X-Ray Structure of a Novel Product formed from 2,5-Dimethylhex-3-yne-2,5-diol by Catalytic Action of Dibromobis(triphenylphosphine)-nickel

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When heated under reflux in toluene in the presence of $[(Bu^n_3P)_2NiBr_2]$, 2,5-dimethylhex-3-yne-2,5-diol is not converted into the expected simple polymerization product. *X*-Ray structural analysis shows the novel product to be 1′-(1,3-dihydro-7-isopropenyl-6-isopropyl-1,1,4,4-tetramethylfuro[3.4-*c*]pyran-3-ylidenemethyl)-1,3-dihydro-7-isopropenyl-6-isopropyl-1,1,4,4,5′,5′-hexamethylfuro[3,4-*c*]pyran-3-spiro-3′-cyclohexene, in agreement with other physical data. The same product was obtained with $[(Ph_3P)_2NiBr_2]$ as catalyst. Crystals are monoclinic, $a = 9.32(1)$, $b = 37.26(3)$, $c = 13.18(1)$Å, $\beta = 118.7(1)°$, $Z = 4$, space group $P2_1/c$. The structure was solved from diffractometer data by direct methods and refined to R 0.054 for 3 583 observed reflections.

In a previous investigation[1] we found that $[(Bu^n_3P)_2NiBr_2]$ acts as a regiospecific catalyst towards monosubstituted α-hydroxyacetylenes, which are cyclotrimerized to 1,3,5-tris(hydroxyalkyl)benzenes in high yields. We now report the catalysis of the analogous disubstituted acetylene: $Me_2C(OH)\cdot C{:}C\cdot C(OH)Me_2$.

In the presence of $[(Bu^n_3P)_2NiBr_2]$ the conversion of this monomer into a cyclic trimer or tetramer, or into linear polymers, would be expected, as was previously observed for similar systems.[2] However, the product obtained had an unexpected structure and was formed by a complex sequence of reactions.

EXPERIMENTAL

Preparation.—2,5-Dimethylhex-3-yne-2,5-diol (5 g), $[(Bu^n_3P)_2NiBr_2]$ (1 g), and toluene (40 ml) were heated under reflux for 48 h. Excess of solvent was eliminated and methanol added to the brown residue. After cooling overnight yellow microcrystals of 1′-(1,3-*dihydro*-7-*isopropenyl*-6-*isopropyl*-1,1,4,4-*tetramethylfuro*[3,4-c]*pyran*-3-*ylidenemethyl*)-1,3-*dihydro*-7-*isopropenyl*-6-*isopropyl*-1,1,4,4,5′,5′-*hexamethylfuro*[3,4-c]*pyran*-3-*spiro*-3′-*cyclohexene* separated from the mixture (0.5 g; 10%, on the monomer). The product was recrystallized from benzene, by addition of methanol, or from methanol (m.p. 186—187 °C) (Found: C, 79.7; H, 9.45. Calc. for $C_{42}H_{60}O_4$: C, 80.2; H, 9.6%). The same product was obtained by use of $[(Ph_3P)_2NiBr_2]$ as catalyst.

Physical Measurements.—^{1}H n.m.r. spectra were measured on a Jeol NMC 60 HL spectrometer with deuteriobenzene as solvent. Mass spectra were carried out with an AEI MS12 mass spectrometer operating at 70 eV. I.r. spectra were recorded on a Beckmann IR 20 spectrophotometer (Nujol mull), u.v. spectra on a Beckmann DK 2 A spectrophotometer; e.s.r. measurements on a Varian E 9 spectrometer. M.p.s were determined with a Köfler hot-stage microscope. Molecular weights were measured with a Mechrolab 301 A osmometer. *X*-Ray intensity data were collected on a Siemens single-crystal computer-controlled diffractometer by use of Ni-filtered Cu-K_α radiation and the ω—2θ scan technique.

Materials.—2,5-Dimethylhex-3-yne-2,5-diol (K & K and Fluka) was recrystallized from toluene. The complexes $[(Bu^n_3P)_2NiBr_2]$ and $[(Ph_3P)_2NiBr_2]$ were prepared according to literature methods.[3] The toluene solvent (Merck and C. Erba) was used without further purification.

