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New Synthesis of Macrocyclic Crown-Formazans from Pyruvic Acid Derivatives

YEHIA A. IBRAHIM*, AHMED H. M. ELWAHY AND ASHRAF A. ABBAS

Department of Chemistry, Faculty of Science, Cairo University, Giza, A. R. Egypt

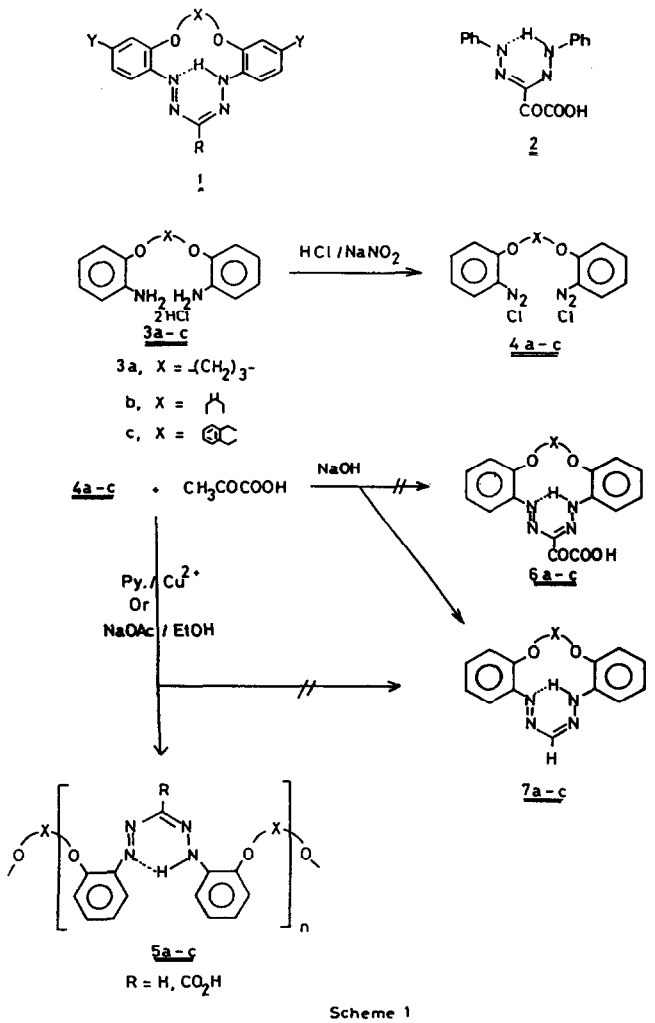
Abstract: The macrocyclic crown-formazans **7a-c, 12a-g** were prepared by the azo coupling of the appropriate bis-diazonium salts **4a-c** with pyruvic acid and arylpyruvic acids **8a-c**. The ready accessability of the latters offers an easy access towards 1,5-symmetrically disubstituted-3-arylformazans e.g. **10a-g** as well as their macrocyclic crown derivatives of expected valuable applications.

INTRODUCTION

The synthesis and diverse applications of formazans have been the subject of many reviews[1a-o]. Moreover, there is recent growing interest in the synthesis of macrocyclic crown-formazans **1** due to their useful applications in selective metal extraction[2-5] and determination[6-15]. Such applications depend mainly on the cavity size of the macrocycles **1** as well as the substituents R and Y. The present study describes new useful approach for the synthesis of a number of crown-formazans of expected useful applications.

RESULTS AND DISCUSSIONS

The known reaction of pyruvic acid with benzenediazonium chloride[16,17] to give 1,5-diphenylformazyl-3-glyoxylic acid **2** stimulated our attention to study the possible synthesis of macrocyclic crown-formazylglyoxylic acid (**1**, R = COCOOH). To achieve this goal the coupling reaction of the bis-diaznium salts **4a-c** with pyruvic acid was now undertaken and the results are summarized in Scheme 1. Thus, the bis-diamines **3a-c** was diazotized with sodium nitrite in hydrochloric acid to give the corresponding bis-diazotized bis(2-aminophenoxy)-1,3-propanes **4a,b** and bis-diazotized 1,2-bis(2-aminophenoxymethyl)benzene **4c**. Upon coupling of **4a** with pyruvic acid in pyridine containing Cu^{+2} (as described for the synthesis of other derivatives of crown-formazans 7,18-20), we failed to separate (by TLC) any identifiable product from the dark brown reaction mixture (probably polymeric formazans **5a-c** were formed). Similar results were obtained when the coupling reaction was performed in ethanolic sodium acetate solution. On the other hand, coupling of each of **4a-c** with pyruvic acid in aqueous sodium hydroxide solution afforded a deep red precipitate, the chloroform



