The Pschorr Cyclization of Aromatic Amines with *t*-Butyl Thionitrate in Nonaqueous Media

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(Received January 23, 1981)

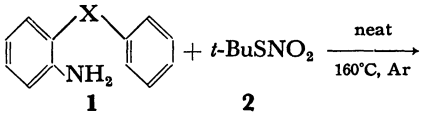
The Pschorr cyclization of various arylamines with *t*-butyl thionitrate under nonaqueous conditions gave the corresponding cyclic products in moderate yields. The same reaction was also found to proceed readily with *p*-toluenesulfonyl nitrite at room temperature. Treatment of *o*-aminophenyl allyl ether or sulfide with *t*-butyl thionitrate resulted in the intramolecular Meerwein arylation to the olefinic bond affording 3-chlorochroman or -thiochroman, though the yield was low. The plausible mechanism of the Pschorr cyclization with *t*-butyl thionitrate is discussed.

During the course of our study on oxidation of aliphatic and aromatic thiols, disulfides and sulfinic acids with N_2O_4, the corresponding thionitrites, thionitrates and sulfonyl nitrites have been found to be the key intermediates, which are also very useful in synthetic reactions. Namely, diazotization reaction of aromatic amines,[1] nitrosation of secondary amines, and sulfenylation of carbanion[2] are readily promoted in good yields in nonaqueous reaction media. These are remarkably effective reagents for diazotization of aromatic amines due partly to the relatively weak S–N bond as compared to O–N bond of alkyl nitrite. The Gomberg-Bachmann reaction which is used for synthesis of biphenyl from aromatic diazonium salt, has also been carried out using the thionitrates.[1] Thus, various aromatic amines have been allowed to react with the thionitrate in aromatic solvents such as benzene affording biphenyl derivatives in good yields.

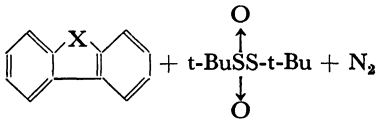
While all these reactions we have studied are intermolecular coupling of two aromatic rings, we now have applied the reaction to an intramolecular reaction, *i.e.* the Pschorr cyclization,[3] which is known to be an effective reaction for one-step synthesis of cyclic compounds, used often for syntheses of natural products.[4,5] This paper deals mainly with the Pschorr cyclization of various aromatic amines with *t*-butyl thionitrate, together with the intramolecular Meerwein arylation to give cyclic products.

Results and Discussion

When various aromatic amines bearing two aromatic rings (**1**) such as 2-aminobenzophenone (**1a**, 1.0 mmol) were treated with *t*-butyl thionitrate (**2**, 1.5 mmol) without solvent at 160 °C for 0.5 h the corresponding cyclization product (**3**) was obtained as the main product. *t*-Butyl thionitrate (**2**) was in turn converted to *S*-*t*-butyl 2-methylpropane-2-thiosulfonate (**4**) during



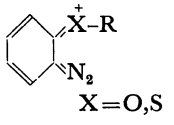
1 **2**



3 **4**

the cyclization. Other unidentified products were in the form of tar or resin. Generally, the Pschorr reaction is known to be accompanied with a few side reactions such as reduction of diazonium ion which produces arene, reductive coupling which affords symmetrical biphenyls, halogenation and phenol formation.[3] Therefore, the yield of the cyclized product in the usual Pschorr reaction is generally low.[3] In this reaction, a small amount of the reduced product, *i. e.* benzophenone, was also obtained, however formation of phenol and reductive coupling derivatives were not observed in this reaction in nonaqueous media.

