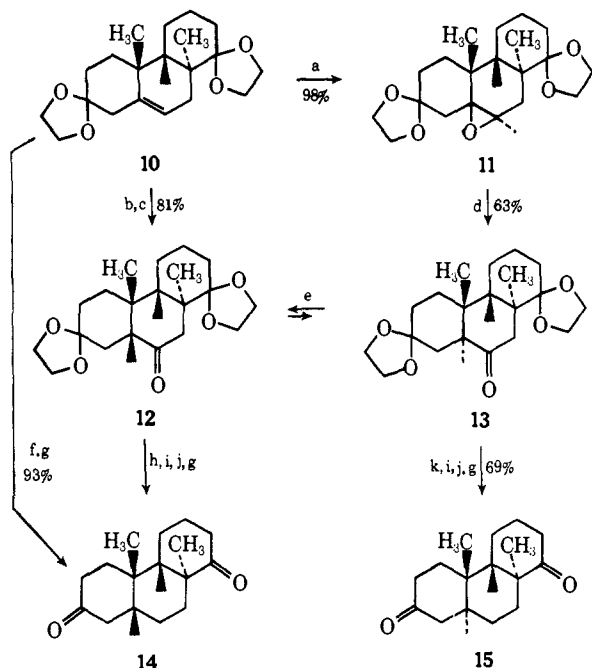


system and clearly show that it is only the β face of the enone portion of the molecule that is unhindered and accessible to intermolecular approach. Thus, catalytic hydrogenation of the ketone ketal **6** results in the formation of the cis-syn-trans ketal ketone **8**, and the same stereochemical outcome attends the metal-ammonia reduction process. This result is probably a reflection of steric strain inherent in such syn-trans tricyclic structures.

Another approach to this problem is through the diketal **10** of the enedione **4** [(CH₂OH)₂, C₈H₈, *p*-TsOH, 93%] (Chart II). Again access to the α face of this

Chart II. Synthesis of Trans-Syn-Trans Diketone **15**^a



^a a, *m*-ClC₆H₄CO₂H, CH₂Cl₂; b, BH₃·THF; H₂O₂, OH⁻; c, CrO₃·Py₂, CH₂Cl₂; d, BF₃·Et₂O, CH₂Cl₂; e, aqueous NaOH, EtOH; f, H₂, 10% Pd/C, EtOH; g, H₃O⁺; h, Li, NH₃; EtOH; i, *n*-BuLi, DME, HMPA, ClPO(NMe₂)₂; j, Li, EtNH₂, THF; k, LiAlH₄, Et₂O. See ref 3.

molecule is severely restricted, and intermolecular reagents may only reasonably approach its β side. Catalytic hydrogenation of the diketal **10** and then deketalization substantiates this analysis, since *only* the cis-syn-trans diketone **14**,³ also available on hydrolysis of the monoketal **8**, is formed.

These observations make it apparent that the formation of the desired trans AB ring fusion through an *intermolecular* process is unlikely, and efficient access to this system would better depend on the *intramolecular* transfer of an α -oriented hydrogen to the ring fusion. Such a sequence was realized when the boron trifluoride catalyzed rearrangement of β oxide **11** afforded the diketal ketone **13**. On treatment of this diketal ketone **13** with aqueous ethanolic hydroxide for 2 hr at reflux, an invariant mixture (90:10 by nmr analysis) of the *cis*-**12** and *trans*-**13** isomers was reached. The *cis* isomer **12** was isolated from this mixture and shown to be identical³ with the diketal ketone prepared by hydroboration and then oxidation of the diketal **10**. Evidence that a mixture of *cis*-syn-*trans*-**12** and *trans*-syn-*trans*-**13** isomers in the ratio of 90:10 is at equilibrium under these basic conditions was apparent

from an identical isomerization study of the pure *cis* isomer **12**.

