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Halogenation with *N*-Halo-2-oxazolidinones. The Chain-carrying *N*-Centered Radicals

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Selectivities in halogenation of 2,3-dimethylbutane, 1-chlorobutane and substituted toluenes with *N*-chloro- or *N*-bromo derivatives of 4,4-dimethyl-2-oxazolidinone (NXDMO), 2-oxazolidinone (NXO), and succinimide (NXS) were examined. In the presence of olefin, halogenation of the substituted butane by these *N*-halo reagents were found to proceed involving hydrogen abstraction by the *N*-centered radicals, since chlorination by the *N*-chloro reagents and bromination by the corresponding *N*-bromo reagents showed the same selectivities. The relative reactivity of a *t*-C–H bond compared with a *prim*-C–H bond RS_p^t markedly depends on the structure of the *N*-radical, being 200, 70, and 11 at 80 °C toward the radicals derived from NXDMO, NXO, and NXS, respectively. Reaction constant ρ of hydrogen abstraction from the toluenes by the *N*-radical from NXDMO was -1.0 at 130 °C.

There has been considerable controversy about the mechanism of halogenations by *N*-halo reagents. At first, for bromination by *N*-bromosuccinimide (NBS), Bloomfield proposed the radical chain mechanism involving the nitrogen centered imidyl radical.[1] In 1953 Goldfinger explained chlorination by *N*-chlorosuccinimide (NCS) by the mechanism in which actual halogenating agent is halogen molecule produced by the reaction of NCS with hydrogen chloride.[2]

Many subsequent studies showed that selectivities or isotope effects in halogenations by various *N*-halo compounds are almost the same as those in photohalogenations by elemental halogens, supporting that the Goldfinger mechanism, if not exclusively, is operative at least as the main path.[3–8]

Bloomfield mechanism

$$\rangle N\cdot + RH \longrightarrow \rangle N\text{-}H + R\cdot$$

$$R\cdot + \rangle N\text{-}X \longrightarrow R\text{-}X + \rangle N\cdot$$

Goldfinger mechanism

$$X\cdot + RH \longrightarrow R\cdot + HX$$

$$R\cdot + X_2 \longrightarrow R\text{-}X + X\cdot$$

$$HX + \rangle N\text{-}X \longrightarrow X_2 + \rangle N\text{-}H$$

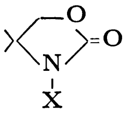
Consequently hydrogen abstraction by *N*-radicals has received only a little attention,[9] except intramolecular abstraction and its application to synthetic chemistry.[10] Recently, however, it has been reported that in some cases selectivities in halogenations by *N*-halo compounds differ from those by elemental halogens. The cases are classified as follows: i) NBS bromination of substrates which are relatively unreactive toward bromine atom:[11] ii) using a good solvent for NBS, for example, CH_2Cl_2;[12] iii) presence of olefin or base which can trap halogen or hydrogen halide.[12,13]

These findings may suggest that under these conditions the Bloomfield mechanism plays an important role in the halogenation by *N*-halo compounds. However, discrepancy in selectivity in halogenation between by halogen and by *N*-halo compound is not necessarily an unequivocal evidence for the contribution of the nitrogen centered radical. Mosher and Estes, for example, demonstrated that selectivity of chlorination by *N*-chlorophthalimide depended on the reaction conditions, and explained the feature in terms of the Goldfinger mechanism complicated by the reversible hydrogen abstraction.[14)

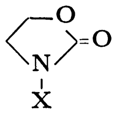
$$X\cdot + RH \rightleftharpoons H\text{-}X + R\cdot$$

If the *N*-radicals are the true chain carrier, selectivity of chlorination by the *N*-chloro reagent should be the same to that of bromination by the corresponding *N*-bromo reagent. From the view of this criteria, in this work, selectivities in halogenations by several *N*-halo reagents were examined, aiming to elucidate the chemical nature of the *N*-radicals.

Besides NBS and NCS, we chose 3-halo-4,4-dimethyl-2-oxazolidinone(NXDMO) and 3-halo-2-oxazolidinone(NXO) as the reagents, since these two *N*-halides have been found to have "lower positive halogens," and to react with hydrogen halides, giving halogens, much slower relative to *N*-halosuccinimides,[15] and consequently are expected to have natures less favorable to take place the Goldfinger processes.