Scheme 1

soluble part of which was readily purified by preparative TLC to give pure crown-formazans 7a-c instead of the expected glyoxylic acid derivatives 6a-c. Compound **7a** obtained now as solid crystals mp. 158-160°C, was reported by Dziomko etal.[18] as an oil by coupling of 4a with malonic acid. By repeating this synthesis using the same experimental conditions and purifying the product with preparative TLC, the same compound 7a was obtained as deep red crystals mp. 158-160°C [identical wth our product (mixed mp., IR, ^{1}H NMR)]. It seems that Dziomko etal. obtained impure formazan, since the IR of 7a contains the same reported bands for this compound.

The previous findings directed our attention to study the behavior of arylpyruvic acids towards the action of diazonium salts as a route for the synthesis of formazans. Thus, treatment of arylpyruvic acids, namely, phenylpyruvic acid (8a), p-methoxyphenylpyruvic acid (8b) and p-nitrophenylpyruvic acid (8c) with

arenediazonium chloride **9a-c** (Method A) gave the corresponding 1,3,5-triarylformazans **10a-g** (Scheme 2). Compounds **10a-g** were found identical with the same compounds reported by coupling of aromatic aldehyde arylhydrazones **11a-g** with arenediazonium chloride[21-27] (Method B). Also, compound **10a** was obtained by coupling of malonic acid with 3.3 mol of benzendiazonium chloride in DMF/pyridine mixture[28] (Method C) (Scheme 2). Table 2 summarizes the yields of formazans obtained by different methods.

The synthesis of 1,5-symmetrically disubstituted formazans from arylpyruvic acids were now extended for the synthesis of macrocyclic crown-formazans substituted with an aryl group in the formazyl carbon. Scheme 3 illustrates the synthesis of these macrocyclic formazans **12a-g**. Thus, bisdiazonium salts **4a-c** were coupled with the appropriate arylpyruvic acids **8a-c** in aqueous sodium hydroxide to give the corresponding cyclic crown-formazans **12a-g** in 4-6% yields. These macrocycles were purified by preparative TLC. In an attempt to increase the yield of these macrocyclic formazans, LiOH was added to the reaction mixture. This was found to raise the yield of only compounds **12a-e** to 10%. However, with compounds **12f,g** LiOH has no detectable effect upon the yield. This can be explained by the tempelate effect of Li^+ which is consistent with the formation of 1:1 complex between 14-crown-formazans and Lithium[9]. The Structure of all macrocyclic formazans were confirmed by mass spectra.

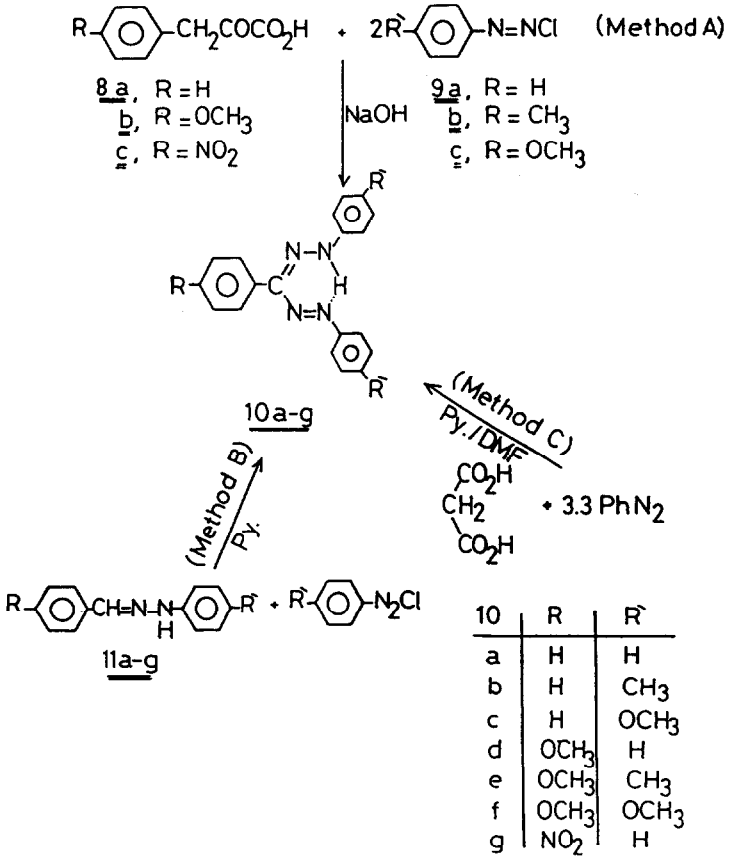
The starting materials needed in this synthesis were prepared as outlined in Scheme 4. Thus, treatment of o-acetamidophenol (**13**) with 1,3-dibromopropane in ethanolic solution containing sodium ethoxide gave the corresponding 1,3-bis(2-acetamidophenoxy)propane (**14**). On the other hand, alkylation of the potassium salt **15** (prepared by treatment of o-acetamidophenol with ethanolic KOH) with each of 2-chloromethyl-3-chloropropene and α,α-dibromo-o-xylene in boiling DMF gave the corresponding 2-methylene-1,3-bis(2-acetamidophenoxy)-propane (**16b**) and 1,2-bis(2-acetamidophenoxymethyl)benzene (**16c**) respectively. Hydrolysis of each of **14**, **16b,c** in ethanolic solution containg HCl gave the corresponding diamine dihydrochlorides **3a-c**.

