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STUDIES TOWARD INTRAMOLECULAR CYCLOADDITION OF *o*-QUINODIMETHANE WITH AN OXAZOLE MOIETY†

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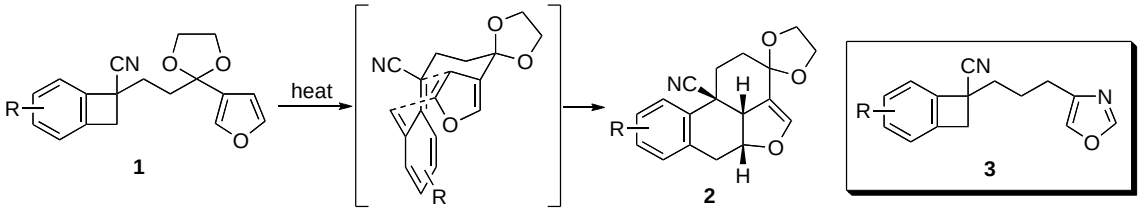
Abstract – Thermal reaction of benzocyclobutene derivatives having an oxazole moiety was investigated. Intramolecular [4+2] cycloaddition of *o*-quinodimethane, generated by thermolysis of the benzocyclobutene, with the oxazole did not proceed, and instead, [1,5]-sigmatropic rearrangement occurred dominantly.

INTRODUCTION

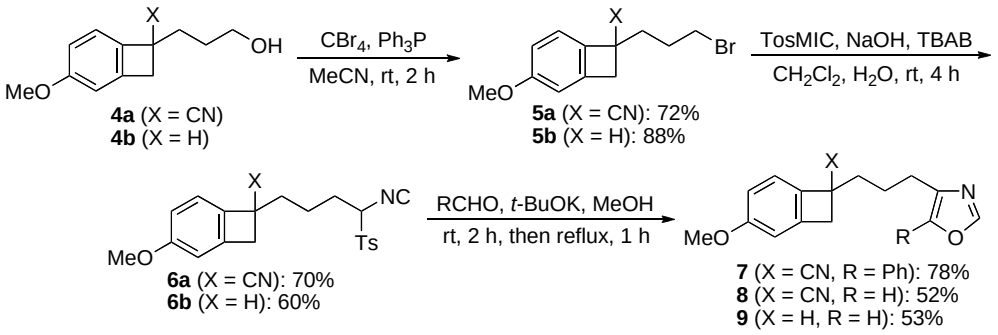
We have for years studied on the formation of *o*-quinodimethane by thermolysis of benzocyclobutene derivatives and its reactivity toward various electrocyclic reactions.[1] These sequential processes have realized efficient syntheses of a variety of polycyclic systems including steroidal bioactive compounds and the relating analogues.[2] We have recently demonstrated that this methodology can be successfully applied for furan-containing benzocyclobutene substrates such as **1**, leading to the stereoselective formation of dihydrofuran-fused tetracyclic compounds **2** through an endo transition state (Scheme 1).[3] These novel compounds have been revealed to exhibit significant biological activities such as antiviral and apoptosis-inducing activities.[4] In this case, the furan ring served as an electron-rich dienophile in the [4+2] cycloaddition with the *o*-quinodimethane. We were interested in whether an oxazole ring worked in a similar manner to produce new condensed heterocyclic compounds. In this paper, we describe the preparation of oxazole-containing benzocyclobutenes **3** and their behavior for the thermal reactions.



Scheme 1. *o*-Quinodimethane Formation and Subsequent Intramolecular Cycloaddition