X: Cl (NCDMO)
Br (NBDMO)



X: Cl (NCO)
Br (NBO)

Results and Discussion

Selectivities in halogenations of 2,3-dimethylbutane, 1-chlorobutane, and substituted toluenes by the *N*-halo reagents were determined by intra- and intermolecular competition methods.

2,3-Dimethylbutane. Halogenations initiated by benzoyl peroxide (BPO) were conducted at 80 °C by using 0.2 equivalent amounts of the *N*-halo regents to avoid dichlorination. In order to eliminate the occurence of the Goldfinger processes, the reaction was carried out in a good solvent for the *N*-halo reagents, CH_2Cl_2,[12] and in the presence of 3,3-dimethyl-1-butene as a halogen scavenger or γ-collidine as a hydrogen halide acceptor.[12,13]

Change in isomer distribution of monohalogenated products was examined as a function of the initial

Table 1. BPO-initiated halogenation of 2,3-dimethylbutane by the *N*-halo reagents (80 °C)

N-Halide	Additive	Product yield/%[b]			Halides/Amide %
		prim-Halide	*t*-Halide	Amide or imide	
NCDMO	None	14	58	72	100
	t-BuCH=CH$_2$	3.1	36	59	66
	γ-Collidine	1.1	13	37	39
NBDMO	None	—[c]	71	79	90
	t-BuCH=CH$_2$	2.6	28	61	51
NCO	None	5.5	84	100	90
	t-BuCH=CH$_2$	1.9	55	100	57
NBO	None	—[c]	68	80	85
	t-BuCH=CH$_2$	1.5	36	100	38
NCS	None	29	36	83	78
	t-BuCH=CH$_2$	4.6	8.6	—[d]	—
	γ-Collidine	3.7	7.8	—[d]	—
NBS	None	—[c]	64	80	80
	t-BuCH=CH$_2$	4.3	7.6	—[d]	—

a) 2,3-Dimethylbutane 1.25 mmol, halogenating agent 0.25 mmol, BPO 0.01 mmol, additive 0.25 mmol, solvent: CH_2Cl_2 5 cm^3 80 °C 15 h. b) Determined by VPC, based on the reagent used. c) Only trace amounts were detected. d) Not determined.

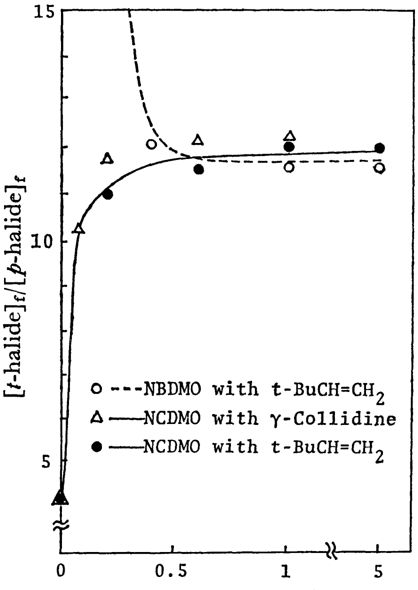


Fig. 1. Dependence of relative yield of tertiary halide to primary halide on relative concentration of additives.

concentration of the olefinic or basic additive. Typical tendencies observed in halogenation with NXDMO are shown in Fig. 1. In the absence of the additives NBDMO halogenated the tertiary C–H of the substrate almost exclusively, while chlorination by NCDMO gave the primary and the tertiary chloride in a ratio of 4:1.

A small amount of the additives brought about marked effects on the distribution of the product, and in the presence of their equimolar amount to the reagents, bromination by NBDMO and chlorination by NCDMO showed the almost same selectivity.

Table 2. Selectivity factor RS_p^t in halogenation of 2,3-dimethylbutane

Reagent	RS_p^t (80 °C)		
	No additive	t-BuCH=CH$_2$ added	γ-Collodine added
NCDMO	25.8±3.6	70.5±1.1	70.8±3.0
NBDMO	—[a]	65.2±4.7	—[b]
NCO	91.6	175±15	—[b]
NBO	—[a]	206±7	—[b]
NCS	7.6±0.1	11.3±0.9	12.8±2.7
NBS	—[a]	10.7	—[b]

a) *prim*-C–H bonds are almost inactive. b) The reaction mixtures are too complex to be analyzed.

