Reaction of Isoprene and Dimethyl Acetylenedicarboxylate in the Presence of Cyclododeca-1,5,9-trienylnickel: Formation of Cyclotetradecatetraene Derivatives and a Novel Rearrangement of an Intermediate π-Allylnickel Complex under the Influence of Carbon Monoxide

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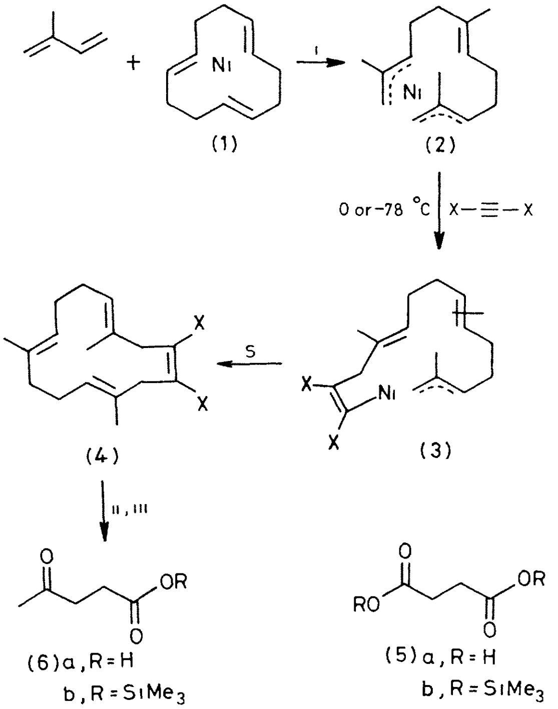
Summary The reaction of dimethyl acetylenedicarboxylate with 2,6,11-trimethyl-α,ω-dodecatrienediyl nickel (**2**), prepared from the reaction of isoprene with cyclododecatrienylnickel, at both 0 and −78 °C yields the fourteen-membered cyclic derivative (**4**) with 85% selectivity, on addition of carbon monoxide at −78 °C a novel rearrangement of the intermediate π-allylnickel complexes is observed which leads, eventually, to cyclic products with different isoprenoid arrangements

Co-oligomerisation of buta-1,3-diene with olefins and acetylenes, catalysed by nickel(0) complex catalysts, has been shown to be a valuable route to the formation of substituted ten-[1] and fourteen-membered[2,3] cyclic derivatives The co-oligomerisation of isoprene with olefins and acetylenes, in the presence of nickel(0) complexes, could provide a synthetic route to valuable fourteen membered cyclic derivatives We report the formation of dimethyl 4,8,13-trimethylcyclotetradeca-*c,t,t,t*-1,4,8,12-tetraene-1,2-dicarboxylate (**4**) by the insertion of dimethyl acetylenedicarboxylate in the tris(isoprene)nickel(0) complex (**2**) and an interesting rearrangement of a π-allylnickel intermediate under the influence of carbon monoxide

Cyclododecatrienylnickel, Ni(cdt) (**1**), has been previously prepared by reaction of cyclododeca-1,5,9-triene in the presence of nickel bis(acetylacetonate) and diethylaluminium ethoxide[4] Isolation of the somewhat unstable red crystalline complex (**1**) is difficult but, in the present work, an ethereal solution of (**1**) was obtained sufficiently pure by decanting the solution of the complex from the insoluble aluminium salts

