(15 900), 352 (10 300), 298 (28 000). The compound was green in solution.

Anal. Calcd for $C_{16}H_{12}O_3S$: C, 67.59; H, 4.25; S, 11.28. Found: C, 67.35; H, 4.27; S, 11.01.

Monothioanthraquinone–2,3-Dimethylbutadiene Adduct (3). To 2.24 g (0.01 mol) of monothioanthraquinone dissolved in 50 mL of warm chloroform was added 0.98 g (0.012 mol) of 2,3-dimethylbutadiene. The solution turned from green to yellow. The solution was treated with Darco and allowed to evaporate. The residue (3.01 g, 98%) was recrystallized from carbon tetrachloride to give 2.71 g (89%) of 3',6'-dihydro-4',5'-dimethylspiro[anthracene-9(10*H*),2'-[2*H*]thiopyran]-10-one: mp 143–146 °C; NMR ($CDCl_3$) 1.96 (s, $2CH_3$), 2.75 (s, CH_2), 3.21 (s, CH_2S) ppm.

Anal. Calcd for $C_{20}H_{18}OS$: C, 78.40; H, 5.92; S, 10.46. Found: C, 78.51; H, 5.90; S, 10.22

Monothioanthraquinone–Cyclopentadiene Adduct (4). To 1.12 g (0.005 mol) of monothioanthraquinone partly dissolved in 25 mL of dichloromethane was added cyclopentadiene until the green color was discharged. The solution was treated with Darco and then allowed to evaporate at room temperature. The residue of pale yellow crystals of spiro[anthracene-9(10*H*),3'-[2]thiabicyclo[2.2.1]-5-heptene]-10-one was washed with pentane: yield 1.30 g (90%); NMR ($CDCl_3$) AB pattern (J = 10 Hz) for CH_2 composed of triplets at 1.39 and 1.55 ppm and singlets at 1.98 and 2.14 ppm; 2.83 (m, H-4), 4.32 (m, H-1), 5.18 (q, H-5), 6.41 (q, H-6) ppm. The compound slowly dissociated back to **2a** and cyclopentadiene at 22 °C.

Anal. Calcd for $C_{19}H_{14}OS$: C, 78.58; H, 4.86; S, 11.04. Found: C, 78.34; H, 5.01; S, 10.89.

Reaction of 2a with Trimethyl Phosphite to Form 5. To 2.24 g (0.01 mol) of monothioanthraquinone dissolved in 30 mL of hot chloroform was added 1.24 g (0.01 mol) of trimethyl phosphite. White crystals separated. The mixture was cooled, and 1.34 g (64%) of crystals was filtered off. Recrystallization from dichloromethane gave 1.26 g (60%) of the thiirane **5**, dispiro[anthracene-9(10*H*),2'-thiirane-3',9''(10''*H*)-anthracene]-10,10''-dione: mp 169.5–170.5 °C dec; IR 3086 (=CH), 1686 (C=O), 1605 (aromatic C=C) cm^{-1}; NMR (CD_2Cl_2) 7.20, 7.67 ppm (anthraquinone-type pattern).

Anal. Calcd for $C_{28}H_{16}O_2S$: C, 80.83; H, 3.87; S, 7.70. Found: C, 80.75; H, 3.85; S, 7.95.

Synthesis of 5 from 1a and 2a. Monothioanthraquinone (0.22 g, 0.001 mol) in 15 mL of dichloromethane was added to 0.22 g (0.001 mol) of 10-diazoanthrone in 10 mL of dichloromethane. Nitrogen was evolved. Crystals deposited when the solution was allowed to stand for 16 h. The solution was reduced in volume by boiling and cooled to give 0.22 g (53%) of **5**: mp 170–171 °C dec; mixture melting point with the $(MeO)_3P$ product above, 170–171 °C; IR spectrum was the same as that for the $(MeO)_3P$ product.

