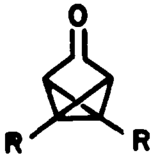
Tetrahedron Letters,Vol.23,No.1,pp 3 - 6,1982 0040-4039/82/010003-04$03.00/0
Printed in Great Britain

REARRANGEMENT OF SUBSTITUTED TRICYCLO[2.1.0.0^{2,5}]PENTAN-3-ONES

Paul Dowd,* Raymond Schappert and Philip Garner
Department of Chemistry, University of Pittsburgh
Pittsburgh, Pennsylvania 15260

Abstract: Treatment of 1,5-bis(hydroxymethyl)tricyclo[2.1.0.0^{2,5}]-pentan-3-one (III) with triphenyl phosphine and carbon tetrachloride results in deep-seated rearrangement to the keto furan, 3-oxybicyclo-[3.3.0]octa-1,4-dien-7-one, VI; the analogous reaction with carbon tetrabromide is normal and yields, the anticipated dibromide IV. Cyclopentadienone intermediates account for the latter reaction and for a dimer formed from 1,5-dimethyltricyclo[2.1.0.0^{2,5}]pentanone (Ia) upon treatment with iodine.

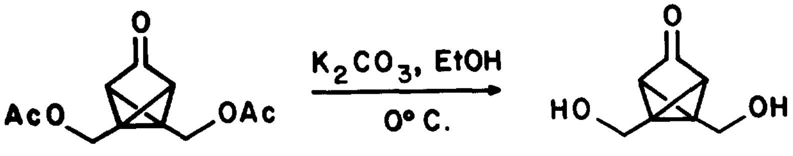
1,5-Dimethyltricyclo[2.1.0.0^{2,5}]pentan-3-one (Ia) was prepared by Doering and Pomerantz[1] in 1963, and 1,5-diphenyltricyclo[2.1.0.0^{2,5}]pentan-3-one (Ib) was made by Masamune[2] at the same time. In spite of this early beginning, the tricyclo[2.1.0.0^{2,5}]pentane system has remained a rare skeletal type as a consequence of its difficult and limited accessibility. Renewed interest in this system arises from the recent observation[3] of an extremely short bridging C_1-C_5 bond in Ia, a bond comparable in length to an aromatic carbon-carbon bond, and because of the synthetic potential inherent in this compact skeleton.



Ia R = CH_3
Ib R = Ph

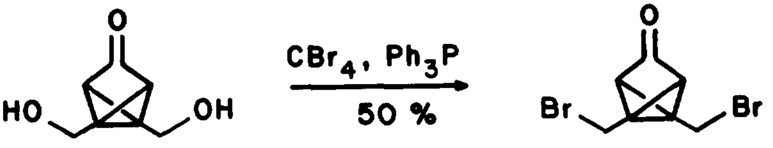
We have now learned[3b] how to prepare functional derivatives of the dimethyl compound Ia. In this Communication, several new members of this class are reported together with a series of rearrangements[4] which provide knowledge of the strain and reactivity inherent in this system.

Preparation of 1,5-bis(hydroxymethyl)tricyclo[2.1.0.0^{2,5}]pentan-3-one (III) proceeded readily (80%) by treatment of the diacetate (II)[3b] with potassium carbonate in cold ethanol. The diol III



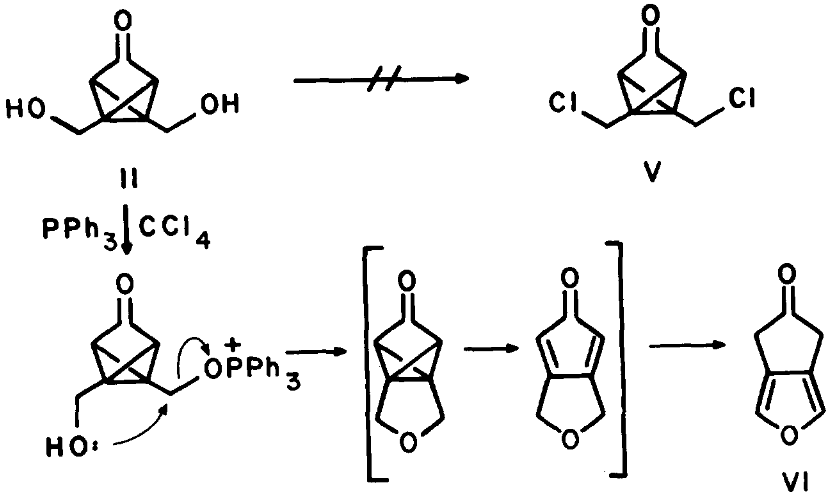
II III

was reacted with carbon tetrabromide and triphenylphosphine in acetonitrile yielding the dibromide IV. When the analogous reaction was attempted using carbon tetrachloride instead of carbon tetrabromide, the keto furan VI was isolated in 37% yield, only 8% of the dichloride V



