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Mechanism of the Thermal Isomerization of Some Diels–Alder Adducts of 1,4-Benzoquinone 2,3-Epoxides

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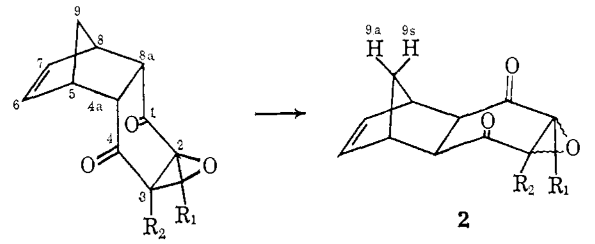
Abstract: The thermal isomerization of some *endo*-cyclopentadiene-1,4-benzoquinone 2,3-epoxide adducts gave the *exo* isomers. The configuration of the epoxide ring in the *exo* adduct is unknown. When the reaction of *endo*-5,8-methano-4a,5,8,8a-tetrahydro-1,4-naphthoquinone 2,3-epoxide was conducted in the presence of tetracyanoethylene, the products were 2,2,3,3-tetracyanonorborn-5-ene and 1,4-benzoquinone 2,3-epoxide. A dissociation–recombination mechanism is indicated. Evidence was obtained that isomerization does not accompany enolization.

Several studies of the isomerization of adducts of cyclopentadiene have been reported.[1–8] The conversion of *endo*-5-norbornene-2,3-dicarboxylic anhydride to the *exo* isomer has been carefully studied.[2,3,7,8] In decalin at 190° under heterogeneous conditions it has been reported to isomerize both by retrogression and by an internal mechanism.[2,3,7] The possibility of epimerization by an enolic species was discounted[2,3] because base catalysis was not observed in the molten state.[1] In *t*-pentylbenzene at 190° under homogeneous conditions no evidence for an internal mechanism was found.[8]



1

2

	R_1	R_2
A,	H	H
B,	CH_3	H
C,	C_6H_5	H
D,	CH_3	CH_3

We wish to report the thermal isomerization of the *endo*-cyclopentadiene-1,4-benzoquinone 2,3-epoxide adduct (**1A**) to its corresponding *exo* isomer (**2A**). The *endo*-cyclopentadiene-1,4-benzoquinone 2,3-epoxide adduct (**1A**),[9] mp 120–121°, may be prepared in high yield by alkaline epoxidation of the *endo*-cyclopentadiene-1,4-benzoquinone adduct,[10] or by reaction of cyclopentadiene with 1,4-benzoquinone 2,3-epoxide in benzene at room temperature. In both precedures the epoxide was homogeneous; no *exo* isomer was produced. Neat **1A** was heated at 220° in a flask under a partial vacuum for 10 min. The product was judged to be approximately 50% **1A** and 50% **2A** from a comparison of its infrared spectrum with the spectra of known mixtures of **1A** and **2A**. Similar results were obtained with **1B**, **1C**, and **1D**. Pure **2** isomers were obtained by fractional recrystallization of each product mixture from ethanol. When pure **2A** was heated at 220° for 10 min, a 63% yield of a mixture of **1A** and **2A** (about 1:1) was obtained. The isomerization of **1A** could not be effected at 125 or 175°, and the rearrangement of **2A** was unsuccessful at 125°.

Treatment of **2B** with 1-phenyl-5-mercaptotetrazole in refluxing ethanol containing a catalytic amount of triethylamine gave the thioetherenedione (**4B**), which was identified by its nmr and infrared spectra. This thioetherenedione was different from that formed from **1B**.[11] Both thioetherenediones may be converted to the same hydroquinone (**5B**).[11]

The nmr spectrum of each *endo* isomer (**1A–D**) displays the 4a, 8a protons at τ *ca.* 6.5, whereas these protons appear at *ca.* 7.3 in the spectra of **2A–D** (Table I). Several authors have observed that *exo* protons are deshielded relative to *endo* protons in various substituted bicyclo[2.2.1]heptanes and bicyclo[2.2.1]heptenes.[12–14] The spectra of the *exo* epoxides (**2**) are distinguished by the appearance of the 9 protons.

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[6] J. A. Berson and A. Remanick, *ibid.*, **83**, 4947 (1961).