This shows, under these conditions both halogenations proceed almost exclusively through the Bloomfield mechanism, involving the common *N*-centered radical as a hydrogen abstracting species.

Table 1 shows the yields of the products of halogenation of 2,3-dimethylbutane by various halogenating agents in the absence and the presence of an equimolar amount of the olefin or the base. Apparently, the presence of the additives reduced the total yield of the halogenated products, and also lowered the relative amount of the halogenated products to the amides (or imide) produced. These facts indicate that the *N*-halo reagents can be consumed also by some side reactions, perhaps, with the additives. Particularly, the presence of γ-collidine gave the complicated mixture containing several unidentified by-products.

Neverthless, in all cases, relative yields of the tertiary to the primary halides fairly coincide with each other between bromination by the *N*-bromo reagent and chlorination by the corresponding *N*-chloro reagent. From the relative yield of the halides obtained in at least three runs for each reaction, selectivity factor between *t*- and *pirm*-C–H bonds, that is the reactivity of a *t*-C–H bond relative to a *prim*-C–H bond in the substrate, RS_p^t was calculated to be as shown in Table 2.

In the absence of the additives, bromination hardly occurs on a *t*-C–H. The tendency is essentially the same to that in bromination by bromine.[16] Therefore, bromination by *N*-bromo amides or imide seems to mainly proceed through the Goldfinger mechanism. Selectivities of chlorination depend on the nature of *N*-chloro reagents and are different from that of chlorination by chlorine ($RS_p^t=3$—4).[17] Thus, chlorinations by *N*-chloro reagents may proceed through both of the Bloomfield and the Goldfinger mechanism.

In the presence of the olefin, halogenation proceed through the Bloomfield mechanism almost exclusively, since the selectivity depends on the structure of the amide or imide groups but not on the nature of halogen.

1-Chlorobutane. Based on the information obtained in the study of halogenation of 2,3-dimethylbutane described above, 1-chlorobutane was halogenated by the *N*-halo reagents in the presence of 3,3-dimethyl-1-butene. From the isomer distribution of the halogenated products, relative reactivity of a C–H bond at each position was estimated. In Table 3 the reactivity values refered to those of a C–H bond at 3-position were listed as well as the results of photochlorination[18] and bromination.[19]

TABLE 3. RELATIVE REACTIVITIES OF C–H BONDS OF 1-CHLOROBUTANE TOWARD HALOGENATIONS[a),b)]

Reagent	$Cl-CH_2-$	CH_2-	CH_2-	CH_3
NCDMO	0.48	0.37	1.00	0.12
NBDMO	0.88	0.40	1.00	0.13
NCO	0.69	0.65	1.00	0.09
NBO	0.70	0.46	1.00	0.12
NCS	0.17	0.56	1.00	0.25
NBS	0.25	0.61	1.00	0.22
Cl_2[c)]	0.09	0.40	1.00	0.19
Br_2(60 °C)[c)]	0.45	0.48	1.00	—

a) 1-Chlorobutane: 1.25 mmol. *N*-halogeno reagent: 0.25 mmol. 3,3-dimethyl-1-butene: 0.25 mmol. BPO: 0.01 mmol. solvent: CH_2Cl_2 5 cm^3, 80 °C 15 h. b) Reactivity of a C–H bond at 3-position was taken as unity. c) Calculated from the results in the references.[18,19]

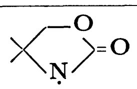
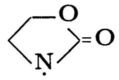
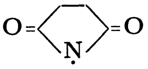
Relative reactivities of C–H bonds toward a *N*-chloro reagent are in tolerable agreement with those toward the corresponding *N*-bromo reagent, except abnormally high reactivity at 1-position toward NBDMO, the reason for which is not clear. It can be seen that the selectivities of these halogenation are quite different from these of photohalogenation, suggesting that hydrogen abstracting species are the *N*-centered radicals.

Selectivity in Hydrogen Abstraction by the N*-Radicals.* Recognizing that halogenations of aliphatic compounds by *N*-halo amide or imide proceed by the Bloomfield mechanism, the selectivities in the halogenation would reveal the relative rates of hydrogen abstraction by the *N*-centered radicals.