Final confirmatory evidence of the accuracy of the structural assignments made for the two diketal ketones **12** and **13** was found in the removal⁷ of the carbonyl group and the formation of the diketones **14** and **15**. In both cases this transformation was accomplished *without* isomerization of the AB ring fusion, since distinctly different diketones resulted and one, the diketone **14**, was identical³ with the *cis*-syn-*trans* material prepared above.

The stereochemical result of this epoxidation-rearrangement sequence relies on the easy intermolecular steric access of the peracid to the β face of the unsaturated diketal **10** and the subsequent concerted intramolecular character of the oxide \rightarrow ketone transformation. *None* of the isomeric *cis* diketal ketone **12** could be detected in the product from this sequence, and the success of the scheme in this functionalized system suggests that the process will generally be applicable to the formation of other *trans*-syn-*trans* structures.

(7) R. E. Ireland and G. Pfister, *Tetrahedron Lett.*, 2145 (1969); D. C. Muchmore, Ph.D. Thesis, California Institute of Technology, 1970.

(8) Fellow of Stiftung für Stipendien auf dem Gebiete der Chemie, Switzerland.

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Regio- and Stereoselective Methyl Migrations in Silver(I)-Promoted Rearrangements of Tricyclo[3.2.0.0^{2,4}]heptanes¹

Sir:

Since the original recognition of the capability of Ag⁺ to promote structural bond reorganizations of molecules endowed only with strained σ bonds,² considerable exploration of the field has occurred³ and other transition metals of equal effectiveness have been found.⁴ Although a general mechanistic theory in explanation of the observed structural changes has progressed into a formative stage,^{1,3b,4a} new aspects of the novel rearrangement capability of Ag⁺ are certain to emerge. We wish now to report just such an unusual, mechanistically informative development in silver(I) chemistry.

In a series of experiments designed to test for substituent effects on the Ag⁺-promoted rearrangement of the tricyclo[3.2.0.0^{2,4}]heptane ring system, we had occasion to treat **1**⁵ with small amounts of silver

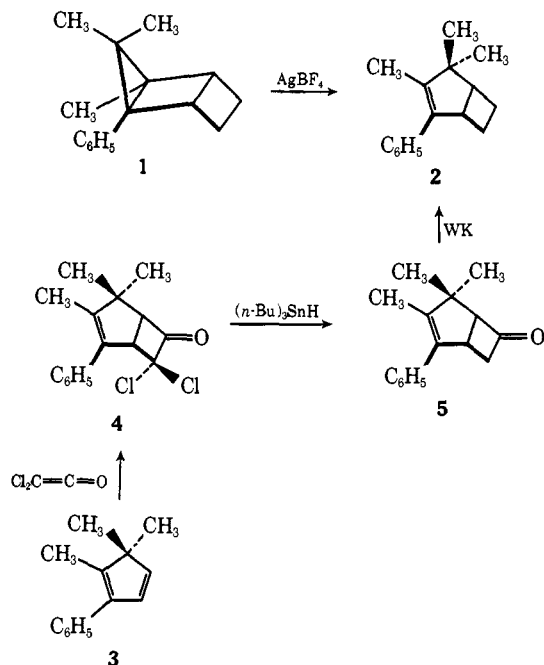
(1) Part IX of the series entitled "Silver(I) Ion Catalyzed Rearrangements of Strained σ Bonds." For the previous paper, see L. A. Paquette and S. E. Wilson, *J. Amer. Chem. Soc.*, **93**, 5934 (1971).

(2) L. A. Paquette and J. C. Stowell, *ibid.*, **92**, 2585 (1970); (b) W. G. Dauben, M. G. Buzzolini, C. H. Shallhorn, D. L. Whalen, and K. Palmer, *Tetrahedron Lett.*, 787 (1970).

(3) (a) L. A. Paquette, R. P. Henzel, and S. E. Wilson, *J. Amer. Chem. Soc.*, **93**, 2335 (1971), and earlier papers from this laboratory; (b) M. Sakai and S. Masamune, *ibid.*, **93**, 4610 (1971), and preceding reports; (c) J. Wrusters, L. Brener, and R. Pettit, *ibid.*, **92**, 7499 (1970); (d) L. Cassar, P. E. Eaton, and J. Halpern, *ibid.*, **92**, 6366 (1970).