[7] J. E. Baldwin and J. D. Roberts, *ibid.*, **85**, 115 (1963).

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[12] J. I. Musher, *Mol. Phys.*, **6**, 93 (1963).

[13] E. W. C. Wong and C. C. Lee, *Can. J. Chem.*, **42**, 1245 (1964).

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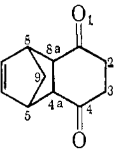
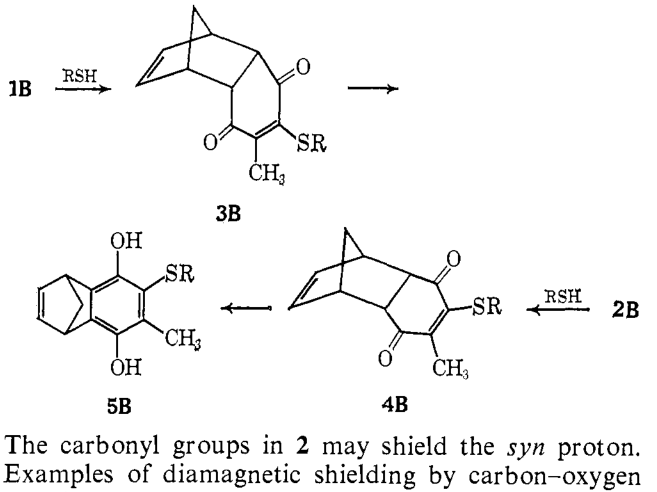
Table I. Peak Positions for *exo* and *endo* Diels–Alder Adducts of Cyclopentadiene and *p*-Benzoquinones[a]



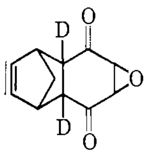
Compound	6,7 olefinic	2,3 epoxy	4a,8a[b]	5,8	9[c]	Other	
1A	3.98	6.50	6.55	6.68	8.40, 8.54,[d] 8.64, 8.79		
2A	3.78	6.26	7.28 (2.1)	6.53	8.58, 8.73,[e] 9.17, 9.33		
1B	3.96	6.62	6.55	6.68	8.41, 8.56,[d] 8.63, 8.78	2-CH_3	8.53
2B	3.79	6.41	7.27 (2.1)	6.55	8.60, 8.74,[e] 9.16, 9.32	2-CH_3	8.42
3B	3.73	...	6.63	6.50	8.50	2-CH_3, Phenyl	7.80 2.33
4B	3.67	...	7.33[f]	6.65	8.60	2-CH_3, Phenyl	7.21 2.32
1C	3.85	6.51	6.44	6.65	8.38, 8.54,[d] 8.63, 8.78	Phenyl	2.62
2C	3.73	6.28	7.10 (2.0)	6.48	8.50, 8.66,[e] 9.00, 9.16	Phenyl	2.55
1D	3.94	...	6.53	6.73	8.40, 8.55,[d] 8.63, 8.78	2,3-CH_3	8.54
2D	3.80	...	7.26 (2.1)	6.58	8.55, 8.72[e] 9.18, 9.33	2,3-CH_3	8.47

[a] The spectra were measured with a Varien 60-Mc high-resolution spectrometer, Model V-4302, or a Varian A-60 spectrometer. Peak positions are expressed in parts per million relative to an internal tetramethylsilane standard (taken at τ 10). The positions indicate the center of the multiplets. The audio-side-band method of calibration was used. The spectra were obtained from 10% solutions in deuteriochloroform. [b] The coupling constant listed in parentheses are $J_{4a,9a}$ in cps. [c] The resonance of the 9 protons in the epoxides is an AB system, each line of which is further split into a multiplet. [d] The resonance is approximately symmetrical. [e] The resonance at lower field (*ca.* 8.6) is more complex than that at *ca.* 9.2. The *anti* proton resonance (A part of an ABX_2 system) has lines of very low intensity at approximately 7.8 and 8.3. [f] The resonance appears as a broadened singlet with a half-height width of 1.5 cps.

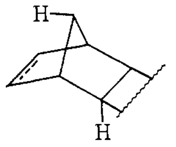
The 9 protons of the *endo* epoxides (**1**) occur as a multiplet at about 8.6. The *syn* and *anti* protons have approximately the same chemical shift. One of these protons is at higher field, about 9.2, in the spectra of **2**.



