# Chemistry of Nitrosoimines. XVI.[1] A New Method for Facile Preparation of Azamonomethinecyanines *via* Nitrosoimines

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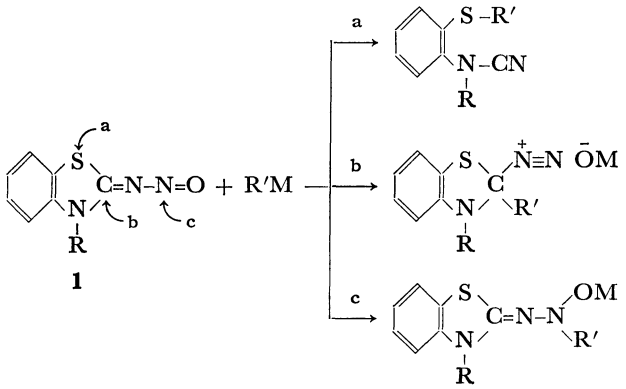
The reaction of 3-substituted 2-nitrosoimino-2,3-dihydrobenzothiazoles (**1**) with Grignard-type reagents of 3-substituted 2-imino-2,3-dihydrobenzothiazoles (**2**) gave azamonomethinecyanines (**3**) in high yields (71—96%). This is a new type of reaction for the preparation of **3**. Hydrolysis of **3** afforded ring-opened disulfides, bis[*o*-{*N*-methyl-*N*-(3-methyl-2,3-dihydrobenzothiazol-2-ylidenecarbamoyl)amino}phenyl] disulfides, in high yields (78—85%). Formation of by-products is explained by the presence of transnitrosation between **1** and **2** and ring-opening equilibrium of Grignard-type reagent of 2-imino-3-phenyl-2,3-dihydrobenzothiazole.

A series of investigations on the reactivity of nitrosoimines has revealed that there are three paths of attack on 3-substituted 2-nitrosoimino-2,3-dihydrobenzothiazoles (**1**) by organometalloids depending on the structure of the latter, *i.e.*, paths a and b by organolithiums[2] and paths b and c by Grignard regents[3] (Scheme 1). The reactivities are recognized by the large contribution of charge separated structures to the ground state of **1** shown by spectroscopic measurements, especially by ESCA.[4]

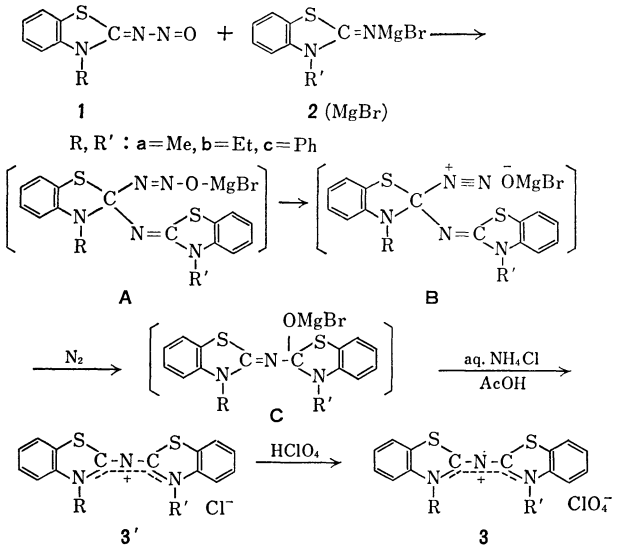


Scheme 1.

In continuation of the research directed to find out conditions under which each path is observed specifically, we report the reaction of **1** with Grignard-type reagents of 3-substituted 2-imino-2,3-dihydrobenzothiazoles (**2**) which followed path b almost exclusively to give the corresponding azamonomethinecyanines (**3**).[5] Concerning the preparation of azamonomethinecyanines, the reaction of 3-methyl-2-phenylsulfonylazobenzothiazolium tetrafluoroborate with sodium azide,[6] that of 2-amino-3-methylbenzothiazolium iodide with 3-methyl-2-methylthiobenzothiazolium iodie,[7] and base-catalyzed decomposition of triazatrimethinecyanine[8] are known.