Monothioanthraquinone S-Oxide (6). A solution of 2.24 g (0.01 mol) of monothioanthraquinone in 125 mL of chloroform was stirred, and 0.01 mol of 40% peracetic acid was added. The solution turned from green to orange-yellow. Drying agent ($MgSO_4$) was added, the solution was filtered, and the solvent was removed under vacuum. The product can be recrystallized from dichloromethane to give yellow-orange needles but remains contaminated with anthraquinone. The sulfine was further purified chromatographically by two passages over 5-μm silica gel using 2:3 CH_2Cl_2–*n*-BuCl as solvent. The sulfine issued from the column after the anthraquinone. The solvent was quickly removed under vacuum to leave the sulfine in 95% purity by sulfur analysis. It decomposed at 209 °C when placed in a hot bath and had IR bands at 3067 (=CH), 1658 (C=O), 1126, 1105 (C=S=O), and 768 (ortho-substituted aromatic band) cm^{-1}. The compound could not be obtained in higher purity by this method as it changes in solution with time, demonstrated by UV absorption.

Anal. Calcd for $C_{14}H_8O_2S$: C, 69.98; H, 3.36; S, 13.34. Found: C, 70.22; H, 3.41; S, 12.71.

Acknowledgment. The author is indebted to N. E. Schlichter and E. W. Matthews for IR and UV spectral interpretations and to A. J. Mical for chromatographic purification of **6**.

Registry No.—**1a**, 1705-82-4; **1b**, 68629-84-5; **2a**, 68629-85-6; **2b**, 68629-86-7; **3**, 68629-87-8; **4**, 68629-88-9; **5**, 68629-89-0; **6**, 68629-90-3; 2,6-dimethoxyanthrone, 961-57-9; *p*-toluenesulfonyl azide, 941-55-9; 2,6-dimethoxyanthraquinone, 963-96-2; 2,3-dimethylbutadiene, 513-81-5; cyclopentadiene, 542-92-7.

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gem-Dinitroenamines. Synthesis of 2-(Arylamino)-1,1-dinitroethylenes

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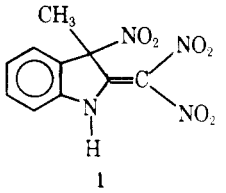
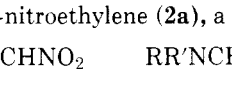
As part of a study of new synthetic routes to *gem*-dinitroolefins, this report describes a synthesis of 2-(arylamino)-1,1-dinitroethylenes. The method involves direct reaction between dinitromethane or its salts, triethyl orthoformate, and aromatic amines. Only one *gem*-dinitroenamine appears to have been reported previously; compound **1** is described as



1

the product of reaction of skatole with tetranitromethane in diethyl ether solvent at room temperature.[2] This structure assignment appears tentative on the basis of the reported data.

Mononitroenamines are known.[3] Severin's reagent, 1-(dimethylamino)-2-nitroethylene (**2a**), a useful reaction in-



2a

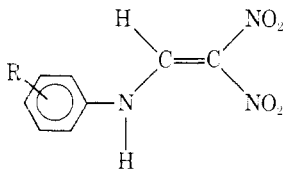
2b

X = CN, $CO_2C_2H_5$

R,R' = H, alkyl, aryl

termediate, is prepared by reaction of nitromethane with dimethyl sulfate–dimethylformamide complex and ethanolic sodium ethoxide.[3a,b] In our hands replacement of dinitromethane for nitromethane in Severin's procedure failed to yield a dinitroenamine. The preparation of substituted mononitroenamines **2b** has recently been reported by Wolfbeis.[3d]

Table I. Properties and Yields of 2-(Arylamino)-1,1-dinitroethylenes

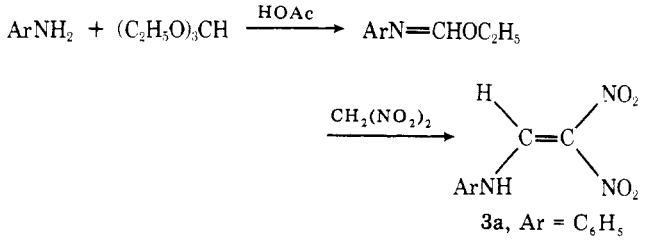


compd no.	molecular formula	R	mp, °C (recrystallization solvent)	yield, %[a]
3a	$C_8H_7N_3O_4$	H	219–221 dec (toluene)	22 (41)[b]
3b	$C_9H_9N_3O_4$	2-CH_3	149–153 dec (CCl_4)	11
3c	$C_9H_9N_3O_5$	4-OCH_3	199–200 dec (CCl_4)	20
3d	$C_9H_9N_3O_4$	4-CH_3	157–159 dec (CCl_4)	10
3e	$C_8H_6ClN_3O_4$	4-Cl	*c*	*d*
3f	$C_8H_6N_4O_6$	4-NO_2	*c*	*d*

[a] Yields are of analytically pure samples (procedure A). [b] The yield in parentheses represents that obtained by the use of dinitromethane instead of the sodium or potassium salt (procedure B). [c] In the reactions of *p*-chloroaniline and *p*-nitroaniline, no analytically pure product could be isolated; however, the mass spectra revealed the presence of the desired dinitroenamines. **3e:** calcd for $C_8H_6ClN_3O_4$, 243.60; found, 243. **3f:** calcd for $C_8H_6N_4O_6$, 254.15; found, 254.

