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SYNTHESIS AND REARRANGEMENT OF FUNCTIONALIZED DISPIRO[2.1.3.3]UNDECANES - PREFERRED C_4-C_5 OVER C_3-C_4 RING ENLARGEMENTS

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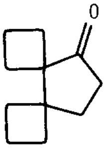
Summary: The functionalized dispiro[2.1.3.3]undecanes 9 and 8 undergo cascade rearrangements to yield the bi- and tricyclic systems 10, 11, 12 and 3, respectively. The rearrangements proceed via an initial enlargement of the four-membered ring.

Within a program devoted to the synthesis of naturally occuring sesquiterpenes via rearrangement routes we recently described 1) the synthesis and rearrangement of dispiro[3.0.3.3]undecanes 1 and 2. Both systems undergo initial C_4-C_5 ring enlargements and thus provide, via two further 1,2-shifts, a new and efficient route to tricycloundecanes 3 and 4, respectively. Several other dispiroundecanes are thought 1) to rearrange to 3 and 4 as well, but only with dispiro[2.1.3.3]undecanes 8 and 9 could the initial reaction involve either C_3-C_4 or C_4-C_5 ring enlargements. We report here the synthesis and rearrangement of both systems and a pronounced preference for an initial enlargement of the four-membered ring.



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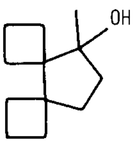

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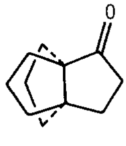

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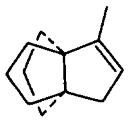

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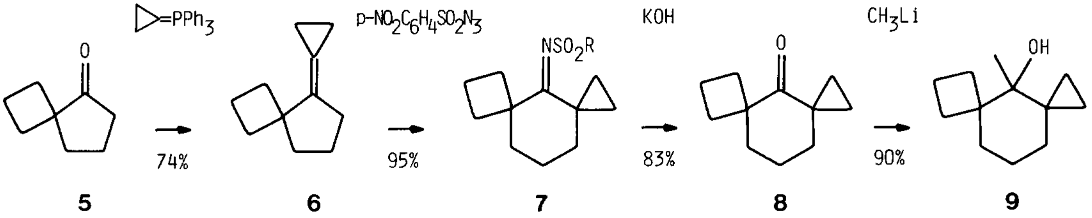
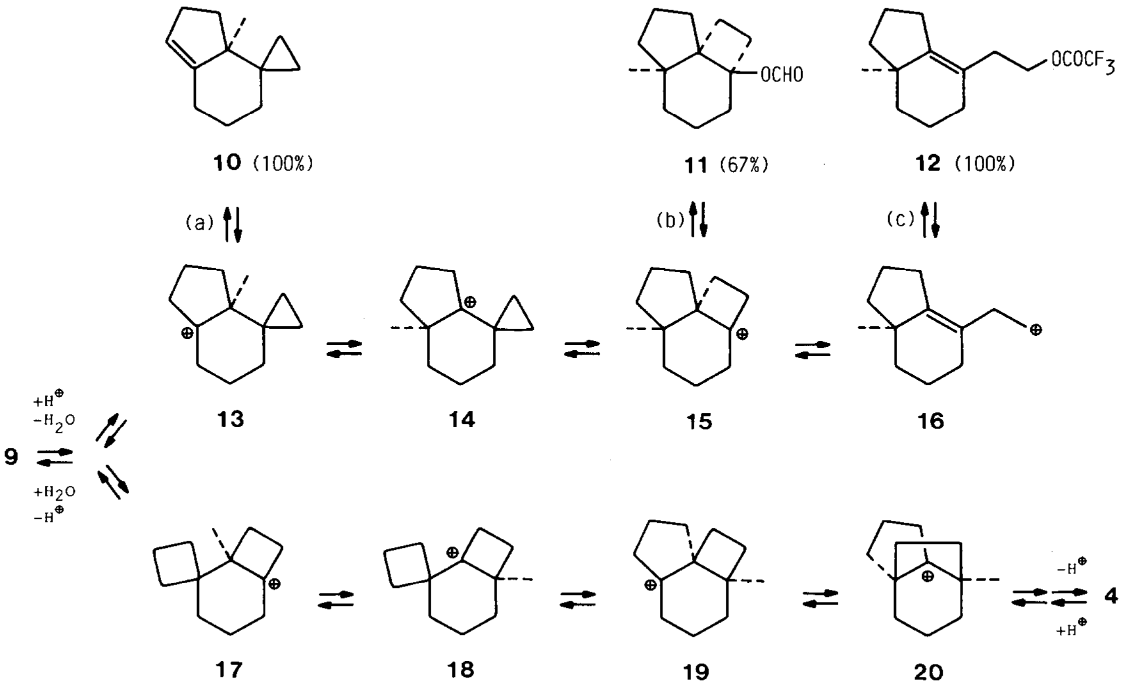
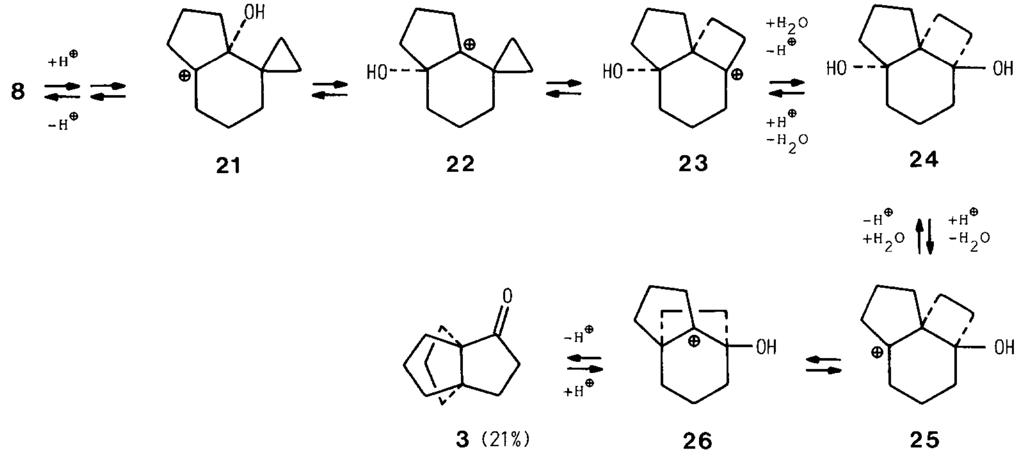
The synthesis of 8 and 9 was achieved as follows: when spiroketone 5 2) was reacted with cyclopropylidene triphenylphosphorane, olefin 6 3) was obtained in 74% yield. Subsequent 1,3-dipolar cycloaddition of p-nitrobenzenesulfonic acid azide proceeded regiospecifically as did the rearrangement of the resulting Δ^2-triazoline. A single imide 7 3,4) arose, and hydrolysis and addition of methyllithium then yielded the desired 8 3) and 9 3), respectively.



