NAME ________________________

ID # ________________________

ORGANIC CHEMISTRY I (CHEM 2301)

9:30 – 10:20 am, August 6, 2014

Exam 4

You will be able to pick up your graded exam from Chemistry department staff in 115 Smith beginning Monday, August 12th at 1 PM. Exams that are not picked up within two weeks will be disposed of.

A periodic table and tables of typical NMR chemical shifts, IR frequencies and atomic isotope compositions are attached to the back of this exam as aids. Otherwise, you are not permitted to use any other materials (including notes, books, or electronic devices of any kind).

Right now, write your name and student ID number at the top of this page. When the exam begins, please write your name at the top of the next page.

You may use pen or pencil. However, re-grades will be considered only for exams completed in pen.

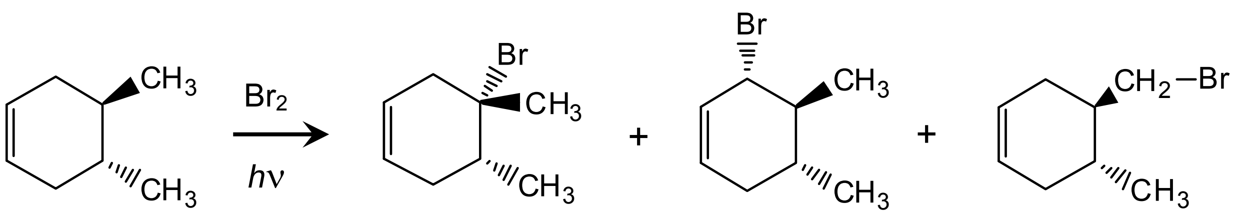
Please write your answers in the boxes/spaces provided. If your answer is not in the appropriate space (say, for example, it's on the back of the page), draw us an arrow and/or note telling us where to look.

NAME ________________________

Scoring: 1. _________ / 35 2. _________ / 65

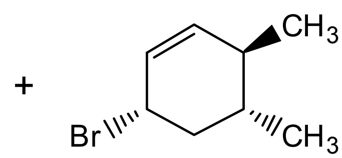
Total Score: _________ / 100

1. (35 pts) When the starting material below is exposed to the conditions of free-radical bromination, four monobrominated products (**A**-**D**) are isolated.



A **B** **C**

a. In the box below, draw a mechanism of **two propagation steps** that explains how product **A** would be made from a combination of starting material, Br_2, and Br• radical. *Because you have been supplied with Br•, you do not need to draw an initiation step.*



D

Mechanism:

b. How would the four molecules **A-D** relate in terms of product ratio? Which product would be most prevalent, and which would be least prevalent? In the boxes below, rank the four molecules (by letter) from highest to lowest product ratio. If any two molecules would be observed at equal ratios, circle the "≈" sign between those two boxes.

highest product ratio [ ] **>** *or* **≈** *(circle one)* [ ] **>** *or* **≈** *(circle one)* [ ] **>** *or* **≈** *(circle one)* [ ] *lowest product ratio*

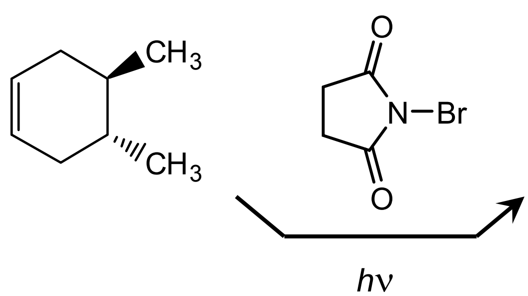
c. The free-radical chain reaction that generates products **A-D** is slowed by termination reactions that remove radicals from the reaction cycle. In the box on the right, draw one termination product that would be observed for the reaction above, *other than* Br_2 *and products* **A-D**. (So, do not draw Br_2 or any of the products **A-D** above as an answer to this part.)

a termination product

d. If the reaction on the previous page were a chlorination instead of a bromination—using Cl_2 instead of Br_2—would your preferred product be made

more selectively , **less selectively** , *or* **with the same selectivity** ?

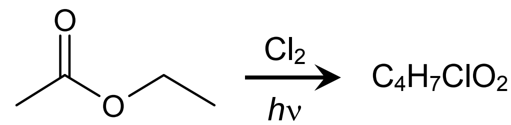
e. If the starting material is halogenated with *N*-bromosuccinimide instead of Br_2, only two of the four products **A-D** would be formed. Which two?