3-Methyl-2-nitrosoimino-2,3-dihydrobenzothiazole (**1a**) reacted with Grignard-type reagent of 2-imino-3-methyl-2,3-dihydrobenzothiazole (**2a**) in THF at room temperature under nitrogen to give azamonomethinecyanine chloride (**3'a, a**) almost quantitatively, which gave the perchlorate (**3a, a**) in 84.5% yield by treatment with excess perchloric acid.

Evolution of nitrogen was followed for the reaction of **1a** with Grignard-type reagent of **2a** by measuring the increase of the gas volume of the reaction vessel set up as a closed system. Gas was evolved continuously during the course of reaction to yield 87% of the calculated amount (3.5 h, at 27.5 °C). No additional gas evolution was observed by injection of excess acetic acid. The cyanine perchlorate (**3a, a**) was obtained in 83% yield by the usual work-up.



Scheme 2.

Table 1. Yields and melting points of azamonomethinecyanine perchlorates (**3**)

| 1 | 2 | 3 | Yield (%)[a] | Mp (°C) | Recovery of **2** (%)[b] |
|---|---|---|---|---|---|
| R=Me | R'=Me | a, a | 84.5 | 319.0—320.0 (dec) | 29.3 |
| Me | Et | a, b | 89.8 | 276.8—278.0 | 29.8 |
| Et | Me | b, a | 95.8 | 276.8—278.0 | 34.7 |
| Et | Et | b, b | 89.3 | 275.0—276.5 | 28.6 |
| Ph | Me | c, a | 70.9 | 312.0—314.0 (dec) | 36.7 |
| Ph | Et | c, b | 78.0 | 253.5—255.0 | 28.2 |
| Ph | Ph | c, c | 80.0[c] | 316.0—317.3 (dec) | 28.2 |

a) After recrystallization from ethanol once. b) Based on **2** initially charged. c) The reaction was carried out at 0 °C.

Formation of **3** can be explained as shown in Scheme 2. The Grignard-type reagent of **2** attacks the *C*-2 of benzothiazoline ring of **1** (path b). The resulting diazotate (**A**) is not stable under the reaction conditions releasing nitrogen to give the alcohol (**C**), where contribution of diazonium character (**B**) to the transition state may be significant. The intermediate alcohol (**C**) is converted into a stabilized cation, *i.e.*, azamonomethinecyanine (**3**).

The results are given in Table 1.

Similar reactions of 2-nitrosoimino-3,4-diphenyl-2,3-dihydrothiazole (**4**) with Grignard-type reagents of **2** also gave the corresponding azamonomethinecyanine perchlorate (**5**) in high yields (Table 2).

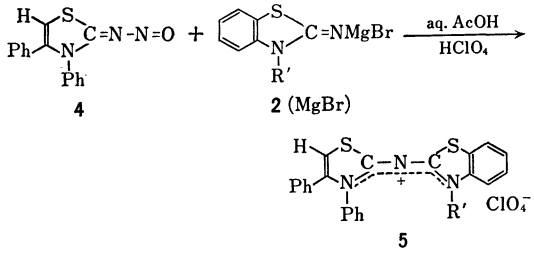
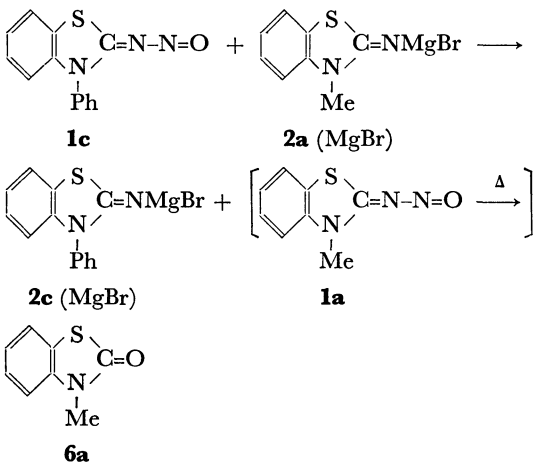



Table 2. Yields and melting points of azamonomethinecyanine perchlorates (**5**)

| 5 | Yield[a] (%) | Mp (°C) | Recovery of 2 (%)[b] |
|---|---|---|---|
| a) R′=Me | 80.5 | 236.8—238.2 | 33.6 |
| b) R′=Et | 74.6 | 274.2—276.0(dec) | 27.7 |

a) After recrystallization once from ethanol. b) Based on **2** initially charged.

