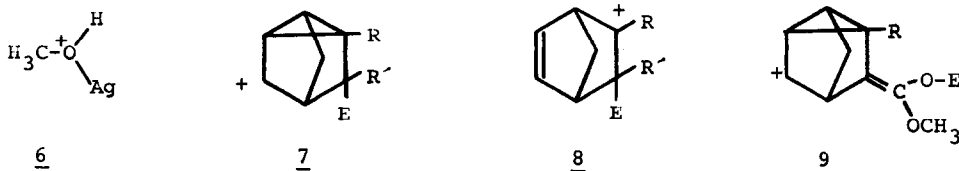
The reactivity of 1b both parallels and contrasts with that of 1c. When 1b (1M) was allowed to react with AgOCCF<sub>3</sub> (1M) in CH<sub>3</sub>OH, Ag<sup>0</sup> was precipitated in 82% yield. Fractional distillation of the crude product gave diene monoester 2b (20%) and nortricyclyl ether 4b (32%) as an equimolar mixture of C-3 epimers. Thus, when one of the ester functions in 1c is replaced by hydrogen, isomerization to

diene becomes competitive with methanolysis. Moreover, methanol adds selectively to the strained  $\sigma$  bond bearing the carbomethoxy group.

The reactivity of lb in acetone differs significantly from that of lc. Treatment of lb (1M) with  $\text{AgOOCF}_3$  (1M) in acetone gave a relatively low yield (32%) of  $\text{Ag}^\circ$  and caused clean conversion of lb to diene 2b (isolated in 81% yield by distillation); no nortricyclenes were identified.

When quadricyclene (1a), the parent hydrocarbon, was allowed to react with  $\text{AgOOCF}_3$  in  $\text{CH}_3\text{OH}$  (0.26M in each reagent), there was 89% reduction of  $\text{Ag}(\text{I})$  to  $\text{Ag}^\circ$ . Several organic products were identified, and their yields were determined by glpc analysis; they were norbornadiene (2a) (34%), 3-exo-methoxynortricyclene (4a) (29%), and 5-exo-methoxynorbornene (5) (7%). By way of comparison, treatment of 1a with concd. sulfuric acid in methanol gave a 90% crude yield of 4a and 5 in a 23:77 ratio.

A most unusual property of the quadricyclene system is its ability to cause silver ion reduction, a process which is apparently regulated by the nature of the quadricyclene substituents and by the reaction solvent.<sup>5</sup> Furthermore, the production of acid in solvent methanol appears to be related to the extent of  $\text{Ag}(\text{I})$  reduction. The results of a pH study on 1a, 1b, and 1c are given in Table I. The formation of silver methoxide, perhaps by proton transfer from Brønsted acid 6 to the substrate, and its subsequent decomposition is a plausible source of  $\text{Ag}^\circ$  in that solvent but we can, as yet, only speculate on this matter.<sup>6</sup> The formation of norbornadienes 2a-2c, nortricyclenes 4a-4g, and norbornene 5 is consistent with the known reactivity of quadricyclenes toward electrophilic agents and may proceed by nucleophilic interception and intramolecular collapse of intermediate



carbocations 7 and 8.<sup>7a-e</sup> With quadricyclyl esters 1b and 1c, bonding of the catalyst to carbonyl oxygen as shown in structure 9 seems possible<sup>4</sup> and is consistent with the observed selectivity of methanol addition to 1b.

We reserve judgment regarding the nature of the active electrophile,  $\text{E}^+$  since

there may, in fact, be several catalytic species. Organosilver carbocations have been implicated as intermediates in Ag(I)-promoted rearrangements of strained hydrocarbons in non-hydroxylic solvents,<sup>2b</sup> but their existence in methanol is equivocal.<sup>2a</sup>

TABLE I

Acidity of Quadricyclene:AgOOCF<sub>3</sub>:Methanol Reaction Mixtures<sup>a</sup>

Quadricyclene	[Quadricyclene] <sub>0</sub> <sup>b</sup>	[AgOOCF <sub>3</sub> ] <sub>0</sub> <sup>b,c</sup>	pH <sup>d</sup>
-----	-----	0.29	6.0
<u>1a</u>	0.28	0.29	1.7
<u>1b</u>	0.28	0.29	1.8
<u>1c</u>	0.27	0.29	4.1

(a) The reaction mixtures (10ml) were allowed to stand for 24 hr at ambient temperature and poured into distilled water (100ml) prior to pH measurements. (b) Initial molar concentrations of 1a, 1b, 1c, and silver trifluoroacetate. (c) Silver trifluoroacetate (Aldrich Chemical CO., 98%) was recrystallized from n-hexane: ethyl acetate and dried *in vacuo* (1mm) just prior to use. (d) The pH meter (Ag/AgCl-Glass electrode) was pre-calibrated with buffer solutions at pH 2,4, and 7.

## References

- (a) L. A. Paquette, *J. Amer. Chem. Soc.*, **92**, 5765 (1970); (b) L. A. Paquette and G. Zon, *ibid.*, **94**, 5096 (1972); (c) W. G. Dauben, D. H. Schallhorn and D. L. Whalen, *ibid.*, **93**, 1446 (1971); (d) E. W. Turnblom and T. J. Katz, *ibid.*, **95**, 4292 (1973).
- (a) Consult the series of papers by L. A. Paquette and his co-workers entitled "Silver(I) Ion Catalyzed Rearrangements of Strained  $\sigma$  Bonds": Paper XVIII; G. Zon and L. A. Paquette, *J. Amer. Chem. Soc.*, **95**, 4456 (1973); (b) L. A. Paquette, *Accts. Chem. Research*, **4**, 280 (1971); (c) K. L. Kaiser, R. F. Childs and P. M. Maitlis, *J. Amer. Chem. Soc.*, **93**, 1270 (1971); (d) J. Wristers, L. Brener, and R. Pettit, *ibid.*, **92**, 7499 (1970); (e) P. G. Gassman and T. Nakai, *ibid.*, **94**, 5497 (1972); (f) G. F. Koser, *Chem. Comm.*, 388 (1971); (g) M. Sakai, H. H. Westberg, H. Yamaguchi, and S. Masamune, *J. Amer. Chem. Soc.*, **93**, 4611 (1971); (h) J. E. Byrd, L. Cassar, P. E. Eaton and J. Halpern, *Chem. Comm.*, 40 (1971).
- B. C. Menon and R. E. Pincock, *Canad. J. Chem.*, **47**, 3327 (1969).
- S. F. Nelsen, J. P. Gillespie and P. J. Hintz, *Tetrahedron Letters*, 2361 (197)
- Ag(I) reduction has been observed with hexamethylprismane; see reference 2c.
- R. S. Macomber, *PRF Annual Research Report*, **16**, 88 (1971).
- For example, see (a) W. G. Dauben and R. L. Cargill, *Tetrahedron*, **15**, 197 (1967); (b) P. G. Gassman, D. H. Aue, and D. S. Patton, *J. Amer. Chem. Soc.*, **90**, 7271 (1968); (c) P. G. Gassman and D. S. Patton, *ibid.*, **90**, 7276 (1968); (d) T. C. Morrill and B. E. Greenwald, *J. Org. Chem.*, **36**, 2769 (1971); (e) S. J. Cristo J. K. Harrington, T. C. Morrill, and B. E. Greenwald, *ibid.*, **36**, 2773 (1971).