The carbonyl groups in **2** may shield the *syn* proton. Examples of diamagnetic shielding by carbon–oxygen double bonds have been reported.[15,16] The 9-*anti* proton of **2** appears as a more complex multiplet than the 9-*syn* proton. This is probably due to long-range coupling of the *anti* proton with the 4a, 8a protons.[12,17,18] The 4a, 8a protons in **2** appear as a doublet with a line separation of 2.1 cps. The possibility that $J_{4a,5}$ is about 2 cps is excluded by the close resemblance of the 5,8 proton resonance in **2A** to that of the 5, 8 protons in **1A**-d_2 (4a, 8a protons >95% deuterated).[9] Further confirmation of this hypothesis was obtained by spin-decoupling experiments performed on **2A**.[19] Irradiation of the multiplets at 8.58 and 8.73 (9-*anti* H) while the band was recorded at 7.28 (4a, 8a H's) caused it to appear as a singlet. The doublet at 7.28 was then irradiated while the resonances were observed at 8.58 and 8.73. The fine structure of the latter bands collapsed. The resonances of the 9-*anti* and 9-*syn* protons were then similar in appearance. Experiments on the bands at 6.53 (5, 8 H's) and 7.28 (4a, 8a H's) revealed no measurable spin–spin interaction ($J_{4a,5}$ < 0.5 cps).[20]



1A-d_2



Although evidence has been presented[9] indicating that the epoxide is *exo* in **1**, no judgment can be made at present as to the configuration of the epoxide in **2**.

Since the isomerization may occur by retrogression or by an internal pathway such as those discussed by Berson and co-workers,[2,3] the thermal reaction was conducted in the presence of tetracyanoethylene, an

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(15) L. Combie and J. W. Lown, *Proc. Chem. Soc.* (London), 299 (1961).

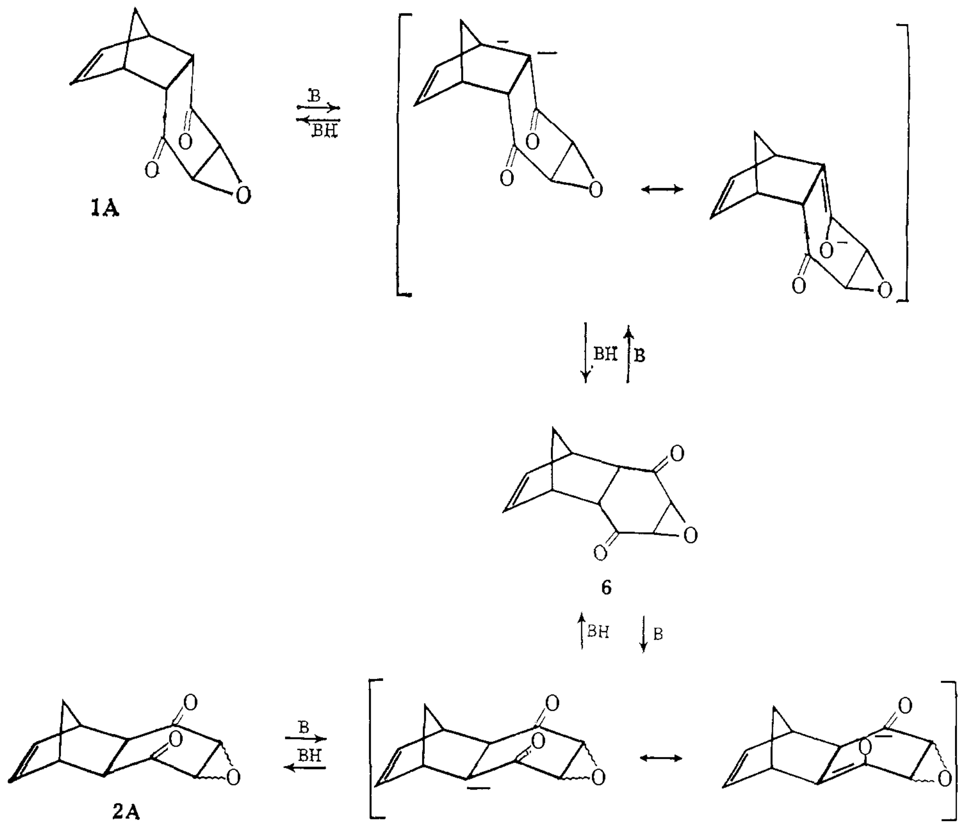
(16) O. L. Chapman, H. G. Smith, and R. W. King, *J. Am. Chem. Soc.*, **85**, 806 (1963).

