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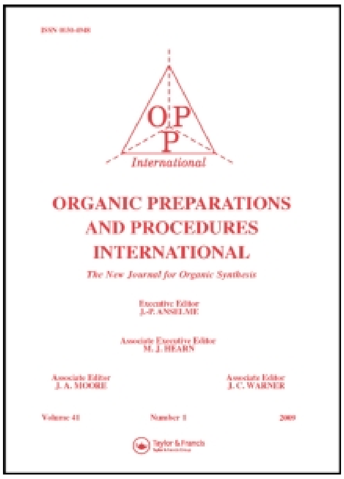

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METACYCLOPHANES AND RELATED COMPOUNDS. 2.† NITRATION AND ACETYLATION OF 2,7-DI(*t*-BUTYL)-*trans*-10b,10c-DIMETHYL-10b,10c-DIHYDROPYRENE

Masashi Tashiro[a]; Takehiko Yamato[a]
[a] Research Institute of Industrial Science, Kyushu University, Kasuga-shi, Fukuoka, JAPAN

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METACYCLOPHANES AND RELATED COMPOUNDS. 2.[†]

NITRATION AND ACETYLATION OF 2,7-DI(*t*-BUTYL)-*trans*-10b,10c-DIMETHYL-10b,10c-DIHYDROPYRENE

Submitted by Masashi Tashiro* and Takehiko Yamato
(9/22/81)
Research Institute of Industrial Science
Kyushu University
Sakamoto, Kasuga, Kasuga-shi
Fukuoka 816, JAPAN

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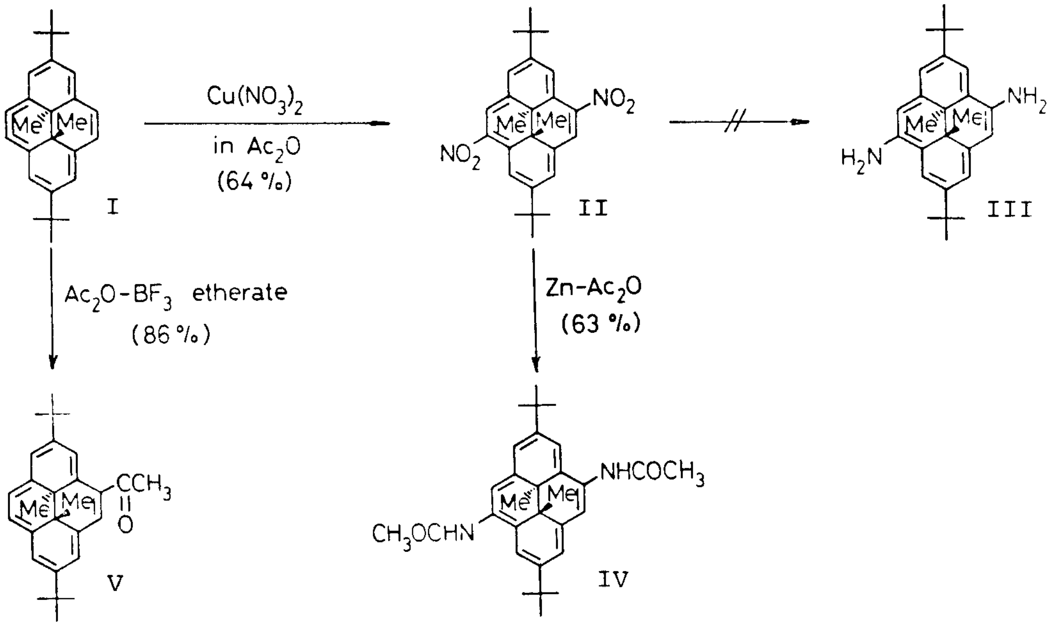
As a part of an investigation of the chemistry of *trans*-10b,10c-dialkyl-10b,10c-dihydropyrenes, we investigated the nitration and acetylation of the title compound (I).



The expected 2,7-di(t-butyl)-4,9-dinitro-trans-10b,10c-dimethyl-10b,10c-dihydropyrene (II) was obtained when 2,7-di-(t-butyl)-trans-10b,10c-dimethyl-10b,10c-dihydropyrene[1] was nitrated under the reported method.[2] Any attempt to obtain the diamine III from the dinitro compound II under various conditions such as Sn in hydrochloric acid, Sn or Zn in acetic acid and Raney Ni-hydrogen systems was unsuccessful. However, the reduction of II with Zn powder in acetic anhydride afforded the corresponding diacetoamide IV. The acetylation of I with acetic anhydride in the presence of boron trifluoride etherate according to the reported method gave the monoacetyl derivative V.