The Pschorr cyclization of several aromatic amines which possess different bridging group of X in (**1**) with *t*-butyl thionitrate (**2**) has been examined and the yields of the corresponding cyclic products are listed in Table 1. Since the Pschorr reaction is an intramolecular condensation reaction, the ready access of the two reaction centers in the ground state is considered to be quite important for successful cyclization. Namely, the two carbon atoms that are eventually linked together would preferably be in a close vicinity with each other. The most favorable bridging group (X, **1**) is the rigid ethylenic linkage of ethyl (*E*)-2,3-diphenylpropenate (**1g**), which would assume a planar structure by conjugation between the two aromatic rings through an ethylenic group, thus placing the two reaction centers of two aromatic rings in a close vicinity. In fact, ethyl (*E*)-2,3-diphenylpropenate (**1g**) gave ethyl 9-phenanthrenecarboxylate (**3g**) as the main cyclic product in a very good yield in the Pschorr reaction with *t*-butyl thionitrate (**2**). In the case of ether (**1b**) and sulfide (**1c**, **1d**, **1e**), the yield of cyclized products were rather low. Contribution of the following *o*-quinonoid structure (**5**)



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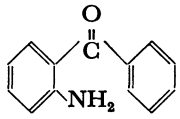
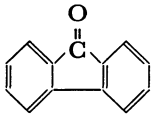
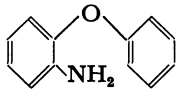
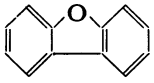
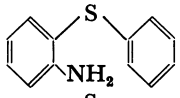
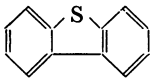
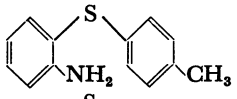
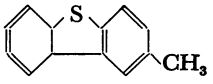
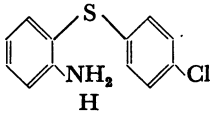
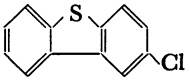
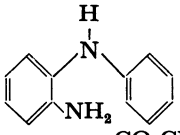
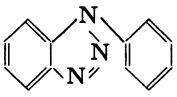
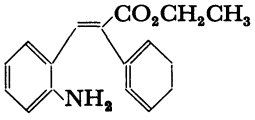
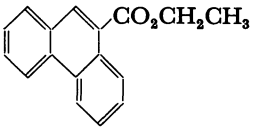
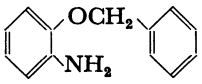
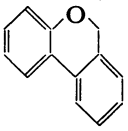
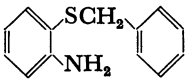
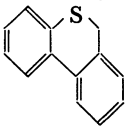
in the ground state of the diazonium salts of both the ether (**1b**) and sulfide (**1c**, **1d**, **1e**) may be partly responsible not only for the low yields of the desired products but also for the undesired resin-forming side reactions, while the distant two reaction centers would not favor the recombination.[3] When 2-aminodiphenylamine (**1f**) was treated with the thionitrate, 1-phenylbenzotriazole (**3f**) instead of carbazol, a desired product,

Table 1. The Pschorr cyclization of various amines (**1**) with *t*-butyl thionitrate (**2**)

Entry	Amine **1**	Product **3**	Yield/%[a]
1	**a** 		34[b]
2	**b** 		5[b]
3	**c** 		16[b]
4	**d** 		20
5	**e** 		17
6	**f** 		26
7	**g** 		70
8	**h** 		21
9	**i** 		10

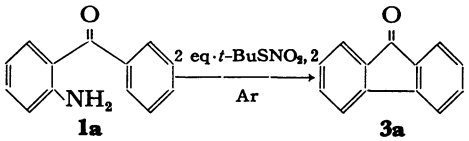
a) Isolated yield. b) Yield by GLC.

was obtained. The same result was obtained in the ordinary Pschorr cyclization with nitrous acid in an aqueous media.[3]

In searching the optimum reaction conditions, several runs were carried out (see Table 2). Although the cyclization is an intramolecular reaction, the reaction without solvent was found to offer higher yield of cyclization at higher temperatures, however the best yield of cyclic product was attained in the reaction in DMSO. The Pschorr reaction with nitrous acid in aqueous media is usually carried out in the presence of copper[3] or copper(I) oxide.[7] However when copper or copper(I) oxide was added into our reaction system, the cyclic adduct, fluorenone (**3a**), was not obtained but a complex mixture was obtained.