In parallel experiments carbinol 9 (2.8 mmol) was treated with (a) silver tetrafluoroborate in methylene chloride (0.3 mmol/10 ml), (b) formic acid in pentane (10 mmol/5 ml), and (c) trifluoroacetic acid in chloroform (10 mmol/5 ml) for 0.5h (a,c) and 2h (b) at room temperature. Quantitative conversions to the bicyclic systems 10 3) (a) and 12 3) (c), and preponderant conversion to the novel tricyclic system 11 3) (b) were observed. 10 and 12 were identified by means of their spectral data, and 11 by means of a crystal structure analysis of a 3,5-dinitrobenzoate 5) derived therefrom.



Clearly, the formation of 10, 11 and 12 is initiated by protonation and dehydration of carbinol 9, followed by enlargement of the four-membered ring. The carbenium ion 13 thus formed then rearranges further to 14, 15 and 16 and thereby not only accounts for the formation of 10, but also for that of 11 and 12. An initial enlargement of the three-membered ring, which would have opened a way to 4, must be excluded since neither 4 nor any other product derived from 17,18,19 or 20 could be detected. Even with the formolysis of 9 (b), the yield of unrearranged 9 (10%), 10 (12%) and a formiate analogous of 12 (11%) complemented the yield of 11 (67%).



From the above, it seemed most likely that a rearrangement of ketone 8 would proceed by the same mechanism as for 9. Formation of a hydroxycarbenium ion 23 could be anticipated but, in contrast to 15, this ion was thought to possibly avoid ring opening by a 1,3-transposition of its hydroxyl group (23→24→25) under aqueous conditions. Indeed, treatment of ketone 8 (6.0 mmol) with 50 perc. aqueous sulfuric acid in methylene chloride (1:1, 10 ml) for 16h at room temperature yielded the [3.3.3]propellane 3$^{1,6)}$, albeit in moderate yield (21%).

In summary, both 8 and 9 undergo cascade rearrangements yielding bi- and tricyclic systems (3,10,11,12) via an initial enlargement of their four-membered rings. This may be explained both by a more favourable alignment of the cyclobutane bonds with respect to the neighbouring cationic center$^{7)}$ and by the greater thermodynamic advantage associated with C_4-C_5 as compared to C_3-C_4 ring enlargements$^{8)}$.

Acknowledgement: Financial support of the Deutsche Forschungsgemeinschaft (project Fi 191/8-3) and the Fonds der Chemischen Industrie is gratefully acknowledged.

References and notes

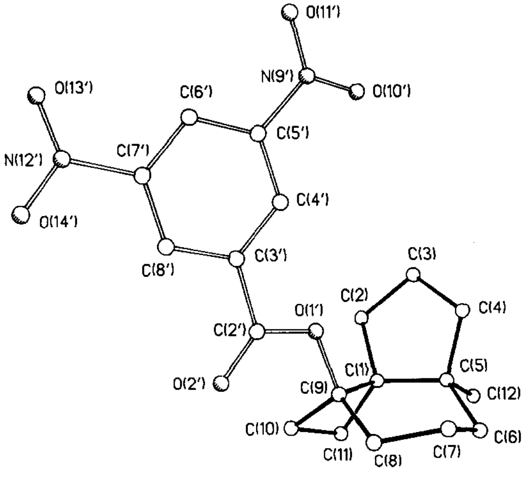
1) Polyspiranes, 11, Cascade Rearrangements, 6; for communications 10 and 5 see L.Fitjer, A.Kanschik and M.Majewski, Tetrahedron Lett. 26, 5277 (1985).