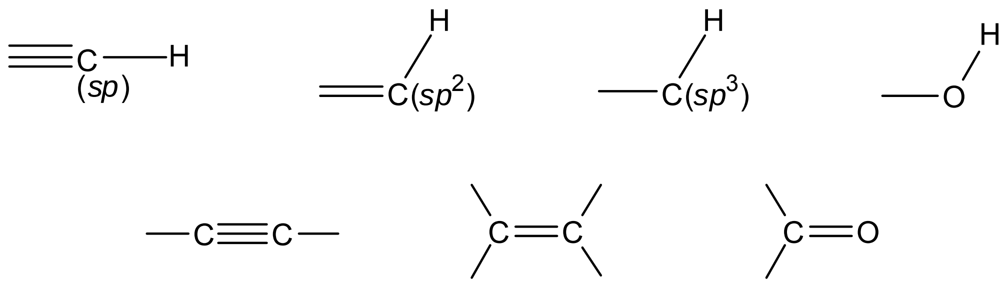
A , **B** , **C** *or* **D**

(Circle two answers.)

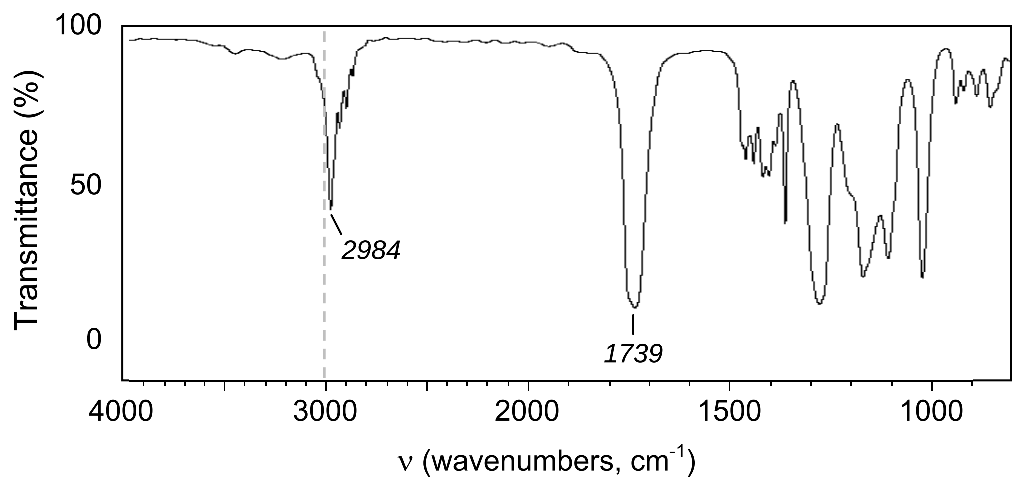
2. (65 pts) Radical chlorination of ethyl acetate ($C_4H_8O_2$, the starting material on the right) gives predominantly one product. This product was isolated and characterized by NMR and IR spectroscopy and mass spectrometry; the spectra of this product are shown on the following pages. High-resolution mass spectrometry determined an exact mass of 122.0135 amu for one of the highest-mass (parent, M^+) peaks in the MS spectrum, which corresponds to a molecular formula of $\mathbf{C_4H_7ClO_2}$.



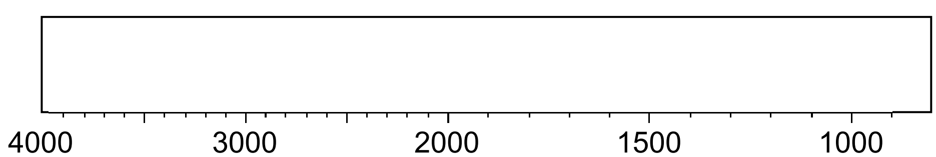
a. Based on the two peaks labeled in the IR spectrum below, what functional groups would you expect the unknown molecule to have? **Circle all answers that apply.**



IR Spectrum:



b. What part of this IR spectrum is the "fingerprint region"? In the box below, color/shade in the range of frequencies that correspond to the "fingerprint region".



c. Compared to NMR, does IR require **MORE** *or* **LESS** material?