The yield of **3c, a** (70.9%) was relatively low. **2c** (18.4%) and 3-methyl-2,3-dihydrobenzothiazol-2-one (**6a**, 13.6%) were obtained from the benzene extract of the reaction mixture along with the recovered **2a** (36.7 %) as shown in Table 1. This can be explained by the attack of Grignard-type reagent on the nitroso group (path c), where the nitroso group is transferred to the imine of stronger basicity.




For the preparation of **3c, c**, the reaction was carried out at 0 °C instead of at room temperature. When the reaction was carried out at room temperature, **3c, c** was obtained in lower yield. Thus the same reaction was carried out at higher temperature (60—80 °C) in order to examine the nature of side reactions. The following products were isolated.

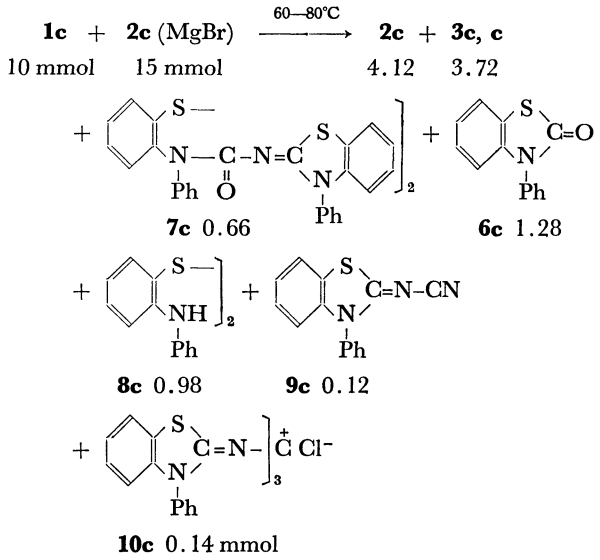
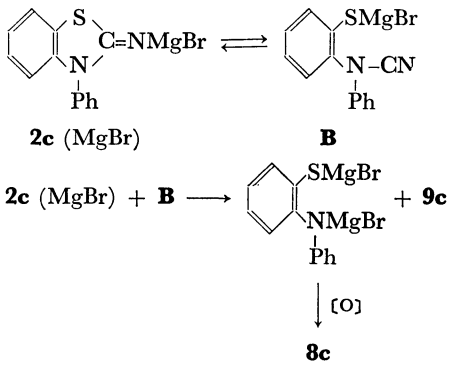


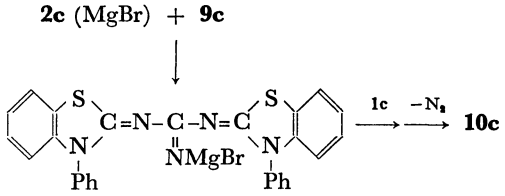

Table 3. Yields and melting points of the disulfides (**7**)

| 7 | Yield (%) | Mp (°C) |
|---|---|---|
| a) R=Me | 84.0 | 253.0—253.5 |
| b) R=Et | 84.5 | 119.5—120.5 |
| c) R=Ph | 78.0 | 230.0—231.0 |

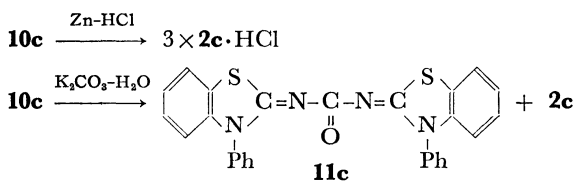
The formation of **8c** and **9c** can be rationalized by assuming the presence of ring-opening equilibrium in Grignard-type reagent of **2c**.[9]



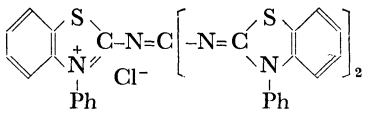

The formation of **10c** can be explained by the following sequence of reactions.




