would be 2-amino-4-arylamino-1,6-dihydro-*s*-triazine-6-thione and the products derived from *p*-alkoxyphenylbiguanide would be 2,4-diamino-1-aryl-1,6-dihydro-*s*-triazine-6-thione. It is assumed that the different behavior of *p*-alkoxyphenylbiguanide is attributed to the increased nucleophilic property of the N^1 atom in which the electron density is increased by the resonance of the electron pair of the oxygen atom of the *p*-alkoxy group with benzene ring. Extensions and developments of this work are in progress.

Experimental

2-Amino-4-arylamino-1,6-dihydro-*s*-triazine-6-thione (I)——1) A solution of 0.002 mole of arylbiguanide and 0.002 mole of 1-morpholinopropylene-2,3-trithiocarbonate in 30 ml of EtOH was heated for 5 hr under reflux. Precipitates deposited gradually from the reaction mixture during heating. After cooling, the precipitates deposited were collected by filtration and recrystallized from DMF. When the both reactants were heated in 1.5 ml of DMF for 3 hr at 100° and then treated by the similar procedure, the yield of the products was somewhat increased. Details of the data were summarized in Table I. These compounds exhibited the abundant corresponding molecular ion peaks in the mass spectra.

2) A solution of 0.002 mole of phenylbiguanide and 0.002 mole of 1-(β-naphthoxy)propylene-2,3-trithiocarbonate in 30 ml of EtOH was heated for 5 hr under reflux. Precipitates gradually deposited from the reaction mixture during heating. After cooling, the precipitates deposited were collected by filtration and recrystallized from DMF to give 0.05 g (11%) of colorless prisms melting at 282°, which was identified with the sample prepared by the procedure described above by mixed melting point determination and infrared comparison. Treatment of another arylbiguanide with 1-(β-naphthoxy)propylene-2,3-trithiocarbonate under the similar conditions gave the corresponding *s*-triazinethiones in low yields.

2,4-Diamino-1-(*p*-alkoxyphenyl)-1,6-dihydro-*s*-triazine-6-thione (II)——A solution of 0.002 mole of *p*-alkoxyphenylbiguanide and 0.002 mole of 1-morpholinopropylene-2,3-trithiocarbonate in 30 ml of EtOH or in 1.5 ml of DMF was heated for 3—5 hr at 100°. Precipitates gradually deposited from the reaction mixture during heating. After cooling, the precipitates deposited were collected by filtration and recrystallized from DMF. Details of the data were summarized in Table I.

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Formic Acid Reduction. XX.[1] Reduction of 2-Benzylidene-1,3-indandiones

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The formic acid reduction of the carbon–carbon double bonds adjacent to carbonyl discovered from this laboratory[3] appears a reaction of considerable synthetic significance. The present work has been directed toward the formic acid reduction of 2-benzylidene-1,3-indandiones possessing substituent on the benzylidene ring.

For preparation of the 2-benzylidene-1,3-indandiones by condensing 1,3-indandione and benzaldehydes, we adopted the previously reported method[4] using boron trioxide as a

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[1] Part XIX: M. Sekiya, M. Tomie, K. Ito, J. Suzuki, K. Suzuki, and Y. Terao, *Chem. Pharm. Bull.* (Tokyo), 21, 1625 (1973).

[2] Location: *2-2-1, Oshika, Shizuoka.*

[3] M. Sekiya and K. Suzuki, *Chem. Pharm. Bull.* (Tokyo), **18**, 1530 (1970).

TABLE I. Preparation[a)] of 2-Benzylidene-1,3-indandiones

X	Reaction time (hr)	Yield (%)
H	0.5	90
p-NO_2	3.0	73
m-NO_2	0.5	86
p-OH	3.0	78
m-OH	1.5	84
p-Cl	3.0	73
m-Cl	2.0	76
p-CH_3O	1.0	81
m-CH_3O	2.0	87

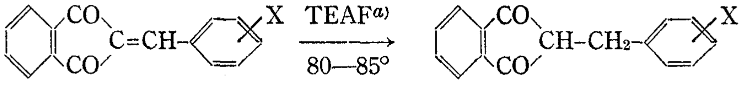
a) 1,3-Indandione, benzaldehyde and boron trioxide were used in 1:1.1:1.5 molar proportion. A benzene solution of 1,3-indandione, aldehyde and catalytic amount of piperidine with a suspension of boron trioxide was refluxed. Details are given in Experimental.

dehydrating agent in the presence of a small amount of piperidine in benzene solution, although they have been reported[5)] to be available by condensation in acetic acid in the presence of sulfuric acid. Preparation of nine 2-benzylidene-1,3-indandiones possessing substituent was performed satisfactorily by this method in 70—90% yields, as can be seen in Table I.