(4) (a) P. G. Gassman and T. J. Atkins, *ibid.*, **93**, 4597 (1971), and other papers by this group; (b) M. Sakai, H. Yamaguchi, and S. Masamune, *Chem. Commun.*, 486 (1971); (c) N. B. Chapman, J. M. Key, and K. J. Toyne, *Tetrahedron Lett.*, 5211 (1970).

fluoroborate in CDCl_3 . Rapid reaction was seen to occur (complete in 0.5 hr, nmr analysis) with formation of the lone isomeric hydrocarbon **2**.⁶ The initial deduction of structure **2** followed from its spectral



data, particularly the presence of a styrene chromophore in the electronic spectrum [$\lambda_{\text{max}}^{\text{isooctane}}$ 247 nm (ϵ 5100)] and the appearance of a single sp^2 -bound methyl group in the nmr [$\delta_{\text{TMS}}^{\text{CDCl}_3}$ 7.25 (br, s, 5, aromatic), 3.58 (m, 1, H_1), 2.63 (m, 1, H_5), 1.25–2.33 (m, 4, H_r and H_7), 1.73 (d, $J = 1.8$ Hz, 3, $=\text{CCH}_3$), 1.04 and 0.96 (s, 3 each, sp^3 CCH_3)]. Ultimate confirmation of this assignment began with the preparation of 2-phenyl-1,5,5-trimethylcyclopentadiene (**3**) according to the elegant method devised by Bays and Cookson.⁷ Dichloroketene, generated *in situ*, added as expected to the less hindered center of unsaturation to give dichlorocyclobutanone **4** in 95% yield: ir (neat) 1805 cm^{-1} ; $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 7.35 (br s, 5, aromatic), 4.48 (dd, $J = 1.5$ and 7.7 Hz, 1, H_1), 3.89 (d, $J = 7.7$ Hz, 1, H_5), 1.79 (d, $J = 1.5$ Hz, 3, $=\text{CCH}_3$), 1.31 and 1.13 (s, 3 each, sp^3 CCH_3). Direct dechlorination of **4** with tri-*n*-butyltin hydride furnished ketone **5** [ir (neat) 1773 cm^{-1}]⁶ which upon Wolff-Kishner reduction (WK) provided authentic **2**, identical in all respects with the original sample.

Although hydride shifts in silver(I)-promoted rearrangements have previously been recognized to occur,^{1,8} net alkyl migrations have heretofore not been encountered (formal "bond switching" processes² not included). The causative origin of the rearrangement clearly resides in the unusual electrophilic and complexing properties of the Ag^+ ion.^{1,3} Most remarkable in the case of **1**, however, is the finding that only that bond reorganization operates in which a methyl group migrates in highly regioselective fashion away from the incipient benzylic carbonium ion center. We interpret this to mean that, in addition to simple

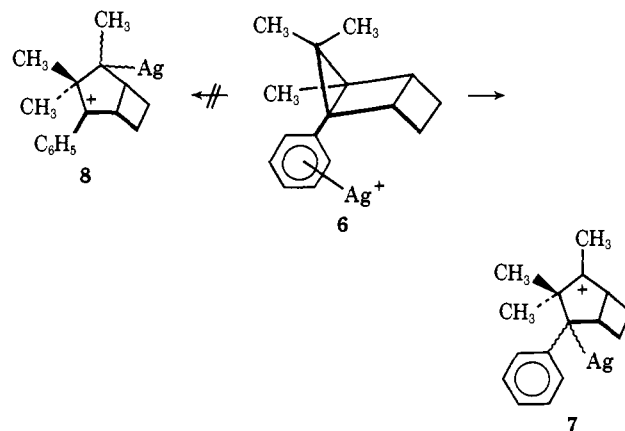
(5) L. A. Paquette and L. M. Leichter, *J. Amer. Chem. Soc.*, **93**, 4922 (1971).

