

TABLE II. CARBANIONS DERIVED FROM KETONES
A. Enolate from Acetone

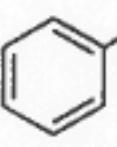
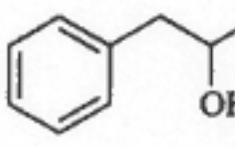
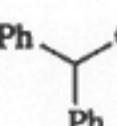
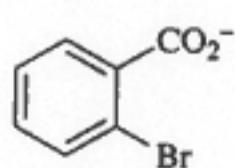
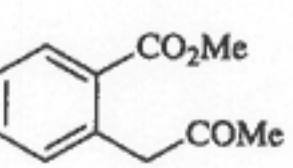
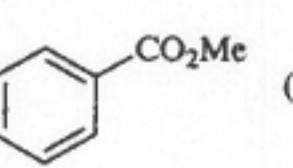
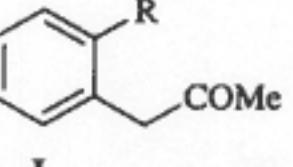
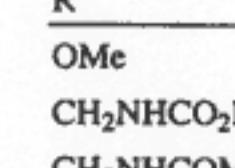
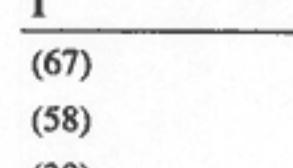
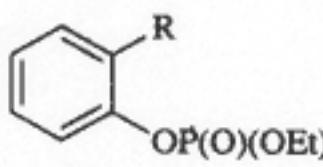
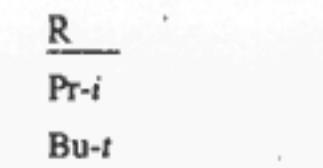
Substrate	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
PhF	$\text{^tCH}_2\text{COMe}$	K, NH_3 , -78°	 I (3) +  II (46)	94
		$h\nu$, NH_3 , 3.3 h	I (60) + C_6H_6 III (31)	136
PhCl	1. K, NH_3 , -78° 2. [O]		I (68)	94
		$h\nu$, NH_3 , 3 h	I (61) + III (31) +  IV (5)	136
PhBr	K, NH_3 , -78°		I (67) + II (10) + IV (14)	94
		$h\nu$, NH_3 , 11 min	I (85) + IV (14)	136
	$h\nu$, NH_3 : Et_2O 1:1, 0.5 h		I (41) + III (13)	108
PhI	1. K, NH_3 , -78° 2. [O]		I (61) + IV (6)	108
		$h\nu$, NH_3 , 5 min	I (71)	94
	$h\nu$, DMSO, 1 h		I (67) + III (20) + IV (10)	136
PhOPh	$h\nu$, DMSO, 1 h		I (88) + IV (4)	138, 340, 41
		DMSO, 1 h	I (50)	62
	FeCl ₂ , DMSO, 10 min		I (60)	75
PhOPh	K, NH_3 , -78°		II (5)	94
	$h\nu$, NH_3 , 4.2 h		I (14) + PhOH (20)	136
PhOP(O)(OEt) ₂	K, NH_3		I (5) + II (56) + III (27)	108, 94
		$h\nu$, NH_3 , 4.2 h	I (13) + III (11) + PhOH (71)	136
PhSPh	K, NH_3 , -78°		I (18) + II (71) + PhSH (84)	94
		$h\nu$, NH_3 , 0.5 h	I (66) + III (26) + IV (5) + PhSH (97)	136
Ph ₃ S ⁺ Cl ⁻	$h\nu$, NH_3 , 1.2 h		I (75) + PhSH (52) + Ph ₂ S (22)	136
PhSePh	$h\nu$, NH_3 , 3.3 h		I (95) + PhSeH (83)	136
PhNMe ₃ I ⁺	K, NH_3		I (46) + II (18) + IV (7)	94
		$h\nu$, NH_3 , 1 h	I (57) + III (37)	136
PhN ₂ SBu- <i>t</i>	Lab. light, DMSO, 1.7 h		I (75)	58
	1. $h\nu$, NH_3 , 1.5 h 2. CH_2N_2		 (85) +  (10)	168, 108
			 I + PhR II	
 <u>R</u> OMe	5-15 min		 I (67) (—)	291
			(58) (11)	291, 290
			(30) (28)	291
 <u>R</u> CH ₂ NHCO ₂ Et	0.8 h			
 <u>R</u> CH ₂ NHCOMe	0.7 h			
 <u>R</u> Pr- <i>i</i>	K, NH_3			
 <u>R</u> Bu- <i>t</i>				