Meanwhile, the Pschorr reaction of *o*-substituted aromatic amines was also found to proceed smoothly with *p*-toluenesulfonyl nitrite (**6**), which has been shown by us to be a new still more powerful nitrosating agent in certain cases, was used instead of *t*-butyl thionitrate.[1] Namely, aromatic amine (**1**, 1.0 mmol) was treated with three equivalents of *p*-toluenesulfonyl nitrite (**6**, 3.0 mmol) at room temperature for 1—2 h in dry acetonitrile under argon atmosphere. In this case, the reaction was carried out at room temperature instead

Table 2. The Pschorr cyclization of 2-aminobenzophenone (**1a**) with *t*-butyl thionitrate (**2**)

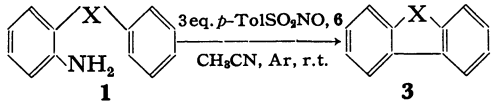


1a **3a**

Entry	Solvent	Temp/°C	Time/h	Yield/%[a]
1	Neat	r.t.	6.0	Trace
2	Neat	120	0.5	15
3	Neat	160	0.5	34
4	CH_3CN	r.t.	2.0	28
5	$(Bu)_2O$	120	4.0	27
6	DMSO	160	1.0	43
7	DMSO Cu or Cu_2O[b]	160	1.0	c)
8	HMPA	160	1.0	Trace

a) Yield by GLC. b) 1.7 Equiv./mol of substrate. c) Complex mixture.

TABLE 3. THE PSCHORR CYCLIZATION OF AMINES (**1a**, **1c**, **1h**) WITH *p*-TOLUENESULFONYL NITRITE (**6**)



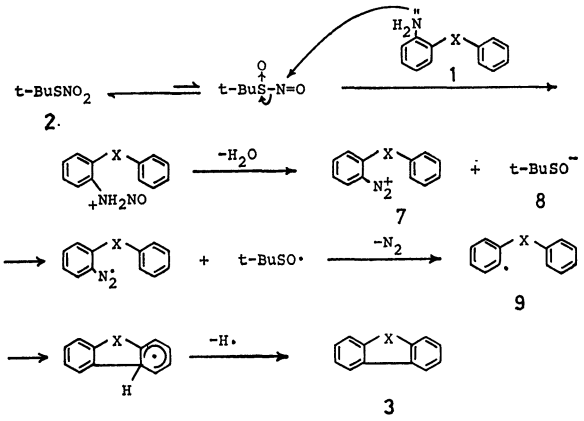
1 **3**

	Amine **1**, X	Yield/%[a)]
1a	X=>C=O	49
1c	-S-	16
1h	$-OCH_2-$	Trace

a) Yield by GLC.

of higher temperatures at which reaction was performed with *t*-butyl thionitrate, since *p*-toluenesulfonyl nitrite (**6**) decomposes at a higher temperature. However the yield of the cyclic adduct was relatively higher than that in the reaction with *t*-butyl thionitrate (see Table 3).

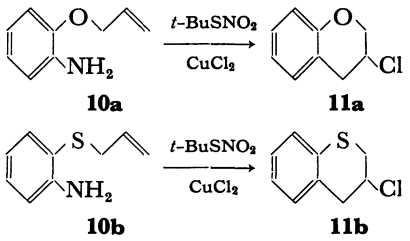
As to the mechanism of the Pschorr cyclization, there are two conceivable pathways, *i. e.* ionic and homolytic paths.[6-8] While thermal decomposition of diazonium salts in acidic media has been believed to take place *via* the ionic process, the reaction has been considered to proceed *via* the homolytic pathway, when the counter anion of diazonium ion is a good reducing agent or the reaction is catalyzed by copper. Since the sulfenate anion derived from the thionitrate (**2**) is considered to be a good reducing agent, while a large amount of tarry material is formed in the reaction, we propose the following free-radical mechanism for this reaction (Scheme 1). The gas evolved in the Gomberg-Bachmann



Scheme 1.