The structure of **10c** is supported by the following reactions where products were obtained almost quantitatively.



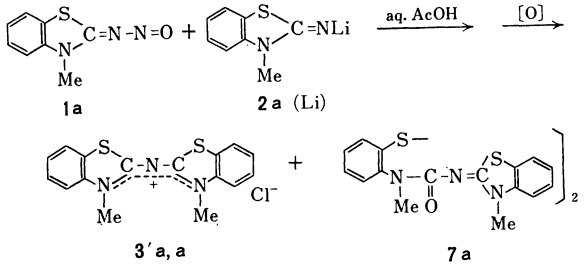

Compound (**10c**) seems to be less stable for alkaline hydrolysis than **3c**, **c**, in spite of the presence of a larger conjugation system for the carbonium ion.



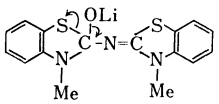

**10c**

The formation of **7c** is due to the thermal decomposition of the intermediate alcohol (*C*) of **3c**, **c**.

Lithium reagent of **2a** reacted with **1a** in THF at 0 °C under nitrogen to give bis [*o*-{*N*-methyl-*N*-(3-methyl-2,3-dihydrobenzothiazol-2-ylidenecarbamoyl)-amino}phenyl] disulfide (**7a**, 78.3%) as a major product and cyanine chloride (**3'a**, **a**, 10.9%) as a minor product.

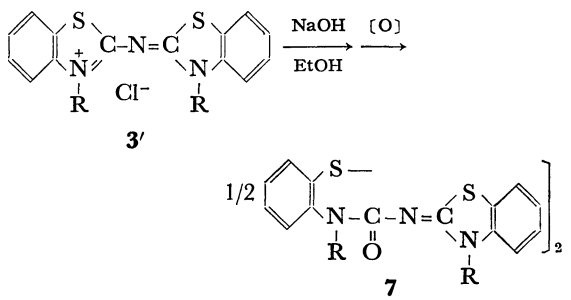



Formation of **7a** during the course of reaction is understandable by simultaneous ring-opening of lithium alkoxide (*C*) which might be produced after extrusion of nitrogen.

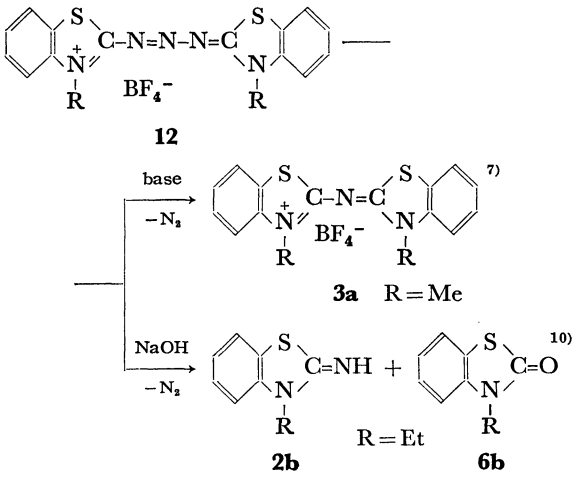



*C*

For the sake of clarification, symmetrical cyanine chlorides (**3'**) were treated with sodium hydroxide in ethanol which gave the disulfides (**7**) in high yields.




Ring-opening reaction of azamonomethinecyanine (**3'**) by sodium hydroxide is in contrast to the decomposition of triazatrimethinecyanine (**12**).




## Experimental

NMR spectra were recorded with Hitachi R-20 B and R-24 spectrometers (60 MHz) using TMS as an internal standard, IR spectra with a Hitachi EPI-G2 spectrometer and MS with a Hitachi RMU-6L mass spectrometer at 70 eV. All the melting points are uncorrected.