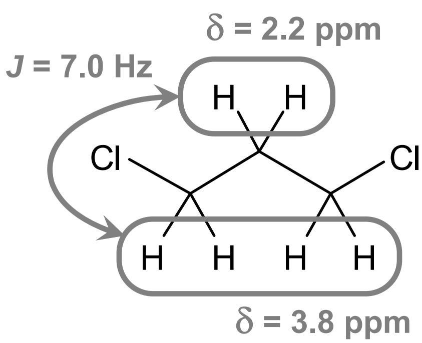
d. Compared to mass spec, does IR require **MORE** *or* **LESS** material?

e. **What is the structure of the product**? In the box below, draw the molecule's structure, <u>including all hydrogens</u>. Then, considering the ^{1}H NMR spectrum below,

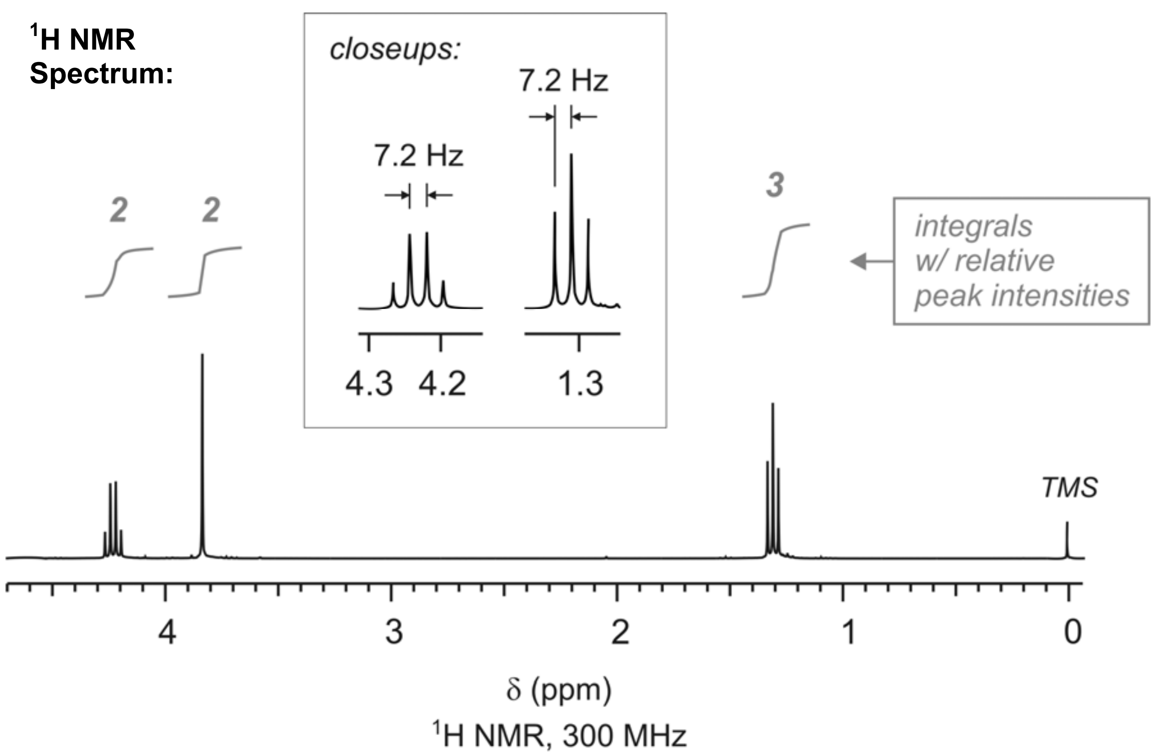
- Circle each group of equivalent H's;
- Assign a ^{1}H chemical shift (δ) to each circled group, within 0.1 ppm;
- Connect any pair of coupled, inequivalent groups of H's with a double-headed arrow, and then label that arrow with the corresponding coupling constant (*J*).

the product
($C_4H_7ClO_2$)

Format for answer to (c):

