Organic Reaction Mechanisms-III

Exercise-1

> Marked questions are recommended for Revision.

PART - I : SUBJECTIVE QUESTIONS

Section (A) : Unimolecular nucleophilic substitution reaction (S_N1)

- A-1. Which compound in the following couples will react faster in S_N1 reaction and why ? (a) 1-Bromopentane or 2-Bromopentane
 - (b) 1-Bromo-2-methylbutane or 2-Bromo-2 methylbutane.
- A-2. What effect do you expect due to following changes in S_N1 reaction of (CH₃)₃CBr with CH₃OH ?
 (a) The concentration of (CH₃)₃CBr is doubled and that of CH₃OH is halved.
 (b) The concentration of both (CH₃)₃CBr and CH₃OH are tripled.
- A-3. Why 3-Chlorocyclopropene is solvolyzed in methanol at much higher rate than 5-Chlorocyclopenta-1,3diene ?

(b)

(d)

CH₃ I

aq. AgNO3

A-4.^> For each of the following solvolysis reaction give the products (major as well as minor)



A-5. Write the mechanism of the following reaction and mention the rate determining step.

(a)
$$CH_3-CH-CH_2-CH_3 \xrightarrow{HBr} CH_3-C-C-CH_2-CH_3$$
 (b) $HI \xrightarrow{HI} CH_3 \xrightarrow{HI} HI$

Section (B) : Bimolecular nucleophilic substitution reaction (S_N2 & S_Ni)

- B-1.★ Arrange the compounds of each set in order of decreasing reactivity towards S_N2 displacement. (a) 2-Bromo-2-methylbutane, 1-Bromopentane, 2-Bromopentane (b) 1-Bromo-3-methylbutane, 2-Bromo-2-methylbutane, 2-Bromo-3-methylbutane
- B-2. Which reacts faster (a) PhCH₂Br or PhCMe₂Br (H₂O / C₂H₅OH) (b) PhCH₂CH₂Br or PhCMe₂Br (NaI / Acetone)

B-3.2 Work out the stereochemistry of following reaction

$$C_2H_3$$
 C_2H_3 C

B-4. What will be the major product of the following reaction ?

(a)
$$CH_3 - CH - CH - CH_3 - \xrightarrow{PC_5} OH$$

(b)









Organic Reaction Mechanisms-III Section (D) : Nucleophilic substitution reaction of Ethers & Epoxides In the given reaction, CH₃–CH₂–CH₂–CH₂–CH₃ $\xrightarrow{\text{HCI}/\Delta}$ [X] + [Y] D-1. [X] and [Y] respectively will be : (A) $CH_3-CH_2-CH_2OH \& CH_3-CH_2-CI$ (C) $CH_3-CH_2-CH_2-CI \& CH_2=CH_2$ (B) CH₃–CH₂–CH₂–CI & CH₃–CH₂–OH (D) CH₃–CH=CH₂ & CH₂=CH₂ H₃0[⊕] D-2.2 The products X and Y are ОН ĎН ОН ОН HBr D-3.3a. Ph-(Q) Alkyl balide ; (P) & (Q) respectively is : – CH. (P) 0 (A) Ph -- OH, CH₃–Br (B) Ph-CH2-OH, CH3-CH2-Br Ċн (C) CH₃-OH, Ph ---CH - CH₃ (D) CH₃-OH, Ph-CH₃-CH₂-Br . Br $(i) Et_2O \rightarrow ;$ D-4. CH₃ - CH - CH₂+ (CH₃)₂CHMgBr -What will be the product : (ii) H₂O (A) CH₃-(CH₂)₄-CH₂-OH (B) $CH_3 - CH = CH - CH - CH_3$ с́н₃ (C) $CH_3 - CH - CH_2 - CH_3$ (D) $CH_3 - CH - CH_2 - CH_3$ L CH(CH₃)₂ òн PART - III : MATCH THE COLUMN 1.2 Match List-I (Alkyl chloride) with List-II (Rates of solvolysis) and select the correct answer using the code given below the lists : List-I List-II (P) (1) 1 °CI 0.07 (Q) (2) CI (R) (3) 7700 CI (S) (4) 91 Ph CI Codes :

