Dehydrogenation of Lindenenyl Acetate by Palladium

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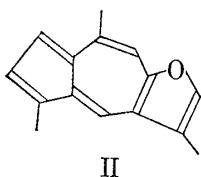
Dehydrogenation of lindenenyl acetate (Ib) by palladium was studied. The reaction was found to proceed directly to a final product (linderazulene (II)) by a main route, and partly to II via a dihydroazulene intermediate (IV), by a concerted mechanism. Dehydrogenation of Ib in deuteropentane showed that palladium has properties of both a dehydrogenation and a hydrogenation catalyst under N_2, at 300°.

About thirty years ago, we reported that lindenenol (Ia), a component of the root of *lindera strychnifolia vill*, was easily dehydrogenated with selenium, palladium or zinc to give linderazulene (II).[2)]
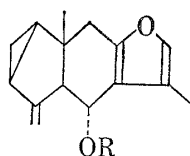
The mechanism of the ring reorganisation involved in dehydrogenation of lindenenyl acetate (Ib) under mild conditions seemed particularly interesting; in an attempt to clarify this have studied the reaction using a palladium metal catalyst.

Ia : R=H
Ib : R=Ac

II

In a previous study of the dehydrogenation reaction of the monoterpene[3)] gas chromatography with a thermal conductivity detector for analysis wang used; as this required several milligrams of sample, in the present work we used a gas chromatograph equipped with a high sensitive flame ionization detector, thereby decreasing the sample required one hundredfold.

The palladium catalyst used was supported on barium carbonate, since lindenenyl acetate is very sensitive to acid. The catalyst (25 mm × 4 mm ϕ) was inserted into the flash heater block of the gas chromatograph, and connected to the column used to separate the reaction products. The performance in dehydrogenation by the catalyst, so combined with a gas chromatograh, was checked under mild condtions (injection block: 285°, flow rate: 50 ml/min) and found to be unsatisfactory because of peak tailing. The application of cholesterol was found to markedly improve peak shape and minimize tailing.

Preliminary experiments using the above catalyst were made to trace the intermediates in the course of the dehydrogenation of lindenenyl acetate (Ib) to linderazulene (II). The results are shown in Fig. 1, with the Kováts index[4)] obtained on a carbowax column, and with molecular weights determined by GC-MS for each peak.

The peak (III) (M^+: 212) which appeared under mild conditions a) (170°, 50 ml/min) seems to be the first intermediate. Under these conditions conversion of Ib to linderazulene (II) was poor. Four major peaks (M^+: 212, 214) appeared in addition to peak (III) under moderate

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1) Location : *Fukushima-ku, Osaka.*
2) H. Kondo and K. Takeda, *J. Parm. Sci.*, **59**, 104 (1939); K. Takeda, *Chem. Pharm. Bull.* (Tokyo), **1**, 244 (1953).
3) T. Okamoto and T. Onaka, *Chem. Pharm. Bull.* (Tokyo), **11**, 1086 (1963); I.C. Nigam, *J. Chromatog.*, **24**, 188 (1966); I. Mizrahi and I.C. Nigam, *ibid.*, **25**, 230 (1966).
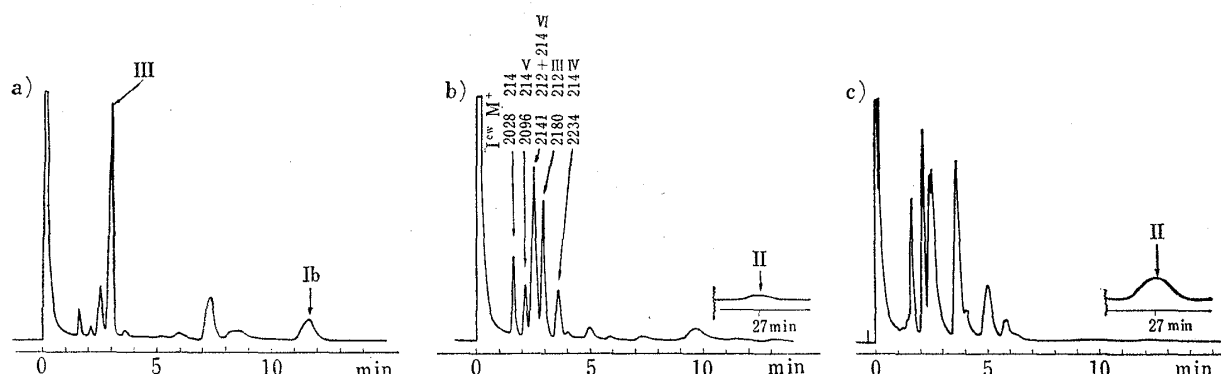4) E. Kováts, *Helv. Chim. Acta*, **41**, 1915 (1958).

Fig. 1. Dehydrogenation of Lindeneyl Acetate by Pd-BaCO₃ Catalyst

	a)	b)	c)
reaction: temp. (°C)	170	220	300
on carrier gas (ml/min)	75	10	10

GC: 1% Carbowax 20M Gas chrom Q (100/120 mesh) 1.5m×4mmφ, column
temp. 170°, injection temp. 180°, detector temp. 250°, N_2 0.7(kg/cm²)

conditions b) (220°, 10 ml/min), and the azulene (II) yield increased. At 300° peaks (IV and V) (M^+: 214) were characteristically increased together with the azulene (II) yield.

The fraction corresponding to the first peak in Fig. 1b) showed M^+: 214, but the NMR spectrum showed it to be a mixture; further purification was not possible owing to insufficient sample.

The second peak (V) in Fig. 1b was determined as lindenene by comparison of the NMR, IR, GC, and GC-MS data with those of an authentic sample[5].

