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THERMAL REARRANGEMENT OF 1-VINYLSPIRO[2.4]HEPTA-4,6-DIENE TO 4,7-DIHYDROINDENE[1]

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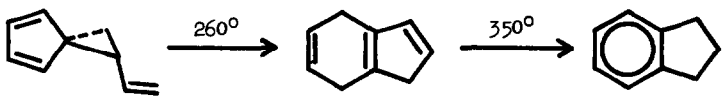
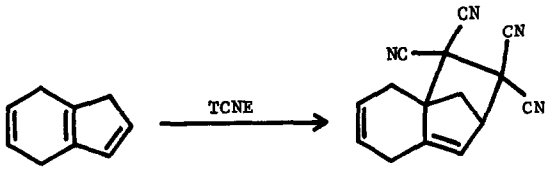
THIS BRIEF NOTE is occasioned by recent observations in Germany and the Soviet Union. Schönleber[3] has remarked the thermal conversion of 1-vinylspiro[2.4]hepta-4,6-diene (1) to indane at 350°. In related work, Mironov, et al.[4] reported the rearrangement of spiro[4.4]nona-1,3-diene to indane at 300-400°. In the latter case, several tetrahydroindene intermediates were isolated. We describe here the isolation of a compound intermediate in the conversion of 1 to indane.



1 2

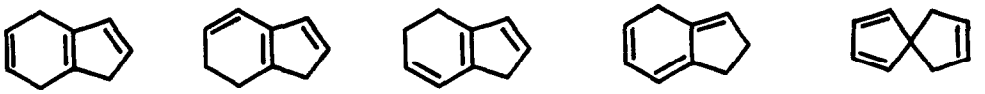
The irradiation of diazocyclopentadiene[5] in butadiene followed by analysis and collection on a 6', 15% Dow-Corning 710 silicone oil column operated at 90° with a flow rate of 100 ml/min He yielded 1 in hundred milligram lots. Pyrolysis of 1 in a flowing system at 260-320° (residence time ca. 20 sec) resulted in 90-100% conversion to 2 which could be recovered in ca. 50% yield. Treatment of 2 under the conditions reported by Schönleber[3] gave indane only. The structure of 2 was assigned on the bases of both spectral and chemical evidence. The nmr spectrum consists of four broad singlets at τ 3.79 (2H), 4.27 (2H), 7.03 (4H) and 7.20 (2H),

and is surprisingly simple. The infrared spectrum shows bands at 3090, 3060, 3025(s) 2962, 2879(s), 2821(s), 2738, 1626, 1520, 1426(s), 1375(s), 1343, 1324, 1262, 1170, 1125, 949(s), 913 and 684(s) cm^{-1}. Addition of a dilute benzene solution of tetracyanoethylene to a benzene solution of 2 gave a white crystalline adduct (3, mp 170-1°, dec) in excellent yield. The nmr spectrum of 3 shows signals for vinyl hydrogens at τ 3.62 (1H) and 4.16 (2H) and is otherwise consistent with the assigned structure.



2 3

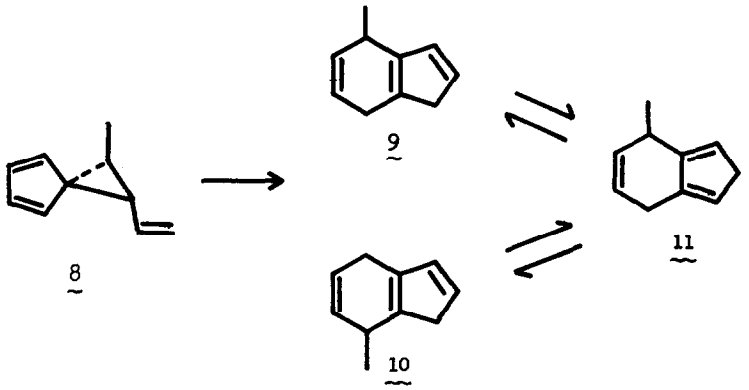
The observations that the colorless compound 2 has four vinyl hydrogens and forms a Diels-Alder adduct with only three vinyl hydrogens serve to reduce the large number of a priori structural possibilities to four (2,4,5 and 6). Of these, 4, 5 and 6 can be eliminated by an examination of



2 4 5 6 7

the ultraviolet spectrum (λ_{max}^{MeOH} 253, ε 3100) which is in good agreement with those recorded by Mironov,[4,6] for disubstituted cyclopentadienes (λ_{max} 254, ε 3400, and significantly to the short wavelength side of that expected for 4, 5 or 6, all of which contain a cyclohexadiene ring.[7]

It is tempting to implicate the known[3] triene 7 in the conversion of 1 to 2. While it seems certain that 7 would indeed rearrange to 2 under the pyrolysis conditions it remains possible that 1 is converted directly to 2 via a concerted or non-concerted sigmatropic shift of order [3.5]. No 7 can be detected in the pyrolysis mixture at any temperature. An attempt to gain information on the mechanistic question through use of the methyl-labelled compound 8 has come to nought as compounds 9 and 10, the likely products of the direct and stepwise mechanisms, are rapidly interconverted under the pyrolysis conditions, doubtless through the unisolated triene 11.



REFERENCES AND NOTES

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