(A) P-2; Q-1; R-4; S-3 (B) P-2; Q-1; R-3; S-4 (C) P-1; Q-2; R-3; S-4 (D) P-1; Q-2; R-4; S-3















iprene	nsion # 3	h., onnrom	vistaly motohing the informatio		in the three columns		
of	the following table.	by approp		n given	in the three columns		
Co	umns 1,2 and 3 contain	reactants,	reagents & products respectively		Calumn 2		
	Column-1		Column-2		Column-3		
(I)	Ph-CH2-CH2-Br	(i)	NaOH/H2O	(P)	Ph–CH–CH ₃ OH (±)		
(11)	CH ₃ HBr Ph	(ii)	HI, H ₂ O/acetone	(Q)	HO-HH Ph		
(111)	H-HOH Ph	(iii)	NaOH/DMSO	(R)	Ph-CH2-CH2-OH		
(IV) Ph-CH2-CH2-OH	(iv)	SOCI ₂ /Pyridine, (NaOH/DMF)	(S)	H H Ph		
S _N (A)	I + S _N 2 mixed mechanis (I), (iii) (P) (E	m is obser) (II) (i) (P)	ved in the reaction : (C) (III) (iv) (Q)	(D) (I\	√) (ii) (S)		
On (A)	ly $S_N 1$ mechanism is obs (I), (i) (R) (B)	served in :) (II) (iii) (P) (C) (IV) (ii) (S)	(D) (II	I) (ii) (P)		
S _N 2 (A)	2 mechanism is observe (I), (iii) (R) (B)	d in :) (IV) (iv) (I	R) (C) (II) (iii) (Q)	(D) al	I		
	xercise-3						
rked c	uestions may have mo	ore than o	ne correct option.				
PART	⁻ - I : JEE (ADVA	NCED)	/ IIT-JEE PROBLEMS (PRE\	/IOUS YEARS)		
An (A) (C)	S _N 2 reaction at an asym an enantiomer of the su a mixture of diastereom	nmetric car Ibstrate Iers	bon of a compound always gives (B) a product with opp (D) a single stereoisor	: [osite op ner	IIT-JEE-2001(S), 1/13		
Th (A)	The compound that will react most readily with NaOH to form methanol is : [IIT-JEE-2001(S), 1/1: (A) $(CH_3)_4N^+I^-$ (B) CH_3OCH_3 (C) $(CH_3)_3S^+I^-$ (D) $(CH_3)_3C-CI$						
. ,	clobutyl bromide on tre anometallic (A) reacts atment of alcohol (B) w	eatment w with etha ith an equ (B) and ex	ith magnesium in dry ether for nal to give an alcohol (B) afte ivalent amount of HBr gives1-br plain how (C) is obtained from (B)	ms an r mild a omo-1-n . [II	organometallic (A). The acidification. Prolonge the acidification. Prolonge (Contention) (Conten		
Cy org trea Wr	ite the structures of (A),						
Cy org trea Wr	ite the structures of (A), ntify X, Y and Z in the fo	llowing sy	nthetic scheme and write their stru	ictures.			
Cy org trea Wr Ide CH	ite the structures of (A), ntify X, Y and Z in the fo $_{3}CH_{2}C\equiv C-H \xrightarrow{(i) NaNH_{2}}{(ii) CH_{3}CH_{2}B}$	$\xrightarrow{H_2}{H_2} X \xrightarrow{H_2}{H_2}$	$\xrightarrow{\text{/Pd.BaSO}_4} Y \xrightarrow{\text{alkaline KMnO}_4} Z$	ictures.			





