EXPERIMENTAL

All melting points are uncorrected. Compounds prepared were characterized by mixed melting points. The IR spectra (KBr) were recorded with a Unicam SP 1200 infrared spectrophotometer. NMR spectra were determined on a VARIAN GEMINI 200 Spectrometer (200 MHz). Mass spectra were determined on Finigan Mat 312, 70 eV or GCMS-QP 1000 EX. Microanalyses were carried out at the Microanalytical Centre, Cairo University. 1,3-Dibromopropane, 2-chloromethyl-3-chloropropene and α,α-dibromo-o-xylene were used as purchased from Aldrich. Arylpyruvic acids **8a-c** were prepared from the corresponding arylaldehydes after reported procedures[29,30].

Potassium o-acetamidophenoxide (**15**)

A solution of o-acetamidophenol (1.5 g, 10 mmol) and KOH (0.56 g, 10 mmol) in ethanol (10 ml) was stirred for 10 min. The solvent was then removed in vacuo. The remaining solid was triturated with dry ether, filtered and dried in air to give 1.7 g (*ca.* 90%) of **15** which was used in the next step without further purification.



10	R	R̂
a	H	H
b	H	CH_3
c	H	OCH_3
d	OCH_3	H
e	OCH_3	CH_3
f	OCH_3	OCH_3
g	NO_2	H

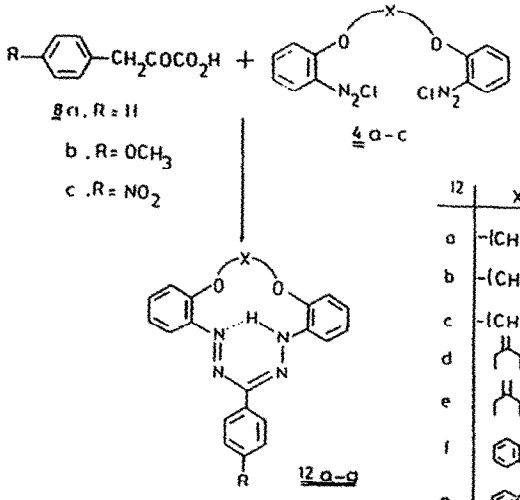
Scheme 2

Table 1

Yield[Ref.]