TABLE II. CARBANIONS DERIVED FROM KETONES (*Continued*)
A. Enolate from Acetone (*Continued*)

Substrate	Nucleophile	Conditions	Product(s) and Yield(s) (%)		Refs.
	$-\text{CH}_2\text{COMe}$	Lab. light, DMSO, 1.5 h	 (10)	 (70)	58
	K, NH ₃		 (6)	 (12)	96
	1. $\text{h}\nu$, NH ₃ , 2 h 2. MeI		 (12)	 (32)	164
	1. $\text{h}\nu$, NH ₃ , 2.3 h 2. CH ₂ N ₂		 (80)	 (8)	108
	$\text{h}\nu$, NH ₃		 (82)		146
	$\text{h}\nu$, NH ₃		 (56)		108
	F	1.2 h			108
	CF ₃	1.5 h		(35) + PhCF ₃ (14)	108
	NH ₂	4 min		(66)	106
	K, NH ₃		 (54)	 (8)	96
	Lab. light, DMSO,				58
	Me	1.5 h			
	OMe	1.5 h			
	COPh	0.7 h		(44) + PhCOPh (36)	
	$\text{h}\nu$, NH ₃		 I (48)	 II (39)	160
	Me	1.75 h			
	OMe	1.25 h			
	e^- , NH ₃ , -78°, mediator		 (48)		85
	K, NH ₃ , -78°		 (57)	 (17)	94
	K, NH ₃ , -78°		(36)	(10)	94
	Na(Hg), NH ₃ , mediator		(57)	(—)	101
	Na(Hg), NH ₃		(78)	(—)	101
	$\text{h}\nu$, NH ₃ , 2.5 h		(69)	(—)	108
	$\text{h}\nu$, NH ₃ , 1.5 h		(—)	(—)	108

TABLE II. CARBANIONS DERIVED FROM KETONES (Continued)
A. Enolate from Acetone (Continued)

Substrate	Nucleophile	Conditions	Product(s) and Yield(s) (%)		Refs.
 	$-\text{CH}_2\text{COMe}$	1. $\text{h}\nu, \text{NH}_3, 1.5 \text{ h}$ 2. H_3O^+		(70)	108
	$\text{h}\nu, \text{NH}_3$			$\frac{\text{R}}{\text{NH}_2} (33)^a$ $\text{NMe}_2 (90)$	106 146
	$\text{h}\nu, \text{NH}_3$			+ 	160
		1.75 h		(38)	
		1.5 h		(50)	
				(28)	
				(16)	
	$\text{K}, \text{NH}_3, -78^\circ$			+ + 	94
				(30)	
				(42)	
 	Lab. light, DMSO,				58
		0.5 h		(42)	
		1.5 h		(86)	
		1.5 h		(69)	
		0.75 h		(78)	
 		1. $\text{h}\nu, \text{NH}_3, 2 \text{ h}$ 2. MeI		(62)	164
		$\text{h}\nu, \text{NH}_3, 2 \text{ h}$		(76)	108
		$\text{h}\nu, \text{NH}_3, 2.2 \text{ h}$		$\frac{\text{R}}{\text{Pr}-i} (78)$ $\text{Bu}-t (26)$	108
		$\text{h}\nu, \text{NH}_3, 1 \text{ h}$		(68)	108
		$\text{h}\nu, \text{NH}_3$			
		2 h		(70)	
		2.5 h		(2)	
				(22)	
				(—)	
	1. $\text{h}\nu, \text{NH}_3$ 2. H_3O^+			+ 	149
		3 h		(60)	
		25 min		(75-80)	
				(40)	
				(20-25)	

