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Diastereoselective Carboxyl Migrations of 3-Arylbenzofuranones

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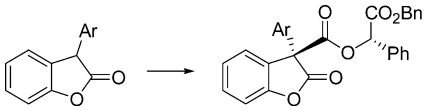
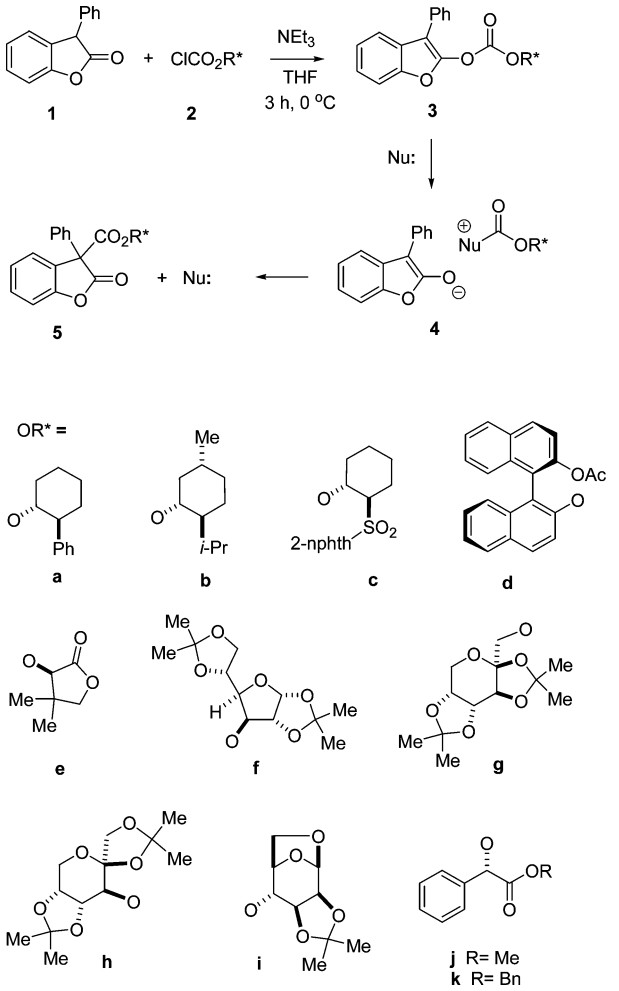


Mixed benzofuranyl carbonates derived from chiral chloroformates rearranged in the presence of nucleophilic catalysts to give *C*-carboxylated benzofurans with variable dr. The use of chiral nucleophilic catalysts gave modest improvement in dr, but better results were obtained by optimizing auxiliary and catalyst. Thus, **8k** was obtained with 9:1 dr.

As part of our effort to access the original (incorrect) structure of diazonamide A,[1,2] we have investigated the DMAP-induced Black rearrangement[3] of 3-arylbenzofuranone-derived enol carbonates. Although the Black rearrangement is limited to the highly stabilized aromatic enolate environment of 3-arylbenzofuranones, this approach has been pursued independently by us and other groups in very similar contexts,[4] as it is particularly well suited to the objective of controlling absolute configuration at the quaternary α carbon adjacent to the benzofuranone carbonyl.

In a model study starting from 3-phenylbenzofuranone **1**,[5] we found that a mixed enol carbonate **3a** derived from the Whitesell chiral auxiliary[2d] rearranged to **5a** with good facial selectivity (8:1 dr, Scheme 1).[2a] However, introduction of additional substituents at the α-phenyl group (i.e., **6**, Scheme 2) resulted in modest diastereoselectivity in the range of 2−3:1.[2a,6] Furthermore, separation of diastereomers was difficult, and key intermediates could not be purified without resorting to preparative HPLC. In an attempt to circumvent these problems,

SCHEME 1



we investigated related rearrangements catalyzed by chiral nucleophiles, including TADMAP (**A**, Figure 1).[7] In those studies, enantioselectivities with catalyst **A** were modest unless the Black rearrangement was conducted at −40 °C. This required 20 mol % catalyst and a time scale of ca. 24 h, even