Crystal Data.—$C_{42}H_{60}O_4$, $M = 628.9$. Monoclinic, $a = 9.32(1)$, $b = 37.26(3)$, $c = 13.18(1)$ Å, $\beta = 118.7(1)°$, $U = 4\,015$ Å^3, $D_m = 1.05$, $Z = 4$, $D_c = 1.04$ g cm^{-3}, $F(000) = 1\,376$. Cu-K_α radiation, $\lambda = 1.5418$ Å; μ(Cu-K_α) = 5.10 cm^{-1}. Space group $P2_1/c$ (from systematic absences). Cell dimensions were determined from rotation and Weissenberg photographs and refined from diffractometer measurements.

Intensity Data Collection.—Three-dimensional intensity data were obtained for a flattened tablet 0.34 × 0.14 × 0.34 mm, aligned with its [100] axis along the ϕ axis of the diffractometer. All reflections with $6 < 2\theta < 120°$ were measured by use of the moving-counter–moving-crystal scan technique with a drive speed related to the number of counts on the peak (lowest speed 2.5° min^{-1}). No significant change in the intensity of a standard reflection monitored every 20 reflections was observed during data collection. For measuring intensities and background the five-points technique was used. Of 5 903 independent reflections measured, 3 583 having $I > 2\sigma(I)$ were considered observed and were used in the analysis. Lorentz and polarization corrections were applied and structure amplitudes derived. Absorption corrections were not applied in view of the low absorbance of the sample ($\mu\bar{r}$ *ca.* 0.1).

Structure Determination and Refinement.—The structure was solved by direct methods of phase determination with the program MULTAN.[4] An E map computed by use of the signs of 100 reflections with $E > 2.27$ showed all non-hydrogen atom positions. Refinement by block-diagonal anisotropic least-squares gave R 0.097. This was improved to 0.060 by adding the contribution of all but three hydrogen atoms located from a Fourier difference map and refined isotropically. It was not possible to locate the hydrogen atoms bound to the carbon C(18A), probably owing to the very high thermal motion of this methyl group. Up to this stage the function minimized in the least-squares calculations was $\Sigma w|\Delta F|^2$, with unit weights. Refinement converged to the final R of 0.054 with the Cruickshank weighting scheme $w^{-1} = A + B|F_o| + C|F_o|^2$, taking values for the coefficients of $A = 0.829\,0$, $B = 0.057\,76$, $C = 0.001\,006$, deduced from the $<|\Delta F|>$ *vs.* $|F|$ distribution.[5]

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[1] P. Bicev, A. Furlani, G. Sartori, *Gazzetta*, 1973, **103**, 849.

[2] C. W. Bird, 'Transition-Metal Intermediates in Organic Synthesis,' Logos–Academic, London, 1967.

[3] K. A. Jensen, *Z. anorg. Chem.*, 1936, **229**, 265.

[4] G. Germain, P. Main, and M. M. Woolfson, *Acta Cryst.*, 1971 **A27**, 368.

[5] G. H. Stout and L. H. Jensen, '*X*-Ray Structure Determination,' Macmillan, New York, 1968, p. 455.

Final positional and isotropic thermal parameters are given in Tables 1 and 2 with their standard deviations. Observed and calculated structure factors and anisotropic thermal parameters are listed in Supplementary Publication No. SUP 21946 (26 pp., 1 microfiche).* Atomic scattering factors used throughout the calculations were taken from ref. 6 for non-hydrogen atoms and from ref. 7 for hydrogen atoms.

All calculations were performed on a CDC 6600 computer at the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale (Bologna).

RESULTS AND DISCUSSION

The value of the molecular weight (628 by mass spectrometry and 610 by osmometry) and the elemental analysis were the first indications that the product was not a simple polymer (calc. for monomer $C_8H_{14}O_2$: *M*, 142; C, 67.6; H, 9.9%). These data were consistent with an empirical formula $C_{42}H_{60}O_4$, containing two carbon atoms more than those required for five monomeric units and only four oxygen atoms.

