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TRICYCLO[6.3.0.0^{1,6}]UNDECAN-2-ONE AND ITS ISOMERIZATION TO TRICYCLO[3.3.3.0]UNDECAN-2-ONE[1]

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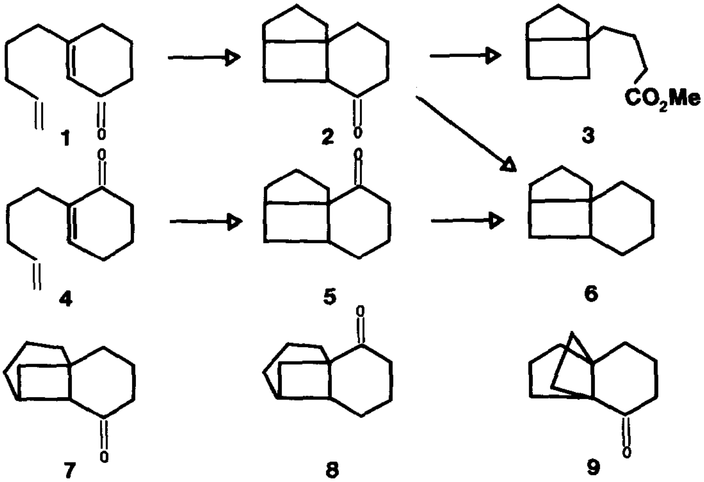
We report the formation of the tricyclo[6.3.0.0^{1,6}]undecanones 2 and 5, and the unusual acid-catalyzed isomerization of 2 to 14.

Irradiation of 1[2] in hexane gave 2[3,4] as the sole product isolated in 92% yield. Similar irradiation of 4[5] gave only 5 (83%). Wolff-Kishner reduction of the new ketones gave the same hydrocarbon, 6. In order to ascertain the orientation of the cycloaddition (whether the cycloadducts are 2 and 5 or 7 and 8[6]) we irradiated 2 in hexane containing 3% methanol at -78° and obtained ester, 3, identical with the ester obtained from the irradiation of 9,[7] confirming the assigned structures.



When a solution of 2 in benzene containing *p*-toluenesulfonic acid was heated at reflux for 15 hours, ketone 14 was produced, along with a trace of other (uncharacterized) material. The identity of 14 was established by comparison with an authentic sample prepared by reduction of the corresponding α,β-unsaturated ketone.[8] Wolff-Kishner reduction of the new ketone gave 15, the ^{13}C-nmr spectrum (in $CDCl_3$) of which exhibits three signals at δ 60.44, 40.37 and 24.64.[9]

The path from 2 to 14 must involve hydride shift(s) since new methylene and quaternary carbons are produced. Ion 10 may undergo hydride shift(s) to give ion 11, which may yield 14 by successive alkyl shifts (a) or by a single 1,3-shift (b). Alternatively, closure of 10 may yield epoxide 12. Protonolysis of 12 to give 13, and alkyl shift(s) as above lead to 14. The experimental distinction among these paths is in progress.

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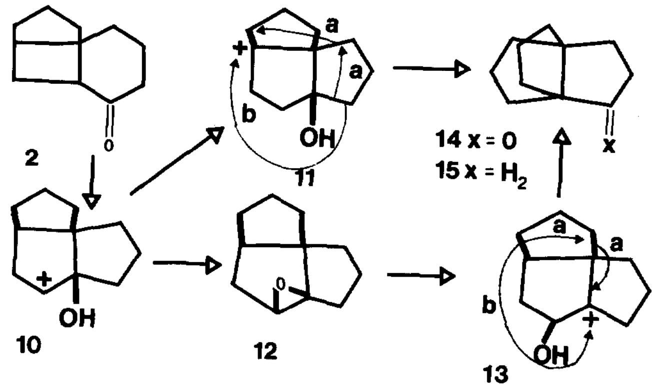
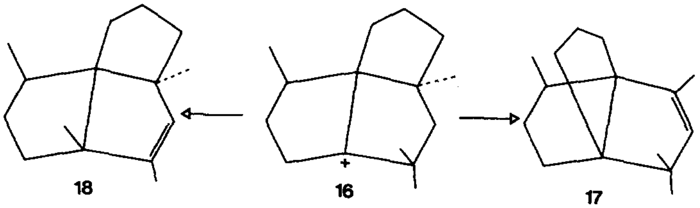


The formation of 14 from 2 may be related to the biosynthesis of modhephene (17),[10] a sesquiterpene isolated from Iscoma Wrightii. Zalkow has suggested that both 17 and isocomene (18) arise from the same cation, 16. We note similarity of ions 11, 13 and 16.



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1. Grateful acknowledgement is made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, and the the National Science Foundation for support of this research.
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3. This conversion was observed earlier by Corey, quoted by W. L. Dilling, Chem. Rev., 69, 845 (1969). We thank Professor Corey for establishing the identity of his and our samples of 2 by comparison of spectra.
4. Satisfactory elemental analyses and spectra (ir, ^{1}H- and ^{13}C-nmr) of all new compounds were obtained.
5. Prepared by the method of D. F. Taber, J. Org. Chem., 41, 2649 (1976), from o-anisic acid and 5-bromopentene.
6. The formation of crossed products from 1,6-heptadienes is unusual, but known. See D. Becker, Z. Harel, and D. Birnbaum, J.C.S. Chem. Commun., 377 (1975).
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