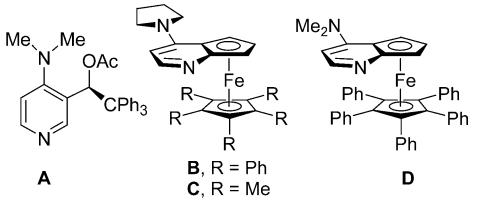


FIGURE 1. Chiral DMAP derivatives.

with the least hindered derivatives of **3**, and there was reason to doubt that rates would be sufficient for the intended application in hindered substrates such as **7** (Scheme 2). A suitably reactive and enantioselective chiral DMAP catalyst (**B**, Figure 1) for the Black rearrangement has been described by

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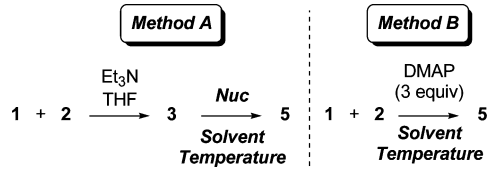
TABLE 1. Chiral Auxiliary and Nucleophile Survey in the Rearrangement of 1 to 5



entry	OR*	Nuc (equiv)	solvent	dr (°C)	method
1	**b**	DMAP (0.2)	DCM	2.2:1.0 (rt)	A
2	**c**	DMAP (0.2)	DCM	1.5:1.0 (rt)	A
3	**d**	DMAP (3)	THF	1.6:1.0 (rt)	B
4	**e**	DMAP (0.2)	DCM	1.4:1.0 (0)	A
5	**f**	DMAP (0.2)	THF	3.1:1.0 (0)	A
6	**f**	DMAP (0.6)	THF	4.0:1.0 (−40)	A
7	**f**	Bu_3P (5)	DCM	5:5:1.0 (0)	A
8	**g**	DMAP (3)	DCM	1.0:1.0 (0)	B
9	**h**	DMAP (3)	DCM	2.0:1.0 (0)	B
10	**i**	DMAP (3)	THF	1.4:1.0 (0)	B
11	**j**	DMAP (0.2)	DCM	2.2:1.0 (0)	A
12	**k**	DMAP (3)	DCM	1.9:1.0 (rt)	B
13	**k**	DMAP (3)	THF	2.8:1.0 (0)	B
14	**k**	Bu_3P (5)	DCM	2.3:1.0 (0)	A
15	**k**	(*R*)-A (0.1)	DCM	2.1:1.0 (rt)	A
16	**k**	(*S*)-A (0.1)	DCM	1.3:1.0 (rt)	A
17	**k**	(*R*)-C (0.1)	DCM	1.0:1.6 (rt)	A
18	**k**	(*S*)-C (0.1)	DCM	4.0:1.0 (rt)	A
19	**k**	(*R*)-D (0.1)	DCM	1.0:1.1 (rt)	A
20	**k**	(*S*)-D (0.1)	DCM	1.3:1.0 (rt)	A

Fu et al.,[8] but the lack of a commercial source, or a short synthesis for the optimum catalyst, raised concerns. We therefore initiated a broader survey of the chiral auxiliary approach to learn whether acceptable diastereoselectivities as well as reaction rates might be encountered.

Chiral chloroformates and the related cyanoformates have been used to carboxylate enolates with mixed success.[9] The best results (9−13:1 dr) were obtained by Braun and co-workers using (+)-menthyl chloroformate for the carboxylation of branched derivatives of phenylacetate enolates or dianions. Of course, these intermolecular carboxylations are mechanistically distinct compared to the Black reaction proceeding via ion pair **4** (Scheme 1) with recombination of enolate and *N*-carboxylpyridinium subunits, but the presence of a conjugated aryl π-system in the substrate enolates of Braun provided an encouraging analogy. Accordingly, the enol menthyl carbonate **3b** was prepared using the commercially available **2b**/Et_3N, and was treated with 20 mol % DMAP at rt. This gave the expected *C*-carboxylated product **5b** as inseparable diastereomers with marginal dr = 2.2:1.0 over 20 min at rt (Table 1, entry 1).

