methyl Sulfide and Cyclohexene.—Photolysis of 1.02 g (6.6 mmol) of diazomalonate in a solution of 9.32 g (0.15 mol) of dimethyl sulfide and 12.01 g (0.15 mol) of cyclohexene was carried out with the high pressure mercury lamp described above. After the diazo band disappeared from the spectrum of the reaction mixture, a known amount of internal standard (biphenyl) was added to the reaction mixture. A white precipitate formed when the reaction was over.

The solid was filtered to give 0.75 g (61% yield) of sulfonium ylide **1** which was identified by comparison of spectra with those of an authentic sample. The reaction mixture was then analyzed directly by gas chromatography. Two major peaks appeared which were found to be the adducts of biscarbomethoxycarbene to cyclohexene. One of them was identified as the adduct of carbomethoxycarbene with the C=C bond of cyclohexene which showed ir (CCl_4) 1735 cm^{-1}; nmr (CCl_4) 1.15 (m, 2 H), 1.85 (m, 8 H), 3.66 (s, 3 H), 3.76 ppm s, 3 H). *Anal.* Calcd for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60. Found: C, 61.79; H, 7.45. The other product was identified as the insertion product of biscarbomethoxycarbene into the allylic carbon–hydrogen bond, which showed ir (CCl_4) 860, 1025, 1740 cm^{-1}; nmr (CCl_4) 1.83 (m, 7 H), 3.15 (d, 1 H), 3.66 (s, 6 H), 5.88 ppm (m, 2 H). *Anal.* Calcd for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60. Found: C, 62.03; H, 7.58.

Photosensitized Reactions of Dimethyl Diazomalonate in Dialkyl Sulfides and Disulfides.—Dimethyl diazomalonate (220 mg) was added to dimethyl sulfide (700 mg) solution with 880 mg of benzophenone. Irradiation of the sample in Pyrex tubes for 40 hr provided a white solid, which was washed with petroleum ether (bp 30–60°) and identified as sulfonium ylide **1** by comparison with an authentic sample. The overall yield of **1** was determined by nmr spectroscopy through addition of dibenzyl ether as an internal standard. The formation of benzopinacol was also observed, but it was neglibible before decomposition of diazomalonate. Irradiation of diazomalonate was also performed in diethyl and di-*tert*-butyl sulfides solution containing benzophenone: 220 mg of dimethyl diazomalonate was dissolved in 1 ml of diethyl or di-*tert*-butyl sulfides and 800 mg of benzophenone and irradiated for 40 hr in a Pyrex tube. Although no significant precipitation could be observed in the solution, the nmr analysis indicated the formation of **2**. On the other hand ethyl or *tert*-butylthiomalonate from the thermolysis of corresponding sulfonium ylides was isolated by preparative gas chromatograph. These were identified by comparison of their spectra with those of authentic samples. When 100 mg of dimethyl diazomalonate in a solution of 300 mg of dimethyl disulfide and 165 mg of benzophenone was irradiated for 40 hr in Pyrex tubes, no corresponding sulfonium ylide formation could be observed. However, the product analysis by gas chromatography indicated the formation of alkylthiomalonate. It was identified by comparison of its spectra with those of authentic samples.

Photosensitized Reaction of Dimethyl Diazomalonate in Dimethyl Sulfide and *cis*-4-Methyl-2-pentene. Competitive Reactions.—Dimethyl diazomalonate (1 mmol) and 4.5 mmol of benzophenone were dissolved in weighed quantities of dimethyl sulfide and *cis*-4-methyl-2-pentene. The solution was irradiated for 40–50 hr until the diazo band in ir spectrum disappeared. The analyses for sulfonium ylide were performed on Varian A-60D nmr spectrometer after the solid that appeared in the reaction mixture was dissolved with deuteriochloroform. The relative integral heights of ylide S^+CH_3 to internal standard CH_2 of dibenzyl ether were compared to obtain the yield of ylide formation. The reaction mixture was concentrated and analyzed by gas chromatograph. Two main products were isolated and shown to be *cis*- and *trans*-cyclopropane derivatives, **29** and **30**, by comparison of their spectra with those of authentic samples.[16]

