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ACCESS TO EQUALLY RING-FUNCTIONALISED PROPELLANES BY DOUBLE THERMOCYCLISATION OF 3,3-DIALKYNYLCYCLOALKANONES.

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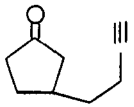
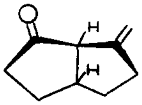
Propellanes bearing several functional groups are attractive stereochemical models, in particular due to their rigid structure ; most of them are prepared through cycloaddition reactions or Dieckmann and acyloin condensations (for a review, see (¹)).

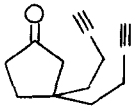
We have recently shown that the double thermocyclisation of convenient dienones as e.g. 3,3-dialkenylcycloalkanones provides a new and simple route to such structures (²) (³). Moreover, other studies (⁴) showed us the ability of 3-butyn-3'-yl-cyclopentanone A to be converted easily into the bicyclo [3,3,0] octanone system B, a result which is qualitatively in line with those reported very recently by Agosta and Wolff (⁵). In the present communication we report on the corresponding double thermocyclisation of diynones, i.e. firstly on the synthesis of the 3,3-dibutynylcyclopentanone 1 and secondly, on its conversion into the [3,3,3] propellane system 2, a key compound from which some equally ring-functionalised propellanes can be derived as e.g. the trimethylene derivative 3.



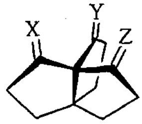
A



B



1



2 X = O, Y = Z = CH_2
3 X = Y = Z = CH_2

The basic problem in the synthesis of 1, i.e. the introduction of the gem-dialkynyl grouping, has been solved by means of a one step double 1,4-addition of the Grignard reagent 10, derived from 3-butyn-1-ol, on the 3-butylthiocyclopent-2-en-1-one 6

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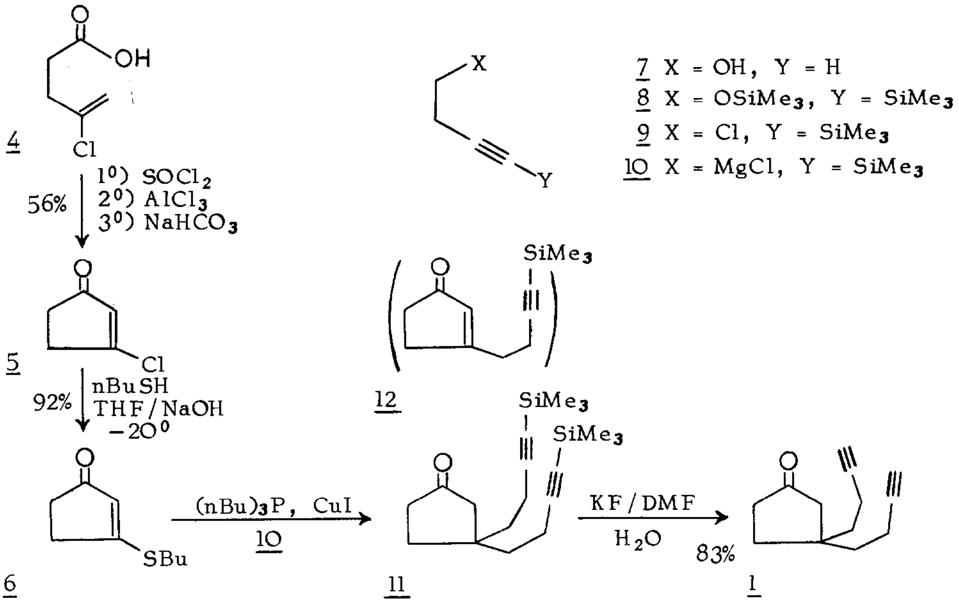
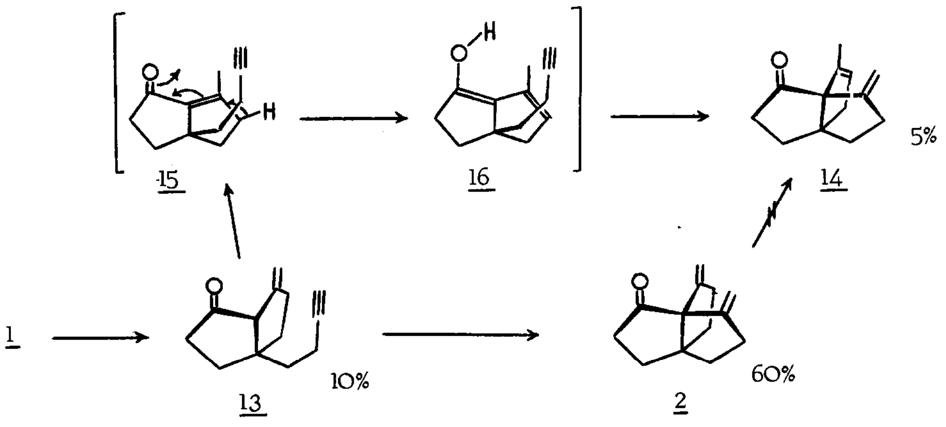
as outlined below. The Lewis acid catalysed cyclisation of 4-chloropent-4-enoyl chloride (1 eq. $AlCl_3$, CH_2Cl_2, -15^0 to O^0, 1.5 h) followed by dehydrochlorination of the resulting 3,3-dichlorocyclopentanone (^{6}) makes the 3-chlorocyclopent-2-en-1-one 5 more easily available than by other existing methods (^{7}). Chlorine-alkylthio group exchange affords the previously unknown ketone 6 in 92% yield (^{8}).