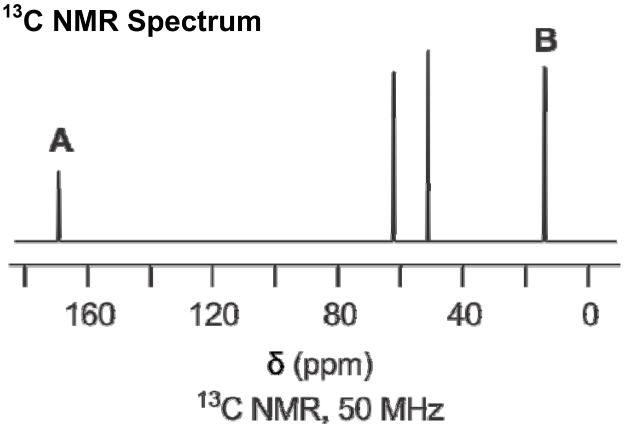


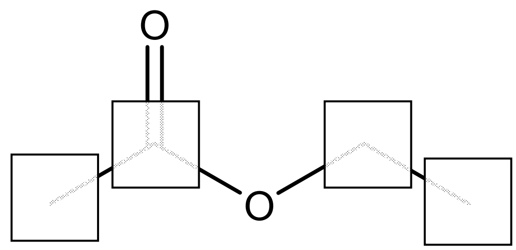
^{1}H NMR Spectrum:



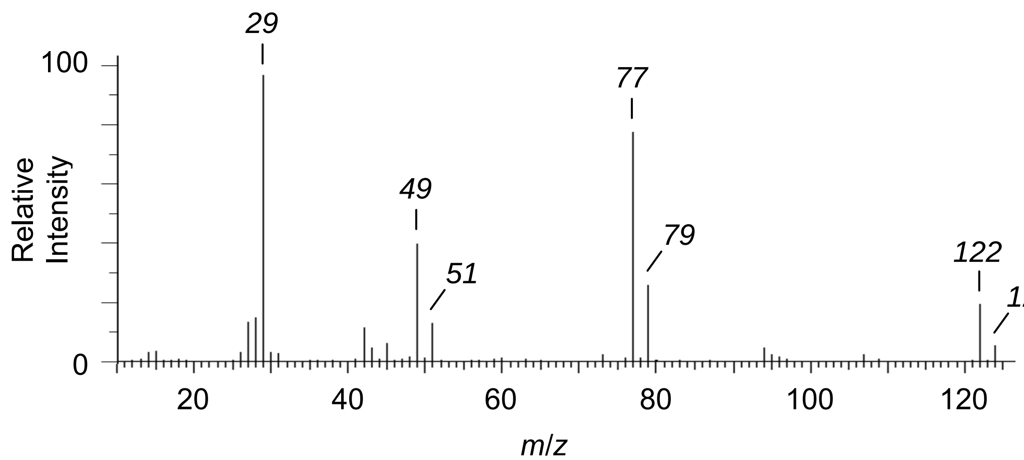
f. The ^{13}C NMR spectrum of the product is shown below, with two peaks labeled **A** and **B**. Which carbons in the product do these peaks correspond to? On the unfinished molecular skeleton on the right, draw the chlorine atom that I've omitted from the product. Then, write the letters "**A**" and "**B**" in the boxes of the carbon atoms that are responsible for the two labeled peaks. *Leave two of the boxes empty.*

^{13}C NMR Spectrum





Mass Spectrum:



g. Some of the peaks in the electron-ionization (EI) mass spectrum (shown above), including the parent peak, are accompanied by a smaller peak that is 2 atomic mass units (amu) higher in mass. (In other words, some peaks with mass *m* are accompanied by another peak, about 1/3 as tall, with mass *m*+2.) Why? *Please be brief; you can probably answer this question in less than 10 words.*

Explain why:

h. The parent mass peak at m/z = 122 corresponds to a radical cation (**M$^{\bullet+}$**) that is generated by removing one electron from the original, neutral molecule **M**. In the box on the right, draw **M$^{\bullet+}$**; re-draw the structure you drew in part (e), but specifically indicate which electron is removed by drawing the molecule with one less electron. *Feel free to omit the hydrogens you drew in part (e).*

M$^{\bullet+}$
($C_4H_7ClO_2^+$)

i. The parent ion fragments to form a daughter ion with m/z = 77. What is the structure of this daughter ion? *You do not need to do electron pushing to answer this part—just draw the cation.*

fragment cation with m/z = 77

j. The parent ion also fragments to form a daughter ion with mass 73 amu (not observed), which then fragments further to give an ion with m/z = 29. In the box below, draw a mechanism (using "arrow pushing") that shows these two sequential fragmentation steps, starting with your answer to part (h).