Registry No.—**1**, 17870-68-7; **2**, 24308-25-6; **3**, 24420-55-1; **4**, 24420-56-2; **5**, 24420-57-3; **6**, 24420-58-4; **7**, 34282-07-0; **8**, 24420-59-5; **9**, 24420-60-8; **10**, 24420-61-9; **11**, 14070-66-7; **12**, 34282-11-6; **13**, 34282-12-7; **14**, 7039-28-3; **15**, 33781-29-2; **16**, 24420-62-0; **17**, 24420-63-1; **18**, 34282-14-9; **22**, 34282-15-0; **24**, 34282-16-1; **25**, 24420-53-9; **26**, 34282-18-3; **27**, 34282-19-4; **28**, 34282-20-4; **29**, 34282-53-6; **30**, 34282-54-7; dimethyl diazomalonate, 6773-29-1; dimethyl methylthiomalonate, 24420-52-8.

Synthesis and Antifungal Properties of Dithiocarboxylic Acid Derivatives. II.[1] Novel Preparation of 2-Alkylamino-1-cyclopentene-1-dithiocarboxylic Acids and Some of Their Derivatives

B. BORDÁS, P. SOHÁR,* G. MATOLCSY, AND P. BERENCSI

Research Institute for Plant Protection, Budapest, and Research Institute for Pharmaceutical Chemistry,[2] Budapest, Hungary

Received July 26, 1971

2-Methylamino-1-cyclopentene-1-dithiocarboxylic acid (II) can be obtained in low yield from cyclopentanone with carbon disulfide and methylamine; no other 2-alkylamino analogs can be synthesized. The amino group of 2-amino-1-cyclopentene-1-dithiocarboxylic acid (I) and that of its methyl ester (VII) can be substituted by the alkylamino group by an amine exchange reaction, yielding the corresponding 2-alkylamino-1-cyclopentene-1-dithiocarboxylic acid (II) or its methyl ester (III–V, VIII–XII), respectively. The structures, including tautomeric forms of the synthesized compounds, were proved by ir and nmr spectroscopy.

In previous research it was found that 2-amino-1-cyclopentene-1-dithiocarboxylic acid (I) synthesized by Takeshima and coworkers[3] exerts a marked antifungal action against various fungi.[4] The steric arrangement of the functional groups in this compound permits the formation of six-membered chelates with metals, which fact may be responsible for the biological activity, too. Chelation plays an important role in the action of several antifungal compounds, among which are the dithiocarbamates.[5–7]

For studying the structure–activity relationship within this group we attempted to prepare the *N*-alkyl and *S*-alkyl derivatives of I. Some of these compounds have been synthesized by Mayer and coworkers[8] by treating *N*-alkyliminocyclopentanes with carbon disulfide. To avoid the tedious preparation of *N*-alkyl-

(1) Part I: G. Matolcsy, M. Hamrán, and B. Bordás, *Acta Phytopathol.*, **5**, 123 (1970).

(2) Address to whom inquiries should be sent.

(3) T. Takeshima, M. Yokoyama, T. Imamoto, and H. Asaba, *J. Org. Chem.*, **34**, 730 (1969).

(4) See part I.[1]

(5) J. G. Horsfall, "Fungicides and Their Action," Chronica Botanica, Waltham, Mass., 1945.

(6) A. Kaars Sijpesteijn, M. J. Janssen, and A. v. Leuwenhoek, *J. Microbiol. Serol.*, **25**, 422 (1959).

(7) A. Kaars Sijpesteijn, *World Ref. Pest Contr.*, **9**, 85 (1970).