The chloroformate **2c** was examined next because the parent alcohol[10] embodied the framework of the Whitesell alcohol precursor of **2a** and **3a**, but with an enlarged π surface and a relatively polar sulfonyl group that might help organize the transition state. After uneventful conversion to the enol carbonate **3c**, treatment with DMAP afforded **5c** with low dr = 1.5:1.0 (Table 1, entry 2). The even more extensive π surface of BINOL derivative **3d** was also ineffective (1.6:1.0 dr for **5d**, Table 1, entry 3).

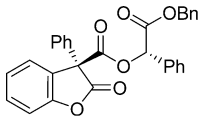


FIGURE 2. Structure of the major diastereomer of *rac*-**5k**.

In principle, greater reactivity allows a broader range of temperatures for optimization of dr with hindered substrates, so heteroatom-substituted chloroformates were investigated based on the premise that electron-withdrawing groups would enhance reaction rates. Electron demand adjacent to the carbonyl group in enol carbonate **3** is expected to accelerate nucleophilic attack. Furthermore, the same electronic effect would increase the rate for recombination of ion pair **4** by destabilizing the cationic fragment. In the event, the pantolactone-derived enol carbonate **3e** rearranged to **5e** within a minute at 0 °C upon treatment with 0.2 equiv of DMAP. Although selectivity was minimal (dr = 1.4:1.0, Table 1, entry 4) and **5e** was contaminated with an unknown byproduct, the dramatic increase in reactivity stimulated the search for chiral auxiliaries containing electron-withdrawing substituents.

D-Glucose acetonide[11] has been used as a chiral auxiliary in other applications,[12] and was easily converted to the chloroformate **2f**. Carboxyl migration to **5f** was very fast (<1 min, 0.2 equiv of DMAP, THF, 0 °C) and diastereocontrol was promising (dr = 3.1:1.0, Table 1, entry 5). The high reactivity allowed evaluation of the carboalkoxyl migration at −40 °C using 0.6 equiv of DMAP, resulting in **5f** with dr = 4.0:1.0 (Table 1, entry 6). Three other carbohydrate derivatives **3g**−**i** were also evaluated. For convenience, these reactions were conducted using excess DMAP as the base for conversion to the enol carbonate as well as to induce the rearrangement. Diastereoselectivity was no better than 2:1 dr (Table 1, entries 8−10), and only one of the product diastereomer pairs (**5h**) could be separated.

Finally, two mandelate-derived auxiliaries[13] were tested under similar conditions. The resulting enol carbonates **3j** and **3k** rearranged effortlessly to **5j** (dr = 2.2:1.0, Table 1, entry 11) and **5k** (dr = 2.8:1.0, Table 1, entry 13), respectively. Although the diastereomers were not separable by chromatography, the major diastereomer of *rac*-**5k** formed from *rac*-**3k** + DMAP was isolated with dr = 24:1 by trituration with ether (49% yield). Relative stereochemistry for the major diastereomer purified by recrystallization was established by X-ray crystallography (Figure 2).

Improved dr in some of the enol carbonate rearrangements was observed using nucleophilic phosphine catalysts. Thus, **3f** (glucose acetonide series) was treated with 0.6 equiv of Bu_3P (THF, 12 h, 0 °C) to give the rearranged product **5f** with dr = 4.9:1.0. However, the parent benzofuranone **1** was also formed, and was already present in the reaction mixture prior to aqueous workup. This side reaction was initially attributed to ion pair enolate protonation in **4f** by adventitious water, but extensive measures to ensure anhydrous conditions did not completely

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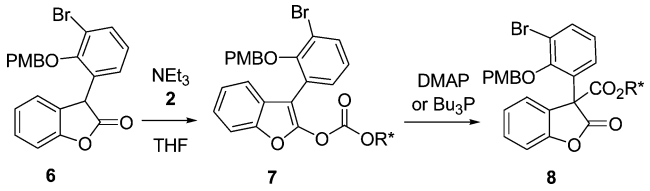
suppress the formation of **1**. The best ratio of **5f**:**1** = 9:1 was obtained in scrupulously dried dichloromethane, and a small improvement in dr (5.5:1.0, Table 1, entry 7) was also observed. Attempts to further improve diastereoselectivity at lower temperature were frustrated by increased formation of **1** (exclusive product at −40 °C). Qualitatively similar results were found in the mandelate series. Thus, when Bu_3P was used to induce the rearrangement of enol carbonate **3k**, conversion to **5k** (dr = 2.3:1.0, Table 1, entry 14) took place (10 min, 0 °C), but formation of **1** could not be avoided (4:1 **5k**:**1**). The same problem was encountered if Bu_3P was replaced by $PhMe_2P$ as the catalyst. The empirical correlation between enolate protonation and the presence of potentially acidic C−H bonds next to positive phosphorus in the intermediate ion pair **4k** (Nu = Bu_3P, $PhMe_2P$) suggests the possibility of internal proton-transfer pathways, but convincing evidence for this conjecture was not obtained. In any event, the Bu_3P-induced rearrangement of **3k** formed the same major diastereomer of **5k** (Figure 2) as in the reaction catalyzed by DMAP.

