Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 1992, 2(2), 51–52

Mendeleev Communications

Synthesis of Pentaspiro[2.0.0.2.0.2.0.0.2.0]tridecane

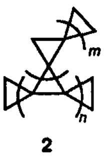
Kirill A. Lukin, Sergei I. Kozhushkov, Andrei A. Andrievski, Bogdan I. Ugrak and Nikolai S. Zefirov*

Department of Chemistry, M. V. Lomonosov Moscow State University, 119899 Moscow, Russian Federation. Fax: +7 095 939 0126

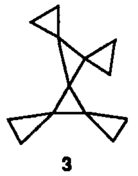
The synthesis of the title pentaspirotridecane and the unique methylenecyclopropane derivatives biscyclopropylidenemethane and 8,9-bismethylenetrispiro[2.0.0.2.1.1]nonane has been accomplished.

Hydrocarbons constructed exclusively from spiroannulated cyclopropanes, which we call *triangulanes*, represent a unique class of strained polycyclic compounds. In the course of systematic studies on these compounds we have developed general approaches for the preparation of both the linear, **1**, and branched triangulanes, **2**. The syntheses are based on three structural transformations, namely (*i*) elongation of the synthetic chain of cyclopropane moieties, (*ii*) chain branching and (*iii*) termination of the synthetic chain.[1,2]

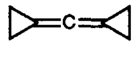
1



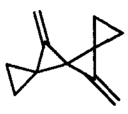
2



3

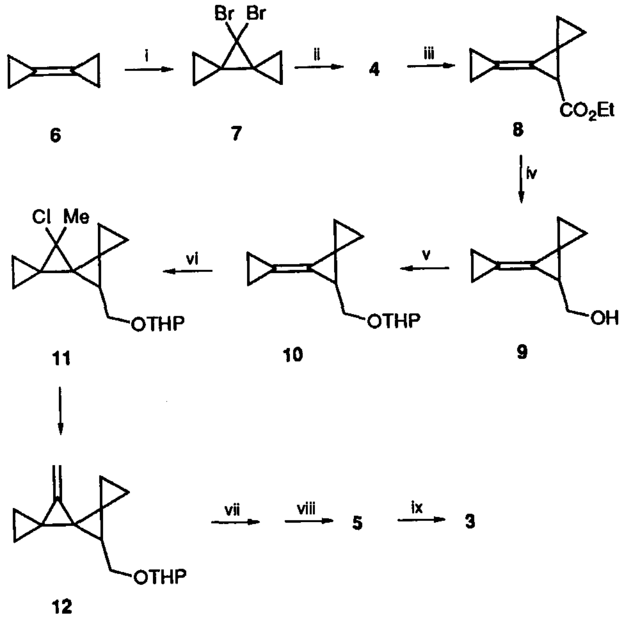


4



5

This communication describes the synthesis of 6-triangulane **3**† using our methodology. This synthesis also involves the



THP = tetrahydropyranyl

Scheme 1 *Reagents and conditions*: i, :CBr$_2$; ii, LiMe; iii, N$_2$CHCO$_2$Et, Rh$_2$(OAc)$_4$; iv, LiAlH$_4$; v, 3,4-dihydro-2*H*-pyran (3,4-DP) H$^+$; vi, :CCH$_3$Cl (Cl$_2$CHMe–LiBu^t); vii, PPh$_3$·Br$_2$; vii, KOBu^t, DMSO; ix, CH$_2$N$_2$, Pd(OAc)$_2$

---

† Prof. A. DeMeijere (University of Göttingen, Germany) recently informed us of his preparation of hydrocarbon **3** from the known 7-cyclopropylidenedispiro[2.0.2.1]heptane.

preparation of two unique methylenecyclopropane derivatives: biscyclopropylidenemethane **4** and 8,9-bismethylenetrispiro[2.0.0.2.1.1]nonane **5** (Scheme 1).

Cycloaddition of dibromocarbene to bicyclopropylidene **6**, which was used as a starting material, gave dibromide **7**, which was in turn treated with methyllithium to give allene **4**. This method of preparation of diene **4** has already been mentioned in the literature,[3] but no information was given on the properties of this compound, or on the experimental details. We found that diene **4** could be obtained in 50% preparative yield when the reaction was carried out at −7 to −5 °C. The structure of **4** was established from ^{1}H NMR [δ 1.48 (s)]; and ^{13}C NMR spectroscopy (δ 7.38, 80.98, 176.57).‡

The double bonds of allene **4** were used to construct two chains of cyclopropane moieties. This was achieved by rhodium acetate catalysed cyclopropanation of diene **4** with ethyl diazoacetate to yield dicyclopropylidene **8** in 65% yield. Ester **8** was reduced to alcohol **9** (78%), which was subsequently transformed into the tetrahydropyranyl derivative **10** (81%). Cycloaddition of chloromethylcarbene, generated in a 1,1-dichloroethane–butyllithium system, to alkene **10** gave trispirononane **11** (60%) which was dehydrochlorinated with potassium *tert*-butoxide in dimethylsulfoxide (DMSO) to give alkene **12** (75%). Treatment of acetal **12** with triphenylphosphine dibromide, followed by potassium *tert*-butoxide in DMSO, gave bismethylenetrispirononane **5** in 25% yield. The structure of this diene was supported by its ^{1}H NMR and ^{13}C NMR spectra.

Finally, palladium acetate catalysed cyclopropanation of diene **5** with diazomethane gave the desired triangulane **3** in 40% yield. Its structure was established from its ^{1}H NMR [δ 0.75–0.9 (m, AA′BB′)] and ^{13}C NMR spectra [δ 3.15 (8 C), 17.58 (4 C), 24.62 (1 C)].‡

In conclusion, we have demonstrated that our methodology can be successfully applied to the synthesis of 6-triangulane **3** which has a rather complex skeleton.

Received: Moscow, 4th July 1991
Cambridge, 19th September 1991; Com. 1/03517G

References

1 N. S. Zefirov, S. I. Kozhushkov, T. S. Kuznetzova, O. V. Kokoreva, K. A. Lukin, B. I. Ugrak and S. S. Tratch, *J. Am. Chem. Soc.*, 1990, **112**, 7702.
2 K. A. Lukin, A. A. Andrievskii, A. Yu. Masunova and N. S. Zefirov, *Dokl. Akad. Nauk SSSR*, 1991, **316**, 379.
3 L. Fitjer and J.-M. Conia, *Angew. Chem.*, 1973, **85**, 832.

---

‡ The structures of compounds 4 and 3 were also confirmed by an X-ray structure determination, the results of which will be published elsewhere.