(8) R. Mayer and J. Jentzsch, *J. Prakt. Chem.*, **23**, 83 (1964).

iminocyclopentanes by the reaction of 1,1-cyclopentanedithiol with aliphatic amines[8,9] we worked out a new synthesis of *N*-alkyl derivatives of I.

The attempted extension of the reaction of cyclopentanone, carbon disulfide, and ammonia[8] to amines succeeded only in case of methylamine; 2-*N*-methylamino-1-cyclopentene-1-dithiocarboxylic acid (II) was obtained in 25% yield. All other primary and secondary aliphatic amines yielded only the corresponding dithiocarbamates, except ethylenediamine, which yielded ethylenethiourea as a result of a well-known reaction.[10-12] Methylation of II by dimethyl sulfate gave the methyl ester (III).

In our search for other synthetic methods we found that *N*-alkyl derivatives of I can be prepared by means of amine exchange reaction. The reaction of I with methylamine, ethylamine, and butylamine gave the corresponding *N*-alkylcyclopentenedithiocarboxylic acids (II, IV, V) in fairly good yield. The melting point of the *N*-butylamino-1-cyclopentene-1-dithiocarboxylic acid was identical with that described by Mayer and Jentzsch.[6] The reaction of I with ethylenediamine resulted in the formation of 2,2′-*N*,*N*′-ethylenebis(amino-1-cyclopentene-1-dithiocarboxylic acid) (VI) even when ethylenediamine was used in excess. Attempts to react I with primary aromatic amines such as aniline and *p*-chloroaniline resulted in decomposition rather than formation of the expected product; secondary aliphatic amines as well as glycine failed to react.

Similar amine exchange reactions proceeded smoothly also when the methyl ester (VII) was used instead of the free acid (I). Thus the methyl esters of 2-methylamino- (III), 2-ethylamino- (VIII), 2-allylamino- (IX), and 2-cyclohexylamino-1-cyclopentene-1-dithiocarboxylic acid (X) were obtained by this way. Reaction of VII with ethylenediamine yielded both the β-aminoethylamino- (XI) and the ethylenebisamino derivative (XII). The N-acetylated product of XI (XIII) was prepared mainly for spectroscopic investigations. Sterically hindered primary aliphatic amines, such as *tert*-butylamine, diacetonamine, primary aromatic amines, and secondary aliphatic amines failed to undergo this reaction even on elevated temperature and prolonged reaction time.

The success of this reaction in aqueous media at room temperature raised the idea whether VII could undergo this reaction also in living organisms with side-chain amino groups on protein surfaces. We found, however, that glycine, glycylglycine, and ethyl glycinate used as simple model substances failed to react.

The usual conditions applied in equilibrium reactions, *e.g.*, the use of an excess of amine or removal of the ammonia formed, are necessary to obtain good yields. However, the reverse reaction was not observed by treatment with an excess of ammonia under similar conditions.

Compound III is highly resistant to alkaline hydrolysis but can be readily decomposed by acids, like the salts of dithiocarbamic acids and in sharp contrast to their esters which show a great stability in the presence of acids and are sensitive to alkaline agents.

The reaction of I and II with formaldehyde and diethylamine yielded the diethylaminomethyl esters (XIV, XV), respectively.

The structure and tautomeric form of the synthesized new compounds was proved by ir and nmr spectroscopy.

The nmr spectrum of compound II contains a two-proton signal of roughly quintet shape at 1.17 ppm due to the methylene group in position 4. The 3- and 5-methylene groups give two almost overlapping triplets at 2.75 ppm. This fact excludes the tautomeric structure IIa since the chemical shift of the 3- and 5-methylene motions should be rather different in this case because of the neighborhood of the C=N and methine group, respectively, and no triplet due to the 1-methyne can be detected in the spectrum. The *N*-methyl signal appears at 3.08 ppm as a doublet (J = 5 Hz), owing to the coupling with the NH proton which can be removed by addition of acid.[13] This proves unambiguously the presence of structure IIb, since in structure IIc, where the methyl signal could give a doublet in consequence of a syn and anti isomer, no collapsing to a singlet should occur by acid. The tautomer IIb has a chelate structure according to the large chemical shift of the NH proton (δ_{NH} 12.4 ppm).

