CHEMISTRY LETTERS, pp. 691-692, 1980.

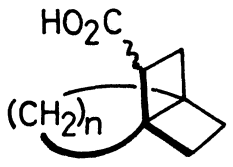
BICYCLO[n.2.2]BRIDGEHEAD ALKENES. SYNTHESIS AND ELECTROPHILIC ADDITION OF ACETIC ACID

Yasuo SAKAI,* Yoshito TOBE, and Yoshinobu ODAIRA
Department of Petroleum Chemistry, Faculty of Engineering
Osaka University, Suita, Osaka 565

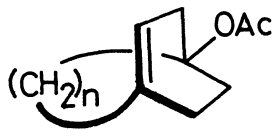
The synthesis of bicyclo[n.2.2]bridgehead alkenes (2a) and (2b) by the solvolytic rearrangement of the corresponding tricyclic acetates (3a) and (3b) in acetic acid and the electrophilic addition of acetic acid to anti-Bredt olefin (2a) are described.

As part of studies on the transformation of readily available [n.3.2]-propellanones into other important carbocyclic ring systems,[1] we recently reported on the synthesis of bicyclo[n.2.2]bridgehead alkenes (2a-c) having an acetoxyl group at the opposite bridgehead position based on the oxidative decarboxylation of [n.2.2]propellane carboxylic acids (1a-c) with lead tetraacetate.[1b] However, the vapor phase thermolysis of the cyclopropylcarbinyl type tricyclic acetates 3a and 3b adopted in the previous paper is inadequate for large-scale preparation of 2a and 2b, albeit in high yield. In this connection, we wish to report here on the improved synthesis of the bridgehead olefins (2a) and (2b) in a preparative scale by the solvolytic rearrangement of 3a and 3b in acetic acid and, moreover, on the electrophilic addition of acetic acid to the obtainable 2a-c.

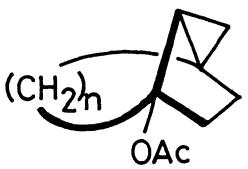
After many trials for the effective conversion of the tricyclic acetates (3a) and (3b) into the bridgehead olefins (2a) and (2b), it appeared that simple treatment of 3a and 3b with acetic acid is the best way for this purpose. Namely, when 3a or 3b (0.10M) was stirred in acetic acid under nitrogen at room temperature for 6 h or 12 h, 2a or 2b was obtained in quantitative yield.[2,3] The reaction followed first-order kinetics and the results are summarized in Table I. As shown in Table I, 3a rearranged 1.6 times faster than 3b at 25°C. By means of the above reaction, the bridgehead olefins 2a and 2b became readily available in a preparative scale.



1 a, b, c



2 a, b, c



3 a, b

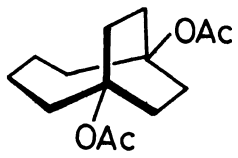
a, n=4; b, n=5; c, n=6

Table I. Kinetic Data for the Rearrangement of 3a and 3b

Acetate	Temp(°C)[a]	$k(sec^{-1})$[b]	k_{rel}	$\Delta H^{\neq}$(kcal/mol)	$\Delta S^{\neq}$(eu)
3a	25.0	7.31×10^{-5}	1.6	26.0	7.8
	33.0	2.37×10^{-4}			
3b	25.0	4.60×10^{-5}	1.0	25.7	5.8
	33.0	1.47×10^{-4}			

a ±0.1°C. b Determined by GLC and the deviations are ±4%.

It has been well known that highly strained bridgehead olefins showed much enhanced reactivity compared with unstrained olefins in addition reactions with various electrophilic reagents.[4] In order to examine the reactivity of a series of the obtainable bridgehead olefins 2a-c, reaction with acetic acid was carried out. In the case of the highly strained olefin (2a) (S=8),[5] addition of acetic acid occurred smoothly at room temperature to afford the bridgehead diacetate (4)[6] almost quantitatively. 4: mp 100-102°C; IR 1715, 1230 cm^{-1}; MS m/e 252(M^+-2), 134(base, M^+-2AcOH); ^{1}H NMR (CCl_4) δ 1.2-2.6(m), s at 1.88; ^{13}C NMR ($CDCl_3$) δ 22.0 (q, 2C), 23.9(t, 2C), 31.0(t, 4C), 38.7(t, 2C), 83.6(s, 2C), 169.3(s, 2C). The kinetic data are listed in Table II. On the contrary, such relatively unstrained olefins as 2b (S=9)[5] and 2c (S=10)[5] failed to undergo acetic acid addition even under severe conditions (reflux, 50 h). Significantly, the above results indicate clearly the category of anti-Bredt compounds.[5]



4

Table II. Kinetic Data for Addition of Acetic Acid to 2a.

Temp(°C)[a]	$k(sec^{-1})$[b]	$\Delta H^{\neq}$(kcal/mol)	$\Delta S^{\neq}$(eu)
25.0	5.72×10^{-6}	23.6	-5.3
33.0	1.67×10^{-5}		

a ±0.1°C. b Determined by GLC and the deviations are ±5%.

References and Notes

(1) (a) Y.Tobe, K.Kakiuchi, Y.Kawakami, Y.Sakai, K.Kimura, and Y.Odaira, Chem. Lett. 1978, 1027.; (b) Y.Sakai, S.Toyotani, Y.Tobe, and Y.Odaira, Tetrahedron Lett. 1979, 3855.; (c) Y.Tobe, Y.Hayauchi, Y.Sakai, and Y.Odaira, J.Org.Chem., 45, 637(1980); (d) K.Kakiuchi, Y.Tobe, and Y.Odaira, ibid., 45, 729(1980).
(2) In the reaction with tetradeuterioacetic acid in place of acetic acid, the corresponding trideuterio derivatives were obtained. Therefore, the reaction is considered to be formally acetolysis of the tricyclic acetates, though the mechanism is not clear at present.
(3) Trace of the diacetate (4) was also formed in the case of 3a.
(4) (a) J.A.Marshall and H.Faubl, J.Am.Chem.Soc., 89, 5965(1967); (b) idem., ibid., 92, 948(1970); (c) J.R.Wiseman, ibid., 89, 5966(1967); (d) J.R. Wiseman and W.A.Pletcher, ibid., 92, 956(1970); (e) Y.Chiang, A.J.Kresge, and J.R.Wiseman, ibid., 98, 1564(1976); (f) K.B.Becker, Helv.Chim. Acta, 60, 94(1977).
(5) (a) G.Köbrich, Angew.Chem., Int.Ed.Engl., 12, 464(1973); (b) G.L.Buchanan, Chem.Soc.Rev., 3, 41(1974).
(6) Satisfactory elemental analysis was obtained.

(Received April 14, 1980)