RESULTS AND DISCUSSION

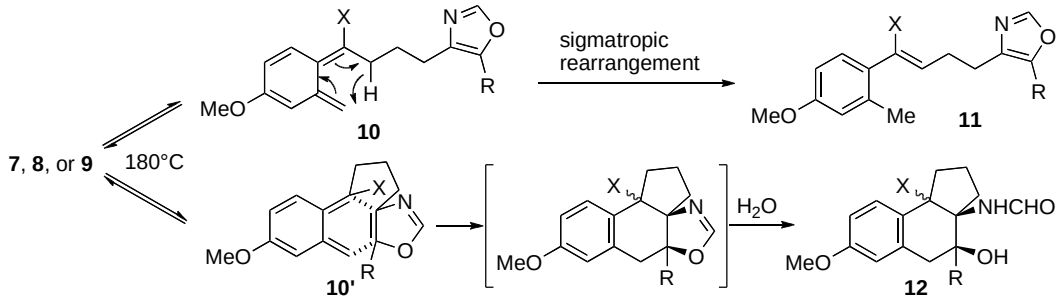
Among a number of methods for the oxazole ring construction, we chose the oxazole synthesis utilizing the reaction of *p*-tolylsulfonylmethyl isocyanide (TosMIC) with aldehydes.[5] Previously reported benzocyclobutenyl alcohol **4a**[2] was converted into the corresponding bromide **5a**, and subsequently allowed to react with a TosMIC anion in the presence of tetra-*n*-butylammonium bromide (TBAB) as a phase-transfer catalyst to give the compound **6a** in satisfactory yields. The oxazole-forming reaction of **6a** with benzaldehyde smoothly proceeded in MeOH to furnish a requisite oxazole-containing benzocyclobutene **7** in 78% yield (Scheme 2). Similarly a compound **8**, having a 5-unsubstituted oxazole moiety, was also synthesized using paraformaldehyde as a reagent. In addition, another compound **9** without a cyano group could be prepared through the same synthetic pathway from a known substrate **4b**, which was easily obtained by reductive decyanation of **4a**.[2]



Scheme 2. Synthesis of Oxazole-containing Benzocyclobutenes **7**–**9**

With three substrates **7**–**9** in hand, we examined *o*-quinodimethane formation from these compounds under thermal conditions and the end of these reactive intermediates (Scheme 3). Initially, the substrate **7** was heated at 180 °C (*o*-dichlorobenzene, reflux), and we observed complete disappearance of **7** and the formation of one isolable product after 2 h. Isolation and purification disclosed that the product was substituted toluene derivative **11**, which obviously originated from [1,5]-sigmatropic rearrangement of the *o*-quinodimethane intermediate **10**.[6] On the other hand, the substrate **8** without a phenyl group afforded another product in addition to **11** under the same condition. This new product was confirmed to be a compound **12** after spectral data analyses, although a relative configuration of the cyano group has not been determined yet. We presumed that the product **12** was formed through an intramolecular cycloaddition of another *o*-quinodimethane intermediate **10'** and subsequent hydrolysis of the cyclic imidate. Because interconversion between *o*-quinodimethanes **10** and **10'** (geometric isomers) may be possible, the product distribution (**11** or **12**) is largely dependent on the transition state energy of the each pericyclic reaction. In the case of **7**, the presence of the bulky phenyl group is likely to be responsible for relatively high energy barrier of the intramolecular cycloaddition of **10'**. Additionally, in both cases, we

could not detect a cycloadduct **13**, which corresponded to the product **2** from the furan-containing substrate **1**. We consider that the [4+2] cycloaddition depicted in Scheme 1 is an inverse electron-demand type reaction, because the dienophile (the furan ring) is electron-rich and the diene (*o*-quinodimethane) is electron-poor due to the cyano group. Therefore, the relatively electron-poor C=N double bond of the oxazole ring is likely to be disadvantageous for the cycloaddition leading to the product **13**. This may be a reason why the [1,5]-sigmatropic rearrangement (formation of **11**) or the cycloaddition involving the C=C double bond of the oxazole ring (formation of **12**) prevailed over the formation of **13** in the cases of the substrates **7** and **8**.[7] In the light of these considerations, the substrate **9** lacking the cyano group seems to be favorable for the formation of the cycloadduct **13**, because the *o*-quinodimethane moiety generated from **9** is conversely considered to have a high electron density due to the conjugated methoxy group. In addition, a contribution of the *o*-quinodimethane intermediate **10**, a precursor of **11**, may be markedly reduced in comparison with that of the geometric isomer **10'** by a steric reason. Thermal reaction of **9**, however, gave the rearrangement product **11** in a 60% yield again, and no other products could be isolated. These results indicate that the energy barrier of the [4+2] cycloaddition of the *o*-quinodimethane with the oxazole moiety is considerably high, and consequently, the reaction course of the *o*-quinodimethane intermediate can converge on the [1,5]-sigmatropic rearrangement pathway.