In the ir spectrum (in KBr and in $CHCl_3$, respectively) of compound II no ν_{NH} band can be detected, being a further evidence of the chelate structure.[14] The ν_{SH} group gives a sharp maximum at 2550 cm^{-1} (2575 in $CDCl_3$), excluding its participation in an association structure. The most intense bands appear at 1610, 1510, and 1360 cm^{-1} which can be assigned to the group frequencies of the chelate structure and approach the character of the $\nu_{C=C}$, ν_{C-N}, ν_{NH}, and $\nu_{C=S}$ bands.[15]

All other N-substituted derivatives gave nmr spectra similar to that of compound II, proving the general validity of the tautomeric structure b.[16] The doublet of the *N*-methyl group in compound III and XV and the *N*-methylene multiplet in compound XII collapsed to a singlet by addition of acid. The same treatment resulted in a simplification of the *N*-methylene multiplets in compounds VIII, IX, XI, and XIII and of the *N*-methyne multiplet in compound X.

The elucidation of the tautomer structure of the compounds carrying no substituent on their nitrogen (I, VII, XIV) is more difficult. In the spectrum of I there are two separated signals due to acidic protons, one of them being shifted downfield (11.0 ppm), which is characteristic for chelates. Structure b can be valid in this case only if one proton of the NH_2 group is presumed to take part in the chelate, as this explains

(9) J. Jentzsch, J. Fabian, and R. Mayer, *Chem. Ber.*, **95**, 1764 (1962).

(10) A. W. Hofmann, *Ber. Deut. Chem. Ges.*, **5**, 242 (1872).

(11) C. F. H. Allen, C. O. Edens, J. VanAllan, and E. C. Horning, "Organic Syntheses, Collect. Vol. III, Wiley, New York, N. Y., 1967. pp 394–395.

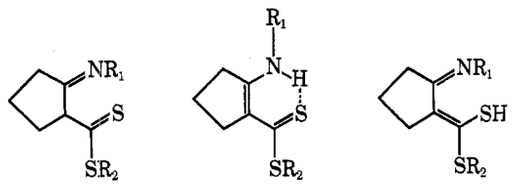
(12) G. Matolcsy, *Chem. Ber.*, **101**, 522 (1968).

(13) H. Suhr, "Anwendung der Kernmagnetischen Resonanz in der Organischen Chemie," Band 8, "Organesche Chemie in Einzeldarstellungen," Springer Verlag, Berlin, 1965, p 114.

(14) P. Sohár and G. Varsányi, *Acta Chim. Acad. Sci. Hung.*, **55**, 189 (1968).

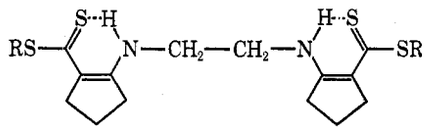
(15) The assignment of these bands as group frequencies is backed by the spectra of the deuterated compounds, where all three bands are shifted to lower wavenumbers, but these shifts (30, 50, and 5 cm^{-1}, respectively) are significantly smaller than those which should originate from XH and XD band frequencies, respectively.

(16) Tables and figures of ir and nmr values will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteeth St., N.W., Washington, D. C. 20036, by referring to code number JOC-72-1727. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.



a b c

Compd	R_1	R_2
I	H	H
II	CH_3	H
III	CH_3	CH_3
IV	C_2H_5	H
V	C_4H_9	H
VII	H	CH_3
VIII	C_2H_5	CH_3
IX	$CH_2CH{=}CH_2$	CH_3
X	cyclohexyl	CH_3
XI	$CH_2CH_2NH_2$	CH_3
XIII	CH_2CH_2NHAc	CH_3
XIV	H	$CH_2N(C_2H_5)_2$
XV	CH_3	$CH_2N(C_2H_5)_2$



VI, R = H
XII, R = CH_3

the nonequivalence of the two NH_2 protons. The tautomeric structure a (suggested by Takeshima, *et al.*,[5] for compound I) can be excluded, as the signal of the 1-methyne proton can be detected neither in the spectrum of compound I, nor in those of compound VII, or XIV. As the ir spectra of these compounds show strong similarity to those of the N-substituted derivatives (Table II),[16] it seems reasonable to suggest for them the same tautomeric structure b.