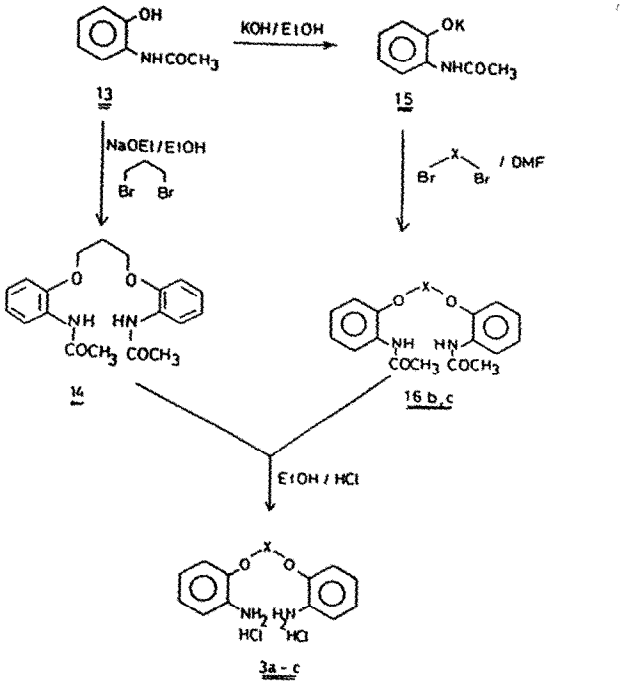
Comp.	Methed A	B	C
10a	75	40[21]	44[26]
10b	80	N[22]	-
10c	79	60[23]	-
10d	75	N[24]	-
10e	79	68[25]	-
10f	82	62[26]	-
10g	66	40[27]	-

The symbol N indicate that the yield was not given in the ref.
A: from arylpyruvic acid and arenediazonium chloride
B: from arylhydrazones and arenediazonium chloride
C from malonic acid and arenediazonium chloride



12	X	R
a	$-(CH_2)_3-$	H
b	$-(CH_2)_3-$	OCH_3
c	$-(CH_2)_3-$	NO_2
d		H
e		OCH_3
f		H
g		OCH_3

Scheme 3



a, X = $-(CH_2)_3-$

b, X = $-CH_2-C(CH_2)-CH_2-$

c X = $-CH_2-C_6H_4-CH_2-$

Scheme 4

1,3-Bis(2-acetamidophenoxy)propane (14)

To a solution of **13** (15.1 g, 0.1 mol) in ethanolic sodium ethoxide solution (prepared from 2.3 g of sodium and 30 ml of absolute ethanol) was added 1,3-dibromopropane (10.1 g, 0.05 mol). The reaction mixture was heated under reflux for 3 h. The solvent was then removed in vacuo, and the remaining precipitate was collected, washed with water and crystallized from acetic acid to give 23.94 g (*ca.* 70%) of colorless crystals of **14**, mp 192-3°C (lit.[31] mp 193.5°C).

2-Methylene-1,3-bis(2-acetamidophenoxy)propane (**16b**) *and 1,2-bis(2-aceta-midophenoxymethyl)benzene* (**16c**)

General Procedure: To a solution of **15** (3.78 g, 20 mmol) in DMF was added the appropriate dihalo compound (10 mmol). The reaction mixture was heated under reflux for 15 min. The solvent was then removed in vacuo and the remaining residue was washed with water.

Compond **16b** crystallized from benzene to give colorless crystals (75%), mp 100-2°C. ^{1}H NMR ($CDCl_3$) δ 2.06 (s, 6H, CH_3CO), 4.27 (s, 4H, OCH_2), 5.45 (s, 2H, CH_2=C), 6,9-8.38 (m, 10H, ArH's, NH) ppm. (Calcd. for $C_{20}H_{22}N_2O_4$: C, 67.78; H, 6.26; N, 7.90. Found: C, 67.6; H, 6.4; N, 7.7).

Compound **16c** crystallized from ethanol to give colorless crystals (70%), mp 138-40°C. (Calcd. for $C_{24}H_{24}N_2O_4$: C, 71.26; H, 5.98; N, 6.92. Found: C, 71.1; H, 5.5; N, 7.1)

Bis(o-aminophenoxy)ether dihydrochloride **3a-c**

General procedure:To asolution of each of **14** and **16b,c** (10 mmol) in absolute ethanol (20ml) was added concentrated hydrochloric acid (16 ml).The reaction was mixture was heated under reflux for 1h and the solvent was removed in vacuo.The remaining solid was collected and crystallized from the ethanol-ether mixture.

Compound **3a** pale yellow crystals (72%) mp 305-7°C (lit.[32] 306-8°C).

Compound **3b** pale yellow crystals (70%) mp 198-200°C. (Calcd. for $C_{16}H_{20}N_2O_2Cl_2$: C, 55..99; H, 5.87; N, 8.16; Cl, 20.66. Found: C, 56.1, H, 5.9; N, 8.2; Cl, 20.7)

Compound **3c** brown crystals (75%) mp 152-4°C. (Calcd. for $C_{20}H_{22}N_2O_2Cl_2$: C, 61.07; H, 5.63; N, 7.12; Cl, 18.02. Found: C, 61.3; H, 5.3; N, 7.4; Cl, 17.9).

