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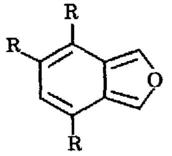
SYNTHESIS AND PHOTOCHEMICAL REACTION OF A STABLE ISOBENZOFURAN DERIVATIVE

Sadao Miki, Masahiro Yoshida and Zen-ichi Yoshida*

Department of Synthetic Chemistry, Kyoto University, Yoshida Kyoto 606 Japan

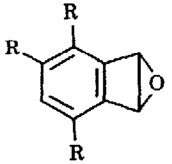
Summary : 4,5,7-Tri-t-butylisobenzofuran (1b) was synthesized as a stable and electronically unperturbed derivative of isobenzofuran. Photolysis of 1b gave (3,4,6-tri-t-butylbenzo)-cyclopropene-3-carbaldehyde (3) as a primary product and not Dewar isobenzofuran.

Photochemical reaction of furan has been of much interest focusing on the primary photoproduct.$^{1)}$ Formation of Dewar furan sounds unequivocal in the recent literature reported by Strausz and his co-workers.$^{1e)}$ However, unfortunately the ^{1}H-NMR of their argon matrix photolyzate does not show the absorptions for Dewar furan, and it seems that there still remains ambiguity. The difficulties in the studies so far were mainly due to the nortoriously unstable nature of Dewar furan.$^{2)}$ Thus, the subject intrigued us to study the photoreaction of isobenzofuran, because expected 4π ring-closing product, Dewar isobenzofuran (2), would be stable as known in the case of diphenyl-di-t-butyl-dibenzoyl derivative.$^{3)}$ However, photolysis of isobenzofuran was known to give dimers.$^{4)}$ We wish to report here the synthesis and photoreaction of 4,5,7-tri-t-butylisobenzofuran (1b), which is stable infinitely at room temperature and undergoes unimolecular photoreaction.

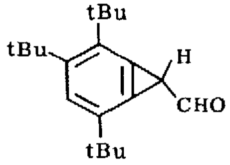


1

a; R = H
b; R = tBu

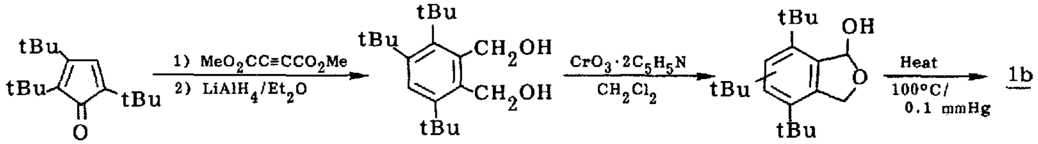


2



3

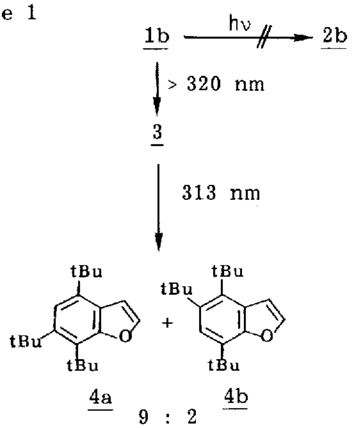
4,5,7-Tri-t-butylisobenzofuran (1b) was synthesized according to the following scheme and pirified by sublimation.$^{5)}$ The electronic spectrum of 1b in acetonitrile exhibited two bands with the maxima at 217 nm (ε ; 31000) and 332 nm (ε ; 5500). The spectrum is very similar to that of 1a$^{6)}$ except for the absence of vibrational progressions, indicating that electronic perturbation by t-butyl groups is small.



Photolyses were performed at -15°C by using a high pressure Hg-lamp with the degassed solution of 1b (ca. 12 mM) in CD_3CN sealed in pyrex NMR tubes, and the ^{1}H-NMR of the photolyzate was measured immediately at the same temperature. Irradiation of the solution through pyrex afforded 4,6,7-tri-t-butylbenzofuran (4a) and 4,5,7-tri-t-butylbenzofuran (4b)$^{7)}$ in main together with the other trivial products. The photolysis by using a $CuSO_4$

solution filter gave a photolyzate, whose ^{1}H-NMR spectrum showed two sets of absorptions : one is assigned to 1b and the other at δ 9.01 (d, 1H, J = 6.3 Hz), 7.64 (s, 1H), 4.11 (d, 1H, J = 6.3 Hz), 1.57 (s, 9H), 1.50 (s, 9H) and 1.30 (s, 9H) assignable to (3,4,6-tri-t-butylbenzo)cyclopropene-3-carbaldehyde (3). As seen in Fig. 1, no other signals were observed at any reaction stages. Subsequent irradiation of the photolyzate without the $CuSO_4$ filter gave a reaction mixture with the same composition to the pyrex photolysis of 1b described above. There were no indications of the formation of Dewar isobenzofuran (2b). The reaction feature is summarized in Scheme 1. Exactly the same results were obtained when the sequencial photolyses were done in CD_2Cl_2 at -65°C. Thus, we conclude that the primary photoreaction of 1b is not 4 π ring closure but furan-cyclopropenylaldehyde rearrangement, even though the ring closure is likely more feasible in isobenzofuran than in furan. Further studies are in progress.

Scheme 1



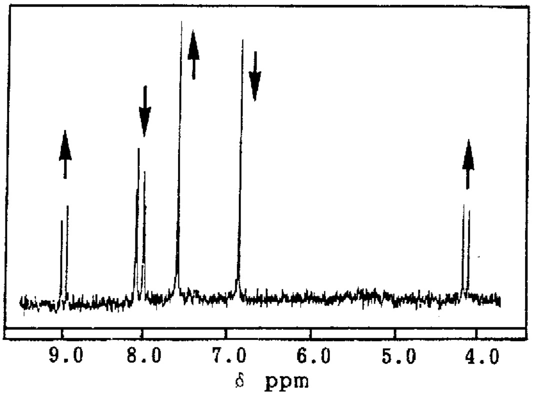


Figure 1 ^{1}H-NMR spectrum following the photolysis ($CuSO_4$ filter) of 1b.

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5) 1b ; mp 58-59°C ; IR (KBr) 2940, 1595, 1075, 885, 845, 740 cm^{-1}; ^{1}H-NMR (CD_3CN) δ 8.13 (d, 1H), 8.05 (d, 1H), 6.88 (s, 1H), 1.60 (s, 9H), 1.46 (s, 9H), 1.38 (s,9H) ; Anal. Calcd for $C_{20}H_{30}O$: C, 83.85; H, 10.56; O, 5.59. Found : C, 84.13; H, 10.49; O, 5.60. MS; m/z (M^+) calcd, 286.2296. obs, 286.2304.

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7) The ratio 4a/4b was 9/2. Assignments of the isomers were done based on the nuclear Overhauser studies for the following ^{1}H-NMR spectra. 4a ; ^{1}H-NMR ($CDCl_3$) δ 7.55 (d, 1H, J = 2.4 Hz), 7.37 (s, 1H), 6.87 (d, 1H, J = 2.4 Hz), 1.72 (s, 9H), 1.57 (s, 9H), 1.44 (s, 9H). 4b : 7.51 (d, 1H, J = 2.4 Hz), 7.37 (s, 1H), 7.01 (d, 1H, J = 2.4 Hz), 1.68 (s, 9H), 1.55 (s, 9H), 1.47 (s, 9H).

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