

Intramolecular Cyclization of Enaminones Involving Arylpalladium Complexes. Synthesis of Carbazoles

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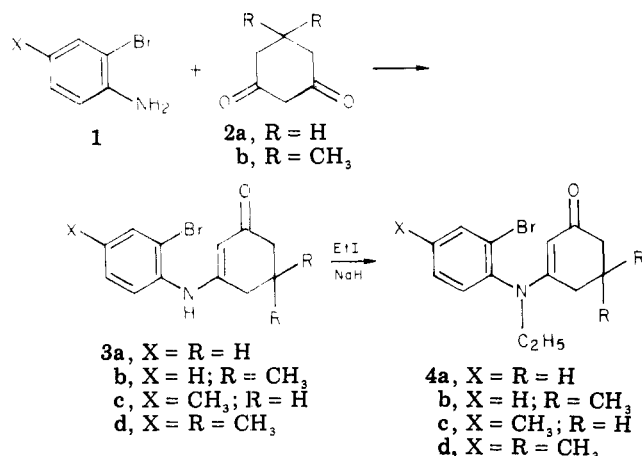
Received January 25, 1980

On treatment of the 3-((2-bromoaryl)amino)cyclohex-2-en-1-ones with a catalytic amount of Pd(0) species, intramolecular cyclization via arylpalladium complexes occurred to yield the 1,2-dihydrocarbazol-4(3H)-ones. Analogous products were also obtained by a similar cyclization of 3-anilino-cyclohex-2-en-1-ones using a stoichiometric amount of Pd(OAc)₂, which could be made catalytic by employing Cu(OAc)₂ and oxygen.

The aromatic substitution of olefins via arylpalladium species has been extensively studied during the past decade.¹ These reactions have been carried out in the presence of either a stoichiometric or catalytic amount of palladium compounds, and the need for utilizing these reactions as an efficient synthetic tool has increased the significance of this area of organometallic chemistry. In both the stoichiometric and catalytic arylations of olefins by way of arylpalladium σ complexes, most of the olefins employed were limited to simple or typical ones including styrenes, allyl alcohols, and acrylic acid derivatives,² and the large majority of the reactions have been carried out in an intermolecular manner.³

We have for some time been interested in utilization of enaminones, the character of which is significantly different from those of both enamines and ketones,⁴ as versatile synthons in the preparation of condensed heterocyclic systems. In connection with this, we have now studied intramolecular cyclization of *N*-arylenaminones via arylpalladium intermediates, which was performed both catalytically and stoichiometrically to afford carbazoles in each case.

Catalytic Cyclization. The substrates for cyclization were prepared according to an analogous procedure previously reported by us.⁵ Thus condensation of 2-bromo-*p*-toluidine (1, X = CH₃) with cyclohexane-1,3-dione (2a) or dimedone (2b) gave the bromo enaminone 3c or 3d, respectively. These products and known compounds⁵ 3a



(1) For current reviews, see: (a) Trost, B. M. *Tetrahedron* 1977, 33, 2615; (b) Heck, R. F. *Acc. Chem. Res.* 1979, 12, 146.

(2) Palladium-catalyzed arylation of enamides was recently reported. See: Ziegler, C. B., Jr.; Heck, R. F. *J. Org. Chem.* 1978, 43, 2949.

