BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 1351—1353 (1969)

Spiro Compound Formation. III.[1] The Formation of Spiro Compounds by the Rearrangement of Bicyclo[5.4.0]-undecene(1,7) and Cyclopentylcyclohexene

Masatomo NOJIMA and Niichiro TOKURA

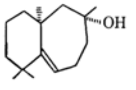
Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka

(Received July 31, 1968)

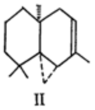
The isomerizations of bicyclo[5.4.0]undecene-(1,7) (IV), spiro[5.5]undecene-1 (V), and 1-cyclopentylcyclohexene (VI) were examined with equivalent amounts of perchloric acid in acetic acid or in ethanol at 75°C. In acetic acid, IV, V, and VI all rearranged to form spiro[5.5]-undecan-1-yl acetate (VII) and spiro[5.5]undecan-2-yl acetate (VIII), together with the three olefins IV, V, and VI. No rearranged product has been obtained by the same procedure in ethanol.

The recent report by Ito[2] on the rearrangement of widdrol (I) or thujopsene (II) to chamigrene (III) under acidic conditions was very suggestive regarding the possibility of spiro-compound formation from bicyclo[5.4.0]undecane derivatives. The formation of 1-cyclopentylcyclohexene (VI) from the reaction of spiro[5.5]undecan-1-ol with zinc chloride had previously been reported by Christol, Jacquier, and Mousseron.[3]

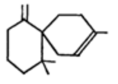
The acetolysis of spiro[5.5]undecan-1-yl tosylate was also examined by Krapcho, McCullough, and Nahabedian[4]; they obtained spiro[5.5]undecane, cyclohexylcyclopentane, and *cis*-bicyclo[5.4.0]undecane in yields of 11, 64, and 25% respectively after the hydrogenation of the reaction mixture.



I

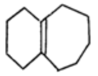


II



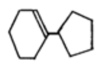
III

From these results, it is expected that bicyclo-[5.4.0]undecene(1,7) (IV), sipro[5.5]undecene-1 (V), and 1-cyclopentylcyclohexene (VI) would all rearrange under acidic conditions. Thus, the present authors attempted the isomerization reaction of IV, V, and VI in the presence of one equivalent mole of perchloric acid in both acetic acid and ethanol.



IV

V



VI

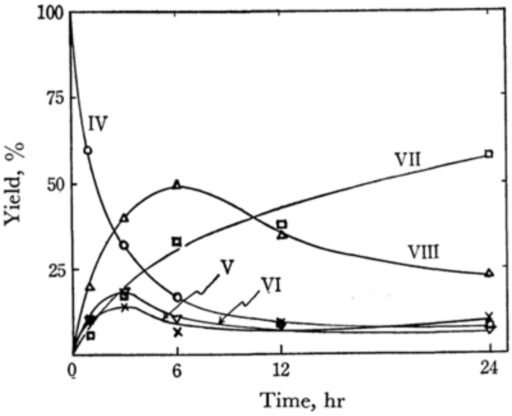


Fig. 1. The Conversion *vs.* reaction time relationship during the isomerization of IV.

IV, V and VI all rearranged with each other and gave a mixture with VII and VIII as the major products after 24 hr.

The behavior of the isomerization of IV is shown in Fig. 1. At the initial stage of the reaction compound IV rearrange to V, VI, and spiro-[5.5]undecan-1-yl acetate (VII), which is then converted to spiro[5.5]undecan-2-yl acetate (VIII). This reaction probably proceeds by way of the carbonium ion B_2. After 24 hr, VIII increased to become 55.8% of the whole reaction product. Similar results were obtained by the reaction of VI in acetic acid. The fact that VIII was formed by the addition of acetic acid to V (after 24 hr an 82.8% yield of VIII was obtained) is comparable to the results in the preceding paper,[1] where V was formed by the reaction of 1-(Δ^4-pentenyl)-

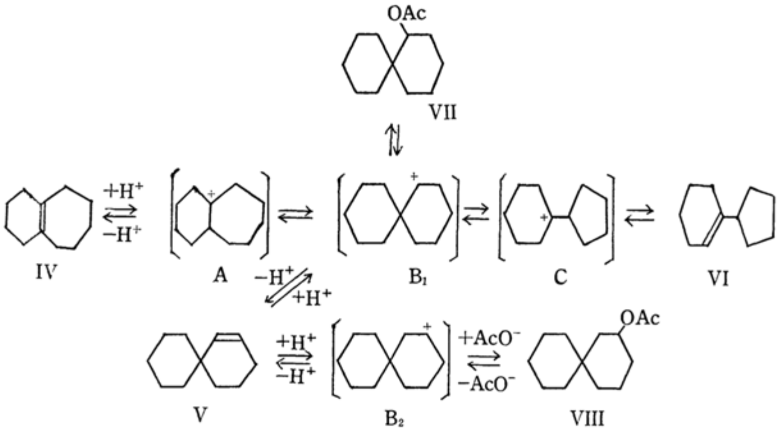
---

[1] M. Nojima, T. Nagai and N. Tokura, *J. Org. Chim.*, **33**, 1970 (1968).

[2] S. Ito, K. Endo, T. Yoshida, M. Yatagai and M. Kodama, *Chem. Commun.*, **1967**, 186.

