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^{3,6}[6.2.0.0]DECA-1,3(6),4,7,9-PENTAENE

Yoshikazu TAKEHIRA, Koichi TANAKA, and Fumio TODA

Department of Industrial Chemistry, Faculty of Engineering, Ehime University,

Bunkyo-cho, Matsuyama 790

The treatment of the title compound (1) with Hg(II), Hg(I), or Ag(I) salt in the presence of ROH, RNH₂, and RCO₂H 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^{3,6}[6.2.0.0]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 1¹⁾ (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^{3,6}[6.2.0.0]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)	$\nu_{\text{max}}^{\text{Nujol}}$ (cm ⁻¹)	$\lambda_{\text{max}}^{\text{CHCl}_3}$ nm ($\epsilon \times 10^{-2}$)	τ_{CDCl_3} (ppm)
MeOH	15	<u>2a</u>	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	<u>2b</u>	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	<u>2c</u>	46	256	1220 (=C-O-) 1060 (ether)	360 (384)	2.2-3.7 (m, Ph) 9.15 (s, Bu ^t)
PhNH ₂	15	<u>2d</u>	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 ₆ H ₄ NH ₂	15	<u>2e</u>	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	<u>2f</u>	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 ₂ H	60	<u>2g</u>	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. ¹³The 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 Hg₂Cl₂ 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 (2) 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

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