Compound (VI),[6] the third peak in Fig. 1b, has a molecular weight 212. The UV absorption at 272, 281, 285, and 291 mμ suggests the existance of an extended conjugation of benzofuran.[7] IR bands at 899 and 787 cm^{-1} indicate a terminal methylene group. The NMR spectrum show in Fig. 2 suggests a $\frac{H}{H}$>C=C<$\frac{H}{}$ moiety. From these data the compound was at first tentatively assumed to be VI'. However, further examination by proton spin

VI'
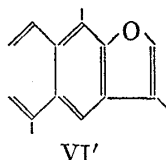
decoupling and nuclear Overhauser effect at 100 Mcps field led to a ressignment of the structure to VI. The results are shown in Fig. 2 and Fig. 3, respectively.

The four vinyl protons spread over ca. 5—4 τ collapsed to single patterns on irradiation at the C_1' methyl proton frequency. From a consideration of the coupling constant these signals can reasonably be assumed to result from a system. It can be seen that the C_4-proton is flanked by C_3 and C_1' methyl groups from the enhancement by the nuclear Overhauser effect, as shown in Fig. 3. Likewise, the C_2' proton may be orientated cis to the C_1' methyl group. The multiplet at 2.70 τ collapsed to a doublet (J=0.6 cps) and showed 28% enhancement by the NOE on irradiation at the C_6 methyl protn frequency, but was not effected by C_1' methyl

5) K. Takeda, H. Ishii, T. Tozyo, and H. Minato, J. Chem. Soc., 1969, 1920.
6) This compound proved to be identical with the "benzofuran compound" reported previously (H. Ishii, M. Nakamura, T. Tozyo, and K. Takeda, Phytochemistry, 8, 2189 (1970) by comparison of their IR, UV, and NMR spectra.
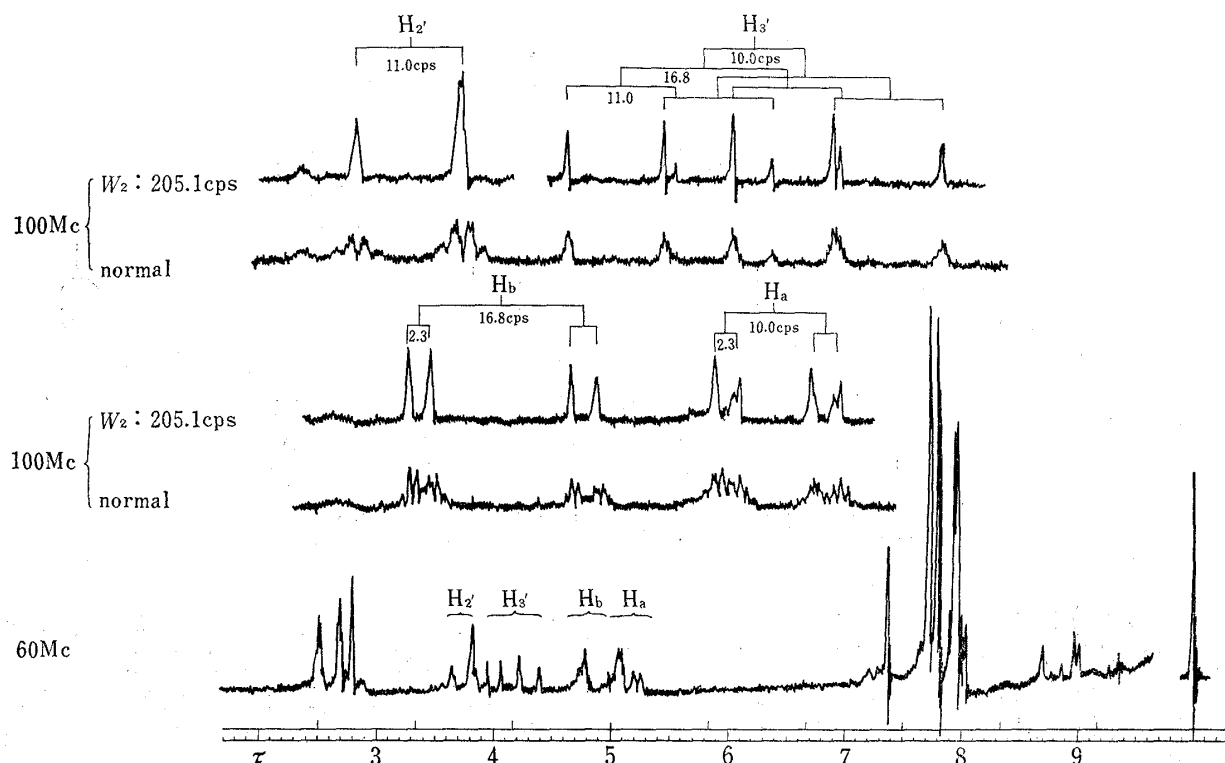7) J.I. Jones and A.S. Lindsey, J. Chem. Soc., 1950, 1836.

Fig. 2. NMR Spectra of Compound (VI)in CD_3COCD_3

protons.   The coupling constant (0.6 cps) can be reasonably ascribed to a proton at the para position of a benzene ring.   Therefore, the proton observed at 2.70 τ should be placed at the C_7 position.   From the results of the NOE on C_2' and C_4 protons by C_1' methyl protons, the butadiene moiety should be placed at the C_5 position of benzofuran.   From the above observations, the third peak (VI) on the gas chromatogram in Fig. 1b may be assigned to 3,6-dimethyl-5-[1'-methyl-buta-1',3'-dienyl]-benzofuran rather than VI'.   Catalytic hydrogenation of compound (VI) by palladium consumed one mole equivalent of hydrogen to give the dihydro-compound(VII), which retains the three aromatic ring protons and one vinyl proton in the NMR spectrum.   Reduction of the dihydro-compound (VII) to the tetrahydro-compound (VIII) by rhodium-platinum catalyst was slow; it gives a mixtue, which was subjected to GC-MS.   The molecular ion peak of VIII was 216 and the base peak was 173 (M^+: -43), implying fission of a propyl group.
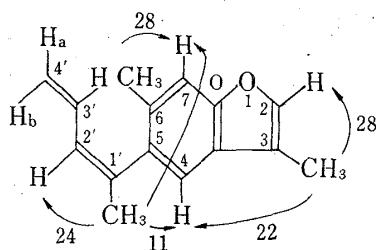
$H_1 \frown H_2$ H_1 : proton irradiated
H_2 : proton observed NOE

