4-(β-Phenylvinyl)-1,4-dihydroxy-2,2,6,6-tetramethylpiperidine was derived from the hydrogenation of radical (II) on Raney Ni after the uptake of 3/2 mole of H_2, mp 112°C.

CONCLUSIONS

1. We have examined the liquid-phase hydrogenation of stable iminoxyl radicals with acetylenic bonds — 4-ethynyl-4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl and 4-phenylethynyl-4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl on Raney Ni, Pt, and Pd catalysts.

2. On Raney Ni the paramagnetic center and the C≡C bond of the radicals are reduced simultaneously; in the presence of Pt the iminoxyl group is preferentially hydrogenated, while on Pd black the C≡C bond is reduced (via the olefinic compound) without affecting the paramagnetic center.

3. In the course of this work we have prepared several new stable iminoxyl radicals: 4-ethynyl-4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl and 4-phenylethynyl-4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl, 4-vinyl-4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl, 4-(β-phenylvinyl)-4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl, and 4-(β-phenylethyl)-4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl, together with 4-vinyl-1,4-dihydroxy-2,2,6,6-tetramethylpiperidine and 4-ethyl-1,4-dihydroxy-2,2,6,6-tetramethylpiperidine.

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CYCLOOLIGOMERIZATION OF 1-VINYL-1-CYCLOPENTENE CATALYZED BY NICKEL COMPLEXES

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Cyclooligomerization forming cyclooctadiene and cyclododecatriene derivatives has been reported only for simple 1,3-dienes (butadiene, isoprene, and their homologs) [1-3]. A reaction involving the rather more complex 1,2-dimethylenecyclohexane was described only recently [4]. We have continued our study of the catalytic cyclooligomerization of vinylarenes [5-7] by examining the reaction of 1-vinylcyclopentene (I) on Ni complex catalysts.

We found that at 80°C in toluene (10 h) on the catalyst system $Ni(acac)_2{-}(C_4H_9)_3P{-}Al(C_2H_5)_3$ (1:1:4) (I) reacted to form a mixture of the hydrocarbons 2(3)-(1-cyclopentenyl)bicyclo-[4.3.0]non-5-ene (II), tricyclo$[9.3.0.0^{4,8}]$tetradeca-1,8-diene (III), and tetracyclo$[16.3.0.0^{4,8}.0^{11,15}]$eicosa-1,8,15-triene (IV) in the ratio 1:8:4. The conversion of (I) was 57%. We isolated pure (II), (III), and (IV) from the reaction mixture by vacuum distillation and verified their structures from their spectra and by ozonolysis. The mass spectra of (III) and (IV) exhibit in addition to the molecular ion an intense $[M - 94]^+$ peak which represents the fragmentation

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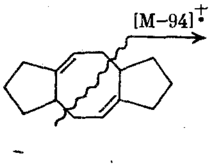
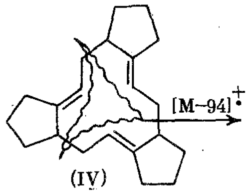
TABLE 1. Effect of the Nature of the Electron-Donating Activator on the Total Yield and Composition of the Reaction Products of 1-Vinylcyclopentene (10 h, 120°C, Ni:P:Al ratio = 1:1:4)

Activator	Total yield, %	Oligomer composition, %		
		(II)	(III)	(IV)
$(PhO)_3P$	35	10	15,5	8,3
Ph_3P	50	18	25	9,1
Bu_3P	57	4,5	35	17
–	60	20	32	–



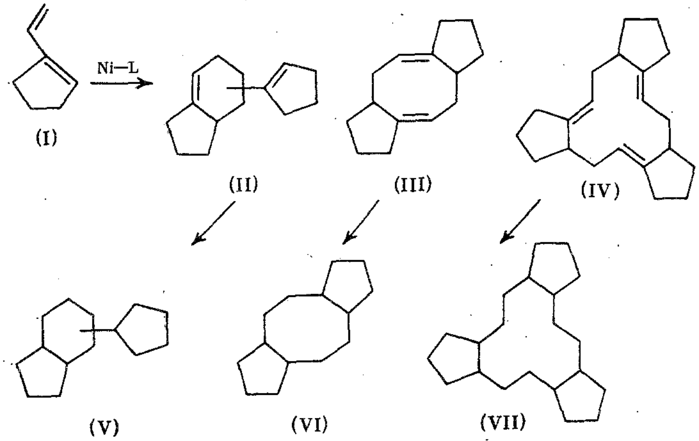
(III)