TABLE II. CARBANIONS DERIVED FROM KETONES (Continued)
A. Enolate from Acetone (Continued)

Substrate	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
 R	CH_2COMe	$h\nu, \text{NH}_3$	 (82)	108
		0.5 h	(10)	
		1.5 h	(—)	
		3 h	(37)	
 N ₂ SBu- <i>t</i>		Lab light, DMSO, 2 h	 (30)	58
			 (50)	
 CO_2H	1. $h\nu, \text{NH}_3$		 (78)	168
	2. H_3O^+		 (11)	
		$h\nu, \text{NH}_3, 3 \text{ h}$	 (42)	166
		$h\nu, \text{NH}_3, 4 \text{ h}$	 (32)	166
	K, NH_3		 $\text{I} (23)$	45
			 $(69)^b$	
		$h\nu, \text{NH}_3, 1.5 \text{ h}$	 $\text{I} (88)$	45
		Na(Hg), NH_3	 $\text{I} (98)$	101
	K, NH_3		 $\text{I} (6) + \text{II} (84)^b$	45
		$h\nu, \text{NH}_3, 1 \text{ h}$	 $\text{I} (76)$	108
		$h\nu, \text{NH}_3, 1.5 \text{ h}$	 (75)	108
 N ₂ SBu- <i>t</i>		Lab light, DMSO, 1 h	 (75)	58
 N ₂ SBu- <i>t</i>	Lab light, DMSO, 0.5 h		 (76)	58
		$h\nu, \text{NH}_3, 1 \text{ h}$	 (98)	108
		$h\nu, \text{NH}_3, 1.3 \text{ h}$	 (62)	108
	Na, $\text{NH}_3, -78^\circ$		 $\text{I} (2)$	152
		$h\nu, \text{NH}_3, 1 \text{ h}$	 (22)	
			 (46)	

TABLE II. CARBANIONS DERIVED FROM KETONES (Continued)
A. Enolate from Acetone (Continued)