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EXPERIMENTAL SECTION

All melting and boiling points are uncorrected. N.M.R. spectra were determined at 100 MHz with the Nippon Denshi JEOL FT-100 NMR spectrometer with Me_4Si as internal references and I.R. spectra were measured as KBr pellets or liquid film on NaCl plates on a Nippon Bunko IR-A-102 spectrometer. Mass spectra were obtained on a Nippon Denshi JMS-01 SA-2 spectrometer at 75 eV using a direct inlet system.

2,7-Di(t-butyl)-4,9-dinitro-trans-10b,10c-dimethyl-10b,10c-dihydropyrene (II).- To a solution of 100 mg (0.29 mmole) of 2,7-di(t-butyl)-trans-10b,10c-dimethyl-10b,10c-dihydropyrene (I) in 20 ml of acetic anhydride held at 0° was added 150 mg of powdered cupric nitrate trihydrate. In about 10 min, the color of the solution had changed from deep green to deep brown. The reaction mixture was stirred at room temperature (20°) for 90 min before adding 5 g of ice and 20 ml of ether. When the reaction of the acetic anhydride with water was completed, ether layer was separated, washed with water, dried, and concentrated. The residue was taken up in dichloromethane and chromatographed over silica gel with benzene to give 144.5 mg of deep brown solid which was recrystallized from hexane to afford 80.8 mg (64.2%) of II as deep brown prisms (hexane), mp. 222-224°; IR (KBr): 3040, 2950, 1600, 1525, 1390, 1290, 1260, 875, 840, 790, 760, 750, 670 cm^{-1}; NMR($CDCl_3$): δ -3.00 (6H, s, CH_3), 1.64 (18H, s, t-Bu), 8.46 (4H, s, ArH), 8.97 (2H, s, ArH); Mass m/e: 434 (M^+).

Anal. Calcd for $C_{26}H_{30}N_2O_4$: C, 71.86; H, 6.96; N, 6.45.
Found: C, 71.78; H, 6.99; N, 6.37.

2,7-Di(t-butyl)-4,9-diacetamide-trans-10b,10c-dimethyl-10b,10c-dihydropyrene (IV).- To a solution of 100 mg (0.23 mmole) of II and 400 mg of sodium acetate in 20 ml of acetic anhydride was added 1.0 g of zinc dust with stirring. The reaction mixture rapidly changed from deep brown to pale green as it was stirred at room temperature for 1 hr. Then, 200 ml of water was added and aqueous suspension was extracted with three 25 ml portions of dichloromethane. The dichloromethane extracts were washed successively with aqueous ammonia and water, dried and concentrated. The resulting green solid was recrystallized from $CHCl_3$ to give 66.4 mg (63%) of (IV) as pale green prisms ($CHCl_3$), mp. 264-265°(dec.); IR(KBr): 3230, 3020, 2950, 1650, 1590, 1530, 1470, 1360, 1280, 1250, 1200, 970, 870, 790, 680 cm^{-1}; NMR($CDCl_3$): δ -3.75 (6H, s, CH_3), 1.66 (18H, s, t-Bu), 2.36 (6H, s, $COCH_3$), 8.20 (2H, broad s, NH), 8.37-8.60 (6H, m, ArH); Mass m/e: 458 (M^+).

Anal. Calcd for $C_{30}H_{38}N_2O_2$: C, 78.56; H, 8.35; N, 6.10.
Found: C, 78.35; H, 8.37; N, 5.78.

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2,7-Di(t-butyl)-4-acetyl-trans-10b,10c-dimethyl-10b,10c-dihydropyrene (V).- To a solution of 100 mg (0.29 mmole) of I in 40 ml of methylene chloride was added 1 ml of acetic anhydride and 0.5 ml of boron trifluoride etherate. The resulting dark blue solution was allowed to stand at room temperature for 3 hr before adding 20 ml of water. The organic layer was separated and concentrated under reduced pressure. The residue was taken up in dichloromethane and chromatographed over silica gel with benzene to give 96.4 mg (86%) of V and 10 mg of recovered I.

V: deep blue prisms (hexane), mp. 185-187°; IR(KBr): 3040, 2950, 1640, 1440, 1375, 1340, 1240, 1220, 930, 880, 790, 660 cm^{-1}; NMR($CDCl_3$): δ -3.89 (6H, s, CH_3), 1.69 (9H, s, t-Bu), 1.70 (9H, s, t-Bu), 3.08 (3H, s, CH_3), 8.44-8.60 (5H, m, ArH), 8.88 (1H, s, ArH), 9.75 (1H, d, J = 2 Hz, ArH); Mass m/e 386 (M^+).

Anal. Calcd for $C_{28}H_{34}O$: C, 86.99; H, 8.87.

Found: C, 87.13; H, 8.93.

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