2) R.Mayer, G.Wenschuh and W.Tölpelmann, Chem. Ber. 91, 1616 (1958); C.F.Wilcox Jr. and G.C.Whitney, J. Org. Chem. 32, 2933 (1967).

3) All new compounds gave correct elemental analyses and/or high resolution mass spectral data. IR, ^1H NMR, UV (10) and mass spectral data are in accord with the structures given. ^{13}C NMR data ($CDCl_3$) are as follows: 6: 0.83, 2.60, 17.50, 24.08, 33.31, 34.60, 42.26, 50.29, 110.37, 138.88; 7: 14.24, 15.16, 20.91, 27.84, 31.54, 38.75, 39.71, 53.00, 124.00, 127.93, 148.48, 149.69, 199.34; 8: 15.23, 16.60, 20.31, 26.70, 30.90, 34.46, 36.99, 50.50, 213.37; 9: 5.38, 8.45, 15.10, 20.22, 20.91, 24.21, 25.64, 27.68, 34.92, 35.47, 47.80, 72.44; 10: 8.25, 17.43, 18.24, 21.86, 23.37, 28.81, 36.85, 41.26, 41.87, 46.61, 116.11, 153.52; 11: 16.74, 20.92, 22.97, 24.58, 33.07, 33.44, 33.86, 33.92, 36.20, 40.15, 55.16, 81.04, 160.35; 12: 19.32, 20.70, 24.16, 28.29, 32.73, 35.96, 41.07, 41.52, 66.34, 113.59 (q, $^1J_{C-F} = 286$ Hz), 120.66, 145.44, 157.47 (q, $^2J_{C-F} = 39$ Hz); 27: 16.91, 21.26, 22.82, 24.38, 32.96, 33.10, 33.67, 34.06, 36.24, 40.30, 55.64, 83.39, 122.04, 129.17, 135.09, 148.66, 161.20.

4) For other examples of this useful homologation sequence see ref. 1 and literature cited therein.

5)



Molecular structure of 27

To this purpose, 11 was reduced to the corresponding alcohol which was reacted with 3,5-dinitrobenzoic acid chloride in pyridine to yield the benzoate 27 3). 27 ($C_{19}H_{22}N_2O_6$, mp 152°C) forms monoclinic crystals from methanol, crystal size 0.5 x 0.4 x 0.2 mm^3, space group $P2_1/n$, a = 801.3(2), b = 760.2(1), c = 3081.5(9) pm, ß = 95.80(2)°, V = 1.867nm^3, Z = 4, $D_C = 1.331$ g·cm^{-3}, μ(Mo-K_α) = 0.09 mm^{-1}, Stoe four-circle diffractometer, $2\Theta_{max} = 50°$, 3257 unique reflections, 2209 with $|F| > 3\sigma(F)$ treated as observed, structure solve by direct methods, riding model with r(C-H) = 96 pm employed for hydrogen atoms, anisotropic refinement converged at R = 0.092 [$R_w = 0.096$; $w^{-1} = \sigma(F)^2 + 0.0007 \cdot F^2$]. All relevant data have been deposited with the Fachinformationszentrum Energie, Physik, Mathematik, D-7514 Eggenstein-Leopoldshafen 2, Nr. CSD-51925.

6) R.L.Cargill, J.R.Dalton, S.O'Connor and D.G.Michels, Tetrahedron Lett. 19, 4465 (1978); K.Kakiuchi, Y.Hato, Y.Tobe and Y.Odaira, J.C.S. Chem. Commun. 1982, 6; K.Kakiuchi, K.Itoga, T.Tsugaru, Y.Hato, Y.Tobe and Y.Odaira, J. Org. Chem. 49, 659 (1984); ^{13}C NMR data were identical with those given in ref. 1.

7) If alternative 1,2-shifts can occur, the bond which forms the smaller dihedral angle with the vacant p-orbital will be broken: M.Saunders, J.Chandrasekhar and P.v.R. Schleyer in Rearrangements in Ground and Excited States (P.de Mayo Ed.), Vol.1, 26ff., 41ff., Academic Press, New York 1980.

8) Compare the heats of formation of ethylcyclopropane ($\Delta H_f^o = 1.1$ kcal/mol) 9), methylcyclobutane ($\Delta H_f^o = -0.6$ kcal/mol) 10) and cyclopentane ($\Delta H_f^o = -18.5$ kcal/mol) 10).

9) R.B.Turner, P.Goebel, B.J.Mallon, W. von E.Doering, J.F.Coburn, Jr. and M.Pomerantz, J. Am. Chem. Soc. 90, 4315 (1968).

10) S.W.Benson, F.R.Cruickshank, D.M.Golden, G.R.Haugen, H.E.O'Neal, A.S.Rodgers, R.Shaw and R.Walsh, Chem. Rev. 69, 279 (1969).

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