substrate	yield (%)		
	11	**12**	**13**
7 (X = CN, R = Ph)	40	0	0
8 (X = CN, R = H)	23	10	0
9 (X = H, R = H)	60	0	0

Scheme 3. Thermal Reaction of Oxazole-containing Benzocyclobutenes **7**–**9**

In this paper, we described thermal reactions of the oxazole-containing benzocyclobutene derivatives *via* the highly reactive *o*-quinodimethane intermediates. Dissimilar to our previous reports on the furan-containing benzocyclobutenes, a main reaction pathway was not intramolecular [4+2] cycloaddition but [1,5]-sigmatropic rearrangement to form substituted toluene products. Further efforts for constructing various heterocyclic systems utilizing *o*-quinodimethane chemistry have been made in our laboratory, and will be reported in near future.

EXPERIMENTAL

All nonaqueous reactions were carried out under an Ar atmosphere. Reagents were purchased from commercial sources and used as received. Anhydrous solvents were prepared by distillation over CaH_2, or purchased from commercial sources. ^{1}H and ^{13}C NMR spectra were obtained on a Varian Gemini 300 instrument, using chloroform peak as an internal reference. Mass spectra were measured on a JEOL D-200 or a JEOL AX 505 mass spectrometer, and the ionization method was electron impact (EI, 70 eV). IR spectra were recorded on a JASCO FT/IR-460Plus spectrometer. Column chromatography was carried out by employing Cica Silica Gel 60N (spherical, neutral, 40-50 μm or 63-210 μm). Preparative methods of the compounds **4a** and **4b** have already been reported.[2]

1-(3-Bromoprop-1-yl)-4-methoxybenzocyclobutene-1-carbonitrile (5a).

To a solution of **4a** (441 mg, 2.03 mmol) in MeCN (9 mL) were added triphenylphosphine (692 mg, 2.64 mmol) and carbon tetrabromide (876 mg, 2.64 mmol) at 0 °C. The mixture was warm to rt and then stirred for 2 h. The reaction was quenched with sat. aq. $NaHCO_3$ and the precipitate were filtered off. The aqueous mixture was extracted with CH_2Cl_2, and the organic layers were combined, dried ($MgSO_4$), and evaporated. The residue was purified with column chromatography to give **5a** (534 mg, 72%) as a colorless oil. ^{1}H-NMR ($CDCl_3$): δ 2.02–2.41 (4H, br), 3.23 (1H, d, *J* = 14 Hz), 3.44 (2H, t, *J* = 6.0 Hz), 3.66 (1H, d, *J* = 14 Hz), 3.81 (3H, s), 6.72 (1H, d, *J* = 1.4 Hz), 6.83 (1H, dd, *J* = 1.4, 8.3 Hz), 7.10 (1H, d, *J* = 8.3 Hz); ^{13}C-NMR ($CDCl_3$): δ 29.50, 32.67, 36.15, 41.41, 55.55, 109.30, 115.01, 121.55, 122.75, 134.72, 141.85, 161.11; IR (neat): 2230 cm^{-1}; MS (EI): *m/z* 279 (M^+); HRMS (EI) Calcd for $C_{13}H_{13}{}^{79}BrNO$: 279.0259 (M^+), found: 279.0223.

4-(1-Cyano-4-methoxybenzocyclobuten-1-yl)-1-(4-toluenesulfonyl)butyl Isocyanide (6a).

To a solution of **5a** (372 mg, 1.13 mmol) in CH_2Cl_2 (2 mL) were added TosMIC (331 mg, 1.70 mmol), tetra-*n*-butylammonium bromide (70 mg, 0.23 mmol), and 30% NaOH aqueous solution (1.2 mL, 9.04 mmol), and the mixture was stirred at rt for 4 h. The reaction mixture was diluted with water and extracted with CH_2Cl_2. The extracts were combined, dried ($MgSO_4$), and evaporated. The residue was purified with column chromatography to give **6a** (310 mg, 70%) as a colorless oil. ^{1}H-NMR ($CDCl_3$): δ 1.80–2.05 (6H, br), 2.48 (3H, s), 3.21 (1H, d, *J* = 14 Hz), 3.67 (1H, d, *J* = 14 Hz), 3.77 (3H, s), 4.50 (1H, m), 6.71 (1H, d, *J* = 2.2 Hz), 6.81 (1H, dd, *J* = 2.2, 8.2 Hz), 7.09 (1H, dd, *J* = 8.2 Hz), 7.42 (1H, d, *J* = 8.1 Hz), 7.85 (1H, d, *J* = 8.1 Hz); ^{13}C-NMR ($CDCl_3$): δ 22.04, 22.61, 28.29, 36.72, 41.77, 42.45, 55.68, 72.56, 109.46, 115.19, 121.48, 122.92, 128.09, 130.06, 130.93, 134.61, 141.90, 146.80, 161.27, 165.51; IR (neat): 2233 cm^{-1}; MS (EI): *m/z* 394 (M^+); HRMS (EI) Calcd for $C_{22}H_{22}N_2O_3S$: 394.1351 (M^+), found: 394.1340.