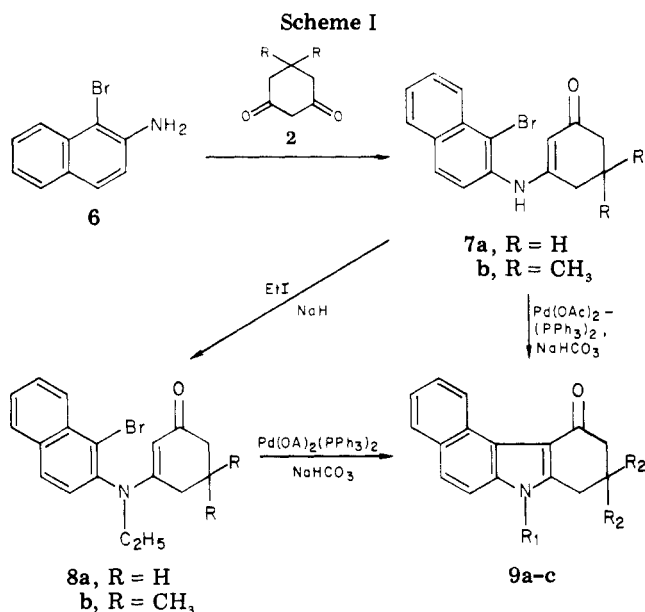
(3) A few reports of an intramolecular version of palladium-catalyzed arylation have recently appeared: Mori, M.; Chiba, K.; Ban, Y. *Tetrahedron Lett.* 1977, 1037; Mori, M.; Ban, Y. *Ibid.* 1979, 1133.

(4) Greenhill, J. B. *Chem. Soc. Rev.* 1977, 6, 277.

(5) Iida, H.; Yuasa, Y.; Kibayashi, C. *J. Org. Chem.* 1979, 44, 1074.

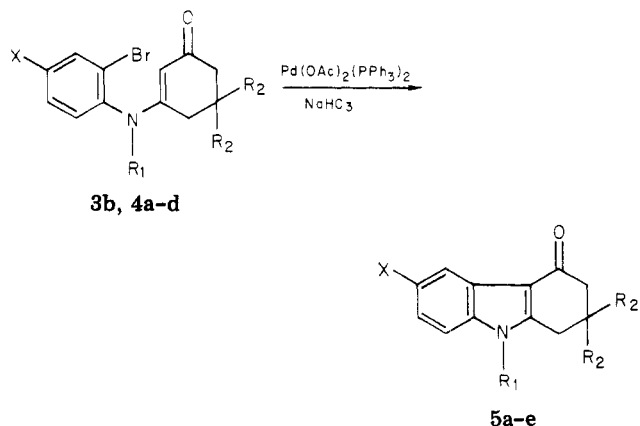
(6) Iida, H.; Yuasa, Y.; Kibayashi, C. *J. Org. Chem.* 1979, 44, 1236.

(7) Meek, E. G.; Turnbull, J. H.; Wilson, W. *J. Chem. Soc.* 1953, 811.



and 3b were then *N*-ethylated with ethyl iodide and sodium hydride to give the tertiary enaminones 4a-d. Otherwise, 1-bromo- β -naphthylamine (6) was condensed with the β -diketones 2a and 2b to give the *N*- β -naphthylenaminones 7a and 7b, respectively, which were converted to the corresponding *N*-ethyl derivatives 8a and 8b by a similar method described above (Scheme I). The conditions and results of these reactions are reported in Tables I and II.

When the bromo enaminone 4 (or 3b) was treated with



2 mol % 2:1 triphenylphosphine-palladium acetate complex (based on substrate) in dimethylformamide in the presence of sodium bicarbonate, the enaminone system was subject to palladium-catalyzed cyclization to yield the carbazole 5. Similar treatment of the *N*- β -naphthylenaminone 8 (or 7b) also gave the benzo[*c*]carbazole 9

Table I. Preparation of Bromo Enaminones by Condensation of Aromatic Amines with β -Diketones

compd	aromatic amine	β -diketone	temp, °C	time, h	yield, %	mp, °C (recrystn solvent)
3c	1	2a	120	3	86	160-162 (CHCl ₃ -hexane)
3d	1	2b	110	3	78	191-193 (CHCl ₃ -hexane)
7a	6	2a	100	2	90	224-226 (CHCl ₃)
7b	6	2b	135	3.5	67	198-198.5 (CHCl ₃)

Table II. Preparation of *N*-Ethylenaminones

compd ^a	starting material	temp, °C	time, h	yield, %
4c	3c	100	5	70
4d	3d	80	2	84
8a	7a	100	3	45
8b	7b	120	4	70

^a All products were isolated as oils.

discontinued when further consumption of the starting material was not observed any longer. Usually the reaction ceased after 20-35 h with 50-60% of the starting material unchanged. Low yields of the cyclized products obtained in the case where the secondary enaminones 3b and 7b were used as substrates may result from, in part, tautomerization of the enaminone system to the imino ketone form with low reactivity.