*Materials.* 2-Imino-3-methyl- (**2a**, mp 122—123 °C),[11] 3-ethyl-2-imino- (**2b**, mp 86—87 °C),[12] and 2-imino-3-phenyl-2,3-dihydrobenzothiazoles (**2c**, mp 73—74 °C)[11,13] were pre pared by reported methods. 3-Methyl-2-nitrosoimino-(**1a**, mp 146—147 °C (dec)),[11] 3-ethyl-2-nitrosoimino(**1b**, mp 147—148 °C (dec))[12] and 2-nitrosoimino-3-phenyl-2,3-dihydrobenzothiazoles (**1c**, mp 139—140 °C (dec))[11,13] were also prepared by reported methods. 2-Imino-3,4-diphenyl-2,3-dihydrothiazole (mp 108—109.5 °C)[14] was nitrosated in acetic acid with an aqueous solution of sodium nitrite to give 2-nitrosoimino-3,4-diphenyl-2,3-dihydrothiazole (**4**), mp 154—155 °C (dec).[15]

All the reactions were carried out under nitrogen except for the alkaline hydrolysis reactions of **3'**.

*General Procedure for the Reaction of 3-Substituted 2-Nitrosoimino-2,3-dihydrobenzothiazole (1) with Grignard-type Reagent of 3-Substituted 2-Imino-2,3-dihydrobenzothiazole (2).* A THF (50 ml) solution of **2** (7.5 mmol) was added dropwise at room temperature to a stirred solution of Grignard reagent prepared from magnesium (0.18 g, 7.5 mmol) and ethyl bromide (0.82 g, 7.5 mmol) in THF (25 ml) and the resulting solution was stirred for 30 min. **1** (5.0 mmol) was then added portionwise. The reaction took place immediately and precipitation appeared meanwhile. The mixture was stirred for 2 h and the solvent was evaporated under reduced pressure. To the residue were added a saturated aqueous solution of ammonium chloride (50 ml), glacial acetic acid (0.5 ml) and benzene (25 ml), and the mixture was stirred vigorously. After separation of the benzene layer, the remaining precipitates were collected by filtration and washed with 10% aqueous acetic acid (10 ml) and with water (25 ml) and then recrystallized from ethanol to give azamonomethinecyanine chloride (**3'**). The chloride was dissolved in ethanol and an excess of 70% aqueous perchloric acid was added to the solution. The resulting precipitates were collected by filtration after cooling in an ice bath and recrystallized from ethanol to give azamonomethinecyanine perchlorate (**3**).

By evaporation of benzene from the benzene layer under reduced pressure, the resulting residue was recrystallized from benzene–hexane (1 : 5) to give recovered **2**.

NMR spectra were recorded for cyanine chlorides (**3'**),

since the solubility of cyanine perchlorates (**3**) in methanol was too small for measurement.

*Measurement of Evolved Gas Volume.* To a THF (25 ml) solution of Grignard reagent prepared from magnesium (182 mg, 7.5 mmol) and ethyl bromide (0.82 g, 7.5 mmol) was added **2a** (1.230 g, 7.5 mmol) in THF (50 ml) at 0 °C under nitrogen. This was carried out in a three-necked 100 ml round bottomed flask equipped with a rubber septum, a gas outlet tube and a Liebig condenser. A small flask containing **1a** (965 mg, 5.0 mmol) was connected to the top with a rubber tube. After the solution had been stirred at 0 °C for 30 min, **1a** was added in small portions from the top and stirring was continued at 0 °C during the course of reaction. Gas was evolved continuously during 3.5 h up to 108 ml measured at 27.5 °C (r.t.) (87.6% based on added **1a**, 5.0 mmol). No additional gas was evolved by addition of excess acetic acid (0.5 ml).

*Reaction of 2-Nitrosoimino-3,4-diphenyl-2,3-dihydrothiazole (**4**) with Grignard-type Reagent of **2b**.* **4** (1.41 g, 5 mmol) was added portionwise at room temperature to a stirred solution of Grignard-type reagent of the imine prepared from ethylmagnesium bromide (7.5 mmol) and **2b** (1.36 g, 7.5 mmol) in THF (75 ml) and the resulting mixture was stirred for 2 h. A similar work-up to that above gave cyanine chloride (**5'b**, mp 298.2—299.5 °C (dec), (7.46 mmol, 74.6%). Treatment of the chloride with 70% aqueous perchloric acid gave cyanine perchlorate (**5**).