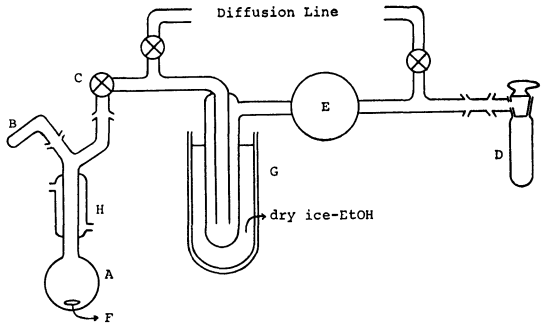
reaction of arylamines with aromatic hydrocarbon using *t*-butyl thionitrate[1] was analyzed as N_2 gas by mass spectrometry upon conducting the reaction carefully in a degassed anhydrous system. Therefore, the Pschorr cyclization of aromatic amine with *t*-butyl thionitrate is considered to be initiated by the nucleophilic attack of aromatic amine to nitrogen atom of *t*-butyl thionitrate, like in the aqueous Pschorr reaction. The diazonium ion (**7**) formed after the dehydration may be reduced to the diazo radical by sulfenate anion (**8**), a good reducing agent, which upon release of N_2 gas, gives aryl radical (**9**) that undergoes intramolecular coupling to afford cyclic product (**3**) after hydrogen abstraction. Besides the intramolecular cyclization there may be some intermolecular arylation or a similar side reaction which may be responsible for the formation of much unidentified tarry materials.

Meanwhile, the reaction of diazonium halides derived from aromatic amines with olefinic compound in the presence of copper salt is known as the Meerwein arylation reaction.[9] The Meerwein arylation to olefinic compounds has been found to take place with *t*-butyl thionitrate and addition products were obtained in moderate yields.[1] When an aromatic amine which possesses allyloxy or allylthio group (**10**) at the ortho position was treated with 1.4 equivalent of *t*-butyl



thionitrate (**2**) in the presence of copper(II) chloride in dry acetonitrile at room temperature, the cyclization product (**11**) was obtained as the result of the intramolecular Meerwein arylation despite the lack of any electron-withdrawing substituent on the vinyl group to enhance the Meerwein addition of aryl group. This may be the first example of the intramolecular Meerwein arylation to afford heterocyclic compounds.

Thus, we may conclude that the Pschorr cyclization of *o*-aminophenyl derivatives proceeds quite well with *t*-butyl thionitrate in nonaqueous media and the reaction is useful especially for ring closure reactions of such compounds as *cis*-stilbene or its ester derivatives which are relatively unstable under acidic conditions used in the usual Pschorr cyclization with nitrous acid in strong acids.



A: Reaction flask, B: bent tube, C: stopcock, D: gas sampler, E: teppler pump, F: magnetic stirrer bar, G: trap, H: water cooler,

Fig. 1. Apparatus for analysis of the gas evolved in the Gomberg-Bachemann reaction with *t*-butyl thionitrate.

Experimental

General. All melting points were taken on a Yanako instrument and were uncorrected. IR spectra were taken on a Hitachi 260-50 spectrometer. NMR spectra were recorded with a Hitachi Perkin-Elmer R-20 spectrometer in $CDCl_3$ using TMS as the internal standard. Mass spectra were

taken with a Hitachi RMU-6MG mass spectrometer. Shimadzu GC-6A instrument was used for gas chromatography using N_2 gas as a carrier gas. Elemental analyses were carried out by the Chemical Analysis Center at this University.

t-Butyl Thionitrate (2) and p-Toluenesulfonyl Nitrite (6). These title compounds were prepared from the corresponding thiol and sulfinic acid with dinitrogen tetraoxide, according to the methods reported earlier.[1]

Preparation of Ethers (1b, 1h, and 10a) and Sulfides (1c, 1d, and 1e). 2-Nitrodiphenyl ethers and sulfides were prepared by the reaction of *o*-chloronitrobenzene with alkaline salts of desired alcohols or thiols in the presence of a catalytic amount of tetrabutylammonium bromide as a phase transfer catalyst.[10] The yields of the ethers and sufides were nearly 90%. The nitro compound was reduced by the Fe–HCl system,[11] yielding the amine in *ca.* 80% yield.