Next, we evaluated the available chiral DMAP derivatives of Figure 1 as catalysts for the rearrangement of the enantiomerically pure mandelate substrate **3k**. Our intent was to amplify the native diasteresoselectivity of the DMAP rearrangement of **3k** to **5k** (DCM, rt, dr = 1.9:1.0, Table 1, entry 12), given that eventual diastereomer separation in related systems would afford enantiomerically pure products. Catalyst (*R*)-**A** proved to be the matched enantiomer for carbonate **3k**. However, the rearrangement produced **5k** with nearly the same dr (2.1:1.0, Table 1, entry 15) as with DMAP, while the mismatched enantiomer (*S*)-**A** afforded **5k** with decreased dr (1.3:1.0, Table 1, entry 16). The major diastereomer of **5k** was the same with (*R*)-**A**, (*S*)-**A**, and DMAP (see Figure 2). These sobering diastereoselectivities reflect the presence of an *O*-carboxyl substituent that is not optimal for TADMAP (**A**) regardless of catalyst configuration.[7]

The commercially available DMAP derivatives **C** and **D** were tested next as surrogates for the highly selective catalyst **B** (vide supra).[8] The (*S*) enantiomer of **C** matched the diastereofacial preference of the mandelate auxiliary, and favored the diastereomer of **5k** shown in Figure 2 with somewhat higher dr = 4.0:1.0 (Table 1, entry 18). On the other hand, (*R*)-**C** reversed selectivity with dr = 1.0:1.6 (Table 1, entry 17; under these conditions the *minor* diastereomer of **5k** is as drawn in Figure 2). A similar experiment was performed with catalyst **D**. Ironically, both enantiomers of this catalyst gave lower dr compared to achiral DMAP (Table 1, entries 19 and 20). Thus, **5k** was obtained with dr = 1.3:1.0 (major diastereromer as in Figure 2) using the "matched" catalyst (*S*)-**D**, while the corresponding reaction using (*R*)-**D** was nonselective (dr = 1.0:1.1; *minor* diastereomer as in Figure 2). Thus, only catalyst (*S*)-**C** gave any significant amplification of dr in the above experiments, and the effect was small compared to the enantiofacial preference reported for the optimal catalyst **B** combined with the optimal *achiral* trichloro-*tert*-butoxycarbonyl migrating group.[8] In view of these findings, no further experiments were carried out with the chiral catalysts.

The best chiral auxiliaries from the experiments of Table 1 were then tested for carboxyl migration in the more hindered substrate **7** (Scheme 2). As expected, the reaction was much slower. Thus, glucose-derived enol carbonate **7f** was prepared from **6** and **2f** as usual. Treatment with 2.5 equiv of DMAP induced rearrangement over 19 h at 0 °C to afford separable

SCHEME 2



diastereomers of **8f** (dr = 2.9:1.0). It was necessary to conduct this experiment in the presence of an added equivalent of chloroformate **2f** to prevent the formation of considerable amounts of the starting benzofuranone **6**. Diastereoselectivity did not improve at −20 °C, and the absolute stereochemistry of the products was not assigned.