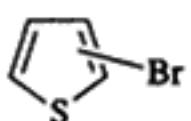
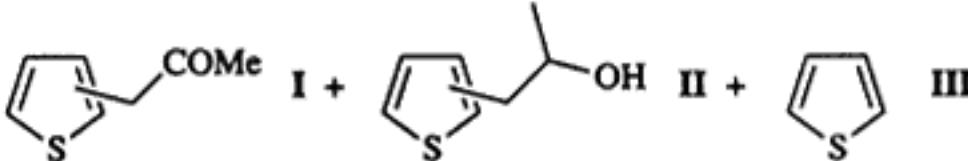
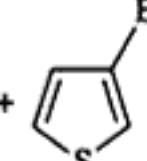
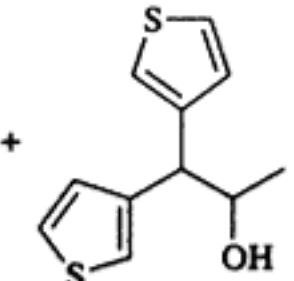
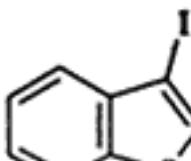
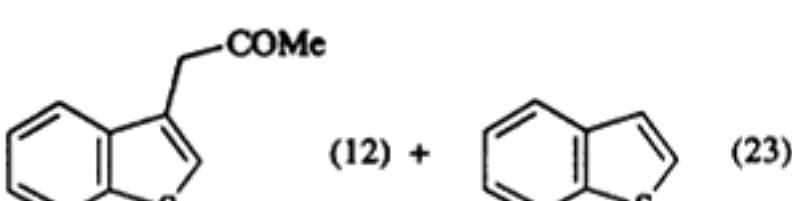
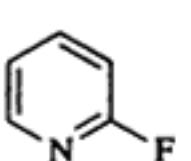
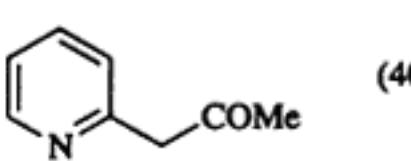
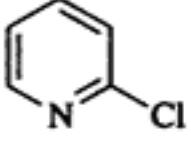
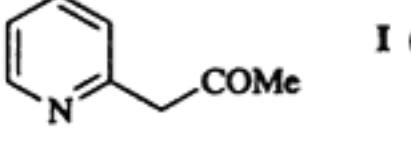
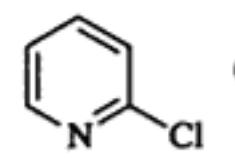
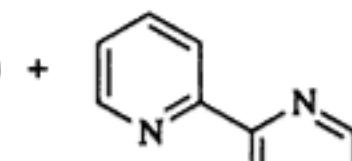
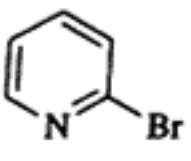
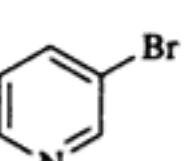
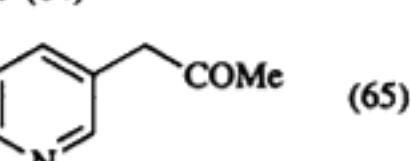
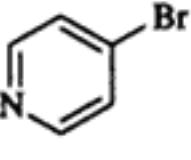
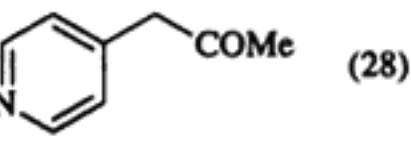
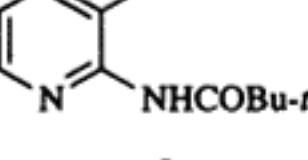
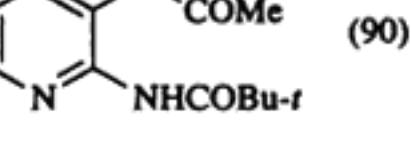
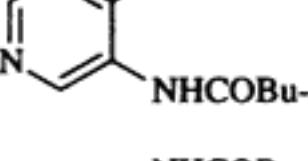
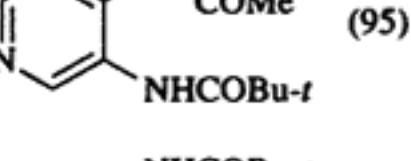
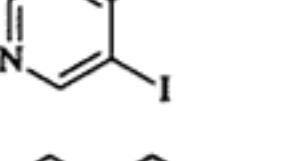
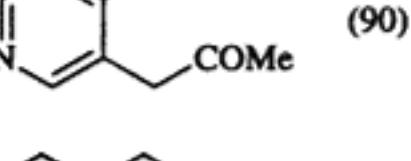
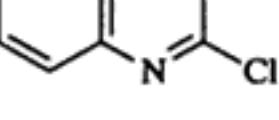
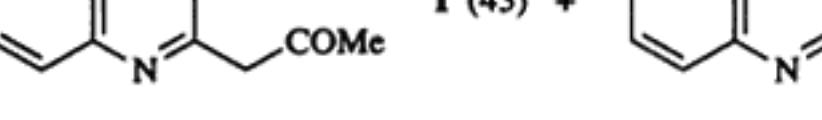
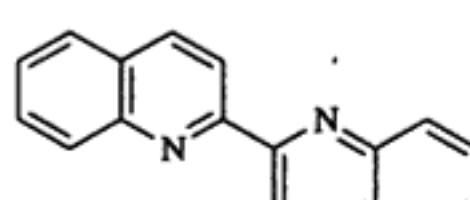
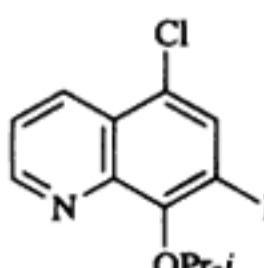
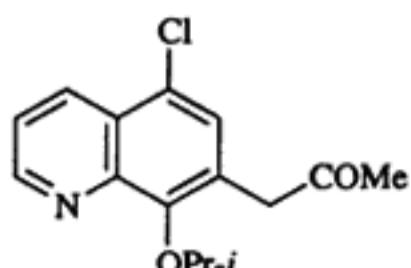
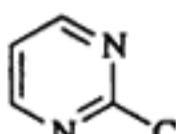
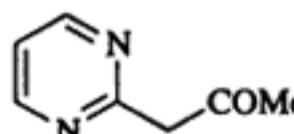
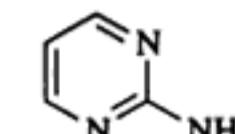
