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Hg(II)-, Hg(I)-, AND Ag(I)-INDUCED 1,8-DIALKOXYLATION, -DIAMINATION, AND -DIACYLOXYLATION OF 2,7-DI-TERT-BUTYL-4,5,9,10-TETRAPHENYLTRICYCLO[6.2.0.0^{3,6}]DECA-1,3(6),4,7,9-PENTAENE

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The treatment of the title compound (1) with Hg(II), Hg(I), or Ag(I) salt in the presence of ROH, RNH_2, and RCO_2H afforded 5,10-dialkoxy- (2a-c), 5,10-diamino- (2d-e), and 5,10-diacyloxy-2,7-di-tert-butyl-4,5,9,10-tetraphenyltricyclo[6.2.0.0^{3,6}]deca-1,3,6,8-tetraene (2f-g), respectively.

We now report novel Hg(II)-, Hg(I)-, and Ag(I)-induced 1,8-dialkoxylation, -diamination, and -diacyloxylation reactions of the title compound (1).

Treatment of 1[1)] (0.5 g) with two molar amounts of $Hg(OAc)_2$ and three molar amounts of nucleophile (NuH) in xylenes (5 ml) at room temperature for 15-60 min afforded 5,10-di-Nu-substituted 2,7-di-tert-butyl-4,5,9,10-tetraphenyltricyclo[6.2.0.0^{3,6}]deca-1,3,6,8-tetraene (2) as yellow crystals in the yields summarized in Table 1.

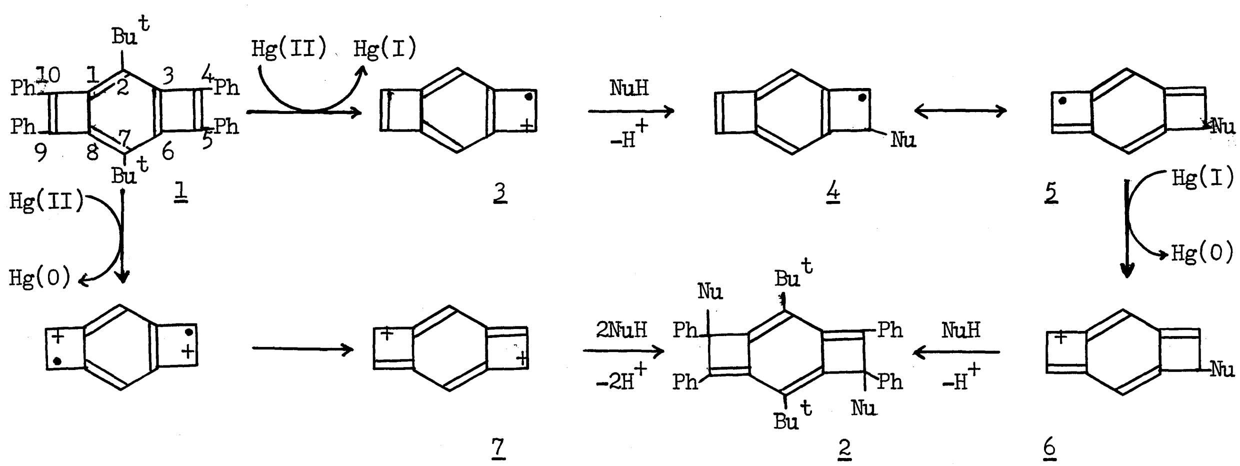

Table 1. Reaction Conditions, and Yields, Melting Points, and Spectral Data of 2

NuH	Reaction time (min)	Product	Yield (%)	Mp (°C)	ν_{max}^{Nujol} (cm^{-1})	$\lambda_{max}^{CHCl_3}$ nm ($\varepsilon \times 10^{-2}$)	τ^{CDCl_3} (ppm)
MeOH	15	2a	68	222	1070 and 1090 (ether)	260 (69) 358 (305)	2.3-3.1 (m, Ph) 6.42 (s, Me), 9.05 (s, Bu^t)
EtOH	60	2b	31	219	1070 and 1095 (ether)	264 (83) 359 (331)	2.6 (m, Ph), 6.13 (q, CH_2) 8.68 (t, Me), 9.05 (s, Bu^t)
PhOH	15	2c	46	256	1220 (=C-O-) 1060 (ether)	360 (384)	2.2-3.7 (m, Ph) 9.15 (s, Bu^t)
$PhNH_2$	15	2d	74	278	3400 (NH) 1300 (C-N)	260 sh (300) 358 (413)	2.4-3.4 (m, Ph) 5.54 (bs, NH), 9.18 (s, Bu^t)
4-Me-$C_6H_4NH_2$	15	2e	63	282	3390 (NH) 1300 (C-N)	356 (400)	3.0 (m, Ph), 4.15 (bs, NH) 7.64 (s, Me), 9.14 (s, Bu^t)
AcOH	30	2f	55	260	1740 (C=O) 1230 (ester)	268 (234) 355 (160)	2.3-3.3 (m, Ph) 7.88 (s, Me), 9.15 (s, Bu^t)
$PhCO_2H$	60	2g	17	256	1730 (C=O) 1270 (ester)	265 (120) 360 (390)	2.1 (m, Ph), 9.06 (s, Bu^t)

The spectral data of 2g were identical to those of the authentic sample[2] which has been previously prepared by 1,8-conjugate addition of benzoyl peroxide to 1. The UV spectral data of 2a-f were comparable to those of 2g. The ^{13}C-NMR spectrum of 2a showed the presence of four kinds of saturated carbons; 29.73 (Me of Bu^t, q), 33.04 (tert-carbon of Bu^t, s), 51.36 (MeO, q), and 92.00 ppm (cyclobutene, s). Stereochemical relationship between the two Nu groups of 2 was uncertain.

Almost the same results as summarized in Table 1 were obtained by using Hg(I) or Ag(I) salt instead of $Hg(OAc)_2$. For example, reaction of 1 with MeOH in the presence of Hg_2Cl_2 and AgOAc afforded 2a in 63 and 82% yields, respectively. Furthermore, when an equimolar amount of $Hg(OAc)_2$ was used for this reaction, 2a and Hg(0) were obtained in 68 and 82% yields, respectively. The formation of 2 can be interpreted by means of one-electron oxidation process. Attack of NuH on the radical cation (3) initially formed by one-electron oxidation of 1 forms radical (4). The second oxidation of the radical (5) derived from 4 gives cation (6), which then reacts with NuH to afford 2. The pathway which proceeds via the dication (7) is also considerable.

References

1) F. Toda and M. Ohi, Chem. Comm., 1975, 506.
2) F. Toda, K. Tanaka, and T. Yoshioka, Chem. Lett., 1976, 657.

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