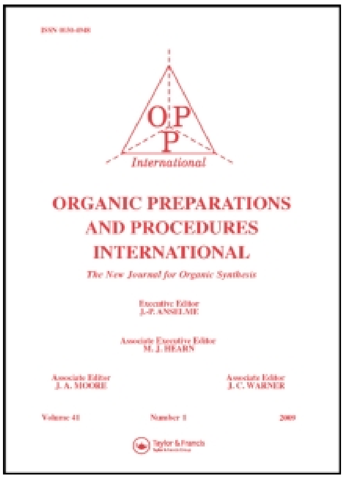

Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

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To cite this Article Yamato, Takehiko , Kobayashi, Kazumasa and Tashiro, Masashi(1986) 'REACTION OF 2,7-DI-*t*-BUTYL-2,4,5,7,9,10-HEXACHLORO-*trans*-10b,10c-DIMETHYL-2,7,10b,10c-TETRAHYDROPYRENE WITH ALCOHOLS AND WATER AND THE CHEMISTRY OF THE PRODUCTS OBTAINED', Organic Preparations and Procedures International, 18: 4, 245 — 252

To link to this Article: DOI: 10.1080/00304948609458149

URL: http://dx.doi.org/10.1080/00304948609458149

ORGANIC PREPARATIONS AND PROCEDURES INT. 18(4), 245-252 (1986)

REACTION OF 2,7-DI-t-BUTYL-2,4,5,7,9,10-HEXACHLORO-trans-10b,10c-DIMETHYL-2,7,10b,10c-TETRAHYDROPYRENE WITH ALCOHOLS AND WATER AND THE CHEMISTRY OF THE PRODUCTS OBTAINED[†]

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2,7-Di-t-butyl-2,3,5,7,9,10-hexachloro-trans-10b,10c-dimethyl-10b,10c-dihydropyrene (I)[1] reacted easily with water and primary alcohols (Eq. 1 and Table 1) to afford good yields of the corresponding 2,7-dihydroxy-(IIa) and 2,7-dialkoxy derivatives (IIb-IId). While only dechlorinated product III was obtained with isoropyl alcohol, t-butyl alcohol failed to react with I. Treatment of I with a mixture of water and

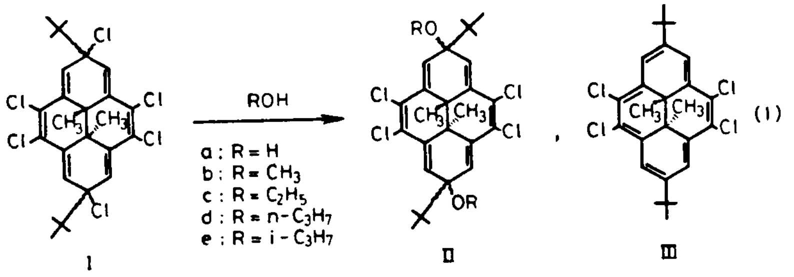
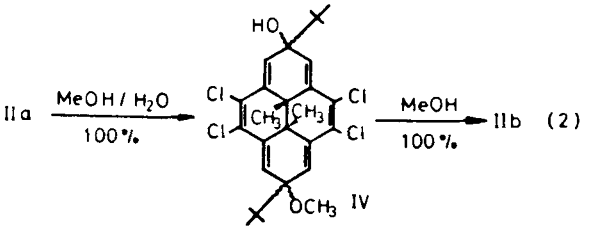


TABLE 1. Reaction of I with Water and Alcohols[a]

H^b	CH_3	C_2H_5	n-C_3H_7[c]	i-C_3H_7[c]	t-C_4H_9
IIa,73%	IIb,93%	IIc,96%	IId,65%	III,88%	N.R.

a) The reaction mixture was refluxed for 10 min unless otherwise indicated. b) Room temperature. c) Reaction time: 2 hrs.

methanol (1:1) yielded 2,7-di-t-butyl-2-hydroxy-7-methoxy-4,5,9,10-tetrachloro-trans-10b,10c-dimethyl-10b,10c-dihydropyrene (IV), which can be converted to IIb in 100% yield by treatment with methanol. When IIb was treated with boiling



ethanol, IIc was formed in 98% yield. While no product was obtained from IIc and boiling methanol; instead, IIc was recovered in nearly quantitative yield. Compound IIa reacted easily with alcohols without catalyst to give the corresponding dialkoxy derivatives IIb-IId.

$$\mathrm{IIb}\ \overset{\longrightarrow}{\underset{\text{MeOH}}{\not\longleftarrow}}\ \mathrm{IIc}$$

$$\mathrm{IIa} \xrightarrow{\text{ROH}} \mathrm{IIb\text{-}IId}$$

b:98%; c:90%; d:52%

Oxidation of IIb and IIc with $FeCl_3$ was carried out under a variety of conditions in the hope of obtaining the corresponding 2,7-dioxo derivative V (Eq. 3, Table 2). The expected compound V was not formed. Instead a mixture of III, VI and VII was obtained. The ratio of the products was dependent upon the amount of $FeCl_3$ used. The above reaction did not afford any useful product when it was carried out at 0°.