Residual **2b** (mp 86—87 °C, 368 mg, 27.7%) was recovered from the benzene layer.

*Reaction of **1c** with Grignard-type Reagent of **2c** at Higher Temperature (60—80 °C).* **2c** (3.30 g, 15 mmol) in THF (100 ml) was added at room temperature to a stirred solution of ethylmagnesium bromide (15.0 mmol) in THF (50 ml). The solution became turbid because of low solubility of Grignard-type reagent of **2c**. **1c** (2.56 g, 10.0 mmol) was then added to the solution portionwise. The mixture was stirred for 10 min at room temperature, and then refluxed for 17 h. The residue obtained by evaporation of the solvent under reduced pressure was extracted with dichloromethane (50 ml × 5) after addition of saturated aq ammonium chloride (100 ml).

By condensation of the extract, greenish yellow ppt were collected to give **3c,c** (0.84 g, 1.86 mmol) after recrystallization from ethanol. The filtrate was chromatographed on silica gel.

The following products were eluted from silica gel chromatography in the described order with the solvents shown in parentheses: bis(*o*-anilinophenyl) disulfide (**8c**, 0.39 g, 0.98 mmol, benzene),[16] 3-phenyl-2,3-dihydrobenzothiazol-2-one (**6c**, mp 73—74 °C, 0.29 g, 1.28 mmol, benzene),[17] bis[*o*-{*N*-phenyl-*N*-(3-phenyl-2, 3-dihydrobenzothiazol-2-ylidenecarbamoyl)amino}pheyl] disulfide [**7c**, mp 231—232 °C, 0.60 g, 0.66 mmol, benzene–ether (5: 1)], 2-cyanoimino-3-phenyl-2,3-dihydrobenzothiazole [**9c**, mp 190—191.2 °C, 0.03 g, 0.12 mmol, benzene–ether (5: 1)], **2c** [mp 74—75 °C, 0.93 g, 4.12 mmol, ether and ether–acetone (2: 1)],[11] tris(3-phenyl-2,3-dihydrobenzothiazol-2-ylideneamino) carbonium chloride [**10c**, mp>360 °C, 0.10 g, 0.14 mmol, UV: $\lambda_{max}^{EtOH}$ 401 nm ($\varepsilon$ $6.4\times10^3$): EA of **10c**: Found: C, 62.77: H, 3.75; N, 10.20: S, 12.06%. Calcd for $C_{40}H_{27}N_6ClO_4S_3$: C, 61.02; H, 3.46; N, 10.67; S, 12.22%, acetone and acetone–ethanol (2: 1)], and **3c, c** [mp 301—302 °C, 1.86 mmol, acetone–ethanol(1:2)]. An authentic sample of **9c** was prepared by refluxing of **2c** (2.78 g, 12.3 mmol) in benzene (20 ml) with cyanogen bromide (0.83 g, 7.79 mmol) in benzene (50 ml) for 3 h. The resulting ppt., hydrobromide of **2c** (1.86 g), were filtered off and the filtrate was shaken with aq sodium hydroxide. The product, **9c**, 1.52 g, mp 190—191.2 °C, was obtained by the usual work-up. EA of **9c**: Found: C, 66.97; H, 3.35; N, 16.46%. Calcd for $C_{14}H_9N_3S$: C, 66.91; H, 3.61; N, 16.72%.

*Reduction of **10c** with Zinc Dust and Hydrochloric Acid.* Zinc dust (100 mg) was added with stirring to **10c** (68 mg, 0.097 mmol) dissolved in acetic acid (10 ml) and ethanol (2 ml).

Since the reaction proceeded very slowly, concd HCl (2 ml) was first added, and then zinc dust (200 mg) and concd HCl (3 ml) were added in two portions over a period of 7 h. The precipitates were filtered and washed with ethanol (10 ml). The filtrate and washings were combined and evaporated to dryness. The residue was extracted with dichloromethane (15 ml × 4) after addition of concd HCl (2 ml) and water (20 ml).