(6) Appropriate combustion analyses ($\pm 0.3\%$) were obtained for all new compounds.

(7) D. E. Bays and R. C. Cookson, *J. Chem. Soc. B*, 226 (1967).

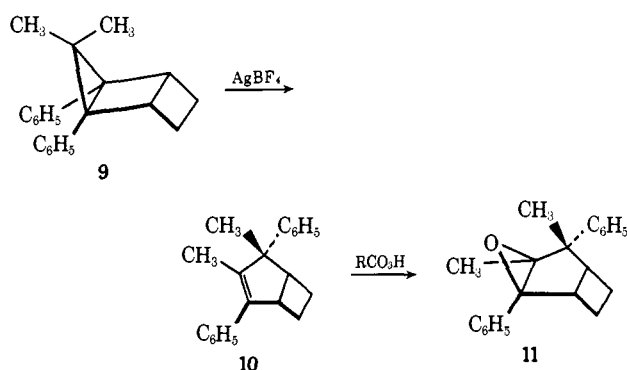
(8) L. A. Paquette, S. E. Wilson, and R. P. Henzel, *J. Amer. Chem. Soc.*, submitted for publication.

metal-strained σ -bond association, there must also exist a significant contribution to bonding which strongly directs Ag^+ to form a covalent bond only at benzylic carbon. Possibly this high level of specificity is the result of initial π -bond coordination of Ag^+ with the phenyl substituent to form a complex (*cf.* **6**, no specification of preferential approach by Ag^+ intended) which is of kinetic consequence in the formation of **2**. Subsequent C_2 - C_4 bond cleavage in intermediate **6** is required for the usual reasons to give rise only to **7** and not to **8**. The data do not rule out, of course, the



closely related possibility that the aromatic ring electronically influences Ag^+ most critically at a time subsequent to its initial oxidative addition to the central bond. Nor is C_3 -methyl migration in concert with this bond cleavage eliminated as feasible; in such an eventuality, the preferential formation of the styrene chromophore could command major significance.

When **9** was treated similarly with AgBF_4 , it was transformed somewhat more slowly than **1** uniquely into isomeric bicyclo[3.2.0]heptene **10**⁶ [$\lambda_{\text{max}}^{\text{isooctane}}$ 251 nm (ϵ 12,200); $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 7.32 (m, 10, aromatic), 3.75 (m, 1, H_1), 2.80 (m, 1, H_5), 1.20–2.33 (br m, 4, H_6 and H_7), 1.82 (d, $J = 1.7$ Hz, 3, $=\text{CCH}_3$), and 1.47 (s, 3, CH_3)]. In an attempt to gain definitive evidence for the stereo-



chemical disposition of the C_4 -methyl group in **10**, this rearrangement product was epoxidized with *m*-chloroperbenzoic acid. Lanthanide-induced differential shifting⁹ of the nmr spectrum of epoxide **11**, mp 99° ,⁶ using $\text{Eu}(\text{fod})_3$ ¹⁰ served to indicate that the two methyl groups were rather similarly shifted to lower field by the weakly coordinating lanthanide ion. Specifically,

(9) For an earlier application of nmr pseudocontact shift reagents to epoxides, see L. H. Keith, *Tetrahedron Lett.*, 3 (1971).

(10) R. E. Rondeau and R. E. Sievers, *J. Amer. Chem. Soc.*, **93**, 1522 (1971).

plots of the chemical shifts of the two singlet methyl absorptions (δ 1.16 and 1.58 in CDCl_3) in hertz downfield from TMS vs. $\text{Eu}(\text{fod})_3$ concentration were linear¹¹ and gave Δ_{Eu} values¹² of -4.09 and -3.62 , respectively. These observations, in tandem with the finding that the protons of one phenyl ring were negligibly affected under these conditions, are consistent in detail with topside complexation of the $\text{Eu}(\text{fod})_3$ to oxygen with attendant comparable influence on $\text{C}_3\text{-CH}_3$ ($R = 2.5$) and $\text{exo-C}_4\text{-CH}_3$ ($R = 3.0$).¹³ In view of the structural rigidity of **11**, the data are entirely incompatible with endo positioning of the methyl substituent at C_4 ($R = 4.2$).¹³ It follows then that **10** has the indicated stereochemistry, the result of methyl migration exclusively from the exo face of the bicyclic structure.