Fig. 3. Nuclear Overhauser Effect (%)
of Compound (VI) in CD_3COCD_3
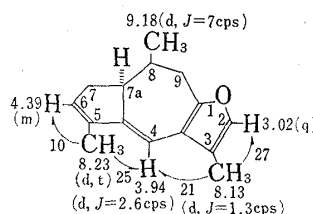
$H_1 \frown H_2$ H_1 : proton irradiated
H_2 : proton observed NOE

Fig. 4.   Chemical Shift (τ) and Nuclear
Overhauser Effect of (%) of Compound
(IV) in C_6D_6 in at 100Mc

The molecular weight of compound (IV), the fifth peak on the gas chromatogram in Fig. 1b, was determined as 214 by GC-MS.   Ehrlich reaction was positive.   The UV spectrum absorbed at 196, 231, 290, and 312 mμ suggesting a conjugated furanodiene moiety.   The NMR spectrum (60 Mc) showed three methyl proton signals, one a secondary methyl at 9.18 τ and

the other on a double bond at 8.13 and 8.23 τ; also two vinyl protons at 3.94 τ (doublet, $J=$ 2.6 cps) and 4.39 τ (multiplet). From above data, two structures regarding the position of the double bond can be assigned. Final assignment was accomplished by NOE technique in NMR. The results are summarized in Fig. 4.

When the vinyl proton observed at 3.94 τ was irradiated at the C_3 methyl proton frequency, it showed 21% enhancement by NOE. Accordingly, this proton must be located at C_4' not at C_9. Likewise, irradiation at the frequency of the methyl proton at 8.23 τ gave a 25% increase of H_4 by NOE; H_4' therefore, should lie between the methyl on the furan ring and the methyl on the double bond. From the above observation we established the structure of compound (IV) as 3,5-8-trimethyl-7,7a,8,9-tetrahydroazuleno[6.5-b]furan. It is interesting that the hydroazulene (IV) is an optical active compound ($[\alpha]_D$ $-164°$), besides having a negative circular dichroism band at 304 mμ ($[\theta]$ -15000), indicating that C_{7a} is the optically active centre.

Configuration of C_{7a} of the hydroazulene (IV) was intended to determined by comparison of the CD bands at the longest wave lengths of IV, XII, and XIII.

The enol acetate (XII) was prepared from cholesta-4,6-dien-3-one. The furano-diene (XIII) was made from the same starting material according to the known method.[8] The 2,4,6-trieno-compound (XII) showed a positive CD band at 302 mμ ($[\theta]$ 11000); on the other hand, the furanodien-steroid (XIII) exhibited a negative CD band at 286 mμ ($[\theta]$ -43000). It has been reported that the 2,4-dieno-steroid (XIV) and a steroid involving a styrene moiety (XV) have the same chirality at the cisoid diene system, but exhibit opposite Cotton effects.[9] If this relationship holds in the case of the extended systems (XII and XVI), compound (XVI) will show a negative CD band at the longest wave length. The relation between the sign of the Cotton effect and chirality in the monoen-conjugated furanosesquiterpene (XVII)[10] is
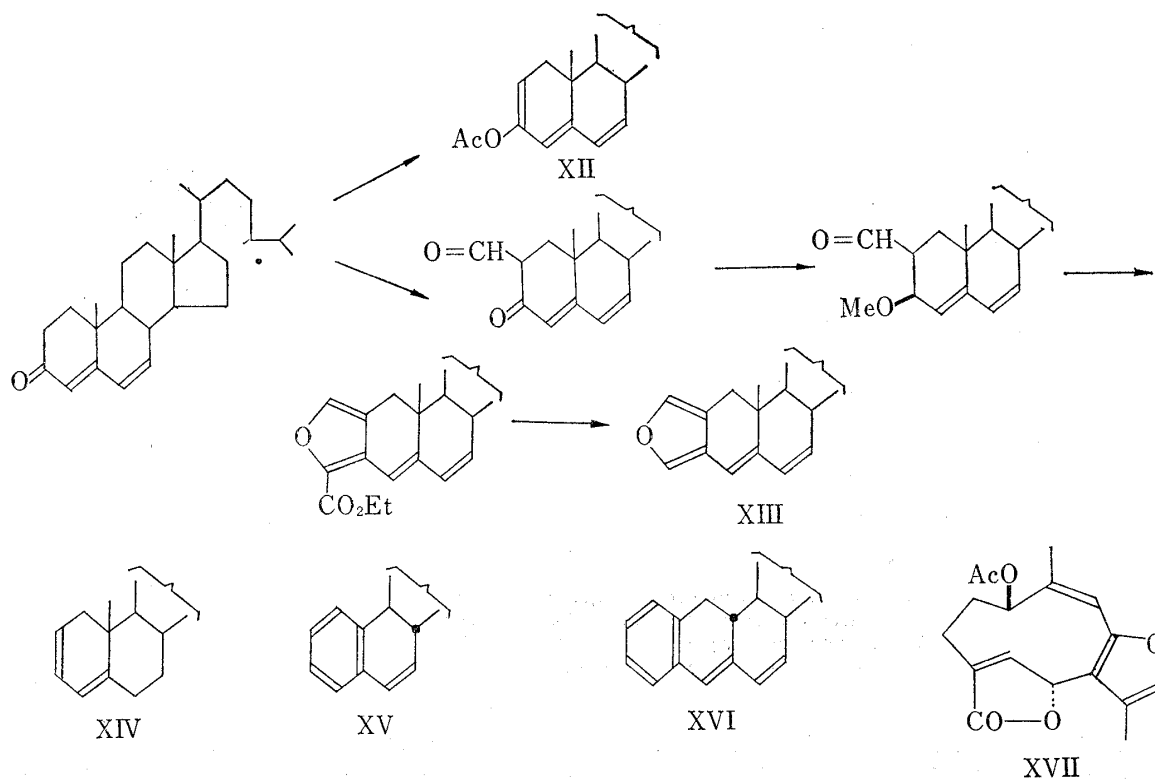
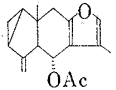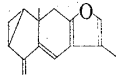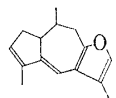8) D.L. Storm and T.A. Spencer, *Tetrahedron Letters*, 1967, 1865.
9) P. Crabbe, "Optical Rotatory Dispersion and Circular Dichroism in Organic Chemistry," Holden-day, San Francisco, 1965, p. 253.
10) Conformational analyses of above compounds were studied by K. Tori, M. Ohtsuru, I. Horibe, and K. Takeda, *Chem. Commun.*, 1968, 943, showing that zeylanine (XVII) has a left handed skew diene. Further, zeylanane and XVII were reported to show a positive CD band at 255 mμ($[\theta]$ 77500 and 61500(shoulder)), respectively. Therefore, it is assumed that the CD band at 255 mμ is responsible for a monoen-conjugated furan.
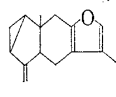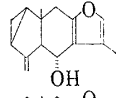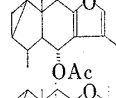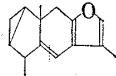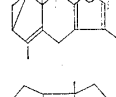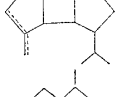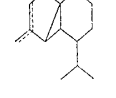
similar to that in the styrene compound (XV). These relations are assumed to be correct also in the case of the furano-dien (XIII and IV). Therefore, the configuration of the hydrogen on C_{7a} of IV will be α.