It requires an activated methylene group in one reactant, i.e., ethyl nitroacetate or nitroacetonitrile. We have found that, under appropriate reaction conditions, dinitromethane can yield dinitroenamines in this reaction.

Treatment of aniline with triethyl orthoformate in acetic acid followed by addition of either the sodium or potassium salt of dinitromethane resulted in formation of 2-anilino-1,1-dinitroethylene (**3a**) (10–20% yield). Extension of this



reaction to other anilines gave enamines **3b–f** (Table I). The reaction is believed to proceed through the ethyl *N*-arylformimidate intermediate.[4] Ethyl *N*-phenylformimidate itself[4a] reacts with pure dinitromethane in acetic acid solvent to produce **3a** in 22% yield. The principal side reaction is the formation of amidines, ArNHCH=NAr;[5] unreacted dinitromethane is ultimately decomposed. The dissociation of *N*-arylformimidates to aniline occurs readily in the presence of acid catalysts such as dinitromethane, a relatively strong acid (pK_a(aci) 1.86; pK_a(nitro) 3.57).[4c,6] The aniline produced reacts rapidly with reactant *N*-arylformimidate to yield the amidine.[4c] Amidines do not react with dinitromethane to yield **3**.

A twofold increase in the yield of **3a** (61% crude, 41% isolated pure) was achieved by reaction of aniline with excess triethyl orthoformate (2 mol equiv) in acetic acid, followed by addition of pure dinitromethane rather than its salts. The reaction proceeds at ambient temperature and avoids the vigorous exotherm which occurs when potassium dinitromethane is employed. Use of excess orthoformate in the presence of aniline leads to an increase in the total amount of ethyl *N*-phenylformimidate ultimately available for reaction.

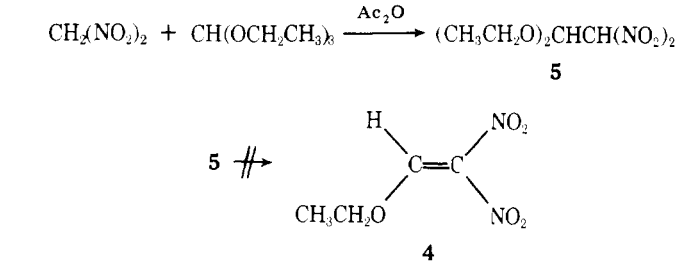
We report an improved procedure for preparation of dinitromethane over that previously described.[6b] Treatment of the potassium salt of dinitromethane[7] suspended in anhydrous ether with trifluoroacetic acid gave 90–95% yields of pure dinitromethane.

Products **3a–f** were characterized and identified by examination of their ^1H NMR and infrared spectra (see Experimental Section). For example, the ^1H NMR of **3a** in $CDCl_3$ showed, in addition to the arene peaks, a doublet centered at δ 9.08 (J = 15.0 Hz) assigned to the vinylic proton and a broad NH peak at approximately δ 11.0; in Me_2SO-d_6 solvent the vinylic proton appeared as a singlet. In all compounds the characteristic asymmetric and symmetric NO_2 stretching frequencies were observed in the infrared spectra near 1520 and 1300 cm^{-1}, respectively. An intense absorption near 1640 cm^{-1} is observed in all compounds and is attributed to the C=C vibration; a similar absorption is observed in mononitroenamines.[3c]

The new *gem*-dinitroenamine synthesis is limited to reactions of primary arylamines. Electron-withdrawing substituents, such as nitro, strongly retard the reaction. The reaction fails with secondary arylamines and with primary and secondary aliphatic amines. A major interfering side reaction, which presents problems during workups, is the formation of amidines.[5]