The disilylated compound 8 was obtained by the standard method (^{9}) and converted into its chloride 9 (1.1 eq. $SOCl_2$) in an overall yield of 93% (^{10}). The 1,4-addition of the Grignard reagent 10 to the ketone 6 always ended up with a mixture of starting compound 6, mono- and diaddition products 12 and 11 when 10 and the catalyst were taken in stoichiometric amounts. But, when 6, 10 and $(nBu)_3P$, CuI were respectively taken in the ratios 1/5.5/6, the compound 11 was the sole final product and could be isolated in 50% yield. This clearly shows a discrepancy in the reactivity of lithioalkylthio(alkyl)cuprates vs.magnesioalkylthio(alkyl)cuprates (^{11}) (^{12}). Finally, cleavage of the trimethylsilyl groups ("KF, 10 H_2O", DMF)(^{13}) led in 83% yield to the 3,3-di (butyn-3'yl)-cyclopentanone 1.

On heating ketone 1 as a 10% solution in decalin (sealed tube, 270^0, 100 min.) the fancy molecule : 8,9-dimethylene [3,3,3] propellan-2-one 2 was obtained as the major product (60% after isolation by G.L.C.), m.p. 57.5-59.5^0. Its structure was established from the following data : M.S. accurate mass M = 188.119 ($C_{13}H_{16}O$ requires 188.120) ; IR (CCl_4) cm^{-1} : 3100, 1740, 1655 and 900 ; NMR (CCl_4) ppm : 1.75 and 2.35 two multiplets (6H and 6H), 4.89 (t, J = 2Hz, 2H), 5.13 (t, J = 2 Hz, 2H) ; UV (cyclohexane) λ max = 215 nm (5380) and 304 nm (128).



Beside the expected double cyclisation compound 2, two minor products have been identified : the monocyclisation product 13 (10%) and the tricyclic compound 14 (5%). Owing to the fact that the dienone 2 is recovered totally unchanged when submitted to the same thermal conditions as diynone 1 (vide supra), compound 14 is presumably formed via the isomerisation 13 ⟶ 15 ⟶ 16 prior to the second cyclisation.

The carbonyl group of the dienone 2 exhibits the usual reactivity pattern towards Wittig reagents. Treated with 2.2 eq. of $Ph_3P^+ CH_3Br^-$ and 2 eq. of sodium t-amylate (14), compound 2 is converted into the 2,8,9-trimethylene-[3,3,3] propellane 3 in 75% yield after isolation by preparative G.L.C. ; NMR (CCl_4) ppm two multiplets at 1.60 and 2.30 (6H and 6H), 4.85 (t, J = 2 Hz, 6H) ; IR (film) cm^{-1} : 3080, 1660 and 895 ; $M^+ = 186$.

The chemistry of these structures, which might exhibit modified properties resulting from an eventual through-space interaction of the π-systems, is presently under active investigation.

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