2-Aminodiphenyl Ether (1b): Colorless crystals; mp 44—45 °C (from benzene–hexane) (lit,[12] 43—44 °C); NMR ($CDCl_3$) δ 3.65 (b, 2H, NH_2), 6.46—7.49 (m, 9H, ArH).

2-Aminodiphenyl Sulfide (1c): Colorless crystals; mp 41 °C (from benzene–hexane) (lit,[13] 41—42 °C); NMR ($CDCl_3$) δ 4.18 (b, 2H, NH_2), 6.51—7.86 (m, 9H, ArH).

2-Aminophenyl p-Tolyl Sulfide (1d): Colorless crystals; mp 47 °C (from hexane–ether) (lit,[14] 48.5—49.0 °C); NMR ($CDCl_3$) δ 2.22 (s, 3H, CH_3), 4.15 (b, 2H, NH_2), 6.52—7.53 (m, 8H, ArH).

2-Aminophenyl 4-Chlorophenyl Sulfide (1e): Colorless crystals; mp 33 °C (from ether), bp 194 °C (bath temp)/4 mmHg† (lit,[15] bp 164—166 °C/0.45 mmHg); NMR ($CDCl_3$) δ 4.20 (b, 2H, NH_2), 6.57—7.59 (m, 8H, ArH).

2-Aminophenyl Benzyl Ether (1h): Colorless crystals; mp 38 °C (from ether) (lit,[16] 39—40 °C); NMR ($CDCl_3$) δ 3.90 (b, 2H, NH_2), 5.60 (s, 2H, CH_2), 6.63—7.58 (m, 9H, ArH); IR (KBr) 3900 and 3730 (NH_2), 1600, 1210, 724 cm^{-1}.

2-Aminophenyl Allyl Ether (10a): Pale yellow oil; bp 136 °C (bath temp)/4 mmHg (lit,[17] bp 129—130 °C/10 mmHg); NMR ($CDCl_3$) δ 3.74 (s, 2H, NH_2), 4.34—4.55 (m, 2H, CH_2), 5.05—5.51 (m, 2H, $=CH_2$), 5.70—6.30 (m, 1H, CH), 6.33—6.93 (m, 4H, ArH); IR (neat) 3890 and 3700 (NH_2), 3100 (=CH), 1600, 1210, 730 cm^{-1}.

2-Aminodiphenylamine (1f). Commercially available 2-nitrodiphenylamine was reduced by the same system of Fe–HCl.[11] Yield *ca.* 80%. Colorless crystals; mp 80 °C (from hexane) (lit,[18] 78—80 °C); NMR ($CDCl_3$) δ 3.36 (b, 2H, NH_2), 5.10 (b, 1H, NH), 6.51—7.34 (m, 9H, ArH).

2-Aminobenzophenone (1a). Commercially available compound (Tokyo Kasei Kogyo Co.) was used.

Ethyl (E)-3-(2-Aminophenyl)-2-phenylpropenate (1g). (*E*)-3-(2-nitrophenyl)-2-phenylpropenic acid was obtained by the Perkin condensation using *o*-nitrobenzaldehyde and phenylacetic acid,[19] and then esterified in ethanol. The nitro compound was reduced to the amino compound by the Fe–HCl system.[11] Yellow crystals; mp 96—97 °C (from benzene–hexane); NMR ($CDCl_3$) δ 1.19 (t, J=6.9 Hz, 3H, CH_3), 3.80 (b, 2H, NH_2), 4.27 (q, J=6.9 Hz, 2H, CH_2), 6.24—7.53 (m, 9H, ArH), 7.82 (s, 1H, =CH); IR (KBr) 3800 and 3690 (NH_2), 1680 (C=O), 1620 (C=C), 1520, 1240, 700 cm^{-1}; Found: C, 76.28; H, 6.38; N, 5.15%. Calcd for $C_{17}H_{17}NO_2$: C, 76.38; H, 6.41; N, 5.23%.