(Scheme I). The conditions and results of these cyclization reactions are summarized in Table III. In each case, the reaction was monitored by gas chromatography and was

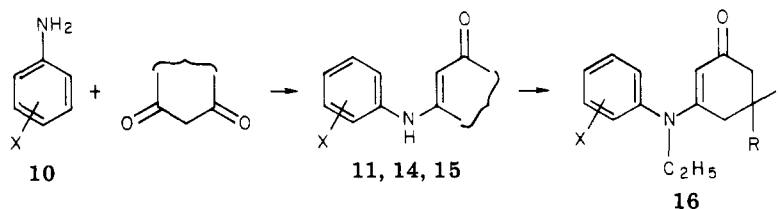
The probable course of the cyclization reaction is related to palladium-catalyzed aromatic substitution which is known as the Heck reaction.¹ As illustrated in Scheme II, the reaction presumably proceeds by oxidative addition of the aryl halide to an in situ produced palladium(0)

Table III. Catalytic Cyclization of *N*-Aryl- and *N*-Naphthylaminones

substrate	temp, °C	time, h	product	X	R ₁	R ₂	yield, ^a %	mp, °C (recrystn solvent)
3b	120-130	22	5a	H	H	CH ₃	9 (26)	209-211 ^b (CHCl ₃ -hexane)
4a ^c	120-130	20	5b	H	C ₂ H ₅	H	15 (40)	107-109 (ether-hexane)
4b ^d	120-130	20	5c	H	C ₂ H ₅	CH ₃	32 (68)	93-95 ^e (ether-hexane)
4c	130	35	5d	CH ₃	C ₂ H ₅	H	14 (38)	149-150 (acetone-hexane)
4d	120	35	5e	CH ₃	C ₂ H ₅	CH ₃	36 (72)	115-117 (ether-hexane)
7b	120	20	9a	H	H	CH ₃	8 (21)	205-206 (CHCl ₃ -hexane)
8a	130	30	9b	C ₂ H ₅	H	H	10 (27)	141.5-143 (acetone-hexane)
8b	120	28	9c	C ₂ H ₅	C ₂ H ₅	CH ₃	35 (78)	231-232.5 (CHCl ₃)

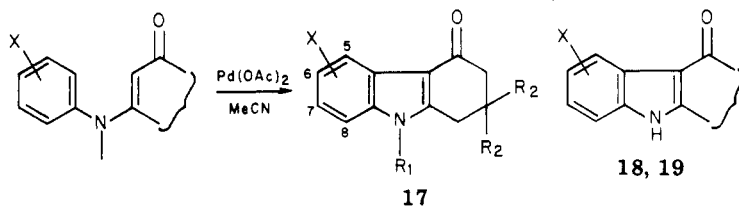
^a Yields are of pure material isolated by column chromatography. Yields in parentheses are corrected for recovered starting material. ^b Lit.⁶ mp 209-211 °C. ^c Prepared from 3a according to our previously reported procedure.⁵ ^d Prepared from 3b according to our previously reported procedure.⁶ ^e 5c was previously isolated as an oil.⁶

Table IV.



arylamine	β -diketone	secondary enaminone ^a	mp, °C	tertiary enaminone ^b
10a (X = <i>o</i> -OCH ₃)	2a	11a, X = 2-OCH ₃ ; R = H	129-131	16a (R = H)
a	2b	b, X = 2-OCH ₃ ; R = CH ₃	136-138	b (R = CH ₃)
b (X = <i>m</i> -OCH ₃)	2a	c, X = 3-OCH ₃ ; R = H	122.5-124	c (R = H)
c (X = <i>p</i> -OCH ₃)	2a	d, X = 4-OCH ₃ ; R = H	164-166	d (R = H)
d (X = <i>o</i> -NO ₂ , <i>p</i> -OCH ₃)	2a	e, X = 2-NO ₂ , 4-OCH ₃ ; R = H	154-155	
c			141-142	
	12 ^c	14		
e (X = H)			239-240	
	13	15		