Chemically, the new *gem*-dinitroenamines appear to be quite stable. Reaction of **3a** with methyllithium in THF solvent at −40 °C followed by treatment with acetic acid gave recovered **3a.** Heating **3a** with excess pyrrolidine in refluxing benzene also resulted in recovery of the enamine; no transamination could be detected. Certain mononitroenamines behave similarly.[3c]

Attempts were made to prepare 1,1-dinitro-2-ethoxyethylene (**4**), a desired intermediate in the preparation of *gem*-



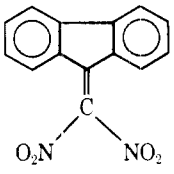
dinitroenamines. Treatment of dinitromethane with triethyl orthoformate in acetic anhydride or acetic acid gave dinitroacetaldehyde diethyl acetal (**5**) in 55% yield. A diethyl acetal group was indicated by a methyl triplet centered at δ 1.18 and the characteristic acetal methylene multiplet centered at δ 3.72. The two methine protons appeared as doublets centered at δ 5.35 (J = 8.0 Hz, acetal methine) and 6.18 (J = 8.0 Hz, dinitro methine). The chemical shift of the dinitro methine proton is in agreement with other observed dinitro methine chemical shifts.[8,9]

Attempts to convert the acidic dinitroacetal **5** to **4** were unsuccessful. Treatment of **5** with trifluoroacetic acid ultimately resulted in C–C bond cleavage, yielding dinitromethane. When **5** was treated in ether with pyrrolidine, a yellow salt formed immediately, mp 85–93 °C dec. The acidic dinitroacetal does not lose ethanol to yield **4**; on prolonged standing at 25 °C it decomposes, ultimately forming dinitromethane.

Our earlier attempts to prepare 1,1-dinitroolefins from 2-alkoxy-1,1-dinitroalkanes and their 1-bromo derivatives were unsuccessful.[8] Five previously reported 1,1-dinitroolefins

have been isolated.[10-15] Their preparations are unique and represent four different preparative methods. They are not applicable as general synthetic methods and appear to be of very limited scope.

We have confirmed the synthesis of dinitroolefins **6** and **7**,

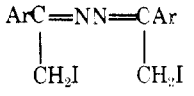


6

$(C_6H_5)_2C{=}C(NO_2)_2$

7

reported by Fridman et al.,[10] by reaction of the appropriate diazo compound with iodonitroform, but have been unable to extend this reaction to synthesis of other types of *gem*-dinitroolefins. Reaction of 1-phenyl-1-diazoethanes with iodonitroform gave the corresponding acetophenones and ω-iodoacetophenone azines (e.g., **8a,b**). No 1,1-dinitro-2-arylpropenes (**9**) were detected. Reactions of diazocyclohexane



$ArC(CH_3){=}C(NO_2)_2$

9

8a, Ar = C_6H_5
b, Ar = 4-$CH_3OC_6H_4$

and dicyanodiazomethane with iodonitroform gave no isolable products. Diazomethane, diazoacetic ester, and diazodimedone do not form 1,1-dinitroolefins by reaction with iodonitroform.[10]

Experimental Section[16]

Caution! All polynitro compounds are considered toxic and potentially explosive and should be handled with appropriate precautions.

2-Anilino-1,1-dinitroethylene (3a). Procedure A. From Sodium or Potassium Dinitromethane. A solution of 0.93 g (0.01 mol) of aniline, 1.9 g (0.013 mol) of triethyl orthoformate, and 2 g (0.033 mol) of glacial acetic acid in 5 mL of toluene was briefly brought to a boil and allowed to cool to room temperature. To this was added 1.28 g (0.01 mol) of potassium dinitromethane,[7] and the mixture was placed on a steam bath. After approximately 5 min a vigorous exotherm occurred, and after an additional 10 min of heating the dark solution was allowed to cool to room temperature. The crude reaction mixture was filtered and the precipitated potassium acetate washed with two 10-mL portions of toluene. The combined filtrates were concentrated, leaving a dark brown solid. This material was triturated with toluene and cooled, yielding 0.53 g of **3a** (25%), mp 183–188 °C dec. Recrystallization of a portion of this material from toluene afforded yellow needles of analytically pure **3a:** mp 219–221 °C dec; NMR ($CDCl_3$) δ 7.52 (m, 5 H), 9.08 (d, 1 H, J = 15.0 Hz), 10.88 (br s, 1 H); IR (KBr) 3200, 1637, 1580, 1510, 1485, 1360, 1275, 1230, 848, 804, 768, 683 cm^{-1}. A similar procedure was used for compounds **3b–d.**

Anal. Calcd for $C_8H_7N_3O_4$: C, 45.93; H, 3.35; N, 20.01; M_r 209.16. Found: C, 45.81; H, 3.41; N, 19.95; M_r 209 (mass spec).