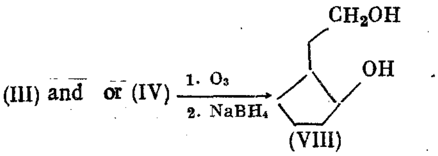


(IV)

Ozonolysis of (III) and (IV) followed by successive treatment with dimethyl sulfide and $NaBH_4$ gave 2-hydroxyethyl-1-cyclopentanol in high yield (VIII), identified by comparison with an authentic sample [8]. The absence of other alcohols from the ozonolysis products implies that the cyclooligomerization of 1-vinylcyclopentene in the presence of Ni complexes is structurally selective. We verified the structure of (II) by comparison with a sample prepared by thermal dimerization of (I). We cannot exclude the possibility that both samples were a mixture of isomers differing in the position (C^2, C^3) of the cyclopentenyl radical. Hydrogenation of cyclooligomers (II), (III), and (IV) on Pd/C involved the uptake of 2, 2, and 3 moles of H_2 respectively, giving the saturated hydrocarbons (VI)-(VIII).

Reduction in the electron-donating ability of the organophosphorus activator in the order $Bu_3P > Ph_3P > (PhO)_3P$ entailed not only diminution in the total yield of cyclooligomers (II)-(IV) but also in the content of (III) and (IV) in the catalyzate (Table 1). The major reaction products here were (II) and (III) in the ratio 3:7. The effect of temperature on the total yield and composition of the cyclooligomers of (I) is shown in Fig. 1.





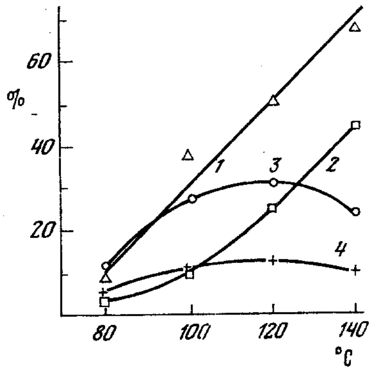


Fig. 1. Effect of temperature on the yield of oligomers (II), (III), and (IV) and the conversion of (I): 1) conversion of (I); 2) yield of (II); 3) yield of (III); 3) yield of (IV).

Thus the cyclooligomerization of (I) on catalysts incorporating Ni complexes could provide a convenient route to difficultly accessible polycyclic unsaturated hydrocarbons.

EXPERIMENTAL

Vinylcyclopentene was prepared after [9]. Hydrocarbon mixtures were analyzed on a Tsvet-102 chromatograph, column length 1 m, Apiezon L on Celite, carrier gas He, flame-ionization detector. Spectra were recorded on: IR: a UR-20 (film); and PMR: a Tesla 480-B in CCl_4, with hexamethyldisiloxane (HMDS) as internal standard. Mass spectra were measured on an MKh-1306, ionizing energy 70 eV and ionization chamber temperature 150°C.

Cyclooligomerization of Vinylcyclopentene (I). To a solution of $Ni(acac)_2$ (0.1 g, 0.39 mmole), the organophosphorus activator (equimolar quantity), and (I) (1 ml) in absolute benzene (5 ml) was added Et_3Al (0.2 g) at −5°C in a stream of Ar. The reaction mixture was stirred for 30 min. The catalyst solution was then transferred to a 17 cm^3 steel autoclave, (I) (2 ml) was added, and the mixture was heated. The autoclave was then cooled. The reaction mixture was filtered through Al_2O_3 (activity III, 10 g) and the column was washed with benzene. The eluates were combined, the solvent was evaporated, and the residue was rectified on a Widmer column. Our results are summarized in Table 1.

The hydrocarbons had the following constants after isolation by vacuum distillation.