(17) R. F. Frazer, *Can. J. Chem.*, **40**, 78 (1962).

(18) J. Meinwald and Y. C. Meinwald, *J. Am. Chem. Soc.*, **85**, 2514 (1963).

(19) The spin-decoupling experiments were performed by Dr. J. K. O'Loane and his associates, using the Varian V-3521 integrator and working on the low-field side band. All decoupling experiments at a given irradiation frequency were done at least twice.

(20) F. A. L. Anet, *Can. J. Chem.*, **39**, 789 (1961).



efficient trap for dienes.[21] When **1A** was heated at 220° for 10 min with an equimolar quantity of tetracyanoethylene, the products were 1,4-benzoquinone 2,3-epoxide and 2,2,3,3-tetracyanonorborn-5-ene, 65 and 72% yields of purified materials, respectively. The crude product mixture was examined by infrared spectroscopy and there was no evidence of **2A**. Similarly, when **2A** was heated at 220° for 10 min with tetracyanoethylene, there was no evidence of the isomeric **1A**. The spectra of known mixtures indicate that about 5% of the isomeric epoxide would be observed. An equimolar mixture of either **1A** or **2A** with tetracyanoethylene, when heated at 175° for 10 min, gave 10–15% recovery of starting epoxide, some 2,2,3,3-tetracyanonorborn-5-ene, and some 1,4-benzoquinone 2,3-epoxide; there was no evidence of isomeric epoxides. The reaction of **1A** with tetracyanoethylene at 125° for 35 min gave recovered starting materials.

These data indicate that the thermal isomerization occurs at 220° by dissociation of the adduct, followed by recombination. It is possible that in a solvent such as decalin an internal pathway involving a complex of diene and dienophile such as that proposed by Berson[2,3] may be followed.

The *exo* epoxide **2A** was treated with sodium carbonate in D_2O–dioxane under nitrogen at 25°. After 35 min, the nmr spectrum of the recovered epoxide showed a decrease in intensity (50%) of the doublet at 7.28 (4a, 8a H's). No isomers were observed. From the mass spectra it was estimated that the sample was 26% undeuterated, 49% monodeuterated, and 25% dideuterated. It has been reported that the *endo* epoxide **1A** undergoes deuterium exchange at the 4a, 8a positions with retention of configuration.[9] The isomeric epoxides give rise to different, nonintervertible anion intermediates. Under conditions where enolization occurs, isomerization is not favored, probably because an intermediate (**6**) having a *trans* ring juncture is unlikely.

Experimental Section

All melting points are uncorrected. Infrared spectra were obtained with a Beckman IR-12 grating spectrophotometer, Baird Models AK-1 or NK-1 spectrophotometers, and a Perkin-Elmer Infracord Model 137 spectrophotometer with sodium chloride optics. Samples were examined as potassium bromide pressings or as chloroform solutions.

2,3-Epoxides of Diels–Alder Adducts of Cyclopentadiene and *p*-Benzoquinones. The Diels–Alder adducts were prepared and epoxidized by the method of Alder.[10]

Reaction of 1,4-Benzoquinone 2,3-Epoxide[2] with Cyclopentadiene. A solution of 0.49 g (4.0 mmoles) of 1,4-benzoquinone 2,3-epoxide in 20 ml of benzene was treated with 3 ml (36 mmoles) of freshly prepared cyclopentadiene. After 4 hr at room temperature the solvent was removed, leaving 0.70 g of a white solid, mp 118–120°, 93% yield. The infrared spectrum of the solid is identical with that of the *endo* adduct **1A**.