CH₃CH(OH)CH A-2. A-7. B-4. B-9. C-4. 2. 2. 7. 12.	H ₂ OH (B) (D) (A) (B) (A) → q,s; (C) (A) (C)	PAF A-3. A-8. B-5. B-10. D-1. D-1. PAF (B) → r ; (C EXER(PAI 3. 8	(ii) $Y = CH_3$ RT - II (B) (C) (B) (B) (A) RT - III C) $\rightarrow p$; (D) \rightarrow CISE - 2 RT - I (B)	CH(OH)C⊢ A-4. B-1. B-6. C-1. D-2. → r	(A) (B) (B) (C) (B)	A-5. B-2. B-7. C-2. D-3.	(D) (B) (C) (C)
A-2. A-7. B-4. B-9. C-4. 2. 2. 2. 7. 12.	(B) (B) (D) (A) (B) (A) $\rightarrow q,s;$ (C) (A) (C)	PAF A-3. A-8. B-5. B-10. D-1. D-1. (B) → r; ((EXER(PAI 3. 8	RT - II (B) (C) (B) (A) RT - III C) $\rightarrow p$; (D) \rightarrow CISE - 2 RT - I (B)	A-4. B-1. B-6. C-1. D-2.	(A) (B) (C) (B)	A-5. B-2. B-7. C-2. D-3.	(D) (B) (C) (C)
A-2. A-7. B-4. B-9. C-4. 2. 2. 7. 12.	(B) (B) (D) (A) (B) (A) $\rightarrow q,s;$ (C) (A) (C)	A-3. A-8. B-5. D-1. D-1. (B) → r; ((EXER(PAI 3. 8	(B) (C) (B) (A) (A) RT - III $C) \rightarrow p; (D) \rightarrow CISE - 2$ RT - I (B)	A-4. B-1. B-6. C-1. D-2.	(A) (B) (C) (B)	A-5. B-2. B-7. C-2. D-3.	(D) (B) (C) (C)
A-7. B-4. B-9. C-4. 2. 2. 7. 12.	(B) (D) (A) (B) (A) $\rightarrow q,s$; (C) (A) (C)	A-8. B-5. B-10. D-1. PAR (B) → r ; ((EXER(PAI 3. 8	(C) (B) (B) (A) RT - III C) $\rightarrow p$; (D) \rightarrow CISE - 2 RT - I (B)	B-1. B-6. C-1. D-2.	(B) (B) (C) (B)	B-2. B-7. C-2. D-3.	(B) (B) (C) (C)
B-4. B-9. C-4. 2. 2. 7. 12.	(D) (A) (B) (A) \rightarrow q,s ; (C) (A) (C)	B-5. B-10. D-1. (B) → r ; (C EXER(PAI 3. 8	(B) (B) (A) RT – III C) $\rightarrow p$; (D) \rightarrow CISE – 2 RT – I (B)	B-6. C-1. D-2.	(B) (C) (B)	B-7. C-2. D-3.	(B) (C) (C)
B-9. C-4. 2. 2. 7. 12.	(A) (B) (A) \rightarrow q,s ; (C) (A) (C)	B-10. D-1. (B) → r ; (0 EXER(PAI 3. 8	(B) (A) RT - III C) $\rightarrow p$; (D) \rightarrow CISE - 2 RT - I (B)	C-1. D-2.	(C) (B)	C-2. D-3.	(C) (C)