Isoprene (0·1 mol) was added to Ni(cdt) (23 mmol) in diethyl ether (30 ml) and stirred at 0 °C for 2 h Dimethyl acetylenedicarboxylate (23 mmol) was added at 0 °C and the deep-red solution quickly darkened to a brown-red After 2 h the reaction was terminated by the addition of a slight excess of sulphur (1 5 mol equiv) The resultant nickel sulphide was removed by filtration and the product was separated by column chromatography (silica, 100—120 mesh), light petroleum–diethyl ether (10: 1) eluted the main diester insertion product (**4**) as a viscous yellow oil [2·3 g, 30% isolated yield based on (**1**)] in 95% purity G l c analysis† of the reaction mixture showed that the main diester insertion product (**4**) was produced with 85% selectivity The product was further purified by either preparative t l c [silica, light petroleum–diethyl ether (1 : 1), R_f 0 5] or preparative g l c At low temperatures (−78 °C) or when the reaction was conducted using a half-molar equivalent of the acetylene diester, the reaction product, selectivity, and yield remained essentially unchanged

The structure of (**4**) was established by ozonolysis and subsequent hydrogenation (5% Pd on $CaCO_3$) of the crude ozonide[5] The resulting fragments, succinic acid (**5a**) and levulinic acid (**6a**), were identified by g l c and mass spectral analysis with coinjection of solutions of authentic samples and by formation and comparison of the trimethylsilyl derivatives[6] The trisubstituted double bonds in (**4**) were assigned *trans* on the basis of the methyl chemical shifts in the ^{13}C n m r spectrum[7] (singlets at 15 097 and 17 870 gave quartets in an off-resonance spectrum) ‡ The tetrasubstituted double bond must result from a *cis* insertion of the acetylene group



$X = CO_2Me$

Reagents i, Et_2O 0 °C, 2 h ii, O_3, −30 °C iii, 5% Pd-$CaCO_3$-H_2

When the same experimental conditions were used but the work-up procedure employed carbon monoxide at 0 °C in place of sulphur, a similar product was obtained By using carbon monoxide at −78 °C, however, with otherwise unchanged conditions the products were drastically changed

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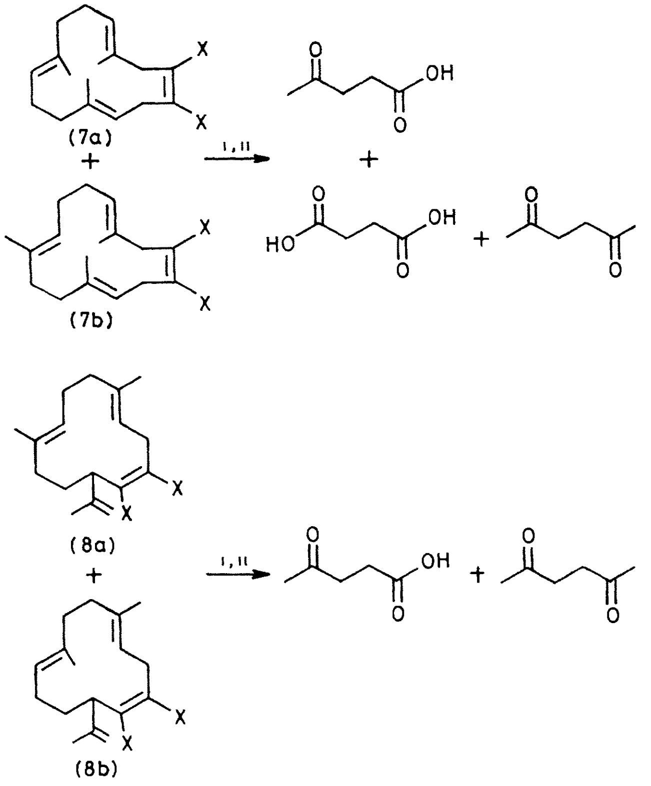
† 5 ft, 3% SE30, 100—250 °C at 16 °C min^{-1}

