Tetrahedron Letters, Vol.22, No.34, pp 3257 - 3260, 1981
Printed in Great Britain

0040-4039/81/343257-04$02.00/0

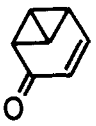
4-ACETOXYTRICYCLO[4.1.0.0^{2,7}]HEPT-4-EN-3-ONE; SYNTHESIS AND NOVEL BOND REORGANIZATION OF A VALENCE ISOMER OF 2-ACETOXYTROPONE

Yoshikazu Sugihara, Akikazu Yamato, and Ichiro Murata*

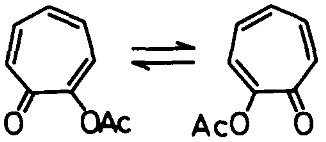
Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan

Summary: 4-Acetoxytricyclo[4.1.0.0^{2,7}]hept-4-en-3-one (3), a valence isomer of 2-acetoxytropone, was synthesized. Upon heating in pyridine at 150°C, 3 rearranged into 1-acetoxybicyclo[3.2.0]hepta-3,6-dien-2-one (9); the mechanism of which was examined by means of deuterium labeling experiments.

Recently, we have reported[1] the facile synthesis and properties of tricyclo[4.1.0.0^{2,7}]-hept-4-en-3-one (tropovalene) (1),[2] a valence isomer of tropone, and some of its derivatives.[3] Photochemical reactions of 1 in acetone gave tropone exclusively[3] suggesting the interaction between enone and bicyclobutane moieties in its excited state. Judging from the ^{1}H- and ^{13}C-NMR spectra of 1, some of the interaction between enone and bicyclobutane moieties appear to exist in the ground state of 1.[1,3] Experimental evidence support of the interaction has recently been reported by Volz et al.[4]



1



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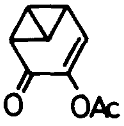
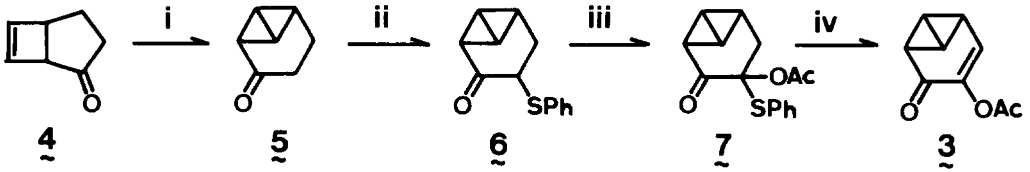


3

Since it is well-known that 2-acetoxytropone (2) undergoes rapid degenerate rearrangement with O,O-acetyl migration,[5] our interest is now turned to examine the thermal behavior of 4-acetoxytricyclo[4.1.0.0^{2,7}]hept-4-en-3-one (3), a valence isomer of 2, in which similar acetyl migration mediated by bicyclobutane and enone moieties might be expected.

The synthesis of 3 could be achieved by a sequence of reactions shown in Scheme I.[6] Tricyclic ketone 5, readily prepared through oxa-di-π-methane rearrangement of bicyclo[3.2.0]-hept-6-en-2-one (4),[7] was sulfenylated to the sulfide 6, pale yellow oil, 67% yield, which was acetoxylated to give acetoxy sulfide 7, pale yellow oil, 94% yield. Since ^{1}H-NMR spectrum of the reaction mixture indicated that the reaction proceeded almost quantitatively, the crude 7 was oxidized with *m*-chloroperbenzoic acid to give sulfoxide which, after routine workup, was pyrolyzed in carbon tetrachloride at 50°C for 10 min.[8] The desired compound 3 was obtained in 30% yield as colorless needles, mp 62-63°C. The structure of 3 was characterized by elemental analysis and usefully by the following spectral data: ^{1}H-NMR (100 MHz, CDCl$_3$, δ-values) 6.57