C-4. 2. 2. 7. 12.	(B) (A) \rightarrow q,s; (C) (A) (C)	D-1. PAF (B) → r ; ((EXER(PAI 3. 8	(A) RT – III C) \rightarrow p; (D) \rightarrow CISE – 2 RT – I (B)	D-2.	(B)	D-3.	(C)
2. 2. 7. 12.	$(A) \rightarrow q, s;$ (C) (A) (C)	PAF (B) → r ; (0 EXER(PAI 3. 8	RT – III C) → p ; (D) → CISE – 2 RT – I (B)	→r			
2. 2. 7. 12.	$(A) \rightarrow q,s$; (C) (A) (C)	PAF (B) → r ; (0 EXER(PAI 3. 8	RT – III C) → p ; (D) → CISE – 2 RT – I (B)	→ r			
2. 2. 7. 12.	$(A) \rightarrow q,s;$ (C) (A) (C)	(B) → r ; (C EXER(PAI 3. 8	C) → p ; (D) → CISE - 2 RT - I (B)	→r			
2. 7. 12.	(C) (A) (C)	EXER(PAI 3. 8	CISE – 2 RT – I (B)				
2. 7. 12.	(C) (A) (C)	PA 3. 8	RT – I (B)				
2. 7. 12.	(C) (A) (C)	3. 8	(B)				
7. 12.	(A) (C)	8		4.	(D)	5.	(D)
12.	(C)	υ.	(C)	9.	(B)	10.	(A)
		PAF	RT – II				
2.	15	3.	3	4.	5 (Except (ii))		
ept (i, iv))		6.	22	7.	2	8.	4
		PAF	RT – III				
2.	(AB)	3.	(AC)	4.	(AB)	5.	(AB
) 7.	(BC)	8.	(CD)	9.	(ABC)	10.	(AB
		PAR	RT – IV				
2.	(C)	3.	(B)	4.	(C)	5.	(B)
7.	(D)	8.	(D)				
		EXER	CISE – 3				
		PA	RT – I				
2.	(C)						
	CH₃,		Brs	CH.			
			\sim				
Mg	IBr H-		()	<u>۱</u>			
	2.) 7. 2. 7. 2.	2. (AB)) 7. (BC) 2. (C) 7. (D) 2. (C) CH₅	PAF 2. (AB) 3.) 7. (BC) 8. PAF 2. (C) 3. 7. (D) 8. EXER(PA 2. (C) 7. PA 2. (C) 8. CH ₃ C - OH	PART - III 2. (AB) 3. (AC) 7. (BC) 8. (CD) PART - IV 2. (C) 3. (B) 7. (D) 8. (D) EXERCISE - 3 PART - I 2. (C) CH ₃ C - OH Br	PART – III 2. (AB) 3. (AC) 4.) 7. (BC) 8. (CD) 9. PART – IV 2. (C) 3. (B) 4. 7. (D) 8. (D) 9. EXERCISE – 3 PART – I 2. (C) CH ₃ MoBr	PART – III 2. (AB) 3. (AC) 4. (AB)) 7. (BC) 8. (CD) 9. (ABC) PART – IV 2. (C) 3. (B) 4. (C) 7. (D) 8. (D) EXERCISE – 3 PART – I 2. (C) $CH_{3} - OH Br CH_{3}$	PART – III 2. (AB) 3. (AC) 4. (AB) 5. 7. (BC) 8. (CD) 9. (ABC) 10. PART – IV 2. (C) 3. (B) 4. (C) 5. 7. (D) 8. (D) 5. 5. EXERCISE – 3 PART – I 2. (C) CH ₃ C – OH Br CH ₃