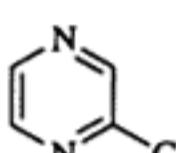
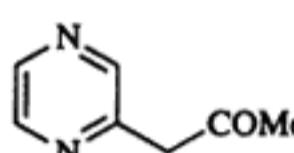
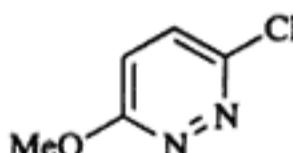
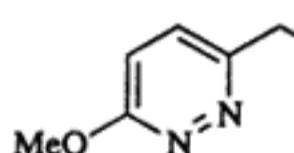
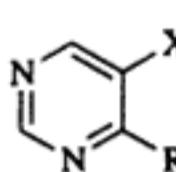
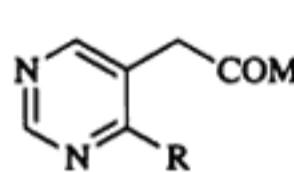
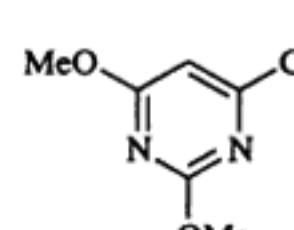
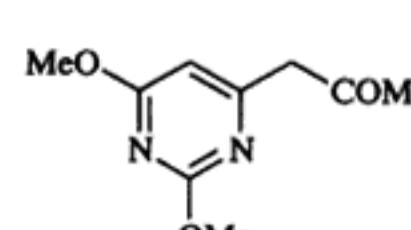
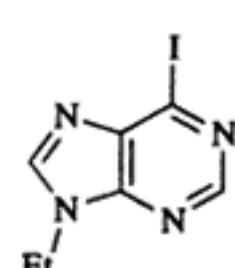
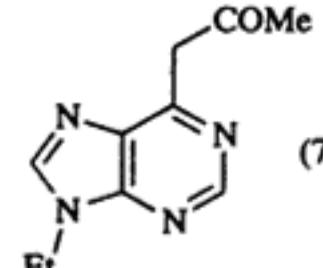
Substrate	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
	$-\text{CH}_2\text{COMe}$		 I + II + III	
		Na, NH ₃ , -78°	2-Br, I (4) + II (3) + III (70) +  (10)	152
		<i>hν</i> , NH ₃ , 1 h	2-Br, I (31)	152
		K, NH ₃ , -78°	3-Br, I (29) + II (23) + III (29) +  IV (10)	152
		<i>hν</i> , NH ₃ , 1 h	3-Br, I (51) + IV (25)	152
		DMSO, 1 h	 (12) + (23)	151
		<i>hν</i> , NH ₃ , 2 h	 (40)	137
		<i>hν</i> , NH ₃ , 1 h	 I (85)	137
		Na(Hg), NH ₃	I (15) +  (10) +  (10) + (55)	101
		K, NH ₃	I (4)	137
		<i>hν</i> , NH ₃ , 15 min	I (100)	137
		<i>hν</i> , THF, 15 min	I (64)	144
		<i>hν</i> , NH ₃ , 15 min	 (65)	137
		<i>hν</i> , NH ₃ , 15 min	 (28)	137
		<i>hν</i> , NH ₃	 (90)	139
		<i>hν</i> , NH ₃	 (95)	139
		<i>hν</i> , NH ₃	 (90)	139
		K, NH ₃	 I (43) + (29)	142
		<i>hν</i> , NH ₃ , ^c 1 h	I (90)	142
		<i>hν</i> , NH ₃ , ^d 1 h	I (62)	157
		Na(Hg), NH ₃	I (49) +  (50)	101