4-Methoxy-1-{3-(5-phenyloxazol-4-yl)prop-1-yl}benzocyclobutene-1-carbonitrile (7).

To a solution of **6a** (50 mg, 0.13 mmol) in MeOH (2 mL) were added potassium *tert*-butoxide (28.5 mg,

0.26 mmol) and then benzaldehyde (0.013 mL, 0.13 mmol). The mixture was stirred at rt for 2 h, and then refluxed for 1 h. The solution was diluted with water and acidified with 10% HCl solution to pH 5. After MeOH was removed by evaporation, the aqueous layer was extracted with CH_2Cl_2. The organic layers were combined, dried ($MgSO_4$), and evaporated. The residue was purified with column chromatography to give **7** (34 mg, 78%) as a colorless oil. ^{1}H-NMR ($CDCl_3$): δ 1.90–2.15 (4H, br), 2.87 (2H, t, *J* = 7.0 Hz), 3.22 (1H, d, *J* = 14 Hz), 3.65 (1H, d, *J* = 14 Hz), 3.82 (3H, s), 6.70 (1H, d, *J* = 2.0 Hz), 6.79 (1H, dd, *J* = 2.0, 8.2 Hz), 7.09 (1H, d, *J* = 8.2 Hz), 7.36 (1H, d, *J* = 7.2 Hz), 7.45 (2H, t, *J* = 8.2 Hz), 7.57 (2H, dd, *J* = 1.1, 8.2 Hz), 7.84 (1H, s,); ^{13}C-NMR ($CDCl_3$): δ 25.52, 26.74, 37.25, 42.20, 42.50, 55.70, 109.38, 115.01, 122.02, 123.05, 125.87, 128.25, 128.68, 128.96, 134.59, 135.38, 142.13, 149.33, 161.14: IR (neat): 2231 cm^{-1}; MS (EI): *m/z* 344 (M^+); HRMS (EI) Calcd for $C_{22}H_{20}N_2O_2$: 344.1525 (M^+), found: 344.1520.

4-Methoxy-1-{3-(4-oxazolyl)prop-1-yl}benzocyclobutene-1-carbonitrile (8).

According to the procedure for the synthesis of **7**, the compound **6a** (620 mg, 1.57 mmol), potassium *tert*-butoxide (388 mg, 3.46 mmol), and paraformaldehyde (424mg, 4.72 mmol) gave **8** (218 mg, 52%) as a colorless oil. ^{1}H-NMR ($CDCl_3$): δ 1.94–2.05 (4H, br), 2.64 (2H, br), 3.22 (1H, d, *J* = 14 Hz), 3.66 (1H, d, *J* = 14 Hz), 3.78 (3H, s), 6.70 (1H, s,), 6.82 (1H, d, *J* = 2.2 Hz), 7.11 (1H, d, *J* = 8.2 Hz), 7.43 (1H, s), 7.81 (1H, s); ^{13}C-NMR ($CDCl_3$): δ 25.46, 25.96, 37.24, 42.18, 42.56, 55.75, 109.45, 115.08, 122.03, 123.05, 134.49, 135.38, 142.14, 151.03, 161.14; IR (neat): 2233 cm^{-1}; MS (EI): *m/z* 268 (M^+); HRMS (EI) Calcd for $C_{16}H_{16}N_2O_2$: 268.1212 (M^+), found: 268.1183.

1-(3-Bromoprop-1-yl)-4-methoxybenzocyclobutene (5b).