•	СН	3–CH2–C≡	CH (i) NaNH (- NH ₃)	¹ ₂→ CH₃–Cŀ	H₂–C≡CNa ⁻	(ii) CH ₃ CH ₂ Br (- NaBr)	7		
	$CH_3 - CH_2$	-C=C-(H H	CH ₂ – CH ₃ ∢	H₂ / Pd. Partial hydi	.BaSO₄ rogenation	— CH3–CH2-	↓ -C≡ C.CH ₂ - (Compour	-CH ₃ nd 'X)	
	y = 0	515 - nex - 3	o – ene	0	НОН				
		H ₂ O + [(with alkaline (Hydroxylat	<mark>O]</mark> ∋ KMnO₄ ➤ CH ion)	 	 -C-CH ₂ - 	CH3			
.	(B)								
							€		
i .	7-bromo-1,	3,5-cycloh	eptatriene o	n ionisation	gives tropy	lium ion	which	is aromatic ⊕	& higl
	stable, but i	ionisation o	of 5-bromo-1	, 3-cyclopen	itadiene give	es 1, 3-cyclop	pentadienyl	cation	which
	anti aromat	ic & unstal	ole. (Non exi	istent)					
7.	anti aromat (A)	ic & unstal	ole. (Non exi	istent)					
7. 3.	anti aromat (A) (A) In 1st S (B) 1st can (C) 2nd pro (D) –NO ₂ is	ic & unstal N ¹ reaction give SN ² A duct has to metadired	ble. (Non exi n is possible Ar but 2nd ca wo antiaroma ting but –N=	so by-produ an not give b atic rings but =O group is c	ct is HBr in : ecause –m t 1st does no ortho-para di	2nd SN ¹ read of –NO ₂ is no ot have antial irecting due t	ction is not p ot opperating romatic syst to +m of –N=	ossible. յ. em. ₌O.	
7. 3. 9.	anti aromat (A) (A) In 1st S (B) 1st can (C) 2nd pro (D) –NO ₂ is (A)	ic & unstal N ¹ reaction give SN ² A duct has to metadirec 10.	ble. (Non exi n is possible Ar but 2nd ca wo antiaroma xting but –N= (D)	stent) so by-produ an not give b atic rings but -O group is c 11.	ct is HBr in t ecause –m t 1st does no ortho-para di (D)	2nd SN ¹ read of –NO₂ is no ot have antia irecting due t 12.	ction is not p ot opperating romatic syst to +m of –N= (A)	ossible. j. em. =O. 13.	(B)
7. 3. 9. 14.	anti aromat (A) (A) In 1st S (B) 1st can (C) 2nd pro (D) –NO ₂ is (A) (D)	ic & unstal N ¹ reactior give SN ² / duct has to metadirec 10. 15.	ole. (Non exi h is possible Ar but 2nd ca wo antiaroma ting but –N= (D) (C)	so by-produ an not give b atic rings but O group is c 11. 16.	ct is HBr in : ecause –m ; t 1st does no ortho-para di (D) (A)	2nd SN ¹ read of –NO ₂ is no ot have antia irecting due t 12. 17.	ction is not p ot opperating romatic syst to +m of –N= (A) (C)	ossible. g. em. =O. 13. 18.	(B) (C)
7. 3. 9. 14. 19.	anti aromat (A) (A) In 1st S (B) 1st can (C) 2nd pro (D) –NO ₂ is (A) (D) (ACD)	ic & unstal N ¹ reaction give SN ² / duct has th metadirec 10. 15. 20.	ole. (Non exi n is possible Ar but 2nd ca wo antiaroma tring but –N= (D) (C) (B)	so by-produ an not give b atic rings but O group is c 11. 16.	ct is HBr in a ecause – m i 1st does no ortho-para di (D) (A)	2nd SN ¹ read of –NO ₂ is no ot have antial irecting due t 12. 17.	ction is not p to opperating romatic syst o +m of –N= (A) (C)	ossible. j. em. =O. 13. 18.	(B) (C)
7. 3. 9. 14. 19.	anti aromat (A) (A) In 1st S (B) 1st can (C) 2nd pro (D) –NO ₂ is (A) (D) (ACD)	ic & unstal N ¹ reaction give SN ² / duct has tr metadirec 10. 15. 20.	n is possible Ar but 2nd ca wo antiaroma ting but –N= (D) (C) (B)	so by-produ an not give b atic rings but -O group is c 11. 16. PAI	ct is HBr in : ecause – m i 1st does no ortho-para di (D) (A) RT – II	2nd SN ¹ read of –NO ₂ is no thave antia irecting due t 12. 17.	ction is not p ot opperating romatic syst to +m of –N= (A) (C)	ossible. J. em. -O. 13. 18.	(B) (C)
7. 3.). 14. 19.	anti aromat (A) (A) In 1st S (B) 1st can (C) 2nd pro (D) –NO ₂ is (A) (D) (ACD)	ic & unstal N ¹ reaction give SN ² / duct has th metadirec 10. 15. 20.	n is possible Ar but 2nd ca wo antiaroma ting but –N= (D) (C) (B) JEE	so by-produ an not give b atic rings but -O group is c 11. 16. PAI	ct is HBr in : ecause – m t 1st does no ortho-para di (D) (A) RT – II FLINE PROI	2nd SN ¹ read of –NO ₂ is no ot have antial recting due t 12. 17. BLEMS	ction is not p pot opperating romatic syst o +m of –N= (A) (C)	ossible. J. em. :-O. 13. 18.	(B) (C)