Synthesis of macrocyclic crown-formazans **7a-c, 12a-g**

General procedure: A solution of the appropriate diamine dihydrochloride **3a-c** (1 mmol) in water (5 ml) and conc. HCl (3 ml) was diazotized at -5°C with a solution of sodium nitrite (0.23 g in 5 ml of water) during 1/2 h. Stirring was continued for 1 h at -5°C and then added dropwise with stirring to a solution containing pyruvic acid or the appropriate arylpyruvic acids **8a-c** (1 mmol) in water (10 ml) containing NaOH (1.2 g) over a period of 1 h. The reaction mixture was then kept in the freezer overnight. The solid precipitated was collected and purified on preparative TLC using silica gel (60 F_{254}) with the proper eluent for each derivative.

16,17-Dihydro-5H,15H-dibenzo[b,i][1,11,4,5,7,8]dioxatetraazacyclotetradecine (**7a**).

With the use of the general procedure **3a** was diazotized and coupled with pyruvic acid to give after chromatographic purification using a mixture of methylene chloride/petroleum ether (40-60) 2 1 as an eluent (R_f = 0.88, red spot) 17 mg (6%) of deep red crystals of **7a**, mp 158-160°C; Ms: m/z 296 (M^+, 100%), 145 (16%), 120 (51%), 92 (27%), 65 (54%), 41 (95.5%), IR: 1600, 1503, 1466 cm^{-1}. (Calcd. for $C_{16}H_{16}N_4O_2$: C, 64.58;

H, 5.44; N, 18.91. Found: C, 64.7; H, 5.3; N, 18.2).

16-Methylene-16,17-dihydro-5H,15Hdibenzo[b,i][1,11,4,5,7,8]dioxatetraazacyclotetradecine (7b).

With the use of the general procedure **3b** was diazotized and coupled with pyruvic acid to give after chromatographic purification using a mixture of methylene chloride/petroleum ether (40-60) 2:1 as an eluent (R_f = 0.88, red spot) 15 mg (5%) of deep red crystals of **7b**, mp 142-4°C; Ms: m/z 308 (M^+, 100%), 131 (44%), 91 (29%), 79 (48%). (Calcd. for $C_{16}H_{16}N_4O_2$: C, 66.22; H, 5.23; N, 18.17. Found: C, 66.1; H, 5.1; N, 17.9).

16,17-Dihydro-11H-tribenzo[b,i,m][1,11,4,5,7,8]dioxatetraazacyclotetradecine (7c).

With the use of the general procedure **3c** was diazotized and coupled with pyruvic acid to give after chromatographic purification using a mixture of methylene chloride/petroleum ether (40-60) 2:1 as an eluent (R_f = 0.94, red spot) 17 mg (5%) of deep red crystals of **7c**, mp 172-4°C; Ms: m/z 358 (M^+, 100%), 250 (10%), 210 (47%), 195 (38%),181 (43%), 164(27%), 134(30%), 104(100%), 78(100%). (Calcd. for $C_{21}H_{18}N_4O_2$: C, 70.38; H, 5.06; N, 15.63 Found: C, 70.4; H, 5.0; N, 15.1).

16,17-Dihydro-5H,15H-7-phenyldibenzo[b,i][1,11,4,5,7,8]dioxatetraazacyclotetradecine (12a)

a- With the use of the general procedure **3a** was diazotized and coupled with phenylpyruvic acid **8a** to give after chromatographic purification using a mixture of methylene chloride/petroleum ether (40-60) 1:3 as an eluent (R_f = 0.94, violet spot) 14 mg (4%) of deep red crystals of **12a**, mp 178-80°C (lit.[19] mp 176-8°C); Ms: m/z 372 (M^+, 74%), 212 (23%), 148 (27%), 133 (37%), 120 (100%), 92 (49%), 77 (74%).

b- With the use of the general procedure **3a** was diazotized and coupled with phenylpyruvic acid **8a** in the presence of 0.024 g (1 mmol) of LiOH in addition to the same reaction mixture using the general procedure to give after TLC purification 35 mg (10%) of **12a**.