From the results of intramolecular competitive reactions of 2,3-dimethylbutane and 1-chlorobutane, relative reactivities of *prim*-, *s*-, and *t*-C–H bonds toward the *N*-centered radicals were found to be as shown in Table 4. Since polar effects of a chlorine substituent in 1-chlorobutane are only slightly operative on 3- and 4-positions,[20] relative reactivities of C–H bonds between these two positions may be used approximately for the selectivity factor between ordinary *s*- and *prim*-C–H bonds. For comparison, selectivity factors in hydrogen abstraction by other radicals are also shown in Table 4.

The *N*-centered radicals are found to be much less selective than bromine atom,[16] but more selective than chlorine atom,[17] *t*-butoxyl[21] and phenyl radicals.[22] The trend is understandable on the basis of the available values of dissociation energies of the bonds forming through hydrogen abstraction: H–Br

TABLE 4. RELATIVE RATE FACTORS IN HYDROGEN ABSTRACTION

Radical	Temp/°C	*prim*-C–H	*s*-C–H	*t*-C–H	Ref.
	80	1	8	70	this work
	80	1	8—11	200	this work
	80	1	4	11	this work
$CH_3CO\backslash N\cdot / CH_3$	25	1	—	95	13
$CH_3CO\backslash N\cdot$ / *t*-Bu	25	1	—	1.6	13
Cl·	25	1	3.5	4.2	17
Br·	150	1	80	1700	16
Ph·	60	1	9	44	21
t-BuO·	40	1	12	44	22

87, average N–H 93.4, *t*-BuOH 102, Ph–H 104, H–Cl 103 kcal mol^{-1}.[23] Comparing with the radicals derived from NXO and NXDMO, succinimidyl radical is less selective. This is perhaps due to that difference in effective electronegativity of the nitrogen atom affects on the bond energy of the forming N–H bond.

The radical derived from NXDMO appears less selective than that from NXO, especially in discrimination between *prim*- and *t*-C–H. This apparent less selectivity can be explained in terms of steric effects. Two methyl groups neighboring the radical center will sterically interfer the attack of the radical center on the more crowded position. As a result, reactivities of a C–H bond at more hindered positions, *e.g.* *t*-C–H, may be apparently lessered. More pronounced similar steric effects have been demonstrated in the selectivities of *N*-methyl- and *N*-*t*-butylacetamidyl radicals.[13] And these acyclic amidyl radicals seem less selective than the cyclic *N*-radicals studied in this work. These can be also considered to be the results of similar steric effects. In the acyclic systems blocking effects of the groups bonded to the nitrogen atom will be much larger. Consequently abstractions by the acyclic radicals are less selective, and more sensitive to steric hindrance by the groups in substrates, than those by the cyclic radicals.

Table 5. Halogenation of toluene by NXDMO

Reagent	Initiator	Temp °C	Time h	Yield of benzyl halide %
NCDMO	BPO	80	15	19
	AIBN	80	3	trace
	DTBP	130	22	73
NBDMO	BPO	80	15	69
	AIBN	80	3	69
	DTBP	130	22	70

Substituted Toluenes. In order to obtain preliminary information about polar selectivities of hydrogen abstraction by the *N*-radicals, substituted toluenes were intended to be halogenated competitively by the *N*-halo reagents in the presence of 3,3-dimethyl-1-butene.

Bromination of toluene by NBDMO was initiated by either BPO or AIBN, and the reaction (at 80 °C) gave benzyl bromide in a reasonable yield. However, chlorination by NCDMO was quite sluggish under these conditions and afforded benzyl chloride in a quite poor yield. Perhaps, this is due to dif-

Table 6. Competitive halogenation of substituted toluenes by NXDMO (130 °C)

$YC_6H_4CH_3$ Y=	NXDMO X= (mol dm^{-3})	Olefin[a] (mol dm^{-3})	Substrates (mol dm^{-3}) $PhCH_3$	$YC_6H_4CH_3$	Molar ratio $YC_6H_4CH_2X/PhCH_2X$	Relative rate const.
p-CH_3	C 0.040	—	0.800	0.402	1.64±0.1	1.63
	B 0.045	—	0.812	0.416	3.21±0.2	3.13
	C 0.041	0.045	0.818	0.600	2.44±0.04	1.83
	B 0.042	0.048	0.810	0.610	2.71±0.01	1.80
p-Cl	C 0.062	0.062	0.604	0.602	0.67±0.01	0.67
	B 0.062	0.074	0.608	0.612	0.76±0.03	0.70
p-CN	C 0.101	0.073	2.006	2.005	0.25±0.01	0.25
	B 0.088	0.104	2.035	1.996	0.25±0.01	0.25

a) 3,3-Dimethyl-1-butene.