7. 3. 14. 19.	anti aromat (A) (A) In 1st S (B) 1st can (C) 2nd pro (D)NO ₂ is (A) (D) (ACD) (1)	ic & unstat N ¹ reaction give SN ² / duct has th metadirec 10. 15. 20. 2. 2. 7.	n is possible Ar but 2nd ca wo antiaroma ting but –N= (D) (C) (B) JEE (2) (2)	stent) so by-produ an not give b atic rings but =O group is c 11. 16. PAI <u>E(MAIN) OFF</u> 3. 8	ct is HBr in : ecause – m i 1st does no rtho-para di (D) (A) RT – II FLINE PROI (1) (3)	2nd SN ¹ read of –NO ₂ is no ot have antial irecting due t 12. 17. BLEMS 4. 9.	ction is not p ot opperating romatic syst io +m of –N= (A) (C) (1) (1)	ossible. em. eO. 13. 18. 5. 10.	(B) (C) (3)
7. 3. 14. 19.	anti aromat (A) (A) In 1st S (B) 1st can (C) 2nd pro (D) -NO ₂ is (A) (D) (ACD) (1) (1)	ic & unstal N ¹ reaction give SN ² / duct has tw metadirec 10. 15. 20. 2. 7. 12.	n is possible Ar but 2nd ca wo antiaroma ting but –N= (D) (C) (B) <u>JEE</u> (2) (2) (3)	so by-produ an not give b atic rings but -O group is c 11. 16. PAI <u>E(MAIN) OFF</u> 3. 8. 13.	ct is HBr in i ecause – m i 1st does no ortho-para di (D) (A) RT – II FLINE PROI (1) (3) (2)	2nd SN ¹ read of –NO ₂ is no ot have antial irecting due t 12. 17. BLEMS 4. 9. 14.	ction is not p to opperating romatic syst o +m of –N= (A) (C) (1) (3) (2)	ossible. em. 13. 18. 5. 10. 15.	(B) (C) (3) (2) (4)
7. 3. 14. 19. 1. 1. 5. 11.	anti aromat (A) (A) In 1st S (B) 1st can (C) 2nd pro (D)NO ₂ is (A) (D) (ACD) (1) (1) (1) (1)	ic & unstat N ¹ reaction give SN ² / duct has th metadirec 10. 15. 20. 2. 7. 12. 12. 17.	n is possible Ar but 2nd ca wo antiaroma ting but –N= (D) (C) (B) JEE (2) (2) (2) (3) (1)	stent) so by-produ an not give b atic rings but =O group is c 11. 16. PAI <u>E(MAIN) OFF</u> 3. 8. 13. 18.	ct is HBr in : ecause – m i 1st does no ortho-para di (D) (A) RT – II FLINE PROI (1) (3) (2) (2)	2nd SN ¹ read of –NO ₂ is no thave antial irecting due t 12. 17. BLEMS 4. 9. 14.	ction is not p to opperating romatic syst (A) (C) (1) (3) (2)	ossible. em. 13. 18. 5. 10. 15.	(B) (C) (3) (2) (4)
7. 3. 14. 19. 1. 6. 11.	anti aromat (A) (A) In 1st S (B) 1st can (C) 2nd pro (D)NO ₂ is (A) (D) (ACD) (1) (1) (1) (1)	ic & unstal N ¹ reaction give SN ² / duct has th metadirect 10. 15. 20. 2. 7. 12. 17.	n is possible Ar but 2nd ca wo antiaroma iting but –N= (D) (C) (B) (B) (2) (2) (2) (3) (1) JEI	stent) so by-produ an not give b atic rings but =O group is c 11. 16. PAI <u>E(MAIN) OFF</u> 3. 8. 13. 18. E(MAIN) ON	ct is HBr in : ecause – m t 1st does no ortho-para di (D) (A) RT – II FLINE PROI (1) (3) (2) (2) LINE PROE	2nd SN ¹ read of –NO ₂ is no ot have antial recting due t 12. 17. BLEMS 4. 9. 14. BLEMS	ction is not p pot opperating romatic syst o +m of –N= (A) (C) (1) (3) (2)	ossible. j. em. :-O. 13. 18. 5. 10. 15.	(B) (C) (3) (2) (4)
7. 8. 9. 14. 19. 1. 6. 11. 16.	anti aromat (A) (A) In 1st S (B) 1st can (C) 2nd pro (D)NO ₂ is (A) (D) (ACD) (1) (1) (1) (1) (2)	ic & unstal N ¹ reaction give SN ² / duct has th metadirec 10. 15. 20. 2. 7. 12. 17. 22.	n is possible Ar but 2nd ca wo antiaroma ting but –N= (D) (C) (B) JEE (2) (2) (2) (3) (1) JEI (3)	stent) so by-produ an not give b atic rings but O group is c 11. 16. PAI <u>E(MAIN) OFF</u> 3. 8. 13. 18. E(MAIN) ON 3.	ct is HBr in : ecause – m i 1st does no ortho-para di (D) (A) RT – II FLINE PROI (1) (3) (2) (2) LINE PROE (4)	2nd SN ¹ read of –NO ₂ is no ot have antial irecting due t 12. 17. BLEMS 4. 9. 14. BLEMS 4.	ction is not p to opperating romatic syst o +m of –N= (A) (C) (1) (3) (2) (2)	ossible. em. 13. 18. 5. 10. 15. 5.	(B) (C) (3) (2) (4) (4)
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