1,1-Dinitro-2-(2-methylanilino)ethylene (3b) was prepared by procedure A: 11% yield; mp 149–153 °C dec; NMR (Me_2SO-d_6) δ 2.53 (s, 3 H), 7.39 (m, 5 H), 8.95 (s, 1 H), 11.25 (br s, 1 H); IR (KBr) 3190, 1635, 1605, 1510, 1360, 1345, 1275, 1205, 972, 788, 769 cm^{-1}.

Anal. Calcd for $C_9H_9N_3O_4$: C, 48.43; H, 4.04; N, 18.83; M_r 223.19. Found: C, 48.87; H, 3.98; N, 18.76; M_r 223 (mass spec).

1,1-Dinitro-2-(4-methoxyanilino)ethylene (3c) was prepared by procedure A: 20% yield; mp 199–200 °C dec; NMR (Me_2SO-d_6) δ 3.84 (s, 3 H), 6.98 (d, 2 H), 7.56 (d, 2 H), 8.94 (s, 1 H), 11.0 (br s, 1 H); IR (KBr) 3200, 1643, 1605, 1505, 1490, 1455, 1380, 1300, 1255, 1220, 1185, 1035, 995, 830, 800, 755, 740 cm^{-1}.

Anal. Calcd for $C_9H_9N_3O_5$: C, 45.19; H, 3.77; N, 17.57; M_r 239.19. Found: C, 45.09; H, 3.91; N, 17.41; M_r 239 (mass spec).

1,1-Dinitro-2-(4-methylanilino)ethylene (**3d**) was prepared by procedure A: 10% yield; mp 157–159 °C dec. 1,1-Dinitro-2-(4-chloroanilino)ethylene (**3e**) and 1,1-dinitro-2-(4-nitroanilino)ethylene (**3f**) were obtained by the same procedure in low yield as crude samples which could not be purified. Their presence was detected by mass spectra (Table I).

Preparation of 3a from Dinitromethane. Procedure B. A solution of 0.33 g (3.5 mmol) of aniline, 1 g (6.8 mmol) of triethyl orthoformate, and 2 g of glacial acetic acid was briefly brought to a boil and allowed to cool to room temperature. To this mixture was added 0.38 g (3.5 mmol) of freshly prepared, undistilled dinitromethane (see below), the resulting solution was stirred for 2 h at room temperature, and then 15 mL of toluene was added. After refrigeration overnight, 386 mg (61%) of crude **3a** was isolated. Recrystallization from toluene afforded 310 mg (41%) of analytically pure **3a,** mp 219–221 °C.

Reaction of Ethyl *N*-Phenylformimidate with Dinitromethane. Freshly distilled ethyl *N*-phenylformimidate[4a] (1.0 g, 6.7 mmol) was added to a solution of freshly prepared, undistilled dinitromethane (0.71 g, 6.7 mmol; see below) in 4.0 mL of acetic acid. A yellow precipitate formed rapidly. After standing for 2 h at 25 °C, the mixture was diluted with 30 mL of toluene and stored at 0 °C overnight. Filtration gave 0.30 g (22%) of pure **3a,** mp 219–220 °C.

Preparation of Dinitromethane. To 25 mL of dry diethyl ether containing 1 g (6.9 mol) of potassium dinitromethane[7] cooled to 0 °C was added slowly with stirring 5 mL of trifluoroacetic acid. The resulting mixture was stirred for 30 min at 0 °C, when an additional 2.5 mL of trifluoroacetic acid was added and the solution stirred for another 30 min. The crude mixture was filtered and the precipitate washed with two 25-mL portions of diethyl ether. The combined filtrates were concentrated at 0 °C on a rotary evaporator using an ice–water bath. The crude residue was treated with 20 mL of CH_2Cl_2, filtered to remove residual potassium trifluoroacetate, and concentrated, yielding 700 mg (95%) of crude dinitromethane. The ^1H NMR ($CDCl_3$) spectrum showed only one major peak at δ 6.2 (recorded value of dinitromethane is δ 6.2 in CCl_4 solvent[9]) contaminated by only trace amounts of impurities. This material was used immediately in subsequent reactions and not stored for prolonged periods. Pure dinitromethane can be stored at low temperatures (−20 °C) for prolonged periods, but decomposes at room temperature in approximately 1 day.