TABLE II. CARBANIONS DERIVED FROM KETONES (Continued)
A. Enolate from Acetone (Continued)

Substrate	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.																																																												
	$-\text{CH}_2\text{COMe}$	$\text{h}\nu$, 1 h		144																																																												
	THF		I (82)																																																													
	DMF		I (74)																																																													
	DME		I (28)																																																													
	Et_2O		I (9)																																																													
	C_6H_6		I (4)																																																													
	DMSO, 5 min		I (37)																																																													
		$\text{h}\nu$, NH_3 , 1 h	 (73)	155																																																												
		$\text{h}\nu$, NH_3 , 15 min	 I (15) +  (4)	55																																																												
		$\text{h}\nu$, THF, 15 min, 0°	I (61)	55																																																												
		NH_3 , 15 min	 (98)	55																																																												
		NH_3 , 15 min	 (60)	55																																																												
				54																																																												
<table border="1"> <thead> <tr> <th>X</th> <th>R</th> <th></th> <th></th> <th></th> </tr> </thead> <tbody> <tr> <td>Cl</td> <td>Bu-<i>t</i></td> <td>K, NH_3</td> <td>(42)</td> <td></td> </tr> <tr> <td>Cl</td> <td>Bu-<i>t</i></td> <td>$\text{h}\nu$, NH_3, 1.25 h</td> <td>(60-65)</td> <td></td> </tr> <tr> <td>Cl</td> <td>Ph</td> <td>NH_3, 16 h</td> <td>(39)</td> <td></td> </tr> <tr> <td>Cl</td> <td>Ph</td> <td>K, NH_3</td> <td>(47)</td> <td></td> </tr> <tr> <td>Cl</td> <td>Ph</td> <td>$\text{h}\nu$, NH_3, 1.25 h</td> <td>(20-25)</td> <td></td> </tr> <tr> <td>Br</td> <td>Bu-<i>t</i></td> <td>NH_3, 16 h</td> <td>(20-25)</td> <td></td> </tr> <tr> <td>Br</td> <td>Bu-<i>t</i></td> <td>K, NH_3</td> <td>(30)</td> <td></td> </tr> <tr> <td>Br</td> <td>Bu-<i>t</i></td> <td>$\text{h}\nu$, NH_3, 1.25 h</td> <td>(70-75)</td> <td></td> </tr> <tr> <td>Br</td> <td>Ph</td> <td>NH_3, 16 h</td> <td>(30)</td> <td></td> </tr> <tr> <td>Br</td> <td>Ph</td> <td>K, NH_3</td> <td>(42)</td> <td></td> </tr> <tr> <td>Br</td> <td>Ph</td> <td>$\text{h}\nu$, NH_3, 1.25 h</td> <td>(25-30)</td> <td></td> </tr> </tbody> </table>					X	R				Cl	Bu- <i>t</i>	K, NH_3	(42)		Cl	Bu- <i>t</i>	$\text{h}\nu$, NH_3 , 1.25 h	(60-65)		Cl	Ph	NH_3 , 16 h	(39)		Cl	Ph	K, NH_3	(47)		Cl	Ph	$\text{h}\nu$, NH_3 , 1.25 h	(20-25)		Br	Bu- <i>t</i>	NH_3 , 16 h	(20-25)		Br	Bu- <i>t</i>	K, NH_3	(30)		Br	Bu- <i>t</i>	$\text{h}\nu$, NH_3 , 1.25 h	(70-75)		Br	Ph	NH_3 , 16 h	(30)		Br	Ph	K, NH_3	(42)		Br	Ph	$\text{h}\nu$, NH_3 , 1.25 h	(25-30)	
X	R																																																															
Cl	Bu- <i>t</i>	K, NH_3	(42)																																																													
Cl	Bu- <i>t</i>	$\text{h}\nu$, NH_3 , 1.25 h	(60-65)																																																													
Cl	Ph	NH_3 , 16 h	(39)																																																													
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Br	Ph	K, NH_3	(42)																																																													
Br	Ph	$\text{h}\nu$, NH_3 , 1.25 h	(25-30)																																																													
		$\text{h}\nu$, NH_3 , 15 min	 (75)	140																																																												
		$\text{h}\nu$, NH_3 , 0.5 h	 (70)	153, 154																																																												

^a This compound decomposes in contact with air.