According to the procedure for the synthesis of **5a**, the compound **4b** (230 mg, 1.2 mmol), triphenylphosphine (627 mg, 2.4 mmol), and carbon tetrabromide (796 mg, 2.4 mmol) gave **5b** (276 mg, 88%) as a colorless oil. ^{1}H-NMR ($CDCl_3$): δ 1.63–1.88 (2H, br), 2.00–2.12 (2H, br), 2.73 (1H, d, *J* = 14 Hz), 3.23 (1H, dd, *J* = 4.7, 14 Hz), 3.40–3.51 (3H, br), 3.80 (3H, s), 6.71–6.78 (2H, m), 7.00 (1H, d, *J* = 7.8 Hz); ^{13}C-NMR ($CDCl_3$): δ 31.67, 33.43, 33.95, 35.65, 41.85, 55.62, 109.17, 113.21, 122.89, 140.64, 144.34, 159.68; MS (EI): *m/z* 254 (M^+); HRMS Calcd for $C_{12}H_{15}{}^{79}BrO$: 254.0306 (M^+), found: 254.0350.

4-(4-Methoxybenzocyclobuten-1-yl)-1-(4-toluenesulfonyl)butyl Isocyanide (6b).

According to the procedure for the synthesis of **6a**, the compound **5b** (265 mg, 1.04 mmol), TosMIC (354 mg, 1.81 mmol), tetra-*n*-butylammonium bromide (100 mg, 0.3 mmol), and 30% NaOH aqueous solution (2.77 mL, 20.8 mmol) gave **6b** (221 mg, 60%) as a colorless oil. ^{1}H-NMR ($CDCl_3$): δ 1.70–1.76 (5H, br), 2.49 (3H, s), 2.67 (1H, d, *J* = 14 Hz), 3.28 (1H, dd, *J* = 5.0, 14 Hz), 3.38–3.40 (1H, br), 3.77 (3H, s), 4.51 (1H, dd, *J* = 3.6, 11 Hz), 6.68–6.74 (2H, m), 6.96 (1H, d, *J* = 7.4 Hz), 7.43 (2H, d, *J* = 8.3 Hz), 7.87 (2H, d, *J* = 8.3 Hz); ^{13}C-NMR ($CDCl_3$): δ 22.00, 24.16, 28.63, 33.76, 33.79, 35.55, 35.64, 41.98, 42.06, 55.55, 72.94, 109.14, 113.20, 122.68, 130.03, 130.16, 140.38, 144.23, 146.58, 159.64, 164.91; MS (EI): *m/z* 369 (M^+); HRMS (EI) Calcd for $C_{21}H_{23}NO_3S$: 369.1399(M^+), found: 369.1357.

4-Methoxy-1-{3-(4-oxazolyl)prop-1-yl}benzocyclobutene (9).

According to the procedure for the synthesis of **7**, the compound **6b** (67 mg, 0.18 mmol), potassium *tert*-butoxide (45 mg, 0.40 mmol), and paraformaldehyde (49mg, 0.54 mmol) gave **9** (34 mg, 53%) as a colorless oil. ^{1}H-NMR ($CDCl_3$): δ 1.65–1.86 (5H, br), 2.61 (2H, t, *J* = 6.5 Hz), 2.67 (1H, d, *J* = 14 Hz), 3.26 (1H, dd, *J* = 5.0, 14 Hz), 3.39–3.41 (1H, br), 3.77 (3H, s), 6.68–6.73 (2H, m), 6.98 (1H, d, *J* = 8.0 Hz), 7.41 (1H, s), 7.81 (1H, s); ^{13}C-NMR ($CDCl_3$): δ 26.41, 27.22, 34.52, 35.78, 42.53, 55.67, 109.19, 113.14, 122.97, 134.23, 140.51, 141.29, 144.56, 150.88, 159.59; MS (EI): *m/z* 243 (M^+); HRMS (EI) Calcd for $C_{15}H_{17}NO_2$: 243.1259 (M^+), found: 243.1288.

Thermolysis of the Compounds 7–9: Formation of 11 and 12.