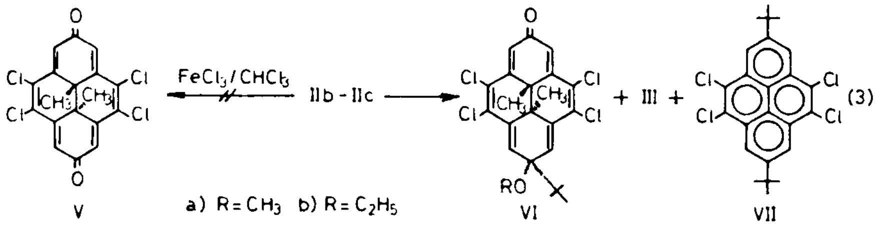
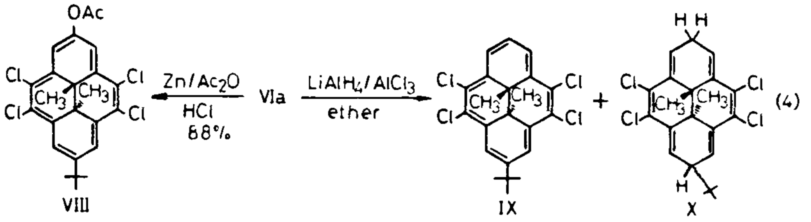


TABLE 2. Reaction of IIb-IIc with $FeCl_3$ in $CHCl_3$[a]

Run	Substrate	$FeCl_3$/II (mole/mole)	Product (%)[b]
1	IIa	1	III(52), VIa(46)
2	IIa	3.3	III(47), VIa(50)
3	IIa	10.0	III(28), VIa(42), VII(20)
4	IIa	33.0	VIa(+)[c], VII(66)
5	IIb	3.3	III(44), VIb(52)

a) The reaction mixture was stirred at room temperature for 1 h. b) The isolated yields are shown. c) Plus sign means less than 1% yield.

The reduction of VIa with Zn powder in acetic anhydride in the presence of conc. HCl (36%) afforded VIII in good yield. On the other hand, the reduction of VIa with $LiAlH_4$-$AlCl_3$ gave a mixture of IX and X (1:1); oxidation of this mixture with DDQ afforded pure IX in 94% yield. Unfortunately the stereochemistry of I and the products and these obtained could not determined from their NMR spectra seem to be mixture of stereoisomers.



EXPERIMENTAL SECTION

Hydrolysis of I.- A solution of 58.3 mg (0.10 mmol) of I in 30 mL of tetrahydrofuran and 10 mL of water was stirred at room temperature for 12 hrs. The reaction mixture was extracted with dichloromethane. The dichloromethane extract was dried over Na_2SO_4 and evaporated <u>in vacuo</u> to leave a residue that crystallized upon addition of a small amount of hexane of IIa as colorless prisms of IIa (37.7 mg, 73%), mp. 210-213° (dec.); IR (KBr): 3590, 3040, 2960, 1550, 1340, 1210, 1160, 970, 930, 905, 790 cm^{-1}; NMR ($CDCl_3$): δ 1.05 (18H, s), 1.07, 1.16 (6H, each s), 1.24 (2H, s), 6.61, 6.68 (4H, each s); Mass spectrum: m/e 459 ($M^+-C_4H_9$).

<u>Anal</u>. Calcd. for $H_{26}H_{30}Cl_4O_2$: C, 60.48; H, 5.86

Found: C, 60.60; H, 5.90

<u>Reaction of I with Alcohols</u>. <u>Typical Procedure</u>.- A suspension of 58.3 mg (0.1 mmol) of I in 30 mL of methanol was refluxed for 10 min. The reaction mixture was cooled to give IIb as colorless prisms (methanol), mp. 277-279° (dec.); IR (KBr): 3040, 2960, 1550, 1455, 1375, 1340, 1160, 1070, 960, 930, 910, 865, 795 cm^{-1}; NMR ($CDCl_3$): δ 1.00 (18H, s), 1.10, 1.15, 1.21 (6H, each s), 3.02, 3.05 (6H, each s), 6.44 (4H, s); Mass spectrum: m/e 487 ($M^+-C_4H_9$).