Table 4. Elemental analyses and spectral data of the cyanines (**3** and **5**)

| Compound 3 and 5 | | 3 Found (Calcd) % C | H | N | S | Mp (°C) of the chloride (3') | NMR data of the chloride (3') in $CD_3OD$ |
|---|---|---|---|---|---|---|---|
| **3a, a** | $C_{16}H_{14}N_3O_4ClS_2$ | 46.64 (46.66) | 3.26 (3.43) | 10.43 (10.20) | 15.60[a] (15.57) | 278.0—279.0 | 4.17 (6H, s, N-Me), 7.4—8.3 (8H, m) |
| **3a, b** | $C_{17}H_{16}N_3O_4ClS_2$ | 47.64 (47.94) | 3.61 (3.79) | 9.77 (9.84) | 14.68 (15.05) | 253.5—254.5 | 1.52 (3H, t, $J$=7), 4.05 (3H, s, N-Me), 4.68 (2H, q, $J$=7), 7.3—8.1 (8H, m) |
| **3b, b** | $C_{18}H_{18}N_3O_4ClS_2$ | 49.36 (49.14) | 3.92 (4.12) | 9.33 (9.55) | 14.31 (14.58) | 272.3—273.2 | 1.62 (6H, t, $J$=7), 4.74 (4H, q, $J$=7) 7.2—8.2 (8H, m) |
| **3c, a** | $C_{21}H_{16}N_3O_4ClS_2$ | 53.48 (53.22) | 3.33 (3.40) | 8.89 (8.87) | 13.20 (13.53) | 245.0—246.5 | 3.74 (3H, s, N-Me), 7.2—8.5 (13H, m) |
| **3c, b** | $C_{22}H_{18}N_3O_4ClS_2$ | 54.14 (54.15) | 3.60 (3.72) | 8.65 (8.61) | — | 262.5—263.8 | 1.20 (3H, t, $J$=7), 4.27 (2H, q, $J$=7), 7.1—8.4 (13H, m) |
| **3c, c** | $C_{26}H_{18}N_3O_4ClS_2$ | 58.13 (58.26) | 3.30 (3.38) | 7.59 (7.84) | 12.20[a] (11.96) | 301.0—302.0 | 7.0—8.5 (18H, m)[b] |
| **5a** | $C_{23}H_{18}N_3O_4ClS_2$ | 55.04 (55.25) | 3.53 (3.63) | 8.46 (8.40) | — | 256.4—257.5 | 3.65 (3H, s, N-Me)[c] 7.2—8.0 (15H, m) |
| **5b** | $C_{24}H_{20}N_3O_4ClS_2$ | 56.31 (56.08) | 3.70 (3.92) | 7.87 (8.17) | — | 298.2—299.5 | 1.14 (3H, t, $J$=7), 4.14 (2H, q, $J$=7)[c] 7.2—8.1 (15H, m) |

a) Chlorine analyzed for **3a,a**, found 8.62 and calcd 8.61; for **3c,c** found 6.77 and calcd 6.61%. b) In $CDCl_3$. c) Perchlorate in ($CD_3OD$+$CDCl_3$). IR (KBr): A very strong band at 1520—1540 $cm^{-1}$ is common to all **3** and **5**. A band at 750—760 $cm^{-1}$ (m) is common to all **3** and **5**, and a band at 690—695 $cm^{-1}$ (m) appears when there is N–Ph, *i.e.*, **3c,a**; **c,b**, and **c,c** and **5a** and **b**. Bands at 1100 (s) and 620 $cm^{-1}$ (m) are ascribed to $ClO_4^-$.

Hexane was added to the concetrated extract dried with anhydrous magnesium sulfate in order to precipitate the hydrochloride of **2c** (mp 278—279 °C, 64 mg, 0.244 mmol, 84%). The hydrochloride was nitrosated to give **1c** almost quantitatively.