A solution of **7**, **8**, or **9** (0.2 mmol) in *o*-dichlorobenzene (3 mL) was refluxed for 2 h on an oil bath (180 °C), and the solvent was removed by evaporation under reduced pressure. The residue was purified with column chromatography to give **11** or **12** in indicated yields (Scheme 3).

Compound 11 from 7: Colorless oil; ^{1}H-NMR ($CDCl_3$): δ 1.90–2.10 (1H, br), 2.22 (3H, s), 2.67–2.83 (3H, m), 3.82 (3H, s), 6.43 (1H, t, *J* = 7.5 Hz), 6.68 (1H, m), 6.80 (1H, dd, *J* = 2.0, 8.0 Hz), 7.05 (1H, d, *J* = 8.0 Hz), 7.36 (1H, d, *J* = 7.2 Hz), 7.46 (2H, t, *J* = 8.2 Hz), 7.58 (2H, dd, *J* = 1.1, 8.2 Hz), 7.83 (1H, s); ^{13}C-NMR ($CDCl_3$): δ 20.42, 32.03, 34.65, 57.20, 109.38, 115.01, 122.02, 123.05, 125.87, 128.25, 128.68, 128.96, 134.52, 135.71, 142.48, 149.33, 160.12, 163.04; IR (neat): 2231 cm^{-1}; MS (EI): *m/z* 344 (M^+); HRMS (EI) Calcd for $C_{22}H_{20}N_2O_2$: 344.1525 (M^+), found: 344.1512.

Compound 11 from 8: Colorless oil; ^{1}H-NMR ($CDCl_3$): δ 1.90–2.20 (1H, m), 2.23 (3H, s), 2.64–2.94 (2H, m), 3.00–3.04 (1H, m), 3.79 (3H, s), 6.40 (1H, t, *J* = 7.2 Hz), 6.73 (2H, m), 7.08 (1H, d, *J* = 9.3 Hz), 7.50 (1H, s), 7.84 (1H, s); ^{13}C-NMR ($CDCl_3$): δ 20.60, 25.41, 30.81, 55.50, 111.87, 116.21, 126.69, 130.58, 134.82, 137.57, 138.76, 149.38, 151.20, 163.00; IR (neat): 2214 cm^{-1}; MS (EI): *m/z* 268 (M^+); HRMS (EI) Calcd for $C_{16}H_{16}N_2O_2$: 268.1212 (M^+), found: 268.1230.

Compound 12 from 8: Colorless prisms, mp 142–143°C (*i*-Pr_2O); ^{1}H-NMR ($CDCl_3$): δ 1.90–2.23 (4H, m), 2.64–2.94 (3H, m), 3.00–3.04 (1H, m), 3.79 (3H, s), 5.20 (1H, d, *J* = 8.5 Hz), 6.33 (1H, s), 6.64 (1H, s), 6.86 (1H, m), 7.11 (1H, d, *J* = 8.2 Hz), 7.38 (1H, m), 8.21 (1H, s); ^{13}C-NMR ($CDCl_3$): δ 20.79, 31.94, 34.52, 40.69, 54.04, 55.35, 67.89, 68.83, 114.06, 114.21, 122.01, 123.38, 129.85, 134.70, 159.50, 163.00; IR (KBr): 2235 cm^{-1}; MS (EI): *m/z* 286 (M^+); HRMS (EI) Calcd for $C_{16}H_{13}N_2O_3$: 286.1317 (M^+), found: 286.1324.

Compound 11 from 9: Colorless oil; ^{1}H-NMR ($CDCl_3$): δ 2.26 (3H, s), 2.52–2.64 (2H, m), 2.71 (2H, m), 3.76 (3H, s), 5.91–6.03 (1H, m), 6.54 (1H, d, *J* = 15 Hz), 6.65–6.74 (2H, m), 7.22–7.36 (1H, m), 7.45 (1H, s), 7.86 (1H, s); ^{13}C-NMR ($CDCl_3$): δ 20.33, 29.97, 34.53, 55.46, 111.65, 115.53, 126.69, 128.25, 128.80, 129.57, 134.51, 136.51, 150.86, 158.65; MS (EI): *m/z* 243 (M^+); HRMS (EI) Calcd for $C_{15}H_{17}NO_2$: 243.1259 (M^+), found: 243.1251.

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REFERENCES AND NOTES

† This paper is dedicated to the late Dr. John W. Daly.

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