Thermal Rearrangement of the *endo*-5,8-Methano-4a,5,8,8a-tetrahydro-1,4-napthoquinone 2,3-Epoxides (1). (a) 220°. The method used was general for all of the epoxides studied. A 1- to 20-g sample of the *endo* epoxide (**1**) was placed in a round-bottomed flask attached to the vacuum system of a water aspirator. A partial vacuum (20–50 mm) was applied while the flask was heated in an oil bath at 220° for 10 min. At the end of the reaction time, the product was a yellowish liquid, and some white crystalline material had sublimed to the upper part of the flask. The oil solidified upon cooling. The infrared spectrum of the product was the same as the spectrum of a mixture of about 50% *endo* epoxide (**1**) and 50% *exo* epoxide (**2**). The pure *exo* epoxide (**2**) was obtained by fractional recrystallization of the crude product from ethanol. The first crops were starting material; the next crops began to show a greater proportion of the *exo* epoxide (**2**). The isolated yield of **2** was 10%. The physical properties of the *exo* epoxides (**2**) are given in Table II.

(b) 175 or 125°. A sample of **1A** was heated at 125° for 30 min. The infrared spectrum of the residue shows only a polymorphic form of **1A**. No rearrangement product was evident.

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[21] See, however, footnote 14 to ref 8.

Table II. Physical Data on the *exo*-5,8-Methano-4a,5,8,8a-tetrahydro-1,4,-naphthoquinone 2,3-Epoxides (**2**)

Epoxide	Mp, °C	C, % Calcd	C, % Found	H, % Calcd	H, % Found
2A	78–80	69.5	69.7	5.3	5.5
2B	100–102	70.6	70.4	5.9	5.9
2C	93–95	Insufficient material			
2D	90–95	71.5	71.9	6.5	6.8

Recrystallization gave only starting material (**1A**). The same results were obtained at 175°.

Thermal Rearrangement of *exo*-5,8-Methano-4a,5,8,8a-tetrahydro-1,4-naphthoquinone 2,3-Epoxide (2A). (a) 200°. A 0.70-g (3.7 mmoles) sample of **2A** was heated at 220° for 10 min by the usual procedure. An infrared spectrum of the crude product shows a 1:1 mixture of **2A** and the polymorphic form of **1A**. Recrystallization from ethanol (after Norit treatment) gave several crops of material, **2A**, **1A**, and mixtures. The total weight of recrystallized material was 0.44 g (63%).

The nmr spectra ($CDCl_3$ or acetone-d_6) of the polymorphic forms of **1A** are identical.

(b) 125°. No change was observed when **2A** was heated at 125° for 30 min.

Reaction of 2-Methyl-*exo*-5,8-methano-4a,5,8,8a-tetrahydro-1,4-naphthoquine 2,3-Epoxide (2B) with 1-Phenyl-5-mercaptotetrazole (HPMT). A solution of 1.0 g (5.0 mmoles) of **2B**, 0.9 g (5.0 mmoles) of HPMT, and 2 drops of triethylamine in 10 ml of ethanol was refluxed for 30 min. The hot solution was filtered and allowed to cool at room temperature. The yellow crystals were filtered and recrystallized from ethanol, giving 0.8 g (45%) of the thioetherenedione **4B**, mp 174–176° dec. The infrared spectrum has a conjugated carbonyl band at 1675 cm^{-1} and no hydroxyl absorption.

Anal. Calcd for $C_{19}H_{16}N_4O_2S$: C, 62.6; H, 4.4; N, 15.4. Found: C, 63.0; H, 4.7; N, 15.2.

A solution of 0.1 g (0.5 mmole) of the thioetherenedione **4B** in 5 ml of benzene with a few drops of triethylamine was warmed for 30 min in a steam bath. The hydroquinone product was isolated and had an infrared spectrum identical with that of **5B**.[11]

Thermal Rearrangement of *endo*-5,8-Methano-4a,5,8,8a-tetrahydro-1,4-naphthoquinone *endo*-2,3-Epoxide (1A) in the Presence of Tetracyanoethylene (TCNE). (a) 220°. A mixture of 1.9 g (0.01 mole) of **1A** and 1.3 g (0.01 mole) of tetracyanoethylene (TCNE) was heated at 220° for 10 min in the apparatus just described. Recrystallization of the black residue from ethanol gave 1.4 g (72%) of 2,2,3,3-tetracyanonorborn-5-ene, mp 219–221° dec. The infrared spectrum and melting point of the product were identical with those of a sample prepared from TCNE and cyclopentadiene. The mother liquors from the recrystallization contained 1,4-benzoquinone 2,3-epoxide; evaporation of the filtrate gave 0.8 g (65%) of the epoxide, and a small sample was purified by sublimation for comparison with an authentic sample. The infrared spectra of the two samples were identical.