Preparation of Sulfides (1i and 10b). *o*-Nitrobenzenethiol was treated with benzyl bromide or allyl bromide, giving the corresponding sulfides in *ca.* 90% yields by the usual method.[20] The nitro compounds then were reduced by the Fe–HCl system.[11]

2-Aminophenyl Benzyl Sulfide (1i): Colorless crystals; mp 45 °C (from benzene–hexane) (lit,[16] 45 °C); NMR ($CDCl_3$) δ 3.87 (s, 2H, CH_2), 4.24 (b, 2H, NH_2), 6.44—7.40 (m, 9H, ArH); IR (KBr) 3860 and 3670 (NH_2), 1595, 1440, 695 cm^{-1}.

2-Aminophenyl Allyl Sulfide (10b): Pale yellow oil; bp 135—138 °C (bath temp)/4 mmHg (lit,[21] bp 120 °C/4 mmHg); NMR ($CDCl_3$) δ 3.34 (d, J=6.4 Hz, 2H, CH_2), 4.27 (s, 2H, NH_2), 4.69—5.12 (m, 2H, $=CH_2$), 5.48—6.22 (m, 1H, =CH), 6.46—7.43 (m, 4H, AtH); IR (neat) 3880 and 3680 (NH_2), 3100 (=CH), 1595, 1465, 740 cm^{-1}.

The Pschorr Cyclization of Amines (1) with t-Butyl Thionitrate (2). *t*-Butyl thionitrate (**2**, 1.5 mmol) was added with syringe to melted 2-aminobenzophenone (**1a**, 1.0 mmol) at 160 °C under argon. Vigorous reaction occurred and gas evolved. After heating and stirring the mixture at the same temperature for 0.5 h, the mixture was cooled and a portion of the mixture was subjected to GLC to determine the yield. Fluorenone (**3a**) was identified by comparing the GLC and TLC with those of authentic samples, and the yields were determined by GLC. Other compounds (**3d—3i**) were isolated by preparative TLC or column chromatography (silica gel, eluent: benzene–hexane=1 : 6) and recrystallized from adequate solvent.

2-Methyldibenzothiophene (3d): Colorless crystals; mp 86 °C (from ethanol) (lit,[22] 88—89 °C); NMR ($CDCl_3$) δ 2.59 (s, 3H, CH_3), 7.20—8.20 (m, 7H, ArH).

2-Chlorodibenzothiophene (3e): Colorless crystals; mp 125—126 °C (from ethanol) (lit,[23] 113—114 °C); IR (KBr) 1420, 1089, 755, 725 cm^{-1}; MS (70 eV) *m/e* (rel intensity) 220 (38%, M^++2), 218 (100%, M^+), 183 (14%, $C_6H_4SC_6H_3^+$).

1-Phenylbenzotriazole (3f): Colorless crystals; mp 85—87 °C (lit,[18] 89—90 °C); IR (KBr) 1592, 1494, 1055, 745 cm^{-1}; MS (70 eV) *m/e* (rel intensity) 195 (23%, M^+), 167 (100%, $C_6H_4N^+C_6H_5$), 77 (25%, $C_6H_5^+$).

Ethyl 9-Phenanthrenecarboxylate (3g): Coloress crystals; mp 58—59 °C (from ethanol) (lit,[23] 61 °C); NHR ($CDCl_3$) δ 1.64 (t, J=7.1 Hz, 3H, CH_3), 4.48 (q, J=7.1 Hz, 3H, CH_2), 7.42—8.97 (m, 9H, ArH); IR (KBr) 1700, (C=O), 1440, 1290, 1240, 1030 cm^{-1}; MS (70 eV) *m/e* (rel intensity) 250 (100%, M^+), 205 (99%, $C_{14}H_9C{\equiv}O^+$), 177 (54%, $C_{14}H_9^+$).