Experimental Section

Preparation of II from Cyclopentanone.—Cyclopentanone (4.2 g, 0.05 mol) was mixed with 31 g (0.2 mol) of 20% aqueous methylamine solution. After 2 hr the mixture was cooled to 5°, 4.6 g (0.06 mol) carbon disulfide was added in portions, and the reaction mixture was shaken for 2 hr. The precipitated yellow product was separated and washed with water. After drying it was suspended in 8 ml of acetic acid and warmed at 50° for several minutes; after the mixture cooled to room temperature, 20 ml of water was added. The yellow solid product was separated, washed with water, and dried, yield 2.2 g (25%), mp 122°. The product was recrystallized from methanol, yield 1 g (12%), mp 125.5°.

Anal. Calcd for $C_7H_{11}NS_2$: C, 48.51; H, 6.39; N, 8.08; S, 37.00. Found: C, 48.31; H, 6.27; N, 8.10; S, 36.74.

Preparation of II from I.—A solution of I (3.2 g, 0.02 mol) in 6 ml of 40% aqueous methylamine solution and 30 ml of methanol was refluxed for 3 hr. The solution was evaporated to dryness under diminished pressure, the residue was taken up in 70 ml of water and filtered, and the solution was acidified with 10% hydrochloric acid. The yellow solid product was separated, washed with water, and dried, yield 1.6 g. The crude product was recrystallized from methanol, mp 125.5°; there was no depression in melting point on admixture with II prepared by the previous method.

Preparation of IV from I.—I (6.3 g, 0.04 mol) and ethylamine (6.75 g, 0.15 mol) in 60 ml of methanol was refluxed for 3 hr. After the mixture cooled 180 ml of water was added and the mixture was filtered. To the filtrate 20 ml of acetic acid was added and the precipitated yellow product was separated by filtration, washed with water, and dried. The crude product was recrystallized from acetone, wt 6.0 g (80.0%), mp 111°.

Anal. Calcd for $C_8H_{13}NS_2$: C, 51.30; H, 7.00; N, 7.48; S, 34.23. Found: C, 51.37; H, 7.02; N, 7.15; S, 33.82.

Preparation of V from I.—I (6.3 g, 0.04 mol) and butylamine (7.3 g, 0.1 mol) in 60 ml of methanol was refluxed for 3 hr and the product was isolated as above, wt 5.5 g (63.9%), mp 90° (EtOH).

Anal. Calcd for $C_{10}H_{17}NS_2$: C, 55.77; H, 7.96; N, 6.50; S, 29.77. Found: C, 55.62; H, 7.96; N, 6.40; S, 29.75.

Preparation of VI from I.—A mixture of I (4.8 g, 0.03 mol), ethylenediamine (1.8 g, 0.03 mol), and 30 ml of methanol was refluxed for 4 hr. The precipitation of a yellow crystalline product began shortly. After cooling the product was separated, washed with methanol, and dried. The crystals (4.8 g) could not be purified by crystallization; they were taken up in a solution of 2.4 g (0.06 mol) of sodium hydroxide and 80 ml of water and filtered, the filtrate was acidified with 10% hydrochloric acid, and the yellow precipitate was separated, washed with water and dried, yield 1.6 g (31%), mp 145–147°.