TABLE 1

Final atomic fractional co-ordinates ($\times 10^4$) for non-hydrogen atoms with estimated standard deviations in parentheses

	x/a	*y/b*	*z/c*
O(1)	6 082(2)	1 304(1)	1 043(2)
O(2)	11 296(2)	865(1)	3 359(2)
O(11)	5 861(3)	2 880(1)	2 252(2)
O(12)	8 721(2)	3 441(1)	648(2)
C(1)	7 601(3)	1 462(1)	1 659(2)
C(2)	6 228(3)	915(1)	1 083(2)
C(2A)	5 488(4)	787(1)	−163(3)
C(2B)	5 280(4)	777(1)	1 679(3)
C(3)	8 970(3)	521(1)	2 095(2)
C(4)	10 574(3)	547(1)	2 866(2)
C(5)	10 648(3)	1 205(1)	2 737(2)
C(5A)	11 309(4)	1 251(1)	1 900(3)
C(5B)	11 359(4)	1 482(1)	3 707(3)
C(6)	8 806(3)	1 177(1)	2 104(2)
C(7)	8 052(3)	858(1)	1 778(2)
C(8)	8 209(4)	163(1)	1 631(3)
C(8A)	8 253(6)	37(1)	576(3)
C(8B)	7 611(5)	−34(1)	2 235(4)
C(9)	11 765(3)	239(1)	3 362(3)
C(9A)	13 189(5)	298(1)	3 098(4)
C(9B)	12 336(5)	195(1)	4 667(3)
C(11)	6 064(3)	2 779(1)	1 257(2)
C(12)	6 426(4)	3 238(1)	2 651(3)
C(12A)	7 769(5)	3 216(1)	3 918(3)
C(12B)	4 956(5)	3 445(1)	2 546(3)
C(13)	7 806(4)	3 710(1)	1 870(2)
C(14)	8 607(4)	3 730(1)	1 261(2)
C(15)	7 359(4)	3 183(1)	171(3)
C(15A)	5 970(4)	3 363(1)	−916(3)
C(15B)	8 042(5)	2 863(1)	−168(3)
C(16)	6 853(3)	3 112(1)	1 084(2)
C(17)	7 039(4)	3 365(1)	1 849(2)
C(18)	7 691(5)	4 033(1)	2 511(3)
C(18A)	6 201(7)	4 256(1)	1 876(5)
C(18B)	8 914(7)	4 113(1)	3 593(4)
C(19)	9 565(4)	4 048(1)	1 170(3)
C(19A)	11 367(5)	3 942(1)	1 609(4)
C(19B)	8 820(5)	4 189(1)	−56(4)
C(20)	7 795(3)	1 822(1)	1 760(2)
C(21)	6 597(3)	2 113(1)	1 298(2)
C(22)	4 834(4)	2 035(1)	451(3)
C(23)	3 639(3)	2 338(1)	286(3)
C(23A)	2 074(4)	2 278(1)	−862(4)
C(23B)	3 208(5)	2 328(1)	1 281(4)
C(24)	4 399(4)	2 698(1)	233(3)
C(25)	7 141(3)	2 450(1)	1 609(2)

The ^1H n.m.r. spectrum [(δ; relative to tetramethylsilane as internal reference) 6.05 (1 H), 5br (4 H, m), 4.75 (1 H), 2.4—3br (4 H, m), 1—2, (50 H, m)] did not change on addition of D_2O. It followed that all the hydroxy-groups of the original monomer had undergone reaction and that water had been eliminated followed by the production of olefinic bonds and ether linkages.

TABLE 2

Fractional atomic co-ordinates ($\times 10^3$) and isotropic thermal parameters (Å^2) for hydrogen atoms, with estimated standard deviations in parentheses