The forth peak (III) in Fig. 1b, was prepared carefully from Ib by the palladium catalyst at 180°, showed high sensitivity to air and temperature, and had a molecular weight of 212 (from GC-MS). The fact that the NMR spectrum exhibited a vinyl proton and an exomethylene group at 3.86 τ (singlet), 4.83 and 5.13 τ respectively is supported by absorption at 863, and 853 cm^{-1} in the IR spectrum. Maximum absorptions in the UV spectrum at 324 and 240 mμ are reasonably ascribed to a conjugated furanodiene. The compound (III), therefore, is assumed to be derived through elimination of acetic acid from lindenenyl acetate (Ib).

TABLE I. Azulene Formation from Various Compounds

Starting materials		Azulenes (%)[a]	Other products (%)[a]
(structure)	Ib	50[b]	5[c]
(structure)	III	50[b]	4[c]
(structure)	IV	17[b]	83[c]
(structure)	V	<0.3[b]	[d]
(structure, OH)		<0.3[b]	[d]
(structure, OAc)		3[b]	(structure)
(structure, CH₂OMe)		<0.1[b] + <0.1[e]	[d]
(structure)	(α-, β-)	0[f]	[d]
(structure)	(α-, β-)	0[f]	[d]

a) Reaction was carried out by a catalyst combined GC.
  Peak area as a percentage of the total peak area eluted up to azulene.
b) linderazulene   c) compound (IV)   d) starting material
e) methoxy linderazulene   f) guaiazulene

Each fraction obtained from the preparative GC, and other various related compounds, were submitted to dehydrogenation combined with gas chromatograph as above. The yields of azulenes are listed in Table I. The compound (IV) was converted to linderazulene(II), in 17% yield with the rest recovered, proving it to be an intermediate. The other fractions were recovered without further conversion to the azulene (II). Compound (III) gave the same products, azulene (II) and the intermediate (IV), and in the same yields as the acetate (Ib) did. Thus, the main reaction path, in the dehydrogenation of Ib by palladium, proceeds to the compound (III) by the elimination of acetic acid, followed by direct dehydrogenation to linder-
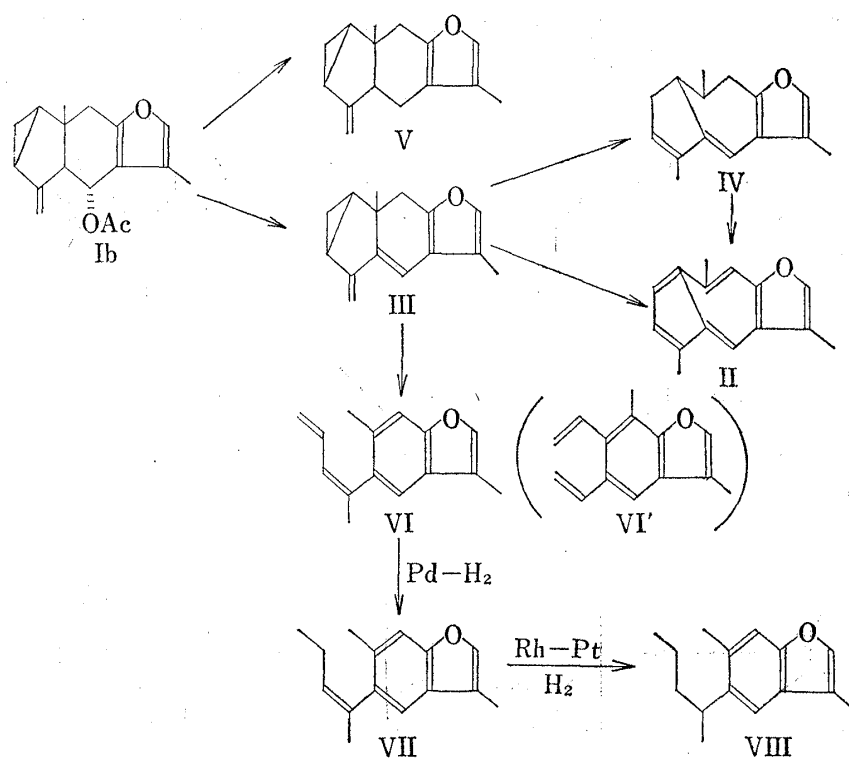
Chart 1

azulene (II), while some of III is dehydrogenated to the final product (II) *via* reduction to the hydroazulene (IV).

