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Reduction of Adducts of Furans and Diisopropyl Acetylenedicarboxylate

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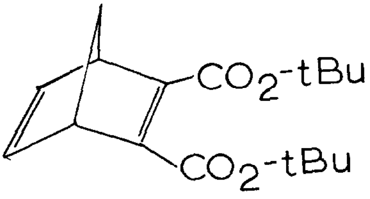
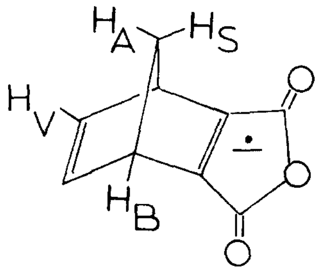
We wish to report esr splitting constants for radical anions of diisopropyl 7-oxanorbornadiene-2,3-dicarboxylate systems, and the reductive elimination of oxygen from these compounds to give phthalates.

We would have preferred using the 2,3-dicarboxylic acid anhydrides[1] as "spin label", but were unable to isolate Diels-Alder adducts from the reaction of furans with either dichloromaleic anhydride or acetylenedicarboxylic acid. The dimethyl acetylenedicarboxylate adducts reduce easily to radical anions, but the heptets (with about 0.7 G splitting) into which all lines of interest are split make analysis of the esr spectra impossible. Di-t-butyl acetylenedicarboxylate is easily prepared from the diacid and isobutylene[2], but its adducts are rather labile, and their radical anions noticably less stable than the dimethyl esters; we believe this to be caused by the cleavage reaction observed with other maleic and fumaric esters[3]. The cyclopentadiene adduct 1 (mp 86-88°, nmr (CCl_4) δ6.88 (2H, t, J=1.3), 3.66 (2, t, J=1.3), 1.9-2.3 (2, broadened AB pattern), 1.48 (18, s) radical anion showed splittings a(1H)=1.4 G, a(2H)=1.0, a(3H)=0.7. The bridgehead splittings and linewidths were clearly larger than those observed for the related anhydride anion 2, which has splittings[1] $a(H_A)=1.4$, $a(H_S,H_V)=0.8$, $a(H_B)=0.4$; these effects are presumably caused by the carbonyl groups not being held planar with the 2,3 double bond. Because of the large linewidths, we have been unable to analyze esr spectra for other di-t-butyl ester adducts. For investigation of the furan adducts, we chose diisopropyl esters as a compromise between stability and resolution. The isopropyl α-hydrogens introduce a small triplet (and the ca. 100-150 mG linewidths seen with all the diesters; the cyclopentadiene adduct was not well enough resolved for analysis). The furan adduct 3a was prepared by heating



1



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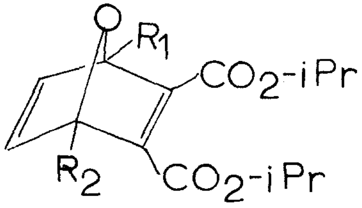

3

a. $R_1=R_2=H$
b. $R_1=CH_3, R_2=H$
c. $R_1=R_2=CH_3$

furan and diisopropyl acetylenedicarboxylate[4] (4) at 100° for 22 hr; mp 35-36° (after two vacuum sublimations), nmr δ7.32 (2, t, J=1.0), 5.63 (2, t, J=1.0), 5.12 (2, hept, J=6.2), 1.32 (12, d, J=6.2), uv (EtOH) λ_m 287 nm (ϵ1400), 222 sh, 205 (7300). Electrolytic reduction in DMSO (Bu_4NClO_4 supporting electrolyte) gave an initial esr spectrum with a(2H)=1.8_8, a(2H)=0.5_2, a(2H)=0.2_0; we assign this spectrum to $(3a)^{\cdot-}$. After a few minutes (a shorter time at higher potential), a second spectrum, showing splittings a(2H)=3.42, a(2H)=0.83, a(2H)=0.33 replaced the first.

We used methyl labeling at the bridgehead positions to assign the splittings in $(3a)^{\cdot-}$. 2,5-Dimethylfuran and 4 gave 3c, mp 42-43°, nmr δ6.95 (2,s), 5.12 (2, hept, J=6.3), 1.78 (6,s), 1.30 (12, d, J=6.3); upon electrolytic reduction a very narrow spectrum, a(2H)=0.6_5, a(2H)=0.1_8 was obtained. 2-Methylfuran and 4 gave 3b, an oil, nmr δ6.8-7.35 (2, 8 peaks), 5.56 (1, d, J=2), 5.08 and 5.18 (2, overlapping heptets), 1.76 (3,s), 1.26 and 1.33 (12, overlapping doublets); it gave upon reduction a broad doublet in the esr, a(1H)= 1.8_7 (the smaller splittings for the other four non-equivalent hydrogens remaining unresolved). These data show that the bridgehead splitting is substantially enhanced by substituting oxygen for carbon at the 7 position, even though this position is in a Hückel nodal plane. We doubt that this difference is entirely caused by geometrical changes; significant spin density is probably present at oxygen.

The second species observed by esr upon reduction of 3a has splittings expected for the radical anion of diisopropyl phthalate. The anion of di-*t*-butyl phthalate has splittings a(2H)=3.37, a(2H)=0.86. To ensure that reduction of 3 systems really does give phthalates, 1.0 g of 3c was reacted with an excess of lithium naphthalenide in DME (room temperature, 30 min) and quenched with iodine. Thin layer chromatogrpahy gave 0.4 g of diisopropyl 3,6-dimethylphthalate (5), independently prepared by refluxing the adduct of 4 and 2,4-hexadiene with 10% Pd/C in p-cymene(5 nmr: δ6.99 (2,s), 2.31 (6,s), and isorpopoxyl absorption). We also observed the esr spectrum of diisopropyl phthalate anion when 4,5-bis(carboixopropoxy)oxepine, prepared by the method of Prinzbach's group[5], was electrolytically reduced. The chance that 3c could be rearranging to the oxepine[6] before cleavage to the phthalate was eliminated, since none of the 4,5-dimethyl isomer of 5 (6, similarly prepared from 2,3-dimethylbutadiene, nmr δ7.30 (2,s), 2.28 (6,s), and isopropoxyl absorptions) could be detected in the reduction product of 3c by nmr or vpc.

The reduction of 5 gave the phthalate anion, a(2H)=3.49, a(small)=0.38 (probably a(CH_3)=2a(iPr)), as did that of 6; a(6H)=3.61, a(2H)=0.34, as expected. We have not yet been able to find the product containing the oxygen atom resulting from cleavage of 3 to phthalate.

References

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5. H. Prinzbach, M. Arguelles, and E. Druckery, Angew. Chem. Int. Ed., 5, 1039(1966); H. Prinzbach and J. Rivier, Tet. Letters, 3713(1967).
6. If $(3)^{\overline{\cdot}}$ were to close to the oxaquadricyclane[5], a photochemical reaction of 3, opening would be expected[5] to give the oxepine which would form 6. The Woodward-Hoffman rules for opening of cis and trans fused bicyclo 6.1.0 nonatriene radical anions[7] are "inverted" (i.e. the photochemical rules apply). Conceivably, then, other photochemical reactions might become thermally allowed for radical anions. Not here.
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