Mechanism that explains m/z = 29 peak

Summary of IR Stretching Frequencies

Frequency (cm^{-1})	Functional Group		Comments
3300	alcohol	O—H	always broad
	amine, amide	N—H	may be broad, sharp, or broad with spikes
	alkyne	≡C—H	always sharp, usually strong
3000	alkane	—C—H	just below 3000 cm^{-1}
	alkene	=C—H	just above 3000 cm^{-1}
	acid	O—H	very broad
2200	alkyne	—C≡C—	just below 2200 cm^{-1}
	nitrile	—C≡N	just above 2200 cm^{-1}
1710 (very strong)	carbonyl	>C=O	ketones, aldehydes, acids esters higher, about 1735 cm^{-1} conjugation lowers frequency amides lower, about 1650 cm^{-1}
1660	alkene	>C=C<	conjugation lowers frequency aromatic C=C about 1600 cm^{-1}
	imine	>C=N—	stronger than C=C
	amide	>C=O	stronger than C=C (see above)

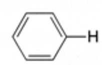
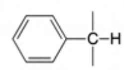
Ethers, esters, and alcohols also show C—O stretching between 1000 and 1200 cm^{-1}.

Isotopic Composition of Some Common Elements

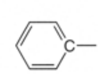
Element	M^+		M+1		M+2	
hydrogen	^{1}H	100.0%				
carbon	^{12}C	98.9%	^{13}C	1.1%		
nitrogen	^{14}N	99.6%	^{15}N	0.4%		
oxygen	^{16}O	99.8%			^{18}O	0.2%
sulfur	^{32}S	95.0%	^{33}S	0.8%	^{34}S	4.2%
chlorine	^{35}Cl	75.5%			^{37}Cl	24.5%
bromine	^{79}Br	50.5%			^{81}Br	49.5%
iodine	^{127}I	100.0%				

^{1}H NMR Absorptions

Compound type		Chemical shift (ppm)
Alcohol		
R–O–H		1–5
R–C(H)–O–		3.4–4.0
Aldehyde		
R–C(=O)–H		9–10
Alkane		0.9–2.0
RCH_3		~0.9
R_2CH_2		~1.3
R_3CH		~1.7
Alkene		
C=C–H	*sp*^{2} C–H	4.5–6.0
C=C–C–H	allylic *sp*^{3} C–H	1.5–2.5
Alkyl halide		
R–C(H)–F		4.0–4.5
R–C(H)–Cl		3.0–4.0
R–C(H)–Br		2.7–4.0
R–C(H)–I		2.2–4.0
Alkyne		
–C≡C–H		~2.5

Compound type		Chemical shift (ppm)
Amide		
R–C(=O)–N–H		7.5–8.5
Amine		
R–N–H		0.5–5.0
R–C(H)–N–		2.3–3.0
Aromatic compound		
	*sp*^{2} C–H	6.5–8
	benzylic *sp*^{3} C–H	1.5–2.5
Carbonyl compound		
–C(=O)–C–H	*sp*^{3} C–H on the α carbon	2.0–2.5
Carboxylic acid		
R–C(=O)–OH		10–12
Ether		
R–C(H)–O–R		3.4–4.0

^{13}C NMR Absorptions

Carbon type	Structure	Chemical shift (ppm)
Alkyl, *sp*^{3} hybridized C	–C–H	5–45
Alkyl, *sp*^{3} hybridized C bonded to N, O, or X	–C–Z Z = N, O, X	30–80
Alkynyl, *sp* hybridized C	–C≡C–	65–100
Alkenyl, *sp*^{2} hybridized C	C=C	100–140
Aryl, *sp*^{2} hybridized C		120–150
Carbonyl C	C=O	160–210

Chemistry Reference Sheet

Key

11 — Atomic number
Na — Element symbol
Sodium — Element name
22.99 — Average atomic mass*