The results in Table I show that high yields of azulene are given by compounds in which the elimination of the C_4 acetoxy group produces a highly conjugated dihydrobenzofuran system. Therefore, further conjugation with dihydrobenzofuran will accelerate the change to a more stabilized system. This is the case with Ib and III.

The hydroazulene (IV) and lindenene (V) are reduction products of the starting material (Ib), not the products of dehydrogenation. Experiments were performed to find out what function is played by the palladium catalyst. Changes in the yields of the products given on repeated dehydrogenations of lindenenyl acetate (Ib) are shown in Fig. 5.

At the earlier stage of this reaction series the yield of linderazulene (II) was extremely high, but with subsequent reactions the yield of II decreased with a simultaneous increase of lindenene (V) and the hydroazulene (IV), the yields of which finally reached a plateau. This result supports the direct conversion of the intermediate (III) into II as the main dehydrogenation route, as mentioned above,
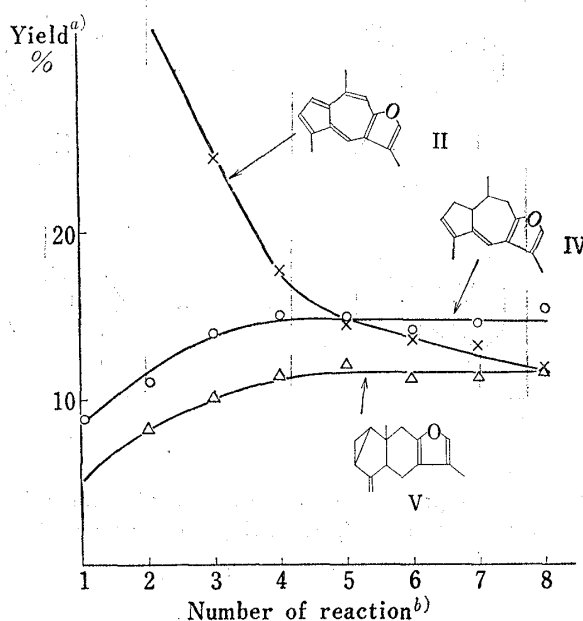
Fig. 5. Relationship of the Career of Palladium Catalyst and Products

a) Yields are peak area as a percentage of the total area of the peaks eluted up to linderazulene.

b) In one reaction, Ib (6 mg) was submitted to a non-priming catalyst at 300°, N_2: 10 ml/min.

since both IV and V are secondary products produced by hydrogenation over palladium hydride or hydrogen chemisorbed.[11]

Chart 2
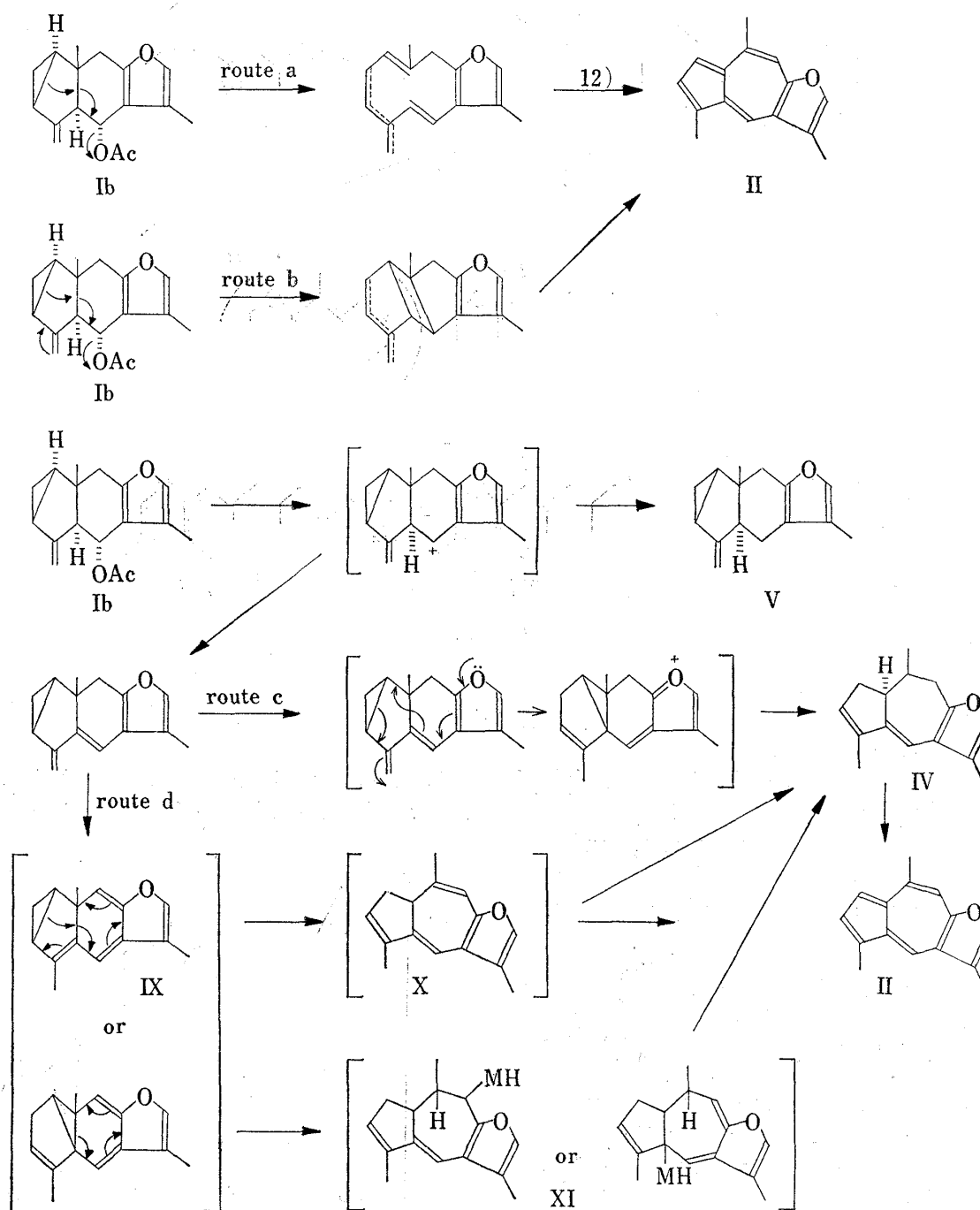
11) Ten milligram of Ib was subject with the Pd catalyst which had passed hydrogen at 300°, at a rate of 10 ml/min for 10′, according to the general method.