(b) 175°. Epoxide **1A** (1.9 g, 0.01 mole) and 1.3 g (0.01 mole) of TCNE were heated at 175° for 10 min in the usual manner. The dark residue was dissoved in hot ethanol, and the solution was treated with Norit and cooled. Several crops of white crystals were obtained: pure **1A**, pure 2,2,3,3-tetracyanonorborn-5-ene, and mixtures of the two. The total weight of isolated material was 1.1 g, of which 0.25 g (13% recovery) was **1A**, and 0.85 g (44% yield) was 2,2,3,3-tetracyanonorborn-5-ene (yields based on weights of pure materials isolated and infrared analysis of the mixtures). Infrared analysis of the residues from evaporation of the mother liquors showed no **2A**.

(c) 125°. Epoxide **1A** (5.7 g, 0.03 mole) and 3.9 g (0.03 mole) of TCNE were heated at 125° for 35 min under the usual conditions. The contents of the flask showed no weight loss on heating. The infrared spectrum of the crude product (in potassium bromide) shows TCNE and a polymorphic form of **1A**. Recrystallization from various solvents (benzene, pyridine, ethanol, dimethyl sulfoxide, carbon tetrachloride, or ethanol–water) gave mixtures of the two forms or only the stable form of **1A**.

Thermal Rearrangement of *exo*-5,8-Methano-4a,5,8,8a-tetrahydro-1,4-naphthoquinone 2,3-Epoxide (2A) in the Presence of Tetracyanoethylene (TCNE). (a) 220°. A mixture of 0.45 g (2.4 mmoles) of **2A** and 0.30 g (2.4 mmoles) of TCNE was heated at 220° for 10 min in the usual apparatus. The dark brown residue was dissolved in hot ethanol and some insoluble charred material was removed by filtration. The filtrate was treated with Norit and cooled, giving 80 mg (17%) of 2,2,3,3-tetracyanonorborn-5-ene. Evaporation of the filtrate left 116 mg (40%) of a dark yellow residue from which a small amount of 1,4-benzoquinone 2,3-epoxide was sublimed for identification. The infrared spectrum of the residue shows absorptions due to 1,4-benzoquinone 2,3-epoxide and 2,2,3,3-tetracyanonorborn-5-ene.

(b) 175°. The preceding reaction was repeated at 175°, with 0.15 g (0.8 mmole) of **2A** and 0.1 g (0.8 mmole) of TCNE. The infrared spectrum of the dark residue shows a mixture of starting materials with some 2,2,3,3-tetracyanonorborn-5-ene.

Deuteration of *exo*-5,8-Methano-4a,5,8,8a-tetrahydro-1,4-naphthoquinone 2,3-Epoxide (2A). A solution of 0.19 g (0.01 mole) of **2A** in 3.0 ml of *p*-dioxane was added to a stirred solution of 0.10 g of anhydrous sodium carbonate in 1.0 ml of 99% D_2O under a nitrogen atmosphere at room temperature. The reaction mixture was stirred for 35 min, then added to 50 ml of ice water. The mixture was neutralized with acetic acid and extracted with ether. The ether extracts were dried with anhydrous magnesium sulfate and the ether was removed on a rotary film evaporator. The solid was crystallized from ethanol, mp 79–80°, 0.17 g.

Comparison of the infrared spectrum of the reactant and that of the product indicates several new bands at 1190, 1060, 905, 870, 790, 780, 757, and 735 cm^{-1}. The nmr spectrum of the product is identical with that of the starting epoxide, except for the decreased intensity (50%) of the doublet at 7.28 and simplification of the bands at 8.58 and 8.73. The mass spectrum of the product has *m/e* peaks at 66, 124, 125, 126, 190, 191, and 192. The reactant displays *m/e* peaks at 66, 124, and 190. The ratio of the *m/e* peaks indicates that the product is 26% $C_{11}H_{10}O_3$, 49% $C_{11}H_9DO_3$, and 25% $C_{11}H_8D_2O_3$.

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