Although the observation of such a remarkably high level of stereoselectivity (and perhaps stereospecificity¹⁴) is frequently considered as suitable evidence against the intervention of a planar carbonium ion, this conclusion must be tempered in the present instance because of possible steric control resulting from the proximate fused cyclobutane ring. The influence of steric and substituent factors on these reactions, as well as the likelihood of the intervention of other organosilver and carbonium ion intermediates, forms the subject of continuing studies. Notwithstanding, Ag^+ is seen to play a definitive, and perhaps uniquely specific, role in these rearrangements which is not shared by Brønsted acids (*p*-toluenesulfonic acid and anhydrous HBr in CDCl_3 at 40° did not rearrange **9** after 30 hr), other transition metals (e.g., **9** was inert to $[\text{Rh}(\text{CO})_2\text{Cl}]_2$), or the fluoroborate anion (no change in the presence of NaBF_4 before and after acidification).

Acknowledgment. We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for their partial support of this research.

(11) Least-squares treatment of these plots gave slopes of 234 and 206 Hz/mol % $\text{Eu}(\text{fod})_3$, respectively.

(12) P. V. Demarco, T. K. Elzey, R. B. Lewis, and E. Wenkert, *J. Amer. Chem. Soc.*, **92**, 5734 (1970).

(13) R is here taken as the vector distance from oxirane oxygen to the most proximate hydrogen of the given methyl group. In this way, we are neglecting the important orientation of Eu , which is of course undefinable in the present instance.

(14) For instance, if a single, configurationally unique, methyl group in **1** and **9** were undergoing the shift to C_3 in **2** and **10**, respectively.

(15) National Institutes of Health Predoctoral Fellow, 1969–1971.

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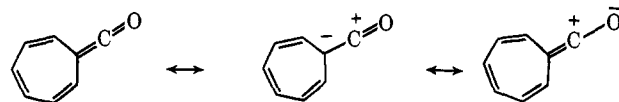
8-Oxoheptafulvene

Sir:

Heptafulvenes having electron-attracting groups at the 8 position are stabilized by the contribution of dipolar structures¹ relative to the ground state in contrast to heptafulvene itself.² Polar structures can also be considered for the previously unknown 8-oxoheptafulvene (**1**) which contains a seven-membered unsatu-

(1) T. Nozoe, T. Mukai, K. Osaka, and N. Shishido, *Bull. Chem. Soc. Jap.*, **34**, 1384 (1961); M. Yamanaka, H. Watanabe, T. Mukai, T. Nozoe, and M. Kubo, *J. Amer. Chem. Soc.*, **82**, 5665 (1960); H. Shimanouchi, T. Ashida, T. Sasada, M. Kakudo, I. Murata, and Y. Kitahara, *Bull. Chem. Soc. Jap.*, **38**, 1230 (1965); **39**, 2322 (1966).

(2) W. von E. Doering and D. W. Wiley, *Tetrahedron*, **11**, 183 (1960).



rated ring and ketene moiety. We have been interested in the properties of compound **1**, and now wish to report our results on its formation and some reactions.