16,17-Dihydro-5H,15H-7-p-methoxyphenyldibenzo[b,i][1,11,4,5,7,8]dioxatetraazacyclotetradecine (12b)

a- With the use of the general procedure **3a** was diazotized and coupled with p-methoxyphenylpyruvic acid **8b** to give after chromatographic purification using a mixture of methylene chloride/petroleum ether (40-60) 4:7 as an eluent (R_f = 0.88, violet spot) 16 mg (4%) of deep red crystals of **12b**, mp 159-61°C ; Ms: m/z 402 (M^+, 78%), 212 (21%), 148 (32%), 133 (78%), 120 (100%), 105 (27%), 92 (62%). (Calcd. for $C_{23}H_{22}N_4O_3$: C, 68.64; H, 5.51; N, 13.92. Found: C, 68.1; H, 5.1; N, 13.0).

b- With the use of the general procedure **3a** was diazotized and coupled with p-methoxyphenylpyruvic acid **8b** in the presence of 0.024 g (1 mmol) of LiOH in addition to the same reaction mixture using the general procedure to give after TLC purification 36 mg (9%) of **12b**

16,17-Dihydro-5H,15H-7-p-nitrophenyldibenzo[b,i][1,11,4,5,7,8]dioxatetraazacyclotetradecine (12c)

a- With the use of the general procedure **3a** was diazotized and coupled with p-nitrophenylpyruvic acid **8c** to give after chromatographic purification using a mixture of methylene chloride/petroleum ether (40-60) 2:1 as an eluent (R_f = 0.94, brown spot) 25 mg (6%) of **12c**, mp 270-2°C (lit.[19] mp 256-286°C).

b- With the use of the general procedure **3a** was diazotized and coupled with p-nitrophenylpyruvic acid **8c** in the presence of 0.024 g (1 mmol) of LiOH in addition to the same reaction mixture using the general procedure to give after TLC purification 45 mg (11%) of **12c**.

16-Methylene-16,17-dihydro-5H,15H-7-phenyldibenzo[b,i][1,11,4,5,7,8]dioxatetraazacyclotetradecine (12d)

a- With the use of the general procedure **3b** was diazotized and coupled with phenylpyruvic acid **8a** to give after chromatographic purification using a mixture of chloroform/petroleum ether (40-60) 1:3 as an eluent (R_f = 0.97,

violet spot) 23 mg (6%) of deep red crystals of **12d**, mp 195-7°C ; Ms: m/z 384 (M^+, 65%), 210 (17%), 160 (31%), 145 (100%), 131 (86%), 120 (65%), 104 (32%), 92 (35%), 79 (82%), 65 (45%). (Calcd. for $C_{23}H_{20}N_4O_2$: C, 71.86; H, 5.24; N, 14.57. Found: C, 71.5; H, 5.1; N, 14.2).

b- With the use of the general procedure **3b** was diazotized and coupled with phenylpyruvic acid **8a** in the presence of 0.024 g (1 mmol) of LiOH in addition to the same reaction mixture using the general procedure to give after TLC purification 42 mg (11%) of **12d**.

16-Methylene-16,17-dihydro-5H,15H-7-p-methoxyphenyldibenzo[b,i][1,11,4,5,7,8]dioxatetraazacyclotetradecine (**12e**)

a- With the use of the general procedure **3b** was diazotized and coupled with p-methoxyphenylpyruvic acid **8b** to give after chromatographic purification using a mixture of methylene chloride/petroleum ether (40-60) 2:1 as an eluent (R_f = 0.96, violet spot) 18 mg (4.5%) of deep red crystals of **12e**, mp 148-50°C ; Ms: m/z 414 (M^+, 63%), 240 (12%), 160 (32%), 145 (100%), 131 (76%), 120 (63%), 103 (25%), 91 (40%), 80 (53%), 65 (42%). (Calcd. for $C_{24}H_{22}N_4O_3$: C, 69.55; H, 5.35; N, 13.52. Found: C, 69.43; H, 5.1; N, 13.0).

b- With the use of the general procedure **3b** was diazotized and coupled with p-methoxyphenylpyruvic acid **8b** in the presence of 0.024 g (1 mmol) of LiOH in addition to the same reaction mixture using the general procedure to give after TLC purification 40 mg (10%) of **12e**.