Tricyclo[$9.3.0.0^{4,8}$]tetradeca-1,8-diene (III): bp 79°C (0.1 mm); n_D^{20} 1.5000. IR spectrum (ν, cm^{-1}): 815, 3060 (C=C), 1450 (CH_2). PMR spectrum (δ, ppm): 5.21 m (2H, CH=C), 2.18 m (6H, CH_2C=C), 1.9 m (4H, CHC=C), 1.53 m (6H, CH_2). Mass spectrum: m/4 188.

Tetracyclo[$16.3.0.0^{4,8}0^{11,15}$]eicosa-1,8,15-triene (IV): bp 123°C (0.05 mm); n_D^{20} 1.5106. IR spectrum (ν, cm^{-1}): 820, 3065 (C=C), 1445 (CH_2). PMR spectrum (δ, ppm): 5.25 m (3H, CH=C), 2.15 m (9H, CHC=C), 1.97 m (6H, CH_2C=C), 1.54 m (12H, CH_2). Mass spectrum: m/e 272.

2(3)-(1-Cyclopentenyl)bicyclo[4.3.0]nonene (II) was prepared by heating (I) in benzene (6 h at 180°C) in 65% yield; bp 76°C (0.1 mm); n_D^{20} 1.4967. IR spectrum (ν, cm^{-1}): 813, 826, 3050, 3010 (C=C), 1450 (CH_2). PMR spectrum (δ, ppm): 5.25 m (2H, CH=C), 2.19 m (6H, CHC=C), 1.95 m (4H, CH_2C=C), 1.65 m (8H, CH_2). Mass spectrum: m/e 188.

Hydrogenation of Hydrocarbons (II), (III), and (IV). Hydrogenation of (II), (III), or (IV) on Pd/C in ethyl acetate at 22°C for 2 h gave the saturated polycycloalkanes (V)-(VII) in ~100% yield.

The individual hydrocarbons had the following constants after purification by vacuum distillation.

Tricyclo[$9.3.0.0^{4,8}$]tetradecane (VI), bp 80°C (0.1 mm); n_D^{20} 1.4928. IR spectrum (ν, cm^{-1}): 1450, 2870, 2920 (CH_2). PMR spectrum (δ, ppm): 1.5 m (20H, CH_2), 1.25 m (4H, CH). Mass spectrum: m/e 192.

Tetracyclo[16.3.0.0^{4,8}0^{11,15}]eicosane (VII): bp 145°C (0.1 mm); n_D^{20} 1.4953. IR spectrum (ν, cm^{-1}): 1440, 2865, 2930 (CH_2). PMR spectrum (δ, ppm): 1.45 m (3H, CH_2), 1.2 m (6H, CH). Mass spectrum: m/e 278.

2(3)-Cyclopentylbicyclo[4.3.0]nonane (V): bp 95°C (0.5 mm); n_D^{20} 1.4905. IR spectrum (ν, cm^{-1}): 1438, 1445, 2860, 2920 (CH_2). PMR spectrum (δ, ppm): 1.55 m (CH_2, CH). Mass spectrum: m/e 192.

Ozonization of Oligomers (III) and (IV). A stream of ozonized oxygen was passed through a solution of (III) (2 g, 10.6 mmole) in MeOH (15 ml) at −65°C until the overshoot of ozone could be detected at the outlet. After removal of the dissolved ozone, dimethyl sulfide (1.3 g, 26 mmole) was added. The mixture was left at 20°C for 16 h and then poured into H_2O (30 ml). The oily product was extracted with ether, washed with H_2O, and dried over $MgSO_4$. After removal of the solvent the residue was dissolved in absolute MeOH and $NaBH_4$ (1 g, 28 mmole) was added. The mixture was stirred for 3 h and then filtered through a column of Al_2O_3 (activity III). The solvent was evaporated and the residue was recrystallized from hexane to give 2-hydroxyethyl-1-cyclopentanol (VIII) (1.4 g), identified by comparison with an authentic sample.

Ozonization of oligomer (IV) (1.6 g) by the method described above gave (VIII) (1.1 g), identical to the sample derived by ozonization of (III).

CONCLUSIONS

The cyclooligomerization of 1-vinylcyclopentene catalyzed by nickel complexes forms a tricyclic dimer and tetracyclic trimer — 1,5-cyclooctene and 1,5,9-cyclododecatriene derivatives.

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