Caution! In one case, an attempted distillation of dinitromethane (less than 1 g of material) resulted in a violent explosion after full vacuum was attained (1–2 mm) and at a bath temperature of 30–35 °C. Serious injury was avoided because adequate safety precautions were in use at the time of explosion.

Dinitroacetaldehyde Diethyl Acetal (5). A mixture of 700 mg of dinitromethane, 2 g of acetic anhydride, and 1.5 g of triethyl orthoformate was stirred overnight at room temperature. The reaction mixture was treated with 25 mL of toluene and concentrated to remove volatiles, leaving 800 mg (55.5%) of **5** as a yellow oil (pure by NMR assay): NMR ($CDCl_3$) δ 1.18 (t, 6 H), 3.72 (m, 4 H), 5.35 (d, 1 H), 6.18 (d, 1 H); IR (neat) 2920, 1575, 1320, 1100, 878, 817, 757 cm^{-1}. The material decomposed slowly on standing at 25 °C and rapidly on heating.

ω-Iodoacetophenone Azine (8a). To a solution of 0.8 g (2.7 mmol) of iodonitroform[17] in 10 mL of anhydrous diethyl ether was added 0.4 g (3.0 mmol) of 1-diazo-1-phenylethane. Upon addition, nitrogen gas evolution was observed and the resulting dark solution was stirred for 2 h. The crude reaction mixture was concentrated to remove ether, iodine, and acetophenone. The acetophenone was identified by comparison of its IR and ^1H NMR spectra with an authentic sample. The residue was dissolved in absolute ethanol and refrigerated to yield 100 mg of **6a** (20%), crystallized as orange needles: mp 142–143 °C dec; ^1H NMR ($CDCl_3$) δ 4.50 (s, 2 H), 7.80 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 8.72 (t, CH_2I).

Anal. Calcd for $C_{16}H_{14}I_2N_2$: C, 39.34; H, 2.86; N, 5.73; I, 52.04; M_r 488.09. Found: C, 39.44; H, 2.94; N, 5.72; I, 52.06; M_r 495 (osmometry).

ω-Iodo-4-methoxyacetophenone azine (8b) was obtained similarly: 14% yield; mp 145–146.5 °C dec; NMR (hot Me_2SO-d_6) δ 3.75 (s, 3 H), 4.50 (s, 2 H), 7.10 (d, 2 H), 8.15 (d, 2 H).

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Registry No.—**3a,** 68408-44-6; **3b,** 68408-45-7; **3c,** 68408-46-8; **3d,** 68408-47-9; **3e,** 68408-48-0; **3f,** 68408-49-1; **5,** 68408-50-4; **8a,** 68408-51-5; **8b,** 68408-52-6; dinitromethane, 625-76-3; aniline, 62-53-3; triethyl orthoformate, 122-51-0; potassium dinitromethane, 32617-22-4; ethyl *N*-phenylformimidate, 6780-49-0; 2-methylaniline, 95-53-4; 4-methoxyaniline, 104-94-9; 4-methylaniline, 106-49-0; 4-chloroaniline, 106-47-8; 4-nitroaniline, 100-01-6; iodonitroform, 39247-25-1; 1-diazo-1-phenylethane, 22293-10-3; 1-diazo-1-(4-methoxyphenyl)ethane, 52506-27-1.

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α Elimination of *N*-Chloro-*N*-sodiourethane in Ethers and in Hydrocarbons