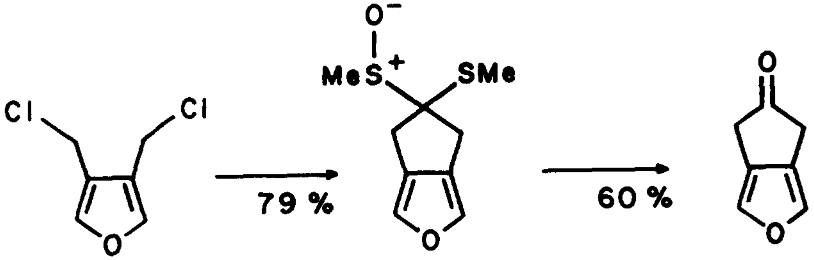
III IV

was formed. When 1.1 eq. of Hunig's base was included in the reaction, no dichloride V was observed and the keto furan VI was obtained in 60% yield.

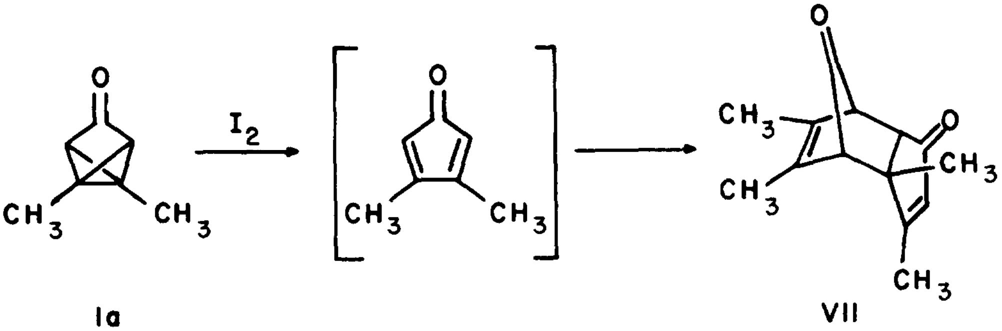


SCHEME I

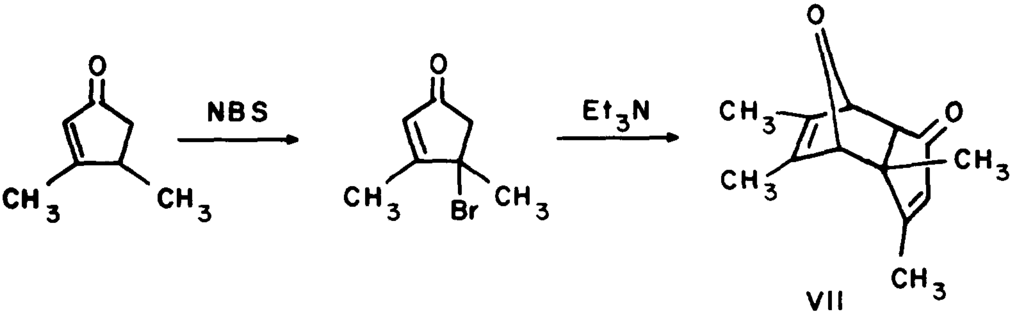
The following rationale accounts for the anomaly. When carbon tetrabromide is used, the counterion is the nucleophilic bromide ion, which displaces the oxaphosphonium ion leaving groups in the fashion expected, yielding the dibromide IV. When carbon tetrachloride is used, the counterion is the less nucleophilic chloride ion. The adjacent hydroxyl group then is able to compete in an internal displacement reaction, thereby forming the tetrahydrofuran ring (Scheme I).[5] The molecule now becomes a (distorted) bicyclo[3.1.1]propellane.[6] To escape from this molecular dilemna, a bicyclobutane to butadiene rearrangement can occur leading to a fused and still highly reactive cyclopentadienone. The protons on the tetrahydrofuran ring are now acidic by virtue of their γ-position with respect to the unsaturated carbonyl group; tautomerization occurs and the keto furan VI is the end product. The structure of VI was demonstrated spectroscopically (ir: 1762 cm^{-1}; nmr ($CDCl_3$): four-proton doublet (J = 1 Hz) at 3.33 δ and two-proton triplet (J = 1 Hz) at 7.29 δ) and by the synthesis (47% overall yield) shown below.