5,21-Dihydro-11H-13-phenyltribenzo[b,i,m][1,11,4,5,7,8]dioxatetraazacyclotetradecine (**12f**)

With the use of the general procedure **3c** was diazotized and coupled with phenylpyruvic acid **8a** to give after chromatographic purification using a mixture of chloroform/petroleum ether (40-60) 1:3 as an eluent (R_f = 0.79, violet spot) 19 mg (4.5%) of deep red crystals of **12f**, mp 208-10°C ; Ms: m/z 434 (M^+, 45%), 210 (50%), 195 (72%), 181 (69%), 165 (35%), 152 (21%), 120 (28%)
104 (100%), 91 (46%), 78 (96%). (Calcd. for $C_{27}H_{22}N_4O_2$: C, 74.64; H, 5.10; N, 12.89. Found: C, 74.2; H, 5.0; N, 12.5).

5,21-Dihydro-11H-13-p-methoxyphenyltribenzo[b,i,m][1,11,4,5,7,8]dioxatetraazacyclotetradecine (**12g**)

With the use of the general procedure **3c** was diazotized and coupled with p-methoxyphenylpyruvic acid **8b** to give after chromatographic purification using a mixture of chloroform/petroleum ether (40-60) 2:1 as an eluent (R_f = 0.93, violet spot) 23 mg (5%) of deep red crystals of **12g**, mp 238-40°C ; Ms: m/z 464 (M^+, 45%), 239 (18%), 210 (38%), 195 (90%), 182 (82%), 165 (37%), 152 (18%), 133 (40%), 120 (24%), 104 (78%). 91(33%), 78(100%). (Calcd. for $C_{28}H_{24}N_4O_3$: C, 72.40; H, 5.21; N, 12.06. Found: C, 72.2; H, 5.1; N, 11.9).

Synthesis of 1,3,5-triarylformazans **10a-g**

General procedure: A solution of the appropriate aromatic amine (10 mmol) in water (5 ml) and conc. HCl was diazotized at -5°C with a solution of sodium nitrite (0.8 g of $NaNO_2$ and 5 ml of H_2O) during (3 ml) 1/2 h. Stirring was continued for 5 min at -5°C. The solution was then added dropwise with stirring to a solution containing the appropriate arylpyruvic acid **8a-c** (5 mmol) in water (10 ml) containing NaOH (1.5 g) over a period of 10 min. The reaction mixture was then kept in the freezer overnight. The solid obtained was collected and crystallized from the proper solvent to give **10a-g**.

1,3,5-Triphenyformazan **10a**: With the use of the general procedure aniline was diazotized and coupled with phenylpyruvic acid **8a** to give crude **10a** which was crystallized from acetone to give 1.1 g (75%) of red crystals mp. 170-2°C(lit.[21] 173-5°C).

1,5-Di-p-tolyl-3-phenylformazan **10b**: With the use of the general procedure p-toluidine was diazotized and coupled with phenylpyruvic acid **8a** to give crude **10b** wich was crystallized from acetone to give 1.3 g (80%) of red crystals mp. 155-2°C (lit.[22] 166°C).

1,5-Di-p-methoxy-3-phenylformazan **10c**: With the use of the general procedure p-anisidine was diazotized and coupled with phenylpyruvic acid **8a** to give crude **10c** wich was crystallized from acetone to give 1.42 g (79%) of red crystals mp. 148-2°C (lit.[24] 165-6°C).

1,5-Diphenyl-3-p-methoxyphenylformazan **10d**: With the use of the general procedure aniline was diazotized and coupled with p-methoxyphenylpyruvic acid **8b** to give crude **10d** wich was crystallized from acetone/methanol (1:1) to give 1.23 g (79%) of red crystals mp. 155-2°C (lit.[24] 154°C).

1,5-p-Tolyl-3-p-methoxyphenylformazan **10e**: With the use of the general procedure p-toluidine was diazotized and coupled with p-methoxyphenylpyruvic acid **8b** to give crude **10e** wich was crystallized from acetone/methanol (1:1) to give 1.4 g (79%) of red crystals mp. 173-2°C (lit.[25] 172-5°C).

1,3,5-Tri-p-methoxyphenylformazan **10f**: With the use of the general procedure p-anisidine was diazotized and coupled with p-methoxyphenylpyruvic acid **8b** to give crude **10f** wich was crystallized from acetone/methanol (1:1) to give 1.56 g (82%) of red crystals mp. 142-2°C (lit.[26] 140°C).

1,5-Diphenyl-3-p-nitrophenylformazan **10g**: With the use of the general procedure aniline was diazotized and coupled with p-nitrophenylpyruvic acid **8c** to give crude **10g** which was crystallized from ethanol to give 1.13 g (66%) of deep red crystals mp. 190-2°C (lit.[27] 204°C).

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