Formic acid reduction of these was carried out by the use of the formate, TEAF, which has been known[6)] as the distillable liquid, bp 98° (18 mmHg), given by $5HCO_2H \cdot 2NEt_3$. When heated the substrate compound in this formate at above 50°, considerable emission of carbon dioxide was observed, indicating occurrence of formic acid reduction. By carring out under the standardized condition of heating a mixture of each 2-benzylidene-1,3-indandione and TEAF in 1: 12 (based on HCO_2H) molar proportion at 80—85°, saturation of benzylidene double bond was successfully effected with nearly quantitative yields of the corresponding 2-benzyl-1,3-indandione as shown in Table II.

Evidence of the saturation of the benzylidene double bonds was seen by disappearance

TABLE II. Reduction of 2-Benzylidene-1,3-indandiones with TEAF



X	Reaction time (hr)	Yield (%)
H	1.5	95
p-NO_2	0.5	93
m-NO_2	2.0	96
p-Cl	1.3	98
m-Cl	0.6	98
p-CH_3O	1.6	96
m-CH_3O	1.6	97
p-OH	2.5	95
m-OH	1.5	97

a) Solution of substrate in TEAF in 1:12 (based on HCO_2H) molar proportion was heated at 80—85°. Procedures are given in Experimental in details.

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4) This method has been shown to be sufficiently effective for condensing β-diketones or secondary amines with aldehydes [M. Sekiya and H. Sakai, *Chem. Pharm. Bull.* (Tokyo), **17**, 32 (1969) and ref. 3)].

5) L. Geita and G. Vanags, *Zhur. Obshchei. Khim.*, **27**, 3109 (1957) [*C.A.*, **52**, 9111 (1958)].

6) K. Ito, *Yakugaku Zasshi*, **86**, 1166 (1966).

of the $\rangle C{=}C\langle$ stretching absorption at *ca.* 1610—1620 cm^{-1} in the infrared (IR) spectra of the starting 2-benzylidene-1,3-indandiones and of the benzylidene absorption at above 340 nm in the ultraviolet (UV) spectra of the same. The higher frequencies of the $\rangle CO$ stretching absorption of the products appeared at 1700—1710 cm^{-1} are also consisted with the structures.

Selectivity of this reduction can be seen by retention of the nitro groups in the two products. Rapidity of the reductions can be roughly deduced from the reaction periods shown in Table II. When compared these values with that of the unsubstituted substrate, the reduction is thought to be accelerated with electron-withdrawing substituent and restrained with electron-releasing substituent. The *m*-nitro substituted substrate is an exception for this deduction, since in this case homogeneous reaction could not be performed because of its sparing solubility in TEAF.

Experimental

Preparation of 2-Benzylidene-1,3-indandiones General Procedure——To a solution of 1,3-indandione (0.02 mole) and a few drops of piperidine in 30 ml of benzene a granular boron trioxide (0.03 mole) and then benzaldehyde (0.022 mole) were added. The mixture was refluxed with stirring. After filtration of the warm mixture, the filtrate was concentrated under reduced pressure. Recrystallization of the resulting crystalline residue from appropriate solvent gave the corresponding 2-benzylidene-1,3-indandione.

In the above procedure the other aromatic aldehydes shown in Table I could likewise be used in place of benzaldehyde. Only *m*-nitrobenzaldehyde formed an exception of the above procedure. In this run, the product was deposited in the warm mixture which was collected by filtration and extracted with chloroform. Evaporation of chloroform and recrystallization of the resulting crystalline residue from dioxane gave needles of *m*-nitrobenzylidene-1,3-indandione.

Reaction time and yield of the products are shown in Table I. Analytical and physical data of the products are summarized in Table III.

Reduction of 2-Benzylidene-1,3-indandiones with TEAF General Procedure——In a flask provided with a thermometer, an inlet tube and an air condenser tube, were placed 0.02 mole each of 2-benzylidene-1,3-indandione and 20.8 g (0.24 mole based on HCO_2H) of TEAF. The mixture was heated at 80—85° with