Catalyst	Yield (%)		
	II	IV	V
Treated with H_2	27.4	11.7	4.3
Non-treated with H_2	33.2	6.7	4.5

Yields of lindenene (V) are the same for both catalyst treated and non-treated with hydrogen, but the yield of the hydroazulene (IV) obtained by the hydrogen-treated catalyst was 1.8 times as large as that by the non-treated catalyst. This experiment will suggest that hydrogen may hydrogenate the intermediate.

12) S. V. Hiremath, G. H. Kulkani, G. R. Kelkar, and S. C. Bhattacharyya, Indian J. Chem., 6, 243 (1968).

In considering the mechanism of dehydrogenation by palladium, the most important result is that the intermediate (IV) has optical activity at C_{7a}. Therefore, this reaction should proceed by a concerted mechanism. As shown in Chart 2, the following four routes may be possible.

In route a, the ten-membered ring intermediate is optically inactive and would result in an optically inactive hydroazulene (IV).

Following route b, the bourbonene type intermediate would be very slow to rearrange to the azulene, since α- and β- bourbonene were found to be unaffected under the dehydrogenation conditions used, as seen in Table I.

By route c, reduction with hydrogen would proceed simultaneously with the electrocyclic process. Therefore, if followed, this route would not result in preferential production of azulene to the intermediate (IV). These three routes are therefore inconsistant with the results obtained.

By route d, the first step calls for a [1, 7]hydrogen shift, which is "forbidden" by the Woodward–Hoffmann rules.[13] But several examples have recently been reported where a system which is symmetry "forbidden" becomes "allowed" when the reaction is catalyzed by various transition metal complexes.[14] Then, the supposed intermediate (IX) is dehydrogenated via an electrocyclic process analogous to the thermolysis of thujene.[15] It is interesting that the dehydrogenation of Ib by palladium proceeds with retention of optical activity, compared with the thermolysis of thujene in which the optical activity is lost. It is difficult to explain reasonably the reduction of the supposed intermediate (IX) to the hydroazulene (IV) according to the above electrocyclic process; as a more complex process would be involved. Valence tautomerization catalyzed by some transition metals have frequently been explained in terms of concerted electrocyclic processes.[14-16]

Fig. 6. Dehydrogenation of 1b and Its Deuterate in Perdeuteriopentane

A: lindenenyl trideuterioacetate
B: lindenenyl acetate (1b)
C: perdueteriopentane
D: pentane

But the isomerization reaction of exo-tricyclo [$3.2.1.0^{3,5}$]octene with a rhodium catalyst[17] was explained by the participation of a carbon-metal insertion reaction. To prove the presence of a route via the σ-bonded metal intermediate (XI), the following experiment wastried.

13) R. B. Woodward and R. Hoffmann, J. Am. Chem. Soc., 87, 395, 2046, 2511, 4388, 4389 (1965).

14) W. Merk and R. Pettit, J. Am. Chem. Soc., 89, 4788 (1967); H. Hogeveen and H. C. Volger, ibid., 89, 2486 (1967); F. D. Mango and J. H. Schachtschneider, ibid., 89, 2484 (1967); F. C. Cowherd and J. L. von Rosenberg, ibid., 91, 2157 (1969).

15) W. von Doering and J. B. Lambert, Tetrahedron, 19, 1969 (1963).

16) H. Hogeveen and H. C. Volger, Chem. Commun., 1967, 1133; H. C. Volger and H. Hogeveen, Rec. Trav. Chim., 86, 830 (1967); H. C. Volger, H. Hogeveen, and M. M. P. Gassbeck, J. Am. Chem. Soc., 91, 218 (1968).

17) T. J. Katz and S. Cerefice, J. Am. Chem. Soc., 91, 2405 (1969).

Lindenenyl acetate (Ib) and lindenenyl trideuterioacetate dissolved in pentane or per-deuteriopentane were dehydrogenated by the palladium catalyst, and the products examined by GC-MS. The intensities of the molecular ion peaks of hydrolinderazulene (IV) and the azulene (II) are shown in Fig. 6. The result that the dehydrogenation of the acetate dissolved in deuteriopentane by the palladium catalyst primed by cholesterol gave products without incorporation of deuterium indicates that the catalyst did not abstract deuterium from the solvent. When the trideuterioacetate dissolved in deuteriopentane was submitted to the primed catalyst, not only the hydroazulene (IV) but the azulene (II) contained deuterium, and high incorporation of deuterium was observed for the nonprimed catalyst at 350°. The high order of incorporation may result from a temperature high enough for the abstraction of deuterium from the solvent. Accordingly, the abstraction of hydrogen from pentane may be possible at 300° by taking account of deuterium isotope effect. It is supposed from these results that the dehydrogenation by palladium at 300° presumably causes not only abstraction of hydrogen from both reactant and sovent but also the donation of hydrogen to the reactant and intermediate simultaneously, leading to the dehydrogenated or hydrogenated products with a scrambling of hydrogen. It should be emphasized that the above results indicate that the dehydrogenation proceeds neither by a single concerted electrocyclic process nor by a single hydrogenation by metal hydride or chemisorbed hydrogen; also the function of the acetate is not clear.