[3] H. Christol, R. Jacquier and M. Mousseron, *Bull. Soc. Chim. France*, **1957**, 1027.

[4] A. P. Krapcho, J. E. McCullough and K. V. Nahabedian, *J. Org. Chem.*, **30**, 139 (1965).



Scheme I

cyclohexanol; it is in equilibrium with VIII in acetic acid in a molar ratio of 4.5 to 95.5.

The instability of VII under these three sets of reaction conditions was confirmed by the finding that VII was converted to VIII in a high yield under the same conditions. This instability of VII may be explained from a sterical point of view.

Scheme I presents what seem to be the most plausible routes for the formation of the products.

The tertiary carbonium ions, A and C, produced by the protonation of IV and VI rearrange to a carbonium ion, B_1, which then affords VII upon the attack of the acetate anion and the compound V upon deprotonation.

The compound VII was also converted to the ion B_1 by the elimination of acetic acid after protonation; the ion was then further rearranged or deprotonated to form the three products, IV, V, and VI. Under the three sets of reaction conditions the tertiary acetate, which may be derived from A and C, is again unstable.

The reactions of IV, V, and VI in ethanol were also attempted. Contrary to the reactions in acetic acid, no rearrangement occurred after 24 hr and the original olefins used were recovered unchanged.

Experimental

Bicyclo[5.4.0]undecene-(1,7) (IV). Bicyclo[5.4.0]-undecan-2-ol was reacted with polyphosphoric acid according to the method of Christol, Jaquier, and Mousseron;[3] bp 107—108°C/25 mmHg. Found: C, 87.90; H, 12.21%. Calcd for $C_{11}H_{18}$: C, 87.92; H, 12.08%.

Spiro[5.5]undecene-1 (V). This compound was prepared from spiro[5.5]undecan-1-yl xanthate according to the procedure described by Alexander and Mudrak;[5] bp 105—106°C/25 mmHg. Found: C, 87.97; H, 11.92%. Calcd for $C_{11}H_{18}$: C, 87.92; H, 12.08%.

1-Cyclopentylcyclohexene. The reaction of cyclopentylcyclohexanol with thionyl chloride and pyridine[6] gave cyclopentylcyclohexene in a 70% yield; bp 104—105°C/25 mmHg, NMR τ=4.8 (broad 1H). Found: C, 87.88; H, 12.19%. Calcd for $C_{11}H_{18}$: C, 87.92; H, 12.08%.

Spiro[5.5]undecan-1-yl Acetate. This acetate was prepared from the corresponding alcohol with acetyl chloride and *N,N*-dimethylaniline according to the procedure of Nevitt and Hammond.[7] The yield was 55%; bp 104—105°C/7 mmHg: NMR τ=7.6 (singlet, 3H), 5.4 (broad 1H). Found: C, 74.50; H, 10.49%. Calcd for $C_{13}H_{22}O_2$: C, 74.30; H, 10.65%.

Isomerization of an Olefin, IV, V, or VI, in Acetic Acid. To 0.5 g (0.33 mmol) of the olefin in 15 m*l* of glacial acetic acid there was added a 5-m*l* portion of an acetic acid solution containing 0.4 g of 60% perchloric acid (d=1.55). The temperature was maintained at 75±2°C, and a 5-m*l* aliquot was withdrawn periodically. The aliquot was rapidly cooled, diluted with 30 m*l* of chilled water, and extracted three times with *n*-hexane. The combined organic layer was washed with saturated brine water and dried over anhydrous sodium sulfate.

The volume of the extract was kept as small as possible so that no concentration was necessary prior to vpc analysis. The products were analyzed on a Hitachi-Perkin Elmer Gas Chromatograph, Model F-6-D, equipped with a hydrogen flame-ionization detector. A 150 ft × 0.01 in. column packed with Silicone DC 550 was employed, and nitrogen was used as the carrier gas. The temperature settings were at 150°C for the olefin analysis and at 200°C for the acetate analysis.

The Reaction of VII in Acetic Acid. A solution of 0.6 g of VII and 0.4 g of 60% perchloric acid (d=1.55) was heated at 75°C for 24 hr. The reaction mixture was then extracted and analyzed as above. The residue after the removal of the solvent was chromatographed over 30 g of alumina. Elution with ether (10×50 m*l*) gave 0.4 g of an oil. The infrared and NMR spectra

---

5) E. R. Alexander and A. Mudrak, *J. Am. Chem. Soc.*, **72**, 1810 (1950).

6) H. Heymann and L. Fieser, *ibid.*, **73**, 5252 (1951).

7) T. D. Nevitt and G. S. Hammond, *ibid.*, **72**, 1810 (1950).

were identical with those of VIII;[1] however, this product found to be 95% pure by vpc analysis on a silicone DC 550 column.

The Attempted Isomerization of Three Olfefins, IV, V, and VI, in Ethanol. To 0.5 g of the olefin and 15 m*l* of ethanol there was added a 5-m*l* portion of an ethanol solution containing 0.5 g of 60% perchloric acid (d=1.55). The reaction temperature was maintained at 75±2°C for 24 hr. The reaction mixture was then treated and analyzed as has been described above.