^a All products were recrystallized from acetone-hexane with the exception of 15 (from DMF-CHCl₃-hexane). ^b All products were isolated as oils. ^c Prepared by a reported method.⁷

Table V. Stoichiometric Cyclization of *N*-Arylenaminones

entry	sub- strate	solvent	time, h	product	yield, ^a %	mp, °C (recrystn solvent)
1	11a	MeCN	4	17a (X = 8-OCH ₃ ; R ₁ = R ₂ = H)	19	248-249 (CHCl ₃ -hexane)
2 ^b	16a	MeCN	8	b (X = 8-OCH ₃ ; R ₁ = C ₂ H ₅ ; R ₂ = H)	20	117-118 (ether-hexane)
3	11b	MeCN	10	c (X = 8-OCH ₃ ; R ₁ = H; R ₂ = CH ₃)	25	245-248 dec (Me ₂ SO-acetone-hexane)
4 ^b	16b	MeCN	5	d (X = 8-OCH ₃ ; R ₁ = C ₂ H ₅ ; R ₂ = CH ₃)	22	147-149 (ether-hexane)
5	11c	AcOH	0.5	e (X = 7-OCH ₃ ; R ₁ = R ₂ = H)	5	280-283 (Me ₂ SO-CHCl ₃)
6	11c	MeCN	4	e	30	same
				f (X = 5-OCH ₃ ; R ₁ = R ₂ = H)	26	212-214 (CHCl ₃ -hexane)
7	16c	AcOH	0.5	g (X = 7-OCH ₃ ; R ₁ = C ₂ H ₅ ; R ₂ = H)	17	146-148 (acetone-hexane)
8	16c	MeCN	4	g	38	same
				h (X = 5-OCH ₃ ; R ₁ = C ₂ H ₅ ; R ₂ = H)	33	117-118 (acetone-ether)
9	11d	AcOH	0.5	i (X = 6-OCH ₃ ; R ₁ = R ₂ = H)	6	245-247 (Me ₂ SO-acetone-hexane)
10	11d	AcOH-MeCN (1:1)	3	i	8	same
11	11d	MeCN	2	i	25	same
12	11e	MeCN	3	j (X = 6-OCH ₃ , 8-NO ₂ ; R ₁ = R ₂ = H)	10	265-266 (CHCl ₃ -hexane)
13	16d	AcOH-MeCN (1:1)	6	k (X = 6-OCH ₃ ; R ₁ = C ₂ H ₅ ; R ₂ = H)	10	99-100 (acetone-hexane)
14	16d	MeCN	3.5	k	30	same
15	14	MeCN	2	k	22	285-287 (CHCl ₃ -hexane)
				18		
16	15	MeCN	2		24	237-240 (DMF-CHCl ₃ -hexane)
				19		

^a Isolated yield based on substrate. ^b 2 mol equiv of Pd(OAc)₂ were required for complete consumption of substrate.

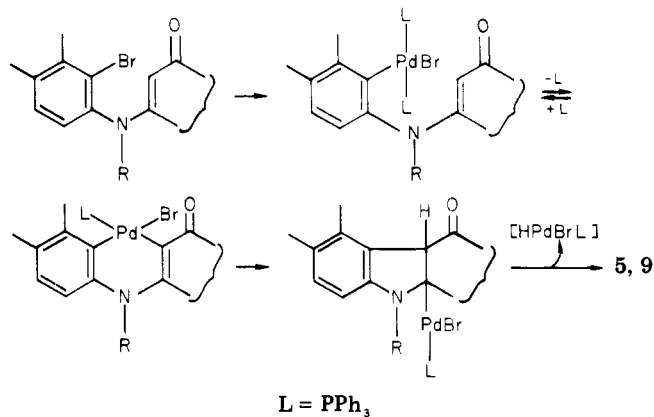
species, followed by insertion of the double bond in the enaminone system into σ aryl-palladium bond and the loss of a palladium hydride species by β -elimination. The palladium hydride species collapses, with a base used (sodium bicarbonate) to regenerate the palladium(0) catalyst.