Experimental

Melting point were measured on a Kofler block (Yanagimoto & Co.). CD sepctra was measured in CH_2Cl_2 with a Jasco model ORD/UV-5 optical rotatory dispersion recorders. NMR spectra were taken in CCl_4 using tetramethylsilane as an internal standard with a Varian A-60 spectrophotometer, unless otherwise stated. Proton spin-decoupling experiments at 100 Mc were made by using a Varian HA-100 spectrometer and a Hewlett-Packard HP 200 ABR audio-oscillator in the TMS locked mode and frequency sweep operation. Gas chromatography was carried out for analytical use; by a Shimadzu GC-4ATF equipped with a flame ionization detector, column: 1% carbowax 20 M and 1% Apiezon L respectively on Gas Chrom Q (100/120 mesh) 1.5m × 4 mm (glass column); for preparative use: by a Varian Aerograph model 1240-B, SE-30, carbowax 20 M, QF-1 respectively 5% coated on Chromosorb W (30/60 mesh, acid-washed, dimethyldichlorosilane treated) 10′ × 3/8″ (glass column). Kováts indices were obtained under column temperature 170°. GC-MS was performed by a Hitachi model K-53 (1% Apiezon L or 1% carbowax 20M on Gas Chrom Q (100/120 mesh), 2 m × 3 mm SS column)-Hitachi model RMU-6E mass spectrometer equipped with a Biemann type separator as a interface, or a Varian Aerograph model 1200 (1% carbowax 20 M on Gas Chrom Q (100/120 mesh), 6′ × 1/8″ SS column)-Varian Matt M-66 mass spectrometer using a Llewellyn type separator. Conditions for GC-MS are as follows: injection temp. 180°, column temp. 160°, He 1.0 kg/cm² (35 ml/min), connecting tube 180°, molecular separator 180°, ion-chamber 70 eV.

Priming of Palladium on BaCO₃ by Cholesterol (for Preparative Use)——Five percent palladium on $BaCO_3$[18) (24/32 mesh) was packed into a preparative column (10 cm × 9 mm) 30 mm in length. The one end of the column have a carrier gas inlet and a sample injector sealed with a silicon rubber septum, and the other end was connected to a glass tube with glass joint, which was fastened by spring. The catalyst column was heated at 300° in a furnace and carrier gas (N₂) was passed at a rate of 10 ml/min. Twenty μl of 3% solution of cholesterol dissolved in CH_2Cl_2 was injected 10 times every half a minutes, then temperature of the column was held at 350° for 1 hr.

Palladium Dehydrogenation Reaction combined with Gas Chromatography——The catalyst of 5% palladium on BaCO₃ (24/32 mesh) primed by cholesterol was packed at 25 mm length in a column (50 mm × 4 mm φ), the catalyst column was inserted into a injection block, and connected to a GC column by a SS pipe with a silicone rubber stopper.

For azulene formation; column; 1% Apizeon L 2.0 m × 4 mm, injection 370°, column 205°, detector 250°, N₂ 12 ml/min. A pentane solution (1—10 μg sample) was injected.

For checking intermediates, 1% carbowax 20 M 2.0 m × 4 mm, injection 170—370°, column 180°, N₂ 12—50 ml/min.

General Method of Dehydrogenation by Palladium Catalyst——The catalyst column used was same as the one mentioned at the priming method of the catalyst. Each 20 μl of 1% solution of sample dissolved in pentane was injected in the catalyst column at any temperature and carrier gas velocity for every half a

18) R. Mozingo, "Organic Synthesis," Vol. 26, 1946, p 77.

minute. The product was trapped at the outlet of the column with dryice–acetone cooling. The product was transferred as a pentane solution.

Dehydrogenation of Lindenenyl Acetate (Ib)——The catalyst column: 200—250°, N_2: 10 ml/min. The product (0.88 g) obtained from Ib (2.2 g) was chromatographed on Al_2O_3 (activity III). The fraction eluted before linderazulene (II) (purple) was fractionated by a preparative GC. The column used was as follows:
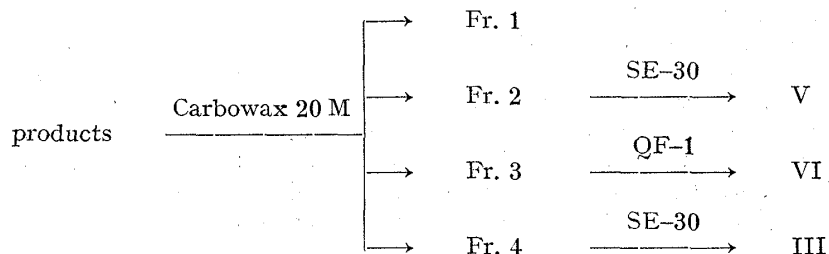
Fr. 2: The second peak on the gas chromatogram Fig. Ib, was identified as lindenene (V) from comparison of NMR, IR, GC, GC-MS spectra.

Fr. 3 (VI): The third peak on the gas chromatogram in Fig. Ib was a pale blue oil. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1643, 899, 879, 856, 787. UV $\lambda_{max}^{heptane}$ mμ (ε): 212.5 (25200), 272 (2840), 281 (2950), 285 (2900), 291 (2800). GC-MS: 212 (M$^+$), 197 (M$^+$-CH$_3$).

Fr. 4 (IV): The fourth peak on the gas chromatogram in Fig. Ib, mp 96—99° (from acetone). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1623, 986, 931, 851, 742. UV λ_{max}^{EtOH} mμ (ε): 195 (8900), 232 (14600), 238 (14000), 290 (10300), 300 (11500), 313 (8200). GC-MS: 214 (M$^+$), 199 (M$^+$-CH$_3$). $[\alpha]_D^{23}$ -164° (c=1.353, CH$_2$Cl$_2$). CD $\lambda[\theta]$ 315 i (-9800), 304 (-15000), 247 (+4800).

VI from Pyrolysis of Lindenenyl Acetate (Ib)——Lindenenyl acetate (975 mg) was pyrolyse according to the general method for dehydrogenation except for the following condition: catalyst: BaCO$_3$ (24/32 mesh) Coulmn 180°, N_2 10 ml/min. The trapped product dissolved in pentane was chromatographed on Al_2O_3 (activity III).The eluate from pentane gave VI 24 mg.

