merization differs from the usual dimerization reactions as observed in different halogen uracils (Feneslau and Wang, 1969; Wang, 1976). The fact that a similar compound was not obtained from VI (Acher and Dunkelblum, 1979) is due to the more facile homolitic cleavage of the *tert*-butyl group as compared to that of the *sec*-butyl group. The formation of V, which is an oligomer, although its exact structure has not yet been elucidated, implies probably a radical reaction mechanism, initiated by RF (Oster, 1954). As the main purpose of this work was to investigate the photodegradation reaction of I under different reaction conditions, the yields of the products were not optimized. The relative amounts of compounds I–V changed with sensitizer, pH, temperature, and time.

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Acid-Catalyzed Alteration of 2,3-Dihydro-2,2-dimethyl-7-benzofuranyl (Di-*n*-butylaminosulfenyl)methylcarbamate via Nitrogen–Sulfur Bond Cleavage. Formation of Polysulfide Derivatives

Noriharu Umetsu, Takaaki Nishioka, and T. Roy Fukuto*

A new experimental insecticide, 2,3-dihydro-2,2-dimethyl-7-benzofuranyl (di-*n*-butylaminosulfenyl)-methylcarbamate (DBSC), was unstable in acidic media, e.g., dichloromethane–acetic acid (9:1), and was converted into a number of alteration products via N–S bond cleavage. The principal products were carbofuran, dibutylamine, a mixture of polysulfide derivatives of DBSC (I), biscarbofuran *N,N'*-disulfide (III), and a mixture of biscarbofuran *N,N'*-polysulfides (IV), the structures being confirmed by MS and NMR analyses of purified products. I and IV, which were indicated to be a mixture of polysulfide derivatives, gave single spots on silica gel thin-layer plates with several different solvent systems. The rates of acid-catalyzed alteration of DBSC and formation of carbofuran, dibutylamine, I, III, and IV were determined by using [*carbonyl*-^{14}C]- or [*dibutylamino*-^{14}C]DBSC. The rate of DBSC decomposition was first order in DBSC.

2,3-Dihydro-2,2-dimethyl-7-benzofuranyl (di-*n*-butylaminosulfenyl)methylcarbamate (DBSC or Marshal) is a sulfenylated derivative of carbofuran which is currently undergoing development as a broad spectrum insecticide. Previous reports from this laboratory described the metabolic and environmental fate of DBSC in plants (Umetsu et al., 1979), soil (Clay et al., 1980), and the rat (Marsden, 1980). These studies indicated that significant nonenzymatic degradation of DBSC was taking place in a biological system. Another study (Umetsu et al., 1980) showed that in an acidic, aqueous environment or one containing sulfhydryl agents, DBSC was readily converted to carbofuran (2,3-dihydro-2,2-dimethyl-7-benzofuranyl methylcarbamate) by N–S bond cleavage but was stable under neutral and alkaline conditions. Since carbofuran was by far the major product observed, these findings pointed to the greater lability of the carbamyl N–S bond compared to the amino N–S bond. Previous studies (Chiu et al., 1975; Umetsu et al., 1979; Mallipudi and Fukuto, 1979) had revealed the ready susceptibility of N–S bonds in sulfenylated methylcarbamates to thiolytic cleavage by attack of the sulfur atom by sulfhydryl-containing agents.

During the course of a study on the behavior of DBSC under different solvent conditions, we discovered that DBSC also was unstable in a dichloromethane–acetic acid (9:1) mixture, being converted into a variety of different products in significant quantities, in addition to carbofuran. Because of the possible significance of acid-catalyzed nonenzymatic alteration on the mode of action and toxicological properties of DBSC, a further probe into the nature