	x/a	*y/b*	*z/c*	*B*
H(2A1)	623(3)	86(7)	−53(2)	7.1(7)
H(2A2)	439(3)	90(7)	−62(2)	6.1(6)
H(2A3)	537(3)	50(7)	−24(2)	6.8(6)
H(2B1)	577(4)	89(8)	254(3)	8.2(8)
H(2B2)	535(4)	50(8)	177(3)	8.2(8)
H(2B3)	403(4)	85(8)	120(3)	8.3(8)
H(5A1)	1 256(4)	127(8)	231(3)	6.6(7)
H(5A2)	1 098(4)	103(8)	132(3)	7.5(7)
H(5A3)	1 086(4)	149(8)	141(2)	7.4(7)
H(5B1)	1 137(3)	174(7)	345(2)	6.2(6)
H(5B2)	1 066(3)	148(7)	417(2)	6.4(6)
H(5B3)	1 257(3)	141(7)	430(2)	5.9(6)
H(8A1)	768(4)	−21(9)	44(3)	9.8(9)
H(8A2)	756(4)	21(10)	−14(3)	9.7(10)
H(8A3)	942(5)	1(10)	69(3)	9.7(10)
H(8B1)	704(4)	−25(9)	194(3)	8.5(9)
H(8B2)	779(4)	5(10)	301(3)	7.5(9)
H(9)	1 114(3)	−1(7)	293(2)	6.5(7)
H(9A1)	1 380(5)	53(10)	352(3)	9.9(10)
H(9A2)	1 401(5)	8(10)	342(3)	10.4(10)
H(9A3)	1 275(5)	32(12)	219(3)	11.3(12)
H(9B1)	1 303(4)	−4(10)	499(3)	9.0(9)
H(9B2)	1 306(4)	42(10)	513(3)	9.6(10)
H(9B3)	1 132(4)	18(10)	483(3)	7.5(10)
H(12A1)	733(4)	312(9)	448(3)	8.9(8)
H(12A2)	868(4)	304(9)	399(3)	8.4(9)
H(12A3)	830(4)	347(10)	421(3)	8.7(9)
H(12B1)	507(4)	370(9)	280(3)	8.7(9)
H(12B2)	404(4)	345(9)	166(3)	9.0(9)
H(12B3)	446(4)	330(9)	303(3)	9.8(9)
H(15A1)	561(4)	361(8)	−69(3)	7.4(7)
H(15A2)	493(4)	317(8)	−129(3)	7.9(7)
H(15A3)	636(4)	342(8)	−157(2)	7.7(7)
H(15B1)	716(4)	266(9)	−58(3)	8.4(8)
H(15B2)	850(4)	294(9)	−75(3)	8.9(8)
H(15B3)	901(4)	277(8)	60(3)	7.7(8)
H(18B1)	868(6)	437(13)	388(4)	13.8(15)
H(18B2)	991(6)	397(13)	406(4)	11.5(15)
H(19)	951(4)	427(8)	174(3)	7.5(8)
H(19A1)	1 155(4)	388(10)	245(3)	11.1(10)
H(19A2)	1 152(5)	373(10)	117(3)	10.8(11)
H(19A3)	1 214(4)	417(10)	166(3)	11.6(10)
H(19B1)	902(5)	397(10)	−54(3)	9.9(10)
H(19B2)	750(4)	424(10)	−42(3)	10.2(10)
H(19B3)	934(5)	443(10)	−13(3)	9.8(10)
H(20)	899(3)	191(6)	224(2)	5.0(6)
H(221)	475(3)	197(8)	−36(3)	7.4(7)
H(222)	447(3)	180(7)	74(2)	7.0(7)
H(23A1)	236(4)	230(9)	−156(3)	9.7(9)
H(23A2)	117(4)	247(9)	−96(3)	9.1(9)
H(23A3)	159(4)	202(9)	−90(3)	9.7(9)
H(23B1)	263(4)	208(10)	126(3)	10.1(10)
H(23B2)	429(5)	236(10)	211(3)	10.7(10)
H(23B3)	241(5)	254(11)	120(3)	10.9(10)
H(241)	467(3)	271(7)	−52(2)	6.5(6)
H(242)	360(3)	292(7)	14(2)	5.9(6)
H(25)	840(3)	250(7)	227(2)	5.3(6)

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* See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1976, Index issue.

[6] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[7] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

This fact was confirmed by the i.r. spectrum: no bands were observed in the region 4 000—3 200 cm^{-1} and at *ca.* 2 100 cm^{-1}, *i.e.* no OH groups and asymmetric triple bonds were present in the molecule. Several bands at *ca.* 1 600 cm^{-1} confirmed the presence of double bonds, and a band at 895 cm^{-1} is probably due to isopropenyl groups. An intense band at *ca.* 1 070 cm^{-1} indicated the presence of C–O–C groups.