Stoichiometric Cyclization. As an alternative version for cyclization, the direct introduction of the aryl group into the enaminone system with a stoichiometric amount of palladium salt was next investigated.

As summarized in Table IV, the required substrates were readily prepared by condensation of the arylamines 10 with the cyclic β -diketones in the same manner as described above for the preparation of the bromo enaminones 3 and 7. Subsequent *N*-ethylation of some of these products, i.e., 11a-d, by a standard procedure using ethyl iodide and sodium hydride provided the corresponding tertiary enaminones 16a-d.

When the *N*-arylenaminones (11, 15, and 16) so obtained were allowed to react with an equimolar amount of palladium acetate in refluxing acetic acid and/or acetonitrile, the cyclization occurred to yield the corresponding carbazoles. When treated under similar conditions, the an-

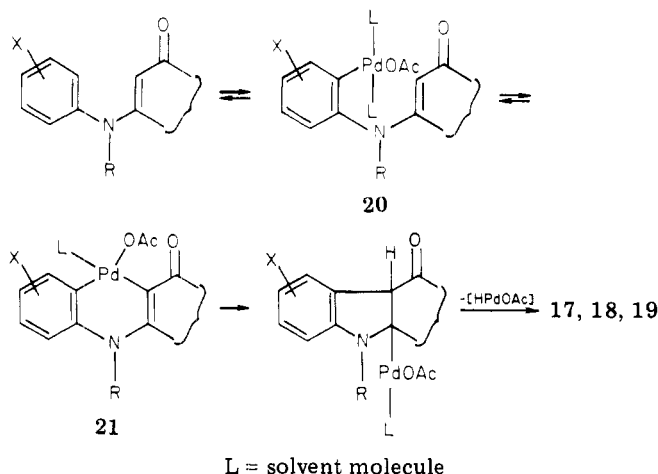
Scheme II. Mechanism for Catalytic Cyclization



ilinocyclopentenone 15 underwent a similar cyclization to give the cyclopenta[b]indole 19. The reaction conditions and results are given in Table V.

Entries 5, 7, 9, 10, and 13 indicate that when acetic acid was used as the solvent the yields of the cyclized products were remarkably decreased; this is probably due to the

Scheme III. Mechanism for Stoichiometric Cyclization



collapse of the enaminone system in the substrates with acetolysis.

Table V also shows that significant influences of the ring substituents were observed in this cyclization reaction, e.g., when either compound 11c or 16c with the methoxy substituent meta to the enaminone nitrogen was used as a substrate (entry 6 or 8, respectively). Namely, these substrates 11c and 16c afforded significantly higher total yields (56 and 71%, respectively) of cyclized products compared with other cases with *o*- or *p*-methoxy substituents. In the case of aromatic substitution of simple olefins with palladium(II) salts, it has been suggested that the reaction involves electrophilic palladation,⁸ and the direction of the palladation is thus affected by substituents such as OCH₃ or NO₂ on the benzene ring, as observed in other electrophilic substitution reactions.^{1a,8,9} On this basis, the position of the methoxy group may be accounted for by electrophilic aromatic substitution by palladium(II). Thus in the substrates with the ortho-para directing group OCH₃ at the meta position, the positions where electrophilic palladation occurs with a preference for positions ortho and para to the methoxy group are consistent with the cyclization sites: it means that these substrates can be caused to undergo the subsequent cyclization more readily than substrates with methoxy substitution at other positions.

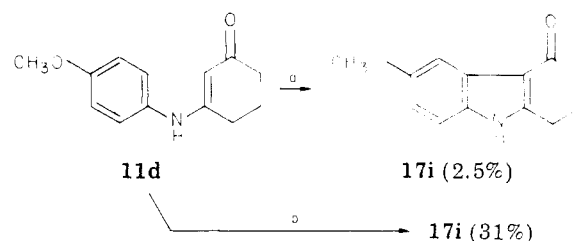
An alternative substituent effect in the cyclization reaction could be observed with reactants containing an electron-attracting group, which serves to decrease the reactivity of the benzene ring for the palladation. Thus as found in entry 12, the cyclization of the nitro enaminone 11e resulted in a 10% lower yield of the cyclized product, although the analogous reactant 11d, lacking the nitro group, gave the product in moderate yield (25%) (entry 11).