Anal. Calcd for $C_{14}H_{20}N_2S_4$: C, 48.88; H, 5.85; N, 8.13; S, 37.22. Found: C, 47.76; H, 6.06; N, 7.31; S, 36.58.

Preparation of VII from I.—I (4.77 g, 0.03 mol) was dissolved in a solution of 1.2 g (0.03 mol) of sodium hydroxide in 50 ml of water; 3.9 g (0.03 mol) dimethyl sulfate was added in portions under cooling and vigorous stirring, with the temperature being kept below 20°. The brown product was then separated, dried (4.19 g), and recrystallized from 1:1 methanol–water, yield 3.3 g (63%), mp 77–79°.

Anal. Calcd for $C_7H_{11}NS_2$: C, 48.51; H, 6.39; N, 8.08; S, 37.00. Found: C, 48.13; H, 6.15; N, .30; S, 36.77.

Preparation of III from II.—II was methylated as described above. The crude product was recrystallized from 2-propanol, yield 58%, mp 143–144°.

Anal. Calcd for $C_8H_{13}NS_2$: C, 51.29; H, 6.99; N, 7.52; S, 34.23. Found: C, 51.27; H, 7.20; N, 7.74; S, 34.31.

Reaction of I and II with Diazomethane.—The acids I and II were treated with an excess of diazomethane in the usual way, with methanol being used as solvent. The methyl esters VII (76%) and III (81%) were identical with those described above.

No reaction took place when the methyl esters III and VII were treated on the similar way, indicating that both dithiocarboxylic acids undergo S-methylation but no N-methylation when diazomethane is used as the methylating agent. No other side reactions such as ring expansion or C-methylation were observed.

Preparation of III from VII.—A mixture of 3.46 g (0.02 mol) of V, 20 ml of 40% aqueous methylamine solution and 20 ml of methanol was shaken for 3 hr. The separation of yellow crystals began shortly after starting the reaction. The product was separated, washed with water and methanol, and dried; 3.5 g of crude product was obtained, which was recrystallized from methanol, yield 2.4 g (69%), mp 143–144°; no depression in melting point was found on admixture with III prepared by the previous method.

Preparation of VIII from VII.—A mixture of 3.46 g (0.02 mol) of VII, 3.8 g (0.06 mol) of 70% aqueous ethylamine solution, and 20 ml of methanol was refluxed for 3 hr. After cooling the yellow product was separated and washed with and recrystallized from methanol, yield 1.9 g (47%), mp 96–97.5°.

Anal. Calcd for $C_9H_{15}NS_2$: C, 53.69; H, 7.51; N, 6.96; S, 31.84. Found: C, 53.42; H, 7.73; N, 6.60; S, 32.01.

Preparation of IX from VII.—A mixture of VII (3.46 g, 0.02 mol), allylamine (3.42 g, 0.06 mol), and 20 ml of methanol was refluxed for 1 hr. After 24 hr, the lustrous yellow plates were separated and recrystallized from methanol, yield 2.9 g (67%), mp 63–65°.

Anal. Calcd for $C_{10}H_{15}NS_2$: C, 56.29; H, 7.08; N, 6.56; S, 30.05. Found: C, 56.23; H, 7.07; N, 6.26; S, 29.94.

Preparation of X from VII.—VII 3.46 g, 0.02 mol) VII was dissolved in 18 ml of cyclohexylamine. After 24 hr, water was added to the dark red solution until precipitation was complete. The yellow crystalline product was separated, washed with water, dried (3.6 g), and recrystallized from methanol, yield 1.9 g (37%), mp 84–86°.

Anal. Calcd for $C_{13}H_{22}NS_2$: C, 60.87; H, 8.65; N, 5.46; S, 25.00. Found: C, 61.31; H, 8.27; N, 5.55; S, 25.60.