Similarly, **6** was treated with the chloroformate **2k** and Et_3N followed by rearrangement of **7k** using excess DMAP in the presence of added **2k** to afford **8k** with dr = 1.8:1.0 as inseparable diastereomers. On the other hand, **8k** was isolated with a much improved dr = 9:1 (44% yield) using Bu_3P as the catalyst in a similar experiment. The parent benzofuranone **6** was also recovered (3:1 **8k**:**6**), as in the other phosphine-catalyzed rearrangements, despite extreme measures taken to maintain anhydrous conditions (glove box conditions; freshly distilled reagents); unfortunately, even after an extensive survey of conditions, diastereomers could not be separated by chromatography at this stage. Nevertheless, the high dr obtained with the Bu_3P/substrate **7**/chloroformate **2k** combination was acceptable from the standpoint of solving the problem of asymmetric diazonamide A quaternary carbon synthesis.

We have shown elsewhere[2a] that the absolute sense of stereoinduction in the rearrangement of **3a** is not affected by the presence of *o*-alkoxy and *m*-Br substituents in the 3-phenyl group of the benzofuranone substrate. On the basis of this analogy and the known sense of stereoinduction of the benzyl mandelate auxiliary (Figure 2), the major diastereomer of **8k** can be tentatively assigned as shown in Figure 3.

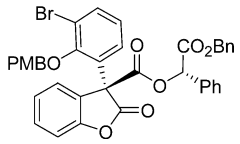


FIGURE 3. Tentative structure of the major diastereomer **8k**.

From the results presented above, we conclude that no one auxiliary or catalyst combination affords consistently high dr in both benzofuranone series (**1** and **6**). Fortunately, moderate to good dr is possible by adjusting the combination of auxiliary and nucleophilic catalyst to match the specific substrate.

Experimental Section

Isolation of *rac*-5k (Major Diastereomer) for X-ray Structure Determination. 3-Phenylbenzofuranone **1**[5] (210 mg, 1.0 mmol, 1.0 equiv) was dissolved in DCM (10 mL, 0.1 M) in a flame-dried round-bottomed flask; chloroformate **2k** (74%/wt, prepared as before,[2a] and used as a solid after evaporation of volatiles under nitrogen stream; 597 mg, 1.5 mmol, 1.5 equiv) was quickly weighed out and added to this solution, which was then cooled to 0 °C. To initiate the carboxylation and rearrangement, solid DMAP (Aldrich, 440 mg, 3.6 mmol, 3.6 equiv) was added to the reaction solution. As DMAP dissolved, blue streaks briefly formed and disappeared in the reaction mixture. After DMAP dissolved, the reaction solution

was placed in the refrigerator at 0 °C. After 18 h, the reaction was diluted with 100 mL of Et_2O and sequentially washed with 100 mL of 10% aq $KHSO_4$ and satd aq $NaHCO_3$. The organic phase was dried over $MgSO_4$, filtered, and concentrated under reduced pressure to yield a yellow oil. This was shown to be a 1.9:1.0 mixture of diastereomers by comparing the relative ratios of the α-carbonyl-proton signals at δ (400 MHz) 6.03 (major dr, 1.9H) and 6.01 ppm (minor dr, 1.0 H). The two diastereomers coelute in several chromatography solvents, and they are somewhat sensitive to silica as determined by the formation of baseline material in 2-D TLC (8:2 hexanes:Et_2O). The major diastereomer was isolated by triturating the crude oil with ∼20 mL of Et_2O and allowing the resulting mixture to stand in the freezer (−23 °C) for 2 days. At this time the precipitate was isolated by pipetting off the supernatant and washing the precipitate with minimal Et_2O, and drying the resulting solid under reduced pressure. This yielded 234 mg (49%) of a white powder highly enriched in the major diastereomer (24:1 dr); the supernatant produced 319 mg of a clear oil enriched in the *minor* diastereomer (1:1.3 dr), and contaminated with minor impurities. X-ray quality crystals of the major diastereomer were obtained by slowly evaporating a dilute Et_2O solution over several days (∼100 mg in ∼4 mL of Et_2O in a capped vial); this process yielded long needles of pure *rac*-**5k** (major diastereomer): analytical TLC, 8:2 hexanes:EtOAc, R_f 0.35. Mp range 65−68 °C. ES molecular ion calculated for $C_{30}H_{22}O_6Na^+$ 501.1314, found *m*/*z* 501.1323, error 2 ppm. IR (neat, cm^{-1}) 3029, 1812, 1743. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (1H, d, J = 7.3 Hz), 7.45−7.17 (18H, m), 6.03 (1H, s), 5.14 (2H, s). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 170.8, 167.4, 166.8, 153.6, 134.8, 134.3, 132.6, 130.7, 129.3, 128.8, 128.7, 128.5, 128.3, 127.8, 127.6, 127.2, 126.7, 124.72, 124.66, 111.2, 76.0, 67.4, 62.2.