^b This product is a mixture of dihydro and tetrahydro derivatives.

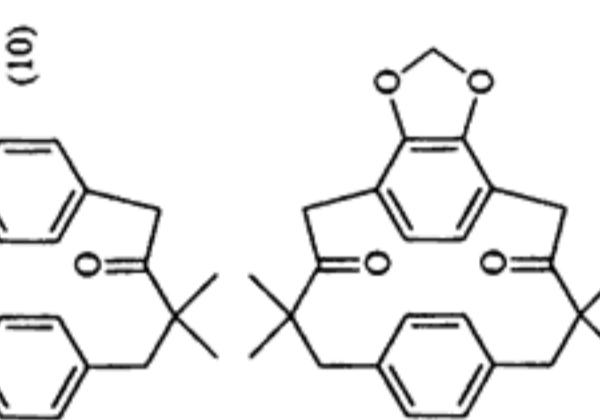
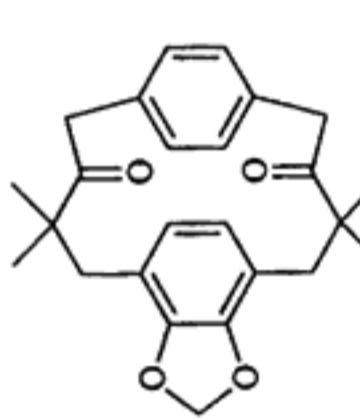
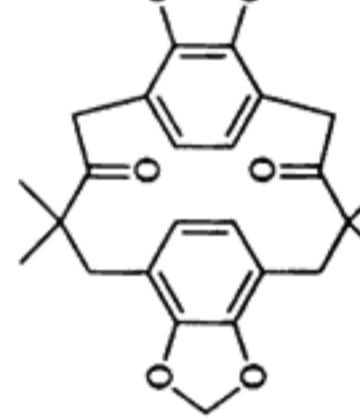
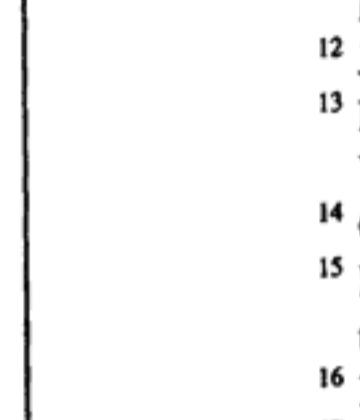
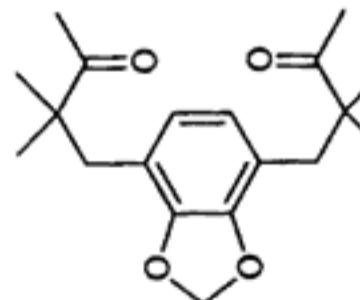
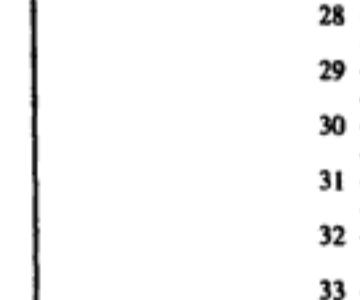
^c The potassium salt of the nucleophile was used.

^d A LiNH_2 :nucleophile ratio of 3 was used.

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TABLE IX. RING CLOSURE REACTIONS (Continued)

Ref.	Product(s) and Yield(s) (%)	Conditions	Nucleophile	Substrate
307	(10)	<i>hv</i> , <i>t</i> -BuOK, NH ₃ , 15 min		
307	(3)	<i>hv</i> , <i>t</i> -BuOK, NH ₃ , 15 min		
307	(7)	<i>hv</i> , <i>t</i> -BuOK, NH ₃ , 15 min		
307	(5)	<i>hv</i> , <i>t</i> -BuOK, NH ₃ , 15 min		
				
				
				
				

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