Preparation of XI and XII from VII.—VII (3.46 g, 0.02 mol) was dissolved in 35 ml of methanol and 6 g (0.1 mol) of ethylene-

diamine was added. After 24 hr, the red solution gradually turned pale yellow; the precipitated yellow crystalline product (XII) was separated, washed with water, dried (0.6 g), and recrystallized from dioxane, yield 0.33 g (9%), mp 210–213°.

Anal. Calcd for $C_{16}H_{24}N_2S_4$: C, 51.56; H, 6.49; N, 7.51; S, 34.42. Found: C, 51.24; H, 6.61; N, 7.84; S, 34.58.

Water (120 ml) was added to the filtrate; the precipitated yellow crystals (XI) were separated, washed with water, and dried. The crude product (XI, 3.1 g) was recrystallized from 3:2 water–methanol, yellow plates, yield 2.1 g (48.5%), mp 94–95°.

Anal. Calcd for $C_9H_{16}N_2S_2$: C, 49.95; H, 7.45; N, 12.95; S, 29.63. Found: C, 50.15; H, 7.72; N, 13.20; S, 29.57.

Preparation of XIII from XI.—XI (3.24 g, 0.015 mol) was dissolved in 35 ml of dioxane and 1.5 g (0.015 mol) of acetic anhydride was added below 30°. The precipitated yellow acetate of XI was separated, washed with methanol and dried, 1.3 g; after repeated recrystallization from 1:2 dioxane–methanol the melting point was 119–122°.

The filtrate was diluted with water and yellow crystals were separated. The product was recrystallized from methanol–water (1:2) and identified as the N-acetylated derivative of XI (XIII), yield 1.0 g (25%), mp 130–132°.

Anal. Calcd for $C_{11}H_{18}N_2OS_2$: C, 51.10; H, 7.00; N, 10.84; S, 24.82. Found: C, 50.80; H, 6.82; N, 10.97; S, 24.31.

Preparation of XIV from I.—I (1.6 g, 0.01 mol) was dissolved in a solution of 0.73 g (0.01 mol) of diethylamine in 20 ml of water; 0.75 g (0.01 mol) of 40% aqueous formaldehyde was added to the solution. After 1 hr, the precipitated yellow product was separated, washed with water, and dried, yield 1.7 g (70%), mp 97–99°.

Anal. Calcd for $C_{11}H_{23}N_2S_2$: C, 54.0; H, 8.24; N, 11.46; S, 26.24. Found: C, 53.76; H, 8.33; N, 11.02; S, 25.86.

Preparation of XV from II.—II (1.73 g, 0.01 mol) was dissolved in a solution of 0.73 g (0.01 mol) of diethylamine in 20 ml of water; 0.75 g (0.01 mol) of 40% aqueous formaldehyde was added. The yellow product, which separated out immediately, was separated, washed with water, dried, and recrystallized from 1:2 water–ethanol, yield 1.5 g (58%), mp 72°.

Anal. Calcd for $C_{12}H_{22}N_2S_2$: C, 55.80; H, 8.59; N, 10.84; S, 24.83. Found: C, 55.71; H, 8.66; N, 11.10; S, 25.04.

The nmr spectra were recorded in $CDCl_3$ solution on a Varian A-60D instrument at 60 MHz, using TMS as internal standard. One drop of TFA was used for acidifying the probes. Ir spectra were recorded on a Perkin-Elmer 457 spectrometer in KBr pellets and in $CDCl_3$ solution (0.1 mol/l.), respectively.

Registry No.—Ib, 20735-33-5; IIb, 34281-24-8; IIIb, 34281-25-9; IVb, 34281-26-0; Vb, 34281-27-1; VIb, 34281-28-2; VIIb, 34281-29-3; VIIIb, 34281-30-6; IXb, 34281-31-7; Xb, 37297-90-0; XIb, 34281-32-8; XIIb, 34281-33-9; XIIIb, 34281-34-0; XIVb, 34281-35-1; XVb, 34281-36-2.