TABLE 3

Bond distances (Å) and angles (°)

(*a*) Distances			
O(1)–C(1)	1.381(4)	C(11)–C(16)	1.514(5)
O(1)–C(2)	1.454(5)	C(11)–C(24)	1.520(4)
O(2)–C(4)	1.363(5)	C(11)–C(25)	1.509(5)
O(2)–C(5)	1.472(5)	C(12)–C(12A)	1.534(5)
O(11)–C(11)	1.461(5)	C(12)–C(12B)	1.520(6)
O(11)–C(12)	1.438(5)	C(12)–C(17)	1.499(6)
O(12)–C(14)	1.381(5)	C(13)–C(14)	1.335(6)
O(12)–C(15)	1.471(5)	C(13)–C(17)	1.465(5)
C(1)–C(6)	1.449(5)	C(13)–C(18)	1.504(6)
C(1)–C(20)	1.352(5)	C(14)–C(19)	1.523(6)
C(2)–C(2A)	1.521(5)	C(15)–C(15A)	1.548(5)
C(2)–C(2B)	1.526(6)	C(15)–C(15B)	1.517(6)
C(2)–C(7)	1.510(4)	C(15)–C(16)	1.512(6)
C(3)–C(4)	1.348(4)	C(16)–C(17)	1.329(5)
C(3)–C(7)	1.463(5)	C(18)–C(18A)	1.484(6)
C(3)–C(8)	1.497(5)	C(18)–C(18B)	1.364(6)
C(4)–C(9)	1.510(5)	C(19)–C(19A)	1.542(6)
C(5)–C(5A)	1.510(6)	C(19)–C(19B)	1.514(6)
C(5)–C(5B)	1.525(5)	C(20)–C(21)	1.463(5)
C(5)–C(6)	1.510(4)	C(21)–C(22)	1.506(4)
C(6)–C(7)	1.342(5)	C(21)–C(25)	1.342(5)
C(8)–C(8A)	1.487(7)	C(22)–C(23)	1.526(5)
C(8)–C(8B)	1.382(7)	C(23)–C(23A)	1.532(5)
C(9)–C(9A)	1.541(7)	C(23)–C(23B)	1.546(8)
C(9)–C(9B)	1.546(6)	C(23)–C(24)	1.534(5)
(*b*) Angles			
C(1)–O(1)–C(2)	110.6(5)	O(11)–C(12)–C(12A)	108.2(5)
C(4)–O(2)–C(5)	120.4(7)	O(11)–C(12)–C(12B)	106.4(6)
C(11)–O(11)–C(12)	112.6(6)	O(11)–C(12)–C(17)	103.4(5)
C(14)–O(12)–C(15)	117.8(6)	C(12A)–C(12)–C(12B)	110.8(6)
O(1)–C(1)–C(6)	107.6(5)	C(12A)–C(12)–C(17)	113.4(6)
O(1)–C(1)–C(20)	122.1(7)	C(12B)–C(12)–C(17)	114.1(7)
C(6)–C(1)–C(20)	130.3(8)	C(14)–C(13)–C(17)	116.5(7)
O(1)–C(2)–C(2A)	106.7(5)	C(14)–C(13)–C(18)	120.3(8)
O(1)–C(2)–C(2B)	106.7(5)	C(17)–C(13)–C(18)	123.2(7)
O(1)–C(2)–C(7)	102.8(4)	O(12)–C(14)–C(13)	122.1(7)
C(2A)–C(2)–C(2B)	112.1(6)	O(12)–C(14)–C(19)	110.4(6)
C(2A)–C(2)–C(7)	113.9(5)	C(13)–C(14)–C(19)	127.5(9)
C(2B)–C(2)–C(7)	113.7(6)	O(12)–C(15)–C(15A)	106.2(5)
C(4)–C(3)–C(7)	116.0(6)	O(12)–C(15)–C(15B)	104.0(5)
C(4)–C(3)–C(8)	120.6(6)	O(12)–C(15)–C(16)	108.0(5)
C(7)–C(3)–C(8)	123.4(7)	C(15A)–C(15)–C(15B)	110.5(6)
O(2)–C(4)–C(3)	122.4(6)	C(15A)–C(15)–C(16)	111.8(5)
O(2)–C(4)–C(9)	111.2(6)	C(15B)–C(15)–C(16)	115.6(7)
C(3)–C(4)–C(9)	126.2(7)	C(11)–C(16)–C(15)	128.5(8)
O(2)–C(5)–C(5A)	107.6(5)	C(11)–C(16)–C(17)	111.3(6)
O(2)–C(5)–C(5B)	102.6(5)	C(15)–C(16)–C(17)	120.2(7)
O(2)–C(5)–C(6)	107.6(4)	C(12)–C(17)–C(13)	127.7(8)
C(5A)–C(5)–C(5B)	111.7(6)	C(12)–C(17)–C(16)	110.9(6)
C(5A)–C(5)–C(6)	111.0(6)	C(13)–C(17)–C(16)	121.4(7)
C(5B)–C(5)–C(6)	115.5(5)	C(13)–C(18)–C(18A)	115.5(7)
C(1)–C(6)–C(5)	128.9(7)	C(13)–C(18)–C(18B)	120.9(7)
C(1)–C(6)–C(7)	109.5(6)	C(18A)–C(18)–C(18B)	123.6(9)
C(5)–C(6)–C(7)	121.3(6)	C(14)–C(19)–C(19A)	110.2(6)
C(2)–C(7)–C(3)	128.9(7)	C(14)–C(19)–C(19B)	111.6(6)
C(2)–C(7)–C(6)	109.5(5)	C(19A)–C(19)–C(19B)	110.4(6)
C(3)–C(7)–C(6)	121.6(7)	C(1)–C(20)–C(21)	131.0(8)
C(3)–C(8)–C(8A)	116.3(6)	C(20)–C(21)–C(22)	120.6(6)
C(3)–C(8)–C(8B)	118.8(7)	C(20)–C(21)–C(25)	117.7(6)
C(8A)–C(8)–C(8B)	124.8(10)	C(22)–C(21)–C(25)	121.6(6)
C(4)–C(9)–C(9A)	109.1(6)	C(21)–C(22)–C(23)	115.1(5)
C(4)–C(9)–C(9B)	110.6(5)	C(22)–C(23)–C(23A)	108.4(5)
C(9A)–C(9)–C(9B)	113.1(7)	C(22)–C(23)–C(23B)	109.3(7)
O(11)–C(11)–C(16)	101.9(5)	C(22)–C(23)–C(24)	109.4(5)
O(11)–C(11)–C(24)	109.3(5)	C(23A)–C(23)–C(23B)	108.8(7)
O(11)–C(11)–C(25)	106.7(5)	C(23A)–C(23)–C(24)	108.9(5)
C(16)–C(11)–C(24)	113.1(5)	C(23B)–C(23)–C(24)	111.9(7)
C(16)–C(11)–C(25)	114.4(6)	C(23)–C(24)–C(11)	115.5(5)
C(24)–C(11)–C(25)	110.9(5)	C(11)–C(25)–C(21)	124.6(7)