*Hydrolysis of* ***10c*** *with Potassium Carbonate.* When a suspension of **10c** (21 mg, 0.03 mmol) in benzene (20 ml) was stirred with potassium carbonate (*ca.* 30 mg) at room temperature, two poducts were obtained: *N,N'*-bis(3-phenyl-2,3-dihydrobenzothiazol-2-ylidene)urea [**11c**, mp 357.5—358.7 °C, 13 mg, 0.027 mmol; MS: *m/e* 478 ($M^+$, 8%) and 253 (100%): IR (KBr): 1470 $cm^{-1}$ (very strong)] and **2c** (5.4 mg, 0.024 mmol).

An authentic sample of the urea (**11c**) was prepared quantitatively from Grignard-type reagent of **2c** (15 mmol) in THF (100 ml) and ethyl chloroformate (0.48 ml, 5 mmol) by refluxing the solution for 30 min, which showed the same character as above. EA of **11c**: Found: C, 68.98; H, 4.11; N, 12.07%. Calcd for $C_{27}H_{18}N_4OS_2$: C, 67.76; H, 3.80; N, 11.71%.

*Reaction of* ***1a*** *with Lithium Reagent of* ***2a***. A solution of butyllithium (12.5 mmol) in hexane (8 ml) and THF (25 ml) was added dropwise at 0 °C to a stirred solution of **2a** (2.15 g, 13 mmol) in THF (100 ml). The solution was stirred for 10 min and then **1a** (2.01 g, 10.5 mmol) was added portionwise. After the mixture had been stirred for 1.5 h, the solvents were evaporated under reduced pressure. The residue was extracted with dichloromethane (50 ml × 3) after addition of water (100 ml) and the extract was dried over anhydrous magnesium sulfate. After the solvent had been evaporated, the residue was chromatographed on silica gel. Bis[*o*-{*N*-methyl-*N*-(3-methyl-2,3-dihydrobenzothiazol-2-ylidenecarbamoyl)amino}phenyl] disulfide (**7a**, 2.70 g, 78.3%) was eluted with dichloromethane and dichloromethane–ether (1: 1), mp 253.0—253.5 °C (from ether–hexane).

Cyanine chloride (**3'a**, **a**, 0.37 g, 10.9%) was eluted with acetone, mp 278.0—279.0 °C (from ethanol).

A trace amount of 3-methyl-2,3-dihydrobenzothiazol-2-one (**6a**, mp 75—76 °C) was eluted with dichloromethane.

*Alkaline Hydrolysis of Azamonomethinecyanine Chloride (****3'****).* Sodium hydroxide (1 g) in water (1 ml) was added to a solution of **3'** (0.35 mmol) in ethanol (30 ml) at room temperature. After being stirred for 4 h, the solvent was evaporated under reduced pressure. The residue was extracted with dichloromethane (20 ml × 3) after addition of water (20 ml).

The extract was dried over anhydrous magnesium sulfate and the solvent was evaporated. The residue was recrystallized from ether–hexane to give disulfide (**7**).

The results are given in Table 3 and elemental analyses and spectral data in Table 5.

Table 5. Elemental analyses and molecular weights of the disulfides (**7**)[a]

| Compound **7** | Found(Calcd) (%) C | H | N | S | MW (Rast) |
|---|---|---|---|---|---|
| a) $C_{32}H_{28}N_6O_2S_4$ | 58.20 (58.51) | 4.54 (4.30) | 12.60 (12.79) | — | 624 657 |
| b) $C_{36}H_{36}N_6O_2S_4$ | 60.48 (60.65) | 5.28 (5.09) | 11.55 (11.79) | — | — |
| c) $C_{52}H_{36}N_6O_2S_4$ | 68.97 (69.00) | 3.84 (4.01) | 9.05 (9.28) | 14.43 14.17 | 881 905 |

a) NMR ($CDCl_3$) of **7a**: 3.14 (3H, s), 3.26 (6H, s), 3.34 (3H, s), and 7.1—7.4 (16H, m). IR (KBr): 1620 $cm^{-1}$ ($\nu$C=O), common to all **7**. Recrystallization solvent: ether–hexane.

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