Catalytic conversion of a tricyclo[2.1.0.0^{2,5}]pentanone to a cyclopentadienone intermediate[1] was also observed when the dimethyl compound Ia was treated with iodine.[7] The product VII is more reasonably formulated as arising by dimerization of a cyclopentadienone intermediate.

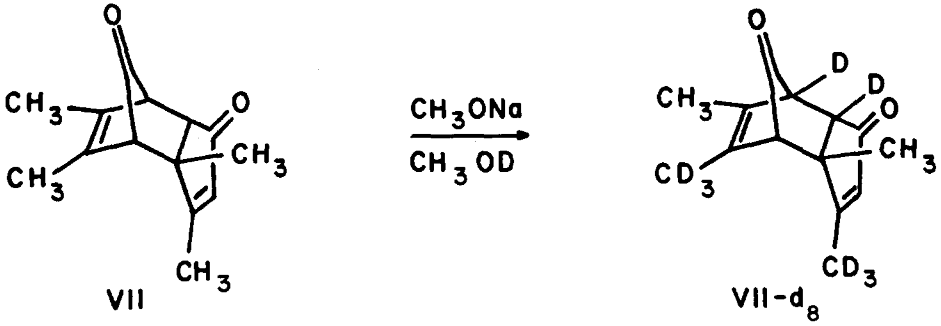


The structure of the dimer VII[8] was established by synthesis of an authentic samples, as shown below, and spectroscopically (ir ($CHCl_3$): 1780, 1692 and 1617 cm^{-1}; nmr ($CDCl_3$, 250 MHz):



one-proton vinyl quartet ($^4J = 1.212$ Hz) at δ 6.023, one-proton bridgehead methine doublet of doublets ($^3J = 5.052$ Hz and $^4J = 1.414$ Hz) at δ 3.112, one-proton bridgehead methine doublet ($^4J = 1.414$ Hz) at δ 2.658, one-proton methine doublet ($^3J = 5.502$ Hz) at δ 2.453, three-proton vinyl methyl doublet ($^4J = 1.213$ Hz) at δ 2.05, three-proton vinyl methyl quartet[9] ($^5J = 1.011$ Hz) at δ 1.708, three-proton vinyl methyl quartet[9] ($^5J = 1.011$ Hz) at δ 1.656 and three-proton methyl singlet at δ 1.357.

Heating the dimer VII with MeONa in MeOD-D_2O for one hour yielded the product VII-d_8



in which substantial exchange has occurred as shown by the nmr spectrum ($CDCl_3$): singlets at δ 6.02, 2.65, 1.71 and 1.36 in a ratio of 1:1:3:3. This is best explained by structure VII-d_8. A facile, degenerate Cope rearrangement is occurring under these conditions.[10]

Acknowledgement. This research was generously supported by the National Science Foundation.

References and Notes

(1) W. von E. Doering and M. Pomerantz, Tetrahedron Letters, 961 (1964).

(2) S. Masamune, J. Am. Chem. Soc., 86, 735 (1964). See also G. Maier, H. P. Resinauer and H. A. Freitag, Tetrahedron Letters, 121 (1978).

(3) (a) H. Irngartinger and K. L. Lukas, Angew. Chem., 91, 750 (1979); Angew. Chem., Int. Ed. Engl., 18, 694 (1979). (b) H. Irngartinger, A. Goldmann, R. Schappert, P. Garner and P. Dowd, J. Chem. Soc., Chem. Comm., 455 (1981).

(4) P. Dowd, R. Schappert and P. Garner, accompanying Communication.

(5) Cf. G. W. Erickson and J. L. Fry, J. Org. Chem., 45, 970 (1980); C. N. Barry and S. A. Evans, Jr., ibid., 46, 3361 (1981).

(6) For stable [3.1.1]propellanes see P. G. Gassman and G. S. Proehl, J. Am. Chem. Soc., 102, 6862 (1980) and K. Minaric-Majerski and Z. Majerski, ibid., 102, 1418 (1980).

(7) For an analogous rearrangement catalyzed by $PdCl_2(C_6H_5CN)_2$ see H. Oma, M. Sakai, M. Suda, and S. Masamune, J. Chem. Soc., Chem. Comm., 45 (1973).

(8) See G. Maier and V. Mende, Angew. Chem., Int. Ed. Eng., 8, 132 (1969).

(9) The two methyls at δ 2.05 and 1.708 appear as doublets but double resonance experiment shows that the two vinyl methyls are coupled to each other.

(10) Cf. D. W. Jones and W. S. McDonald, J. Chem. Soc., Chem. Comm., 417 (1980).

(Received in USA 23 September 1981)