The u.v. spectrum (nm; log ε in parentheses) in $CHCl_3$ exhibits maxima at 363 (4.30) and 264 (4.06). The former band strongly suggested the existence of conjugated bonds in the molecule.

However, these data were still not sufficient to assign a structure, and it was for this reason that an *X*-ray crystal-structure analysis was carried out. This showed that discrete molecules of formula $C_{42}H_{60}O_4$ were present in the crystals. Each molecule (Figure 1) consists of three parts: two equal terminal moieties formed by two systems of substituted pyran and furan condensed rings, linked to a cyclohexene central part. The greatest differences in the two ends are about the C(1) and C(11) carbon atoms, the other regions having closely similar values for structural parameters (Table 3). The observed differences are due to the different hybridisation states of these two carbon atoms, C(1) being sp^2, and C(11) sp^3. The central cyclohexene ring on one side is settled at C(11), and on the other is linked to a bridging CH group bonded to C(1) through a double bond. The spiro-carbon C(11) is at a centre of asymmetry, but the structure is centrosymmetric, both enantiomers being present and related by the symmetry of the crystal space.

TABLE 4

Equations of least-squares planes and, in square brackets, distances (Å) from these planes *

Plane (1): furan ring, O(1), C(1), C(6), C(7), C(2)

$$0.550\,3X + 0.027\,7Y - 0.834\,5Z = 1.875\,9$$

[O(1) 0.008, C(1) −0.005, C(6) −0.001, C(7) 0.007, C(2) −0.009]

Plane (2): furan ring, O(11), C(11), C(16), C(17), C(12)

$$-0.693\,7X + 0.363\,3Y - 0.621\,9Z = -0.515\,5$$

[O(11) −0.005, C(11) 0.005, C(16) −0.005, C(17) 0.003, C(12) 0.002]