Table 7. Competitive halogenation of substituted toluenes by NXO (130 °C)

$YC_6H_4CH_3$ Y=	NXO X= (mol dm^{-3})	Olefin[a] (mol dm^{-3})	Substrates (mol dm^{-3}) $C_6H_5CH_3$	$YC_6H_4CH_3$	Molar ratio $YC_6H_4CH_2X/PhCH_2X$	Relative rate const.
p-CH_3	C 0.044	—	1.02	0.479	1.70±0.03	1.88
	C 0.047	0.048	0.979	0.481	2.00±0.04	2.03
	C 0.042	0.049	1.04	0.447	1.68±0.05	1.95
	B 0.022	—	1.00	0.233	0.94±0.02	2.22
	B 0.022	0.025	1.03	0.238	0.90±0.03	1.93
p-Cl	C 0.043	—	0.426	0.796	1.16±0.01	0.62
	C 0.040	0.045	0.425	0.993	1.04±0.03	0.56
	C 0.046	0.045	0.407	0.429	0.49±0.04	0.46
	B 0.050	—	0.424	0.620	1.16±0.04	0.79
	B 0.049	0.041	0.405	0.592	1.21±0.04	0.83
p-CN	C 0.021	—	0.225	1.00	1.44±0.04	0.32
	C 0.022	—	0.220	1.00	1.38±0.03	0.30
	B 0.046	—	0.427	1.26	0.12±0.05	0.04
	B 0.041	0.046	0.414	1.30	0.17±0.10	0.06

a) 3,3-Dimethyl-1-butene.

TABLE 8. COMPETITIVE BROMINATION OF SUBSTITUTED TOLUENES BY NBS (130 °C)

$YC_6H_4CH_3$ Y=	NBS (mol dm^{-3})	Olefin[a] (mol dm^{-3})	Substrates(mol dm^{-3}) PhCH$_3$	$YC_6H_4CH_3$	Molar ratio $YC_6H_4CH_2Br/PhCH_2Br$	Relative rate const.
p-CH$_3$	0.044	—	1.00	0.390	2.92±0.07	3.75
	0.042	—	1.02	0.320	2.17±0.03	3.45
	0.040	0.039	1.01	0.400	2.61±0.02	3.24
p-Cl	0.042	—	0.435	0.818	1.22±0.01	0.67
	0.039	0.039	0.404	0.806	1.64±0.02	0.82
p-CN	0.023	—	0.214	2.02	0.83±0.03	0.087
	0.022	0.028	0.231	1.89	0.56±0.03	0.069

a) 3,3-Dimethyl-1-butene.

ficulty in chlorine abstraction from the N–Cl bond by the relatively stable benzyl radical. However, when the reaction was carried out at 130 °C using di-*t*-butyl peroxide (DTBP) as a radical generator, toluene was smoothly halogenated by either NCDMO or NBDMO, giving benzyl halides in good yields, as shown in Table 5. Even under these conditions NCS could not chlorinate toluene in an appreciable yield. On the basis of the observations, competitive experiments were conducted with NXDMO and NXO at 130 °C in CH_2Cl_2 solvent using DTBP as an initiator, and relative reactivities of substituted toluenes were compared between bromination and chlorination.

Table 6 shows the results obtained about halogenation by NXDMO. Relative reactivity of each substituted toluene was obtained with satisfactory reproducibility, and the values obtained for chlorination and bromination were coincide with each other. This obviously supports that the reagent attacking benzylic hydrogen in both reactions is the common *N*-radical, and the radical has fairly electron seeking nature ($\rho=-1.0$).