Scheme I



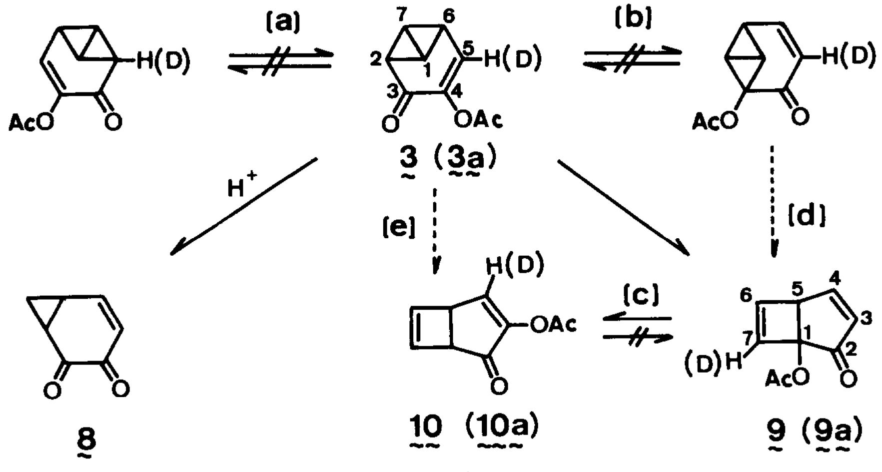
i, hν/acetone; ii, LDA/THF-HMPA/-78°C then Ph-SS-Ph/THF/0°C;
iii, Pb(OAc)$_4$/benzene/reflux ; iv, MCPBA/CH$_2$Cl$_2$ then Δ/CCl$_4$

(1H, d, J=5.0 Hz), 3.43 (2H, t, J=2.5 Hz), 2.83 (1H, dt, J=5.0, 2.5 Hz), 2.60 (1H, dtd, J=5.0, 2.5, 5.0 Hz), 2.18 (3H, s); ^{13}C-NMR (22.5 MHz, CDCl$_3$, δ-values) 20.5 (q, J-130 Hz), 31.1 (d, J= 215 Hz), 33.1 (d, J=160 Hz), 48.8 (d, J=160 Hz), 129.7 (s), 134.1 (d, J=165 Hz), 169.3 (s), 191.1 (s); IR (KBr) $\nu_{C=O}$ 1762, 1690 cm^{-1}; UV (cyclohexane) λ_{max} (log ε) 254 nm (3.65), 324 (1.80), 337 (1.79), 352 (1.68).

It seems to be interesting that the acetoxylation with lead tetraacetate is applicable to the molecule having a bicyclobutane skeleton9) in spite of the presence of Pb^{4+} and Pb^{2+} ions in the reaction mixture.

Treatment of 3 with a catalytic amount of p-toluenesulfonic acid in benzene at room temperature for 1 day afforded 3,4-homo-*o*-benzoquinone (8) quantitatively which was identical in all respects with those reported by Engelhard and Lüttke.10) This finding suggests that the compound 3 acts as a vinylog of cyclopropanol acetate,11) namely, the acid catalyzed cleavage of bicyclobutane ring synchronously takes place with the formation of new enone structure.12)