A plausible mechanism for this stoichiometric cyclization can be depicted as in Scheme III by analogy with the known olefinic arylation^{1a,9} and, partly, on the basis of the presumed substituent effect. It involves the direct electrophilic palladation of the aromatic ring to generate the arylpalladium acetate 20 to which the vinyl group in the enaminone system presumably coordinates in an intramolecular manner. The reactive intermediate 21 thus produced can be subsequently incorporated into a sequence similar to that of catalytic cyclization (see Scheme II) to give the carbazole.

Improvement of Stoichiometric Cyclization. The

ready availability of the reactants without halogen substitution in the stoichiometric cyclization is indeed of advantage; however, the reaction would achieve much greater synthetic utility if it could be carried out by utilizing a catalytic amount of palladium because the cost of the latter is a significant factor. Since the equivalent of a palladium(0) species is formed in the palladium(II) cyclization (Scheme III), the overall sequence is expected to be made catalytic by employing oxidizing agents such as cupric or silver acetate and oxygen as previously adapted in simple olefinic arylation.¹⁰ The catalytic reaction of this type is related to the Wacker process which involves the cupric chloride reoxidation of palladium(0).

For the blank experiment, the enaminone 11d was heated with 0.1 mol equiv of palladium acetate in acetonitrile to give the corresponding carbazole 17i only in 2.5%



a, Pd(OAc)₂ (0.1 mol equiv), MeCN, reflux; b, Pd(OAc)₂, (0.1 mol equiv), Cu(OAc)₂ (0.1 mol equiv), O₂, MeCN, reflux

yield. When this cyclization with the same substrate was carried out with catalytic amounts of palladium acetate and cupric acetate (0.1 mol equiv of each) under oxygen, the cyclized product 17i was obtained in 31% yield. These results indicate that the cyclization reaction, which is stoichiometric in palladium, can be effected by using only a catalytic amount of palladium acetate if cupric acetate and oxygen are employed.

Experimental Section

Melting points were determined on a Yanagimoto micro apparatus and are uncorrected. ¹H NMR spectra were recorded on a Varian T-60 or JEOL JNM-PS-100 spectrometer in CDCl₃, unless otherwise stated, with tetramethylsilane as internal reference. IR spectra were run on a Hitachi 215 grating spectrophotometer. Mass spectra were obtained from a Hitachi KMU-7L double-focusing spectrometer at 70 eV.

General Procedure for Preparation of 3-(2-Bromo-4-methylanilino)- (3c,d) and 3-((1-Bromo-2-naphthyl)amino)cyclohex-2-en-1-ones (7a,b) (Table I). A mixture of the aromatic amine (27 mmol) and the β-diketone (26 mmol) was heated under nitrogen. The reaction mixture was allowed to cool to room temperature, and the solidified product was crushed and washed with acetone-ether (1:1). The material obtained was sufficiently pure for further reaction. Recrystallization provided the analytical sample.

General Procedure for Preparation of 3-(2-Bromo-4-methyl-N-ethylanilino)- (4c,d) and 3-((1-Bromo-N-ethyl-2-naphthyl)amino)cyclohex-2-en-1-ones (8a,b) (Table II). A sample of sodium hydride (36 mmol) which had been washed free of mineral oil was suspended with stirring in toluene (30 mL) under nitrogen. To this suspension was added a solution of the secondary enaminone (18 mmol) in the same solvent (50 mL), and the mixture was refluxed for 1 h. After the mixture cooled, ethyl iodide (36 mmol) was added. The mixture was heated with stirring. The crude oil obtained on removal of the solvent by rotary evaporation was chromatographed on a silica gel column with chloroform-benzene (1:1).