Competitive experiments with NXO gave, however, poorer reproducible results, as shown in Table 7. Although there can be seen the tendencies that the presence of the olefin makes the chlorination with NCO more selective and the bromination with NBO less selective, no numerical coincidence in relative reactivity was obtained between chlorination and bromination. This may arise probably from that both of the Bloomfield and the Goldfinger processes proceed concurrently even in the presence of the olefin. Contrasting with 3-halo-4,4-dimethyl-2-oxazolidinone, 3-halo-2-oxazolidinone, bearing α-hydrogens, is though to take place dehydrohalogenation at higher temperature.[10] Hydrogen halide thus formed will accelarate the Goldfinger process through the reaction with NXO producing halogen molecule. Under the drastic conditions used in this study, therefore, halogen will form too rapidly to be entirely scavenged by the olefin added. Increasing the amount of the olefin might suppress the Goldfinger process. Under these circumstances, however, yield of the benzyl halides became too low for reliable competitive study.

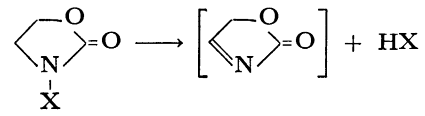


Table 8 shows the results of bromination with NBS in the absence and the presence of the olefin. The reaction constant obtained in the absence of the olefin are derived to be *ca.* -1.8 ($r=0.95$), being somewhat larger negative compared with the values reported so far ($\rho=-1.46$,[4] $\rho^+=-1.38$[6] at 80 °C in CCl_4). This is perhaps due to that a more polar solvent, CH_2Cl_2 was used in this work. The presence of the olefin makes the reaction slightly more electron seeking ($\rho=-1.9$, $r=0.97$). We feel, this reveals the polar selectivity of hydrogen abstraction by the succinimidyl radical, although comparison with chlorination by NCS could not be accomplished owing to the difficulty described above.

Experimental

Materials. NCO and NCDMO were prepared by the modified known method.[24] The precipitated NCO was filtered, dried under reduced pressure, and crystallized from dichloromethane-petroleum ether. Yield 50%, mp 62.5—63.5 °C. The sample in a vacuum sealed tube wrapped with aluminum foil was reserved in a refrigerator. NCDMO was recrystallized from benzene–petroleum ether. Yield, 70%, mp 69—70 °C. NBDMO was prepared by the known method[15] and recrystallized from dichloromethane–petroleum ether. Yield 76%, mp 118—119 °C. NBO was prepared by bromination of 2-oxazolidinone (7 g) with *t*-butyl hypobromite[25] in dichloromethane. The crystal was filtered and recrystallized from dichloromethane–petroleum ether. The sample was reserved in a evacuated tube wrapped with aluminum foil. Yield 50%, mp 115—120 °C (partially decomposed).[15] NCS were prepared by the usual method.[26] NBS was commercially available and purified by recrystallizing from water. All substrates were purified by distilling the commercial materials.

Halogenation of 2,3-Dimethylbutane and 1-Chlorobutane. A solution of an *N*-halo reagent (0.25 mmol), 2,3-dimethylbutane (1.25 mmol), BPO (0.01 mmol), and γ-collidine or 3,3-dimethyl-1-butene (0.25 mmol) in dichloromethane (5 cm^{-3}) was taken in a reaction tube and degassed by successive freezing-thawing processes. The tube was sealed under vacuum, and immersed in a thermostat at 80 °C for 15 h. The products were collected by GLPC, identified spectroscopically and determined by GLPC. All products were well known in the literature.[3-8] The results were summarized in Tables 1—3.

Competitive Halogenation of Substituted Toluenes. In a

5 cm^{-3} graduated flask, an *N*-halo reagent (0.2—0.5 mmol), DTBP (0.2 mmol), 3,3-dimethyl-1-butene (0—0.5 mmol) and precisely weighed toluene (*ca.* 5 mmol) and a substituted toluene were taken, and the mixture was diluted with dichloromethane to 5 cm^{-3}. Then the solution was devided to 3—4 fractions. Each fraction was degassed in a tube, which then was evacuated and sealed. The tube was immersed in a thermostat at 130 °C at 15 h. Molar ratio of halogenated products was determined by GLPC using calibration curves. From the molar ratios of initial concentration of toluenes and final concentration of benzylic halides, relative reactivity of the substituted toluene was calculated. The results were tabulated in Tables 6—8. In the reaction with NXO, the fractions from the same solution did not necessarily give the results in reasonable agreement with each other.

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