Dropwise addition of 1.4 equiv of NEt_3 to a stirred solution of tropyl-7-carboxylic acid chloride (**2**) and cyclopentadiene in anhydrous ether or *n*-hexane at ca. -20° immediately afforded triethylamine hydrochloride. The mixture was stirred at room temperature for 1 hr, and chromatography of the ether extract on silicic acid gave about 60% of an adduct **3** as a colorless liquid.³ Compound **3** exhibits infrared bands (neat) at 1778 (four-membered cyclic ketone) and 1600, 723, and 695 cm^{-1} (tropilidene moiety); the nmr spectrum (CDCl_3) at 100 MHz includes signals at δ 2.33 (1 H, d, d, q, $J = 17, 9, 2$ Hz, exo H-5'), 2.66 (1 H, d, d, m, $J = 17, 2$ Hz, endo H-5'), 2.94 (1 H, d, m, $J = 8$ Hz, H-2'), 3.83 (1 H, d, d, d, $J = 9, 8, 2$ Hz, H-6'), 5.09 (1 H, d, m, $J = 9$ Hz, H-2 or H-7), 5.22 (1 H, d, m, $J = 9$ Hz, H-7 or H-2), 5.29 and 5.70 (2 H, m, H-3' and H-4'), 6.23 (2 H, m, H-3 and H-6), and 6.58 (2 H, m, H-4 and H-5). The chemical-shift assignments and couplings were verified by double and triple resonance experiments and by comparison with the spectra of tropilidene⁴ and the adducts of cyclopentadiene with ketenes.⁵ Adduct **3** also exhibits $\lambda_{\text{max}}^{\text{cyclohexane}}$ 274 nm (ϵ 2610) as expected for a tropilidene chromophore, and a mass spectral parent ion at m/e 184 (relative intensity 41) as well as major fragment ions at 156 (19), 155 (19), 141 (27), 118 (84), 115 (23), 91 (22), 90 (100), and 89 (22).

A similar reaction in the presence of indene instead of cyclopentadiene gave 24% of crystalline adduct **4**, mp $95\text{--}97.5^\circ$. Compound **4** showed an infrared band (KBr) at 1770 cm^{-1} ; $\lambda_{\text{max}}^{\text{isooctane}}$ 264 nm (ϵ 3720), 269 (4200), 275 (3730); nmr (CDCl_3), δ 2.96 (1 H, d, d, $J = 16.8, 9.2$ Hz, exo H-7'), 3.31 (1 H, br d, $J = 16.8$ Hz, endo H-7'), 3.46 (1 H, d, $J = 8$ Hz, H-2'), 4.14 (1 H, d, d, $J = 9.2, 8, 2$ Hz, H-8'), 5.01 (1 H, d, m, $J = 9.2$ Hz, H-2 or H-7), 5.43 (1 H, d, m, $J = 9.2$ Hz, H-7 or H-2), 6.15–6.45 (2 H, m, H-3 and H-6), and 6.6–7.2 (6 H, m, H-4, -5, -3'-6'); mass spectral parent ion at m/e 234 (1.4), and fragment ions at 206 (1), 205 (1.4), 119 (9), 118 (49), 116 (100), 115 (90), 91 (17), 90 (84), 89 (30), and 63 (24). The chemical-shift assignments and couplings were also confirmed by double resonance technique and by comparison with the spectra of tropilidene derivatives⁴ and the adduct of indene and dichloro-ketene.⁶

Hydrogenation of **3** over palladium/charcoal led to the uptake of 4 mol of hydrogen and afforded oily tricyclic saturated ketone **5**: mol wt 192 (mass spectrum); ir (neat) 1770 cm^{-1} ; dinitrophenylhydrazone mp $91\text{--}92^\circ$.

The formation of the adducts **3** and **4** can be explained by a cycloaddition reaction of olefins with 8-oxohepta-

(3) All new compounds gave satisfactory elemental analyses.

(4) G. Fraenkel, R. E. Carter, A. McLachlar, and J. H. Richard, *J. Amer. Chem. Soc.*, **82**, 5846 (1960); H. Günther, M. Görlitz, and H.-H. Hinrichs, *Tetrahedron*, **24**, 5665 (1968).

(5) M. R. S. Roberts, A. Dieffenbacher, and A. S. Dreiding, *Helv. Chim. Acta*, **53**, 417 (1970), and references cited therein.

(6) R. W. Turner and T. Seden, *Chem. Commun.*, 399 (1966).