Table III. Physical and Analytical Data of 2-Benzylidene-1,3-indandiones

X	Appearance (recryst. solv.)	mp (°C) (lit. mp (°C))	Analysis (%) Calcd. (Found)			IR ν_{max}^{KBr} cm^{-1}			UV λ_{max}^{MeOH} nm (log ε)
			C	H	N or Cl	$\rangle C{=}C\langle$	$\rangle CO$	Others	
H	pale yellow plates (EtOH)	150 (153[a,b])	82.04 (82.11)	4.30 (4.20)		1615	1690 1730		239(4.32) 341(4.58)
p-NO_2	pale yellow needles (C_6H_6)	225—227 (230[a,c])	68.82 (68.61)	3.25 (3.22)	5.02 (5.08)	1619	1683	1348 1511 (NO_2)	266(4.11) 344(4.52)
m-NO_2	pale yellow needles (dioxane)	243—246 (246—247[a,c])	68.82 (68.91)	3.25 (3.30)	5.02 (5.06)	1618	1688	1350 1525 (NO_2)	340(4.42)
p-Cl	pale yellow needles (C_6H_6)	176—177 (177[a])	71.49 (71.48)	3.37 (3.44)	13.19 (13.31)	1616	1684		347(4.56)
m-Cl	pale yellow needles (C_6H_6)	173—175 (178—179[a])	71.49 (71.61)	3.37 (3.54)	13.19 (13.27)	1612	1682		337(4.55)
p-OCH_3	pale yellow needles (C_6H_6)	152—155 (155[a])	77.26 (77.31)	4.58 (4.60)		1614	1680		383(4.58)
m-OCH_3	pale yellow needles (C_6H_6)	139—141 (143[c])	77.26 (77.04)	4.58 (4.52)		1622	1680		339(4.39)
p-OH	pale yellow needles (dioxane)	233—234 (234[a])	76.79 (76.79)	4.03 (4.13)		1618	1652	3246 (OH)	386(4.52)
m-OH	pale yellow needles (dioxane)	219—222 (222[a])	76.79 (76.73)	4.03 (4.05)		1617	1658	3262 (OH)	338(4.38)

a) M.V. Ionescu, *Bull. Soc. Chim.*, **47**, 210 (1930)

b) Y. Poirer and N. Lozac'h, *Bull. Soc. Chim. France*, **1966**, 1062; D. Radulescu and V. Georgescu, *ibid.*, **37**, 1072 (1925)

c) V. Petrow, J. Saper, and B. Sturgeon, *J. Chem. Soc.*, **1949**, 2134

Table IV. Physical and Analytical Data of 2-Benzyl-1,3-indandiones

X	Appearance (recryst. solv.)	mp (°C) (lit. mp (°C))	Analysis (%) Calcd. (Found)			IR ν_{max}^{KBr} cm^{-1}	UV λ_{max}^{MeOH} nm (log ε)
			C	H	N or Cl		
H	pale yellow prisms (EtOH)	95—96 (96—97[a])	81.34 (81.46)	5.12 (4.92)		1713 (CO)	
p-NO_2	pale yellow needles (EtOH)	139—141 (142[a])	68.32 (68.29)	3.94 (3.97)	4.88 (4.76)	1703 (CO) 1505 1348 (NO_2)	252(3.46)
m-NO_2	pale yellow needles (EtOH)	121—122	68.32 (68.33)	3.94 (4.00)	4.88 (4.77)	1700 (CO) 1532 1348 (NO_2)	278(3.36)
p-Cl	pale yellow needles (MeOH)	116—118 (119—120[a])	71.01 (70.74)	4.10 (4.18)	13.10 (13.30)	1702 (CO)	
m-Cl	pale yellow needles (MeOH)	138—139	71.01 (70.78)	4.10 (3.98)	13.10 (12.98)	1705 (CO)	
p-CH_3O	pale yellow neeldes (MeOH)	101—102 (102—104[a,b])	76.67 (76.71)	5.30 (5.44)		1704 (CO)	
m-CH_3O	pale yellow needles (MeOH)	58—59	76.67 (76.54)	5.30 (5.28)		1706 (CO)	
p-OH	pale yellow needles (MeOH)	181—183	76.18 (76.35)	4.80 (4.86)		1698 (CO) 3230 (OH)	
m-OH	prisms (MeOH)	114—116	76.18 (76.07)	4.80 (4.92)		1701 (CO) 3348 (OH)	

a) J. Strandings, E. Ermanc, T. Dumpis, J. Linabergs, and G. Vanags, *Zh. Organ. Khim.*, **1** (2), 388 (1965)
b) G. Vanags and T. Dumpis, *Doklady. Akad. Nauk.*, **135**, 549 (1959)

stirring. A stream of dry air free from CO_2 was passed through the reaction mixture so as to check emission of CO_2 by $Ba(OH)_2$ solution. Heating was continued until emission of CO_2 was almost ceased. The reaction solution was concentrated under reduced pressure to remove triethylamine and excess of TEAF. Trituration of the resulting residue with water gave fine powder which was recrystallized from appropriate solvent to give the corresponding 2-benzyl-1,3-indandione.

Reaction time and yield of the products are shown in Table II. Analytical and physical data of the products are summarized in Table IV.

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An Improved Method for the Analysis of Dansyl Polyamines

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Recently, increasing attentions have been directed to the significance of polyamines in various biological processes including DNA replication, RNA synthesis, and protein synthesis.[2]

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[1] Location: *Yayoi-cho, Chiba.*

[2] H. Tabor and C.W. Tabor, *Ann. Rev. Pharmacol.*, **16**, 245 (1964); U. Bachrach, *Ann. Rev. Microbiol.*, **24**, 109 (1970); S.S. Cohen, "Introduction to the Polyamines," Prentice-Hell, Englewood Cliffs, N. J., 1971; T.A. Smith, *Endeavour*, **31**, 22 (1972).