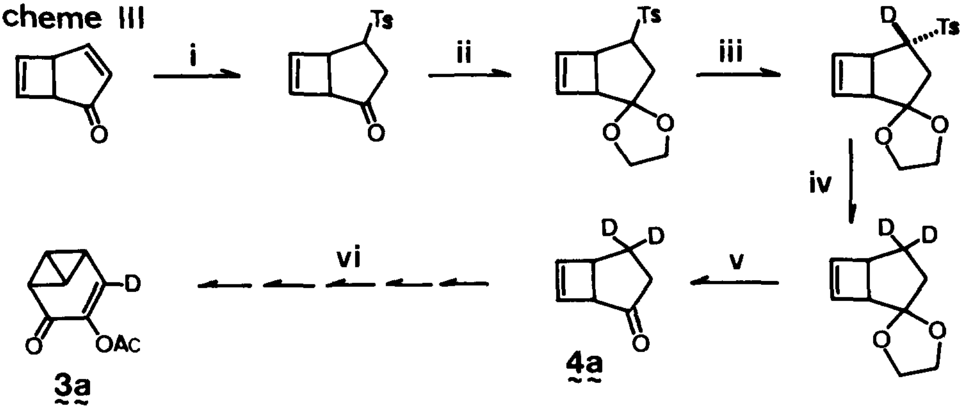
Scheme II



Since ^{1}H-NMR spectrum of 3 does not show any change up to 120°C, a priori expected rapid equilibria with O,O-acetyl transfer such as path-a and/or path-b [Scheme II] are not present. On the other hand, upon heating in dry pyridine at 150°C for 24 h, compound 3 rearranged into 1-acetoxybicyclo[3.2.0]hepta-3,6-dien-2-one (9), instead of 3-acetoxy derivative (10) expected as a normal product for the thermolysis of bicyclobutane,13) in 48% yield. Since the compound 10, which was prepared from 4 by sulfenylation-acetoxylation-desulfenylation sequence similar to those used for the synthesis of 3, does not show any rearrangement into 9 but decomposes slowly ($t_{1/2} \sim 3$ h) into a polymeric material, an intermediate formation of 10 during the thermal rearrangement of 3 into 9 can be ruled out.

There are two plausible mechanisms by which 3 can proceed on to 9. One involves an acetyl migration along with bond relocation of bicyclobutane [path-b] followed by bicyclobutane-cyclobutene rearrangement [path-d] of 3 to give 9. A second possibility for the formation of 9 involves the initial C(1)-C(6) bond cleavage followed by construction of cyclobutene ring via C(2)-C(7) cleavage and then C(4)-C(7) bonding. Examination of the two alternative mechanisms indicated that they might be differenciated by certain deuterium labeling studies. Fortunately, acetoxytropovalene by deuterium at C-5, 3a, could be prepared by a sequence of reactions depicted i Scheme III.[6,15] The ^{1}H-NMR spectrum of 3a showed the complete absence of any signal due to an unlabeled vinyl group. Pyrolysis of 3a in pyridine at 150°C gave 9a which was devoid of any ^{1}H-NMR signal at δ 6.33 where 9 has doublet signal for the vinylic proton at C(7). This experiment clearly ruled out the mechanism involving path-b and path-d. Provided that the mechanism proposed by Christl et al.[13] for one of the possibilities of the thermal rearrangement of tricyclo[4.1.0.0^{2,7}]hept-3-ene (homobenzvalene) is actually involved in our case, 3a should collapse via an intermediate *cis,trans,cis*-2-acetoxytropone into both 9a and 10a. Since 10 is not so stable under the pyrolytic conditions used, whether 10 is produced on the pyrolysis of 3 [path-e] or not has remained obscure.[16]

Scheme III



i, TsNa/EtOH-HOAc/reflux 4 h[a]; ii, $HOCH_2CH_2OH$/benzene/TsOH; iii, ^{n}BuLi/THF/-78°C then D_2O; iv, Na-Hg/MeOD/NaH_2PO_4/THF/reflux 1 h[b]; v, H_3O^+; vi, same with those shown in Scheme I.

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In any case, the results of this study indicated that, in sharp contrast to the case of homobenzvalene,[13] the thermolysis of 3, in which a methylene carbon of homobenzvalene was substituted by carbonyl carbon, provides novel bond reorganization of a bicyclobutane with the participation of an enone moiety.

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8) B. M. Trost and G. S. Massiot, *J. Am. Chem. Soc.*, 99, 4405 (1977).
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11) C. H. Depuy, *Accounts Chem. Res.*, 2, 33 (1968).
12) Attempts to obtaine a valence isomer of tropolone under various methods were unsuccessful so far.
13) M. Christl, U. Heinemann, and W. Kristof, *J. Am. Chem. Soc.*, 97, 2299 (1975).
14) The reverse isomerization, **9** → **10** [path-c], which was regarded as antara-antara Cope rearrangement, could be performed at 420°C under flash vacuum pyrolysis. Cf. T. Miyashi, M. Nitta, and T. Mukai, *J. Am. Chem. Soc.*, 93, 3441 (1971).
15) **4a** was obtained in a 46% overall yield. The deuterium incorporation was found to be > 95% by NMR examination.
16) Analysis of flash vacuum pyrolysis of **3** at 290°C and 400°C showed that a ratio of the products, **9**, **10**, and **3**, was 1.2:0.8:3.0 and 1:2:0, respectively.

(Received in Japan 20 May 1981)