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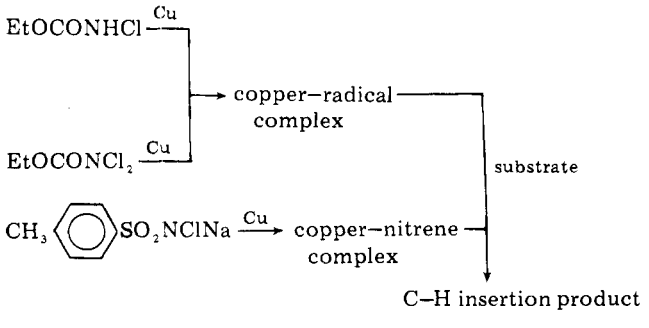
We reported that, in the presence of copper, the reactions of *N*-chloro- and *N,N*-dichlorourethanes with several substrates such as hydrocarbons and ethers proceeded via a copper–radical complex involving no nitrene.[2] Furthermore, Carr et al. reported that the reaction of chloramine-T with dioxane gave the N-substituted sulfonamide in the presence of copper, suggesting that a copper–sulfonylnitrene complex was formed as an intermediate.[3] In these reactions, the presence of copper gave the C–H insertion products, while it was found that the reaction of *N*-chloro-*N*-sodiourethane gave the C–H insertion product in spite of the absence of copper.



Results and Discussion

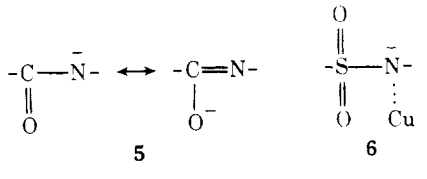
As shown in Table I, the reactions of *N*-chloro-*N*-sodiourethane (**1**) with ethers and hydrocarbons gave the respective N-substituted urethanes **2** and urethane **3**, whose yields were compared with those of the photolyses of ethyl azidoformate (**4**). In the reactions with cyclic ethers, tetrahydrofuran, tetrahydropyran, and dioxane, the preferential formations of α-substituted derivatives parallel those in the photolyses of **4**.[4,5] The reactions of *cis*- and *trans*-2,5-dimethyltetrahydrofurans were found to proceed nonstereospecifically in the formation of **2**.[6] In the reactions with aromatic hydrocarbons, none of the azepines were detected, contrary to the photolyses of **4**. In the reaction of the azide, the formation of the azepine is explained by the addition of singlet ethoxycarbonylnitrene to an aromatic double bond followed by cleavage of the C–C bond.[7,8] In sharp contrast with the photolyses of **4**, the reaction of **1** with cyclohexene gave preferentially the abstraction product **3** without the cycloadduct. This finding shows that the nitrene mechanism may be ruled out since both the singlet and triplet nitrenes react with olefins to give cycloadducts.[9]

Heating chloramine-T in the presence of copper in dimethyl sulfoxide furnished the sulfoximine in 80% yield.[3] An analogous experiment omitting the copper catalyst gave the sulfoximine in 6% yield.[3] Then, the reaction of **1** was carried out in the presence of copper to know the influence of the catalyst. The results are listed in Table I. The same products as formed in the absence of copper were obtained in slightly higher yields than those in the absence. The azepines were also not detected even under this condition. The findings indicate that the influence of copper is not essential contrary to that in the case of ref 3.

The reactions of **1** with ethanol in the absence and in the presence of copper gave urethane in the yields of 80.6 and 81.8%, respectively, and those with 1-butanol gave urethane in the yields of 73.1 and 96.3%, respectively, accompanied by the corresponding aldehydes. None of the O–H insertion products, *N*-ethoxyurethane and *N*-butoxyurethane, were detected in these reactions, whereas the photolyses of **4** in ethanol and 1-butanol gave the O–H insertion products in the yields of 11.0 and 27.0%, respectively, accompanied by urethane.[5] The O–H insertion products have been formed by singlet nitrene but not by any radicals.[5]

The results mentioned so far can be explained tentatively by a radical-like mechanism. Then **1** was treated with dioxane in the presence of radical inhibitors, nitrobenzene and hydroquinone. The addition of nitrobenzene decreased the yields of both N-substituted urethane (**2C**, 14.3%) and urethane (28.6%), and the addition of hydroquinone gave only urethane in high yield (64.9%). As for the decomposition of **4**, where the singlet nitrene was generated, the effect of the additives such as nitrobenzene and sulfur led to the increased yield of the insertion products and to the decreased yield of the abstraction product.[10]

The influence of copper on the present reaction was not so great as that on the reaction of chloramine-T, where the copper–nitrene complex had been proposed. This difference can be explained as follows. For *N*-chloro-*N*-sodiourethane, a resonance as presented by formula **5** is permitted. Consequently, the nitrogen atom of **1** is not easy to coordinate with copper, while the nitrogen atom of chloramine-T, whose resonance is not considered other than d-orbital expansion of the



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