General Procedure for Catalytic Cyclization of 3-(2-Bromoanilino)- (3b and 4) and 3-((1-Bromo-2-naphthyl)amino)cyclohex-2-en-1-ones (7b and 8). Formation of 1,2-

(8) Fujiwara, Y.; Asano, R.; Moritani, I.; Teranishi, S. *J. Org. Chem.* 1976, 41, 1681.

(9) Moritani, I.; Fujiwara, Y. *Synthesis* 1973, 524.

(10) Fujiwara, Y.; Moritani, I.; Danno, S.; Asano, R.; Teranishi, S. *J. Am. Chem. Soc.* 1969, 91, 7166.

Dihydro-9H(or -ethyl)-carbazol-4(3H)-ones (5) and 8,9-Dihydro-7H(or -ethyl)-benzo[*c*]carbazol-11(10H)-ones (9) (Table III). A mixture of the bromo enaminone (5 mmol), palladium acetate (0.1 mmol), triphenylphosphine (0.2 mmol), and sodium bicarbonate (10 mmol) in DMF (50 mL) was heated. The reaction mixture was filtered through Celite and the solvent was distilled under reduced pressure. The residue was chromatographed on a silica gel column with chloroform.

Preparation of 3-Anisidino-cyclohex-2-en-1-ones (11a-e and 14) and 3-Anilinocyclohex-2-en-1-one (15) (Table IV). The arylamine and the β -diketone were treated in a manner similar to that stated above for the general procedure for the bromo enaminones listed in Table I.

General Procedure for Stoichiometric Cyclization of *N*-Arylenaminones. Formation of 1,2-Dihydro-9H(or ethyl)-carbazol-4(3H)-ones (17 and 18) and 1,2,3,4-Tetrahydrocyclopent[*b*]indol-1-one (19) (Table V). A mixture of the enaminone (5 mmol) and palladium acetate (5 mmol) in an appropriate solvent was refluxed. After cooling to room temperature, the reaction mixture was filtered through Celite and the solvent was evaporated under reduced pressure. The residue was chromatographed on a silica gel column with chloroform.

Preparation of 3-(*N*-Ethylanisidino)cyclohex-2-en-1-ones (16) (Table IV). The secondary enaminone was treated in a manner similar to the general procedure described above for the *N*-ethylenaminones listed in Table II.

Treatment of 3-(4-Methoxyanilino)cyclohex-2-en-1-one (11d) with a Catalytic Amount of Palladium Acetate. A mixture of the enaminone 11d (1.5 g, 6.9 mmol) and palladium acetate (155 mg, 0.69 mmol) in acetonitrile (50 mL) was refluxed with stirring for 6 h. The reaction mixture was filtered through

Celite and the solvent was removed by evaporation. Chromatography of the residue on silica gel (CHCl₃) afforded 6-methoxy-1,2-dihydro-9H-carbazol-4(3H)-one (17i) (37 mg, 2.5%) and the unreacted starting material (~80%).

Catalytic Cyclization of 11d with Palladium Acetate in the Presence of Cupric Acetate and Oxygen. A mixture of 11d (1.0 g, 4.6 mmol), palladium acetate (103 mg, 0.46 mmol), and cupric acetate (84 mg, 0.46 mmol) in acetonitrile (40 mL) was refluxed with bubbling of oxygen for 40 h. After workup according to the above procedure, silica gel column chromatography eluting with chloroform gave 17i (310 mg, 31%).