Plane (3): pyran ring, O(2), C(3)—(7)

$$0.677\,5X + 0.068\,5Y - 0.732\,3Z = 3.113\,5$$

[O(2) −0.044, C(4) 0.047, C(3) 0.011, C(7) −0.078 C(6) 0.064, C(5) 0.427]

Plane (4): pyran ring, O(12), C(13)—(17)

$$-0.490\,1X + 0.385\,0Y - 0.782\,0Z = 0.617\,8$$

[O(12) −0.050, C(14) 0.053, C(13) 0.028, C(17) −0.104, C(16) 0.073, C(15) 0.485]

Plane (5): cyclohexene ring, C(11), C(21)—(25)

$$0.688\,3X + 0.080\,2Y - 0.720\,9Z = 3.216\,6$$

[C(22) −0.080, C(21) 0.000, C(25) 0.055, C(11) −0.091, C(24) 0.116, C(23) −0.546]

* The transformation matrix from monoclinic *x*, *y*, *z* to orthogonal *X*, *Y*, *Z* is:

$$\begin{pmatrix} 1 & 0 & \cos\beta \\ 0 & 1 & 0 \\ 0 & 0 & \sin\beta \end{pmatrix}$$

One of the furan rings [O(11), C(11), C(16), C(17), C(12)] is strictly planar, the distortions of the other [O(1), C(1), C(6), C(7), C(2)] being at the limits of significance (Table 4). Both pyran groups show a nearly half-chair conformation: C(5) and C(15) being 0.43 and 0.48 Å out of the best planes through them. These two planes form dihedral angles of 10 and 15° with their condensed furan rings. The isopropenyl side-chains exhibit different conformations, the rotation angles around the C(8)–C(3) and C(18)–C(13) bonds being −87 and 85° respectively. The conformations of rings A, B, and C are shown in Figure 2.

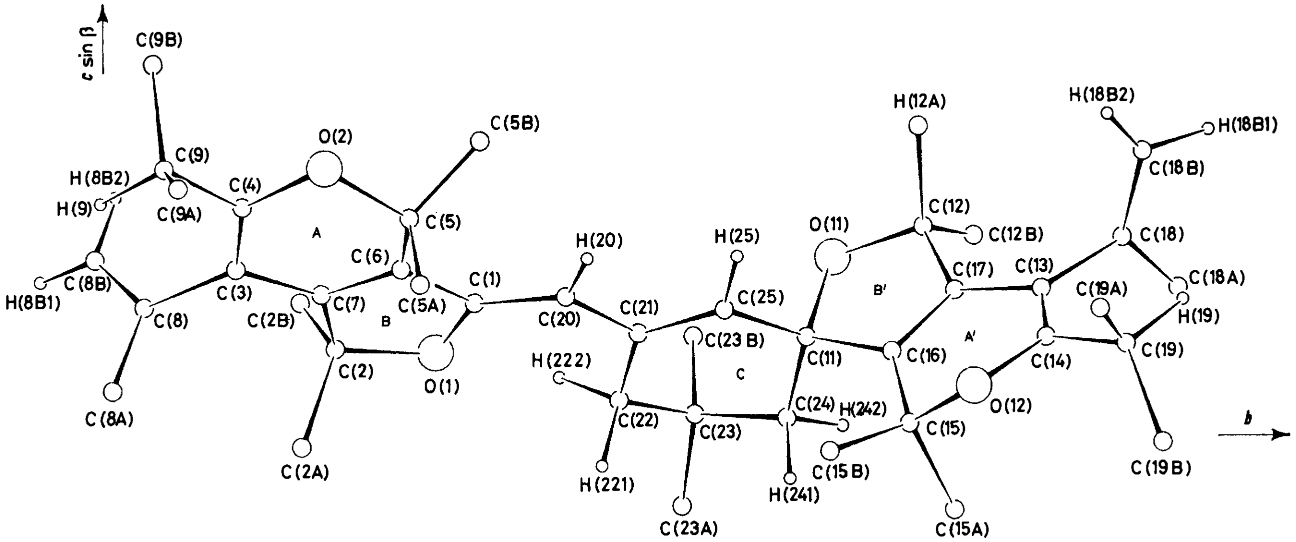

FIGURE 1 Projection of the molecule along [100]; methyl hydrogen atoms are omitted for clarity

The double bond in the cyclohexene moiety occurs between C(21) and C(25) and the ring presents a half-chair conformation, C(23) being 0.55 Å out of the plane through the ring carbon atoms. The orientation of the cyclohexene moiety with respect to the furan ring containing C(11), is determined by the tetrahedral character of this atom as shown by the dihedral angle (89°) between the respective planes.