‡ δ values in p p m relative to Me_4Si

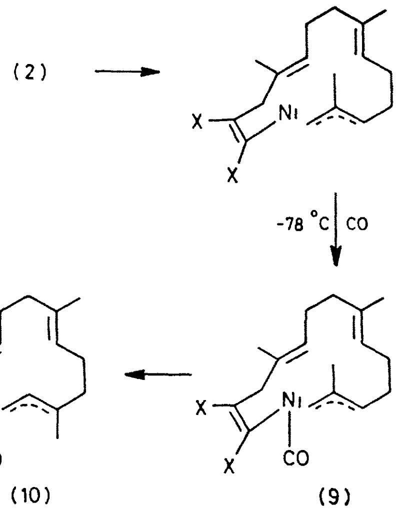
to a mixture of (**4**) (10%), (**7**) (40%), and (**8**) (50%) in an overall yield of 27% After separation by silver nitrate–silica gel column chromatography followed by preparative g l c both (**7**) and (**8**) were shown from spectral considerations and ozonolysis, to be pairs of inseparable isomers A mixture of levulinic acid, succinic acid, and acetonylacetone was obtained from ozonolysis of (**7**) indicating the presence of two isomers (**7a**) and (**7b**) Similarly, levulinic acid and acetonylacetone were obtained from (**8**) indicating the presence of the mixture (**8a**) and (**8b**)



X = CO_2Me

Reagents i O_3 ii Pd–$CaCO_3$–H_2

The elucidation of structure (**4**) leads to the conclusion that the initially formed bis-π-allylnickel complex from isoprene trimerisation must have structure (**2**) This new complex has not been isolated and fully characterised, but its structure is assumed to be similar to the complex obtained in an analogous reaction of butadiene with bis(cyclooctadienyl)nickel[8] After the insertion of dimethyl acetylenedicarboxylate, either ring closure to form (**4**) occurs or at −78 °C after addition of carbon monoxide, a rearrangement of the unchanged π-allyl group leads on to ring closure to either (**7a**) or (**7b**) The other isomer of (**7**) is probably formed by rearrangement of the complex formed by initial reaction at the other π-allylnickel group A comparable situation clearly explains the formation of a pair of isomers by ring closure of the intermediate complexes to form C_{12}-ring products



This type of rearrangement, which has not been previously observed may well be due to the relative stabilities of the nickel intermediates, (**9**) and (**10**), co-ordinated to a ligand such as carbon monoxide We have previously shown that bis-π-allylnickel complexes take up only one molecule of carbon monoxide at −78 °C and remain indefinitely stable without carbon–carbon coupling[9] This type of rearrangement might have wide implications in the control of co-oligomerisation reactions of isoprene

We thank the Department of Education (N I) for financial support (M G K)

(*Received*, 17*th January* 1980, *Com* 055)

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[1] P Heimbach, P W Jolly, and G Wilke, *Adv Organometal Chem* , 1970, **8**, 29, 63, W Brenner, P Heimbach, K J Ploner, and F Thomel *Angew Chem Internat Edn* , 1969, **8**, 753, P Heimbach and W Brenner, *ibid*, 1966, **5**, 961

[2] R Baker, P Bevan, and R C Cookson, *J Chem Soc Chem Commun* , 1975, 752

[3] For synthesis of 14-, 15-, and 16-membered rings by reaction with allene and isocyanides, see R Baker, R C Cookson, and J R Vinson, *J Chem Soc Chem Commun* , 1974, 515, R Baker, P Bevan, R C Cookson, A H Copeland, and A D Gribble, *J Chem Soc* , *Perkin Trans I*, 1978, 480

[4] B Bogdanovic and G Wilke, *Annalen* , 1966, **699**, 1

[5] B P Moore and W V Brown, *J Chromatogr* , 1971, **60**, 157

[6] C C Sweely, R Bently, M Makita, and W W Wells, *J Am Chem Soc* , 1963, **85**, 2497

[7] E Breitmaier and W Voelter, '^{13}C n m r Spectroscopy,' Vol 5, Verlag Chemie, Frankfurt, 1973

[8] B Bogdanovic, P Heimbach, M Kroner, and G Wilke, *Annalen*, 1969, **727**, 143

[9] R Baker and A H Copeland, *Tetrahedron Letters*, 1976, 4535