3-[3-Bromo-2-(4-methoxybenzyloxy)phenyl]-2-oxo-2,3-dihydrobenzofuran-3-carboxylic Acid Benzyloxycarbonylphenylmethyl Ester (8k). Benzofuranone **6**[2c] (104 mg, 0.245 mmol, 1.0 equiv) was placed in an oven-dried flask, dissolved in THF (1.2 mL), and cooled to 0 °C. Then, the chloroformate **2k** (1.35 mL of a 0.2 M solution in THF, 0.270 mmol, 1.1 equiv) and Et_3N (38 μL, 0.270 mmol, 1.1 equiv) were sequentially syringed in. After 10 min at 0 °C, volatiles were removed under reduced pressure and the resulting crude oil was purified by flash column chromatography (8:2 hexanes:Et_2O) to yield 170 mg (100%) of the enol carbonate **7k** as a white foam. A portion of this material (80 mg, 0.115 mmol, 1.0 equiv) was exposed to high vacuum for 12 h before the reaction flask was transferred to the glovebox. The enol carbonate was dissolved in DCM (freshly distilled from P_2O_5, 1.2 mL, 0.1 M) and Bu_3P (distilled from LAH, 0.14 mL, 0.576 mmol, 5.0 equiv) was slowly syringed in. After 1 h the solution was removed from the glovebox, diluted with 4 mL of DCM, and quenched with 0.8 mL of CH_3I. The reaction was concentrated under reduced pressure and the resulting clear oil purified by flash column chromatography (85:15 Hex:Et_2O) to yield 36 mg of **8k** (44%) as an inseparable 9:1 mixture of diastereomers: analytical TLC, 8:2 hexanes:EtOAc, R_f 0.22. ES molecular ion calculated for $C_{38}H_{29}O_8BrNa^+$ 715.0943, found *m*/*z* 715.0950, error 1 ppm. IR (neat, cm^{-1}) 1814, 1743, 1514, 1214. ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.61 (0.1H, dd, J = 7.8, 1.9 Hz), 7.55 (0.9H, dd, J = 7.8, 1.5 Hz), 7.45 (2H, d, J = 8.8 Hz), 7.42−7.35 (2H, m), 7.31−7.23 (5H, m), 7.18−7.08 (6.6H, m), 7.05−7.02 (0.3H, m), 6.94 (0.1H, t, J = 7.8 Hz), 6.88−6.82 (3.9H, m), 6.68 (0.1H, d, J = 8.8 Hz), 5.66 (0.9H, s), 5.64 (0.1H, s), 5.25 (1H, d, J = 9.8 Hz), 5.11 (1H, d, J = 9.8 Hz), 5.03 (1.8H, ABq, J = 12.2 Hz, $\Delta\upsilon$ = 24 Hz), 5.03 (assume 0.1H, d, J = 12.2 Hz), 4.96 (0.1H, d, J = 10.7 Hz), 4.84 (0.1H, d, J = 12.2 Hz), 3.79 (2.7H, s), 3.76 (0.3H, s). ^{13}C NMR (only major diastereomer signals are reported, 126 MHz, $CDCl_3$, ppm) δ 170.7, 167.9, 165.8, 159.5, 154.3, 153.7, 135.1, 132.9, 131.7, 130.7, 130.4, 129.3, 129.0, 128.7, 128.5, 128.4, 128.2, 128.1, 127.8, 127.7, 126.9, 126.6, 125.0, 124.9, 117.9, 113.5, 111.0, 75.7, 75.3, 67.0, 61.2, 55.2.

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Supporting Information Available: Complete experimental details, characterization data, and X-ray data tables for *rac*-**5k**. This material is available free of charge via the Internet at http://pubs.acs.org.

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