Acknowledgment.—We are indebted to Miss M. Fodor for the microanalyses. Thanks are due to Mrs. C. Méhesfalvi, Miss A. Bede, Mr. I. Echter, and Mr. A. Fürjes for valuable technical assistance.

Synthesis and Some Reactions of 3,3-Dimethoxycyclopropene[1,2]

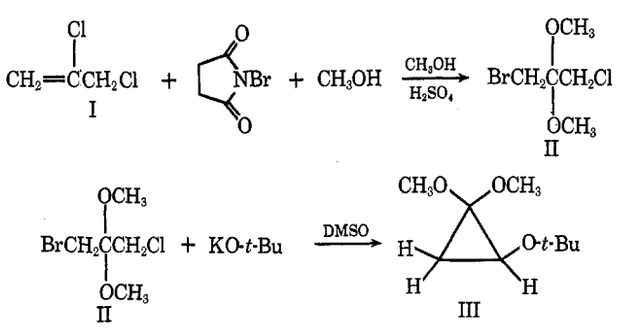
KEITH B. BAUCOM AND GEORGE B. BUTLER*[3]

Department of Chemistry, University of Florida, Gainesville, Florida 32601

Received October 5, 1971

During the course of attempts to synthesize compounds potentially capable of intramolecular charge-transfer interaction, an easy and relatively simple procedure for the preparation of 3,3-dimethoxycyclopropene (IV) was developed. The starting material for this synthesis is the commercially available 2,3-dichloropropene (I). Reaction of I with methanol and *N*-bromosuccinimide, using an acid catalyst, yields 1-bromo-3-chloro-2,2-dimethoxypropane (II) in 33–40% yield. Reaction of II with potassium *tert*-butoxide (KO-*t*-Bu) in dimethyl sulfoxide (DMSO) led to 1,1-dimethoxy-2-*tert*-butoxycyclopropane (III) which has been identified and characterized by nmr, ir, mass spectroscopy, and elemental analysis. IV was considered to be an intermediate and subsequent attempts to isolate this compound were successful. Cyclization of II was achieved using KNH_2 in liquid NH_3. IV was obtained in yields up to 50% and its identity has been well established. When IV was hydrolyzed, cyclopropenone was obtained. Reaction of IV with 1,3-diphenylisobenzofuran gave the adduct V which was converted to 1,4-diphenyl-2-carbomethoxynaphthalene (VI) using trifluoroacetic acid. VI was identified by conversion to its known hydrazide derivative. IV dimerizes at room temperature to 3,3,6,6-tetramethoxytricyclo[3.1.0.0^{2,4}]cyclohexane (VII) which was characterized by its spectral properties and elemental analysis. Reaction of IV with anhydrous dimethylamine led to 1,1-dimethoxy-2-(dimethylamino)cyclopropane (VIII).

An easy and relatively simple procedure for the preparation of 3,3-dimethoxycyclopropene (IV) was developed during the course of attempts to synthesize compounds potentially capable of intramolecular charge-transfer interaction. The starting material for this synthesis is the commercially available 2,3-dichloropropene (I). Reaction of I with methanol and *N*-bromosuccinimide, using an acid catalyst, yields 1-bromo-3-chloro-2,2-dimethoxypropane (II) in 33–40% yield. Reaction of compound II with KO-*t*-Bu in DMSO led to 1,1-dimethoxy-2-*tert*-butoxycyclopropene (III), which has been identified and characterized by nmr, ir, mass spectroscopy, and elemental analysis. IV was postulated to be an intermediate in the formation of III and subsequent attempts to isolate this compound were successful. Cyclization of II was achieved using KNH_2 in liquid NH_3. IV was obtained in yields up to 50% and its identity has been well established.



Formation of IV can be accounted for on the following basis.

(1) We acknowledge the support of this work by the National Institutes of Health under Grant No. CA-06838.

(2) Presented before the Organic Division, 159th National Meeting of the American Chemical Society, Houston, Texas, Feb 1970, No. 139.

(3) To whom all correspondence should be addressed.