<u>Anal</u>. Calcd. for $C_{28}H_{34}Cl_4O_2$: C, 61.78; H, 6.30

Found: C, 61.46; H, 6.35

Similarly, I reacted with ethanol and <u>n</u>-propyl alcohol to gave IIc and IId in 96% and 65%, respectively.

IIc: colorless prisms (ethanol), mp. 295-298° (dec.); IR (KBr): 3040, 2980, 2880, 1540, 1480, 1340, 1160, 1120, 1060, 1010, 985, 930, 905, 785, 660 cm^{-1}; NMR ($CDCl_3$): δ 1.00 (18H, s), 1.12 (6H, t, J = 7 Hz), 3.15 (4H, q, J = 7 Hz), 6.45 (4H, s); Mass spectrum: m/e 513 ($M^+-C_4H_9$).

<u>Anal</u>. Calcd. for $C_{30}H_{38}Cl_4O_2$: C, 62.94; H, 6.69

Found: C, 62.80; H, 6.50

IId: colorless prisms (n-propyl alchol), mp. > 300°; IR (KBr): 2980, 1540, 1480, 1340, 1160, 1110, 1075, 1020, 910, 660 cm^{-1}; NMR ($CDCl_3$): δ 0.87 (6H, t, J = 7 Hz), 1.00 (18H, s), 1.12 (6H, s), 1.30-1.70 (4H, m), 3.05 (4H, t, J = 6 Hz), 6.44 (4H, s); Mass spectrum: m/e 541 (M^+-C_4H_9).

Anal. Calcd. for $C_{32}H_{42}Cl_4O_2$: C, 64.00; H, 7.05

Found: C, 63.90; H, 7.00

Reaction of IIa with Methanol and Water.- A suspension of 58.3 mg (0.1 mmol) of IIa in a mixture of 15 mL of methanol and 15 mL water was refluxed for 10 min. The reaction mixture was cooled to give quantitative yield of IV as colorless prisms (MeOH-H_2O), mp. 216-218°, IR (KBr): 3670, 3600, 3040, 2960, 1550, 1460, 1375, 1340, 1160, 1080, 970, 930, 910, 865, 825 cm^{-1}; NMR ($CDCl_3$): δ 1.00, 1.04 (18H, each s), 1.08, 1.12, 1.15 (6H, s), 1.24 (1H, s), 3.00, 3.04 (3H, each s), 6.44, 6.61 (3H, each s); Mass spectrum: m/e 473 (M^+-C_4H_9).

Anal. Calcd. for $C_{27}H_{32}Cl_4O_2$: C, 61.15; H, 6.08

Found: C, 60.90; H, 6.12

Reaction of IIa with Alcohols. Typical Procedure.- A suspension of 50 mg (0.097 mmol) of IIa in 30 mL of methanol was refluxed for 2 hrs. The reaction mixture was cooled to give 51.6 mg (98%) of IIb.

Similarly compound IIa reacted with ethanol and n-propylalchol to give IIc and IId in 90% and 52% yield, respectively.

Reaction of IIb with Ethanol.- A suspension of 50 mg (0.092 mmol) of IIb in 30 mL of ethanol was refluxed for 12 hrs. The reaction mixture was cooled to give 56.1 mg (98%) of IIc.

Reaction of IIc with Methanol.- A suspension of 50 mg (0.087

mmol) of IIc in 30 mL of methanol was refluxed for 12 hrs. The reaction mixture was cooled to give 50 mg (100%) of IIc. Similar treatment of IV afforded IIb in near quantitative yield.

Oxidation of II with Ferric Chloride. Typical Procedure.- To a solution of 217.6 mg (0.4 mmol) of IIb in 80 mL of chloroform was added 216 mg (1.33 mmol) of ferric chloride while stirring at room temperature. After the reaction mixture was stirred for 1 hr, it was washed with water, dried over Na_2SO_4 and evaporated *in vacuo* to leave the residue, which was chromatographed on silica gel with hexane and benzene as the eluent. The deep green crystals isolated from the hexane eluate were recrystallized from hexane to give 90 mg (47%) of III.[2] The pale yellow crystals isolated from the benzene eluate were recrystallized from hexane to give 95 mg (50%) of VIa as pale yellow prisms (hexane), mp. 255-257° (dec.); IR (KBr): 2980, 1660, 1580, 1540, 1340, 1290, 1160, 1070, 885, 795, 660 cm^{-1}; NMR ($CDCl_3$): δ 1.02 (9H, s), 1.32 (3H, s), 1.48 (3H, s), 3.05 (3H, s), 6.65 (2H, s), 6.78 (2H, s); Mass spectrum: m/e 413, 415, 417, 419, 421, ($M^+-C_4H_9$).