6H-Dibenzo[b, d]*pyran (3h):* Oil; NMR ($CDCl_3$) δ 5.07 (s, 2H, CH_2) (lit,[25] δ 5.07, s), 6.84—7.81 (m, 8H, ArH); MS (70 eV) *m/e* (rel intensity) 182 (74%, M^+), 181 (100%, $C_6H_4O^+CHC_6H_4$).

6H-Dibenzo[b, d]*thiopyran (3i):* Colorless crystals; mp 73—74 °C (lit,[26] 75.5 °C); MS (70 eV) *m/e* (rel intensity) 198 (91%, M^+), 197 (100%, $C_6H_4S^+CHC_6H_4$).

The Pschorr Cyclization of Amines (1a, 1b, and 1h) with p-Toluenesulfonyl Nitrite (6). A mixture of 2-aminobenzophenone (**1a**, 1.0 mmol) and dry acetonitrile (5 ml) was added onto *p*-toluensulfonyl nitrite (**6**, 3.0 mmol) under argon. Evolution of the gas was observed. Then the solution was stirred for 1 h at room temperature. The cyclic products were identified by comparison of the GLC and TLC with those of authentic samples, and yields were determined by GLC.

The Intramolecular Meerwein Arylation of Amines (10a and 10b) with t-Butyl Thionitrate (2) and Copper (II) Chloride. *t*-Butyl thionitrate (**2**, 1.4 mmol) was added slowly to the solution of 2-aminophenyl allyl ether (**10a**, 1.0 mmol) and well-dried anhydrous copper (II) chloride (1.2 mmol) in dry acetonitrile (10 ml) under argon with vigorous stirring at room temperature. The solution was stirred further for 1 h. Then cyclic product, 3-chlorochroman (**11a**), was directly isolated by column chromatography (silica gel, eluent: hexane).

3-Chlorochroman (11a): Pale yellow oil; NMR ($CDCl_3$) δ 3.43—3.90 (m, 3H, CH_2 and CH), 4.29—4.71 (m, 2H, OCH_2), 6.67—7.35 (m, 4H, ArH); MS (70 eV) *m/e* (rel intensity) 200

† 1 mmHg=133.322 Pa.

13%, $M^+ +2$), 168 (38%, M^+), 119 (100%, $[C_7H_5{=}O]CH_2^+$), 91 (31%, $C_6H_5CH_2^+$); Found: C, 63.65; H, 5.45%. Calcd for C_9H_9ClO: C, 64.10; H, 5.38%.

*3-Chlorothiochroman (**11b**)*: Pale yellow oil; NMR ($CDCl_3$) δ 3.16—3.75 (m, 5H, CH_2, CH and SCH_2), 6.97—7.27 (m, 4H, ArH); MS (70 eV) *m/e* (rel intensity) 186 (11%, $M^+ +2$), 184 (27%, M^+), 135 (100%, $[C_7H_5{=}S]CH_2^+$), 91 (14%, $C_6H_5CH_2^+$); Found: C, 58.51; H, 4.92%, Calcd for C_9H_9ClS: C, 58.53; H, 4.91%.

Determination of Gas Evolved in The Gomberg-Bachmann Reaction of p-*Chloroaniline with* t-*Butyl Thionitrate.* A mixture of *t*-butyl thionitrate (1.4 mmol) in dry benzene (1 ml) was placed in the flask A of the special apparatus shown in Fig. 1, freezed with liquid nitrogen bath and degassed three times using the vacuum line. After the stopcock C was closed, solid *p*-chloroaniline (0.7 mmol) was added from bent tube B, then the mixture was stirred and heated at 80 °C with an oil bath for 5 h. The gas evolved was pumped into the gas sampler D by teppler pump E. The gas obtained was introduced into the mass spectrometer for identification.

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