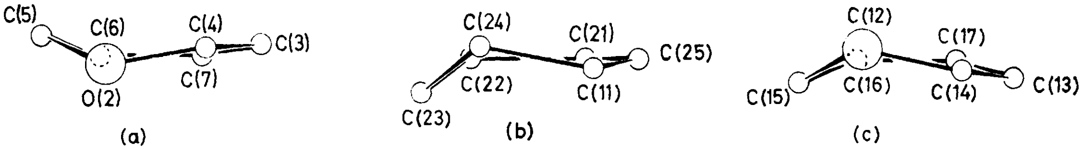

FIGURE 2 Conformations of (a) ring A, (b) ring C, and (c) ring A'

There is in the molecule a system of alternate double bonds, C(4)–C(3), C(7)–C(6), C(1)–C(20), C(21)–C(25) which are almost coplanar (max. deviation 0.05 Å); the internal rotation angles around the system are: C(3)⟩C(7) −9, C(6)⟩C(1) 179, and C(20)⟩C(21) −175°. Nevertheless the values of bond distances seem to indicate π localization rather than a conjugative effect. The characters of the bonds in the molecule were assigned on the basis of the values of distances and angles and confirmed by the location of the hydrogen atoms. As can be seen from Table 3, the bond length ranges are as expected for the different bond types: $C(sp^3)$–$C(sp^3)$ 1.51—1.54, $C(sp^3)$–$C(sp^2)$ 1.49—1.51, $C(sp^2)$–$C(sp^2)$ (single) 1.46—1.50, $C(sp^2)$–$C(sp^2)$ (double) 1.33—1.38, $C(sp^3)$–O 1.44—1.47, and $C(sp^2)$–O 1.36—1.38 Å.

Packing is determined by normal van der Waals contacts.

Reaction Mechanism.—It is not easy to suggest a reaction mechanism to explain the formation of the product. The fragment of group A (Figure 3), defined by the line Z, corresponds to one monomeric unit in which one water molecule has been eliminated to produce an isopropenyl group. The triple bond has been broken up and two new bonds formed, one involving an oxygen atom. The tertiary alcoholic group is changed into an isopropyl group, indicating that the oxygen of the hydroxy-group has migrated in the course of the reaction. The same thing probably takes place during the formation of the similar fragment of A'. The second fragment of groups A, B and A', B' defined by the lines X, Z and X', Z', may be derived from a molecule of the monomer in which an OH group and a H atom (in total a water molecule) have been eliminated from the two tertiary

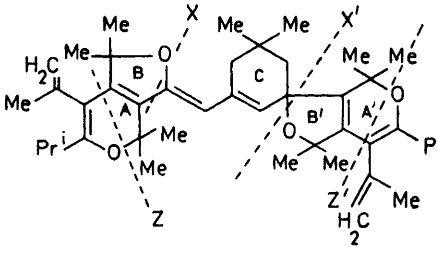

FIGURE 3 Suggest reaction pathways in the molecule

alcoholic groups. Although the triple bond has been destroyed, no migration reaction needs to be invoked.

The formation of the central part of the molecule is unprecedented. The possibility that fragments of the catalyst molecule enter to form part of the compound may be excluded since the same product is obtained by use of $[(Ph_3P)_2NiBr_2]$ as catalyst. Participation by the solvent, toluene, can also be excluded. Gas chromatographic analysis reveals the presence of acetone in the reaction mixture, probably formed in a decomposition reaction which is the reverse of the reaction synthesis of the monomer: $Me_2C(OH){\cdot}C{\vdots}C{\cdot}CMe_2(OH) \rightleftharpoons HC{\vdots}CH + 2Me_2CO$. The most likely possibility is that different fragmentations take place, catalysed by the complex, and generating free radicals which are rearranged by the catalyst to give the substituted cyclohexene group C. Nevertheless, if free radicals are formed, they must be very reactive, because e.s.r. measurements on samples of the reaction mixture during the reaction, did not reveal the presence of stable free radicals.

The synthesis of this compound is the first example of a catalytic reaction involving Ni complexes in which such complex reaction mechanisms occur.

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