Registry No. 1, 583-68-6; 2a, 504-02-9; 2b, 126-81-8; 3b, 68890-20-0; 3c, 73825-18-0; 3d, 73825-19-1; 4a, 68890-21-1; 4b, 69083-41-6; 4c, 73825-20-4; 4d, 73825-21-5; 5a, 40429-04-7; 5b, 73825-22-6; 5c, 69083-42-7; 5d, 73825-23-7; 5e, 73825-24-8; 6, 20191-75-7; 7a, 73825-25-9; 7b, 73825-26-0; 8a, 73825-27-1; 8b, 73825-28-2; 9a, 73825-29-3; 9b, 73825-30-6; 9c, 73825-31-7; 10a, 90-04-0; 10b, 536-90-3; 10c, 104-94-9; 10d, 96-96-8; 10e, 62-53-3; 11a, 73825-32-8; 11b, 61997-80-6; 11c, 51409-74-6; 11d, 36646-77-2; 11e, 73825-33-9; 12, 14203-46-4; 13, 3859-41-4; 14, 73825-34-0; 15, 73825-35-1; 16a, 73825-36-2; 16b, 73825-37-3; 16c, 73825-38-4; 16d, 73825-39-5; 17a, 73825-40-8; 17b, 73825-41-9; 17c, 73825-42-0; 17d, 73825-43-1; 17e, 73825-44-2; 17f, 73825-45-3; 17g, 73825-46-4; 17h, 73825-47-5; 17i, 35556-81-1; 17j, 73825-48-6; 17k, 73825-49-7; 18, 73825-50-0; 19, 61364-20-3; ethyl iodide, 75-03-6; palladium acetate, 3375-31-3; cupric acetate, 142-71-2.

Supplementary Material Available: Spectral characterization data (IR, ¹H NMR, and mass spectral) and C, H, N analyses for all compounds in Tables I-V (11 pages). Ordering information is given on any current masthead page.

Occurrence of the S_NANRORC Mechanism in the Amination of 2-Substituted Purines with Potassium Amide in Liquid Ammonia¹

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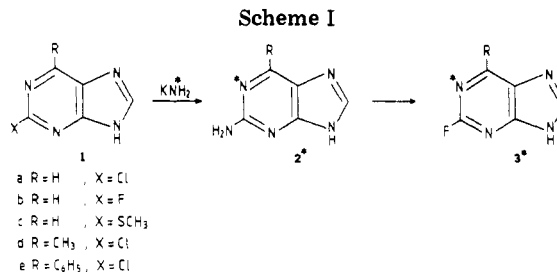
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Received February 27, 1980

The reactions of 2-chloro-, 2-fluoro- and 2-(methylthio)purine with potassium amide in liquid ammonia lead to the formation of 2-aminopurine. When these reactions are carried out with ¹⁵N-labeled potassium amide, ring-labeled 2-aminopurine is found. This demonstrates that a ring opening occurs during the amination. Formation of an anionic σ adduct at position 6 is proven by low-temperature NMR spectroscopy, and evidence is obtained for the formation of an open-chain intermediate, although this intermediate could not be isolated in a pure state. Reaction of the open-chain intermediate with hydriodic acid gives the thus far unknown 2-iodopurine. 2-Chloro-6-phenylpurine also reacts via ring opening into 2-amino-6-phenylpurine. However, 2-chloro-6-methyl- and 2-chloro-6,8-di-*tert*-butylpurine are found to be unreactive.

Introduction

We have recently found that purine and its derivatives containing a leaving group at position 6 or 8 easily undergo amination with potassium amide in liquid ammonia.^{2,3} From purine and the 6-substituted purines, adenine is obtained, being formed by an addition-elimination reaction at position 6.^{2,3} Interestingly 8-chloro- and 8-(methylthio)purine do not undergo amination at position 8, but



(1) Part 27 on the S_NANRORC mechanism. For Part 26 see: Rykowski, A.; van der Plas, H. C. *J. Org. Chem.* 1980, 45, 881. Pyrimidines, Part 81. For Part 80 see: van der Stoep, R. E.; van der Plas, H. C.; Jongejans, H.; Hoeve, L. *Recl. Trav. Chim. Pays-Bas*, in press.

(2) Kos, N. J.; van der Plas, H. C.; van Veldhuizen, A. *J. Org. Chem.* 1979, 44, 3140.

(3) Kos, N. J.; van der Plas, H. C.; van Veldhuizen, A. *Recl. Trav. Chim. Pays-Bas.*, in press.

at position 6, giving 8-chloroadenine (together with adenine) and 8-(methylthio)adenine, respectively. These reactions have been explained by an initial addition of the amide ion at position 6, leading to a σ adduct, which undergoes either aromatization into 8-chloro- or 8-(methyl-