Anal. Calcd. for $C_{23}H_{22}Cl_4O_2$: C, 58.50; H, 4.70
Found: C, 58.60; H, 4.65

Compound VIb was synthesized in the same manner as described above and was obtained as pale yellow plates (hexane), mp. 244-245° (dec.); IR (KBr): 3050, 2900, 1660, 1580, 1540, 1460, 1380, 1350, 1300, 1170, 1120, 1100, 915, 890, 670 cm^{-1}; NMR ($CDCl_3$): δ 1.00 (9H, s), 1.12 (3H, t, *J* = 7 Hz), 1.29

(3H, s), 1.44 (3H, s), 3.15 (2H, q, *J* = 7 Hz), 6.65 (2H, s), 6.76 (2H, s); Mass spectrum: *m/e* 427, 429, 431, 433, 435 (M^+-C_4H_9).

Anal. Calcd. for $C_{24}H_{24}Cl_4O_2$: C, 59.28; H, 4.98
Found: C, 59.24; H, 5.01

Reduction of VIa with Zinc Powder.- To a solution of 50 mg (0.106 mmol) of VIa in 10 mL of acetic anhydride was added 200 mg of zinc powder and 0.1 mL of concentrated hydrochloric acid and the solution was heated on the water bath for 2 hrs. The reaction mixture was filtered and concentrated to leave the residue, which was extracted with dichloromethane. The dichloromethane extract was washed with water, dried over Na_2SO_4 and evaporated *in vacuo* to leave a residue which was chromatographed on silica gel with hexane as the eluent. The deep green crystals isolated from the eluate were recrystallized from methanol to give 45 mg (87.7%) of VIII: deep green prisms (methanol), mp. 207-208°; IR (KBr): 3040, 2960, 1765, 1580, 1440, 1360, 1335, 1230, 1180, 1140, 1015, 915, 890, 870, 670 cm^{-1}; NMR ($CDCl_3$): δ -3.48 (3H, s), -3.42 (3H, s), 1.72 (9H, s), 2.52 (3H, s) 8.62 (2H, s), 8.98 (2H, s); Mass spectrum: *m/e* 481, 483, 485, 487, 489 (M^+).

Anal. Calcd. for $C_{24}H_{22}Cl_4O_2$: C, 59.53; H, 4.58
Found: C, 59.35; H, 4.78

Reduction of IVa with $AlCl_3$-$LiAlH_4$.- Fresh 1:1 mixed hydride reagent was prepared from 133 mg (1 mmol) of anhydrous aluminium chloride in 2.5 mL of ether and 38 mg (1 mmol) of lithium aluminum hydride in 2.5 mL of ether. A solution of 47.2 mg

(0.1 mmol) of VIa in 5 mL of ether was added dropwise with gentl reflux while stirring with magnetic stirrer and the refluxing was then confirmed for 30 min. After the reaction mixture was cooled, poured on ice and extracted with dichloromethane, the organic extract was washed with water and 10% HCl solution, dried over sodium sulfate and evaporated in vacuo to give green crystals (50 mg). An nmr spectrum of the crystalline green residue showed the presence of 7-t-butyl-4,5,9,10-tetrachloro-trans-10b,10c-dimethyl-2,7,10b,10c-tetrahydropyrene (X); NMR ($CDCl_3$): δ 1.00 (3H, s), 1.05 (9H, s), 1.11 (3H, s), 2.88-2.98 (1H, m), 3.07-3.14 (2H, m), 6.42-6.54 (4H, m), and 7-t-butyl-4,5,9,10-tetrachloro-trans-10b,10c-dihydropyrene (IX), which could not be separated.

Reaction of IX and X with DDQ.- A solution of 50 mg of the mixture of IX and X and 50 mg of DDQ in 10 mL of benzene was refluxed for 2 hrs under nitrogen. After cooling, the reaction mixture was concentrated and the residue was chromatographed on silica gel using hexane as the eluent to give 40 mg (94% from VIa) of IX as deep green prisms (MeOH), mp. 150-151° (dec.); NMR ($CDCl_3$): δ 3.58 (3H, s), 1.71 (9H, s), 8.13 (1H, d, J = 8 Hz), 8.85 (2H, d, J = 8 Hz), 8.97 (2H, s).

Anal. Calcd. for $C_{22}H_{20}Cl_4$: C, 62.00; H, 4.73

Found: C, 61.99; H, 5.00

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1. M. Tashiro et al., ibid., 49, 3380 (1984); J. Am. Chem. Soc., 104, 3701 (1982).

(Received September 16, 1985; in revised form March 3, 1986)