Catalytic Hydrogenation of VI——Compound (VI), (10 mg) dissolved in methanol (0.5 ml) was hydrogenated with 5% Pd-C (5 mg). After 30′, 1 mole eq. hydrogen was absorbed, the solution was filtered, the filtrate was evaporated to leave oil (10 mg). GC: $I^{carbowax20M}$2025, $I^{ApiezonL}$ 1576. GC-MS 214 (M$^+$). NMR τ: 9.07 (3H, J=7 cps), 7.72 (3H, singlet), 4.55 (1H, triplet—multiplet, J=7 cps), 2.99 (1H, singlet), 2.83 (1H, multiplet), 2.23 (1H, multiplet).

Catalytic Hydrogenation of VII——Compound (VII) (10 mg) dissolved in EtOH (0.5 ml) was hydrogenated with Rh-Pt catalyst [19] (15 mg). After 2 hr, the catalyst was filtered the resulting filtrate was evaporated to give an oil. GC: a new peak (VIII) (accompanying with VII) $I^{carbowax20M}$ 2100, $I^{ApiezonL}$ 1641. GC-MS: 216 (M$^+$) 173 (M$^+$-C$_3$H$_7$).

Preparation of III——Lindenenyl acetate (Ib), (150 mg) was treated according to the general methods of dehydrogenation: catalyst: 50% Pd on Chromosorb W (30/60 mesh), 180°, N_2 30 ml/min. The product traped was dissolved in pentane, chromatographed on Al_2O_3 (activity III). III was obtained as an oil (9 mg). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1629, 863, 853. UV $\lambda_{max}^{heptane}$ mμ (ε): 202 (7800), 222 (8000), 240 (10000), 324 (5800). GC-MS: 212 (M$^+$), 197 (M$^+$-CH$_3$). NMR τ: 8.97 (3H, singlet), 8.03 (3H, d, J=1 cps), 5.13 (1H, multiplet), 4.83 (1H, multiplet), 3.86 (1H, singlet), 3.10 (1H, triplet).

2-Formyl-cholesta-4,6-dien-3-one——Cholesta-4,6-dien-3-one (1 g) was dissolved in benzene (20 ml), ethyl formate (1 ml), NaH (50%, o.6 g) was added with stirring under N_2 atmosphere. After 3 hr, methanol was added to decompose NaH, further H_2O added, and the precipitate was collected, washed with ether. The aqueous layer combined with the precipitate was acidified with 2N HCl, extracted with ether–CH$_2$Cl$_2$. The organic layer was washed with H_2O, dried over Na_2SO_4, and evaporated. 975 mg, mp 117—118°, yellow prisms (from hexane). Found: C, 82.06; H, 10.23. Calcd. for C$_{28}$H$_{42}$O$_2$: C, 81.89, H, 10.31.

2-Formyl-3-methoxy-cholesta-2,4,6-triene——A solution of 2-formyl-cholesta-4,6-dien-3-one (470 mg) was dissolved in methanol (20 ml), added p-toluenesulfonic acid (1 mg), and refluxed 10 min. After cooling, one drop of pyridine was added, followed addition of water, the mixture was extracted with CH$_2$Cl$_2$–MeOH. The extract was washed with H_2O, dried over Na_2SO_4. 395 mg, mp 120.5—122°, needles from pentane. Found: C, 82.13; H, 10.52. Calcd for C$_{29}$H$_{44}$O: C, 82.09: H, 10.44. UV λ_{max} mμ (ε): 296 (21000), 326 (shoulder) (7160). NMR (CDCl$_3$) τ: 6.17 (3H, singlet), 4.30 (1H, singlet), 3.91 (2H, singlet), 2.65 (doublet—multiplet, J=2 cps).

5-Ethoxycarbonylfurano[3′, 4′-2, 3] cholesta-4, 6-diene——To a solution of above 3-methoxy compound (2.0 g) dissolved in diglyme (30 ml) at 170° with stirring, CuSO$_4$ (one bit) was added, followed addition of

19) S. Nishimura, *Bull. Chem. Soc. Japan*, **31**, 1356 (1960).

a solution of ethyl diazoacetate (2.1 g) dissolved in diglyme (20 ml) in a period of 30′, further stirring and heating was continued for 1.5 hr.   After cooling, the mixture was extracted with ether, and the extract was evaporated to dryness.   Recrystallization from pentane gave 1.2 g, mp 132—134°.   Found: C, 80.64: H, 9.69.   Calcd. for $C_{32}H_{46}O_3$: C, 80.27; H, 9.69. $[\alpha]_D^{27}$ -323.6° (0.5322%, CH_2Cl_2).   NMR τ: 5.70 (2H, quartet, $J=7$ cps), 4.25 (1H, doublet—multiplet, $J=10$ cps), 3.85 (1H, doublet—multiplet, $J=10$ cps 3.46 (1H, multiplet), 2.85 (1H, multiplet).

Furano[3′,4′-2,3]cholesta-4,6-diene (XV)———To a solution of above ester (300 mg) dissolved in benzene (2 ml), 2% KOH–EtOH solution (30 ml) was added, refluxed 30′ min.   After cooling, the precipitate was collected, washed with EtOH, extracted with 10% AcOH–CH_2Cl_2.   The extract was washed with water, dried over Na_2SO_4, evaporated to leave a residue 233 mg. The residue was mixed with copper powder, heated at 240—260° for 5′ min.   After cooling the product was dissolved in pentane, chromatographed on Al_2O_3. Fraction eluted with pentane (156 mg) was recrystallized from ether–MeOH mp 80—82°.   Found: C, 85.71; H, 10.40.   Calcd. for $C_{29}H_{42}O$: C, 85.65: H, 10.41. $[\alpha]_D^{23}$ -149°.   CD: mμ [θ] 280 (-43000).   UV $\lambda_{max}^{CH_2Cl_2}$ mμ (ε): 281 (28900). NMR τ: 4.40 (1H, doublet—multiplet, $J=10$ cps), 3.99 (1H, doublet—multiplet, $J=10$ cps), 3.89 (1H, singlet), 2.92 (1H, multiplet), 2.82 (1H, doublet, $J=1.5$ cps).