Period	1 1A	2 2A	3 3B	4 4B	5 5B	6 6B	7 7B	8 8B	9 8B	10 8B	11 1B	12 2B	13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
1	1 **H** Hydrogen 1.01																	2 **He** Helium 4.00
2	3 **Li** Lithium 6.94	4 **Be** Beryllium 9.01											5 **B** Boron 10.81	6 **C** Carbon 12.01	7 **N** Nitrogen 14.01	8 **O** Oxygen 16.00	9 **F** Fluorine 19.00	10 **Ne** Neon 20.18
3	11 **Na** Sodium 22.99	12 **Mg** Magnesium 24.31											13 **Al** Aluminum 26.98	14 **Si** Silicon 28.09	15 **P** Phosphorus 30.97	16 **S** Sulfur 32.07	17 **Cl** Chlorine 35.45	18 **Ar** Argon 39.95
4	19 **K** Potassium 39.10	20 **Ca** Calcium 40.08	21 **Sc** Scandium 44.96	22 **Ti** Titanium 47.87	23 **V** Vanadium 50.94	24 **Cr** Chromium 52.00	25 **Mn** Manganese 54.94	26 **Fe** Iron 55.85	27 **Co** Cobalt 58.93	28 **Ni** Nickel 58.69	29 **Cu** Copper 63.55	30 **Zn** Zinc 65.39	31 **Ga** Gallium 69.72	32 **Ge** Germanium 72.61	33 **As** Arsenic 74.92	34 **Se** Selenium 78.96	35 **Br** Bromine 79.90	36 **Kr** Krypton 83.80
5	37 **Rb** Rubidium 85.47	38 **Sr** Strontium 87.62	39 **Y** Yttrium 88.91	40 **Zr** Zirconium 91.22	41 **Nb** Niobium 92.91	42 **Mo** Molybdenum 95.94	43 **Tc** Technetium (98)	44 **Ru** Ruthenium 101.07	45 **Rh** Rhodium 102.91	46 **Pd** Palladium 106.42	47 **Ag** Silver 107.87	48 **Cd** Cadmium 112.41	49 **In** Indium 114.82	50 **Sn** Tin 118.71	51 **Sb** Antimony 121.76	52 **Te** Tellurium 127.60	53 **I** Iodine 126.90	54 **Xe** Xenon 131.29
6	55 **Cs** Cesium 132.91	56 **Ba** Barium 137.33	57 **La** Lanthanum 138.91	72 **Hf** Hafnium 178.49	73 **Ta** Tantalum 180.95	74 **W** Tungsten 183.84	75 **Re** Rhenium 186.21	76 **Os** Osmium 190.23	77 **Ir** Iridium 192.22	78 **Pt** Platinum 195.08	79 **Au** Gold 196.97	80 **Hg** Mercury 200.59	81 **Tl** Thallium 204.38	82 **Pb** Lead 207.2	83 **Bi** Bismuth 208.98	84 **Po** Polonium (209)	85 **At** Astatine (210)	86 **Rn** Radon (222)
7	87 **Fr** Francium (223)	88 **Ra** Radium (226)	89 **Ac** Actinium (227)	104 **Rf** Rutherfordium (261)	105 **Db** Dubnium (262)	106 **Sg** Seaborgium (266)	107 **Bh** Bohrium (264)	108 **Hs** Hassium (269)	109 **Mt** Meitnerium (268)									

58 **Ce** Cerium 140.12	59 **Pr** Praseodymium 140.91	60 **Nd** Neodymium 144.24	61 **Pm** Promethium (145)	62 **Sm** Samarium 150.36	63 **Eu** Europium 151.96	64 **Gd** Gadolinium 157.25	65 **Tb** Terbium 158.93	66 **Dy** Dysprosium 162.50	67 **Ho** Holmium 164.93	68 **Er** Erbium 167.26	69 **Tm** Thulium 168.93	70 **Yb** Ytterbium 173.04	71 **Lu** Lutetium 174.97
90 **Th** Thorium 232.04	91 **Pa** Protactinium 231.04	92 **U** Uranium 238.03	93 **Np** Neptunium (237)	94 **Pu** Plutonium (244)	95 **Am** Americium (243)	96 **Cm** Curium (247)	97 **Bk** Berkelium (247)	98 **Cf** Californium (251)	99 **Es** Einsteinium (252)	100 **Fm** Fermium (257)	101 **Md** Mendelevium (258)	102 **No** Nobelium (259)	103 **Lr** Lawrencium (262)

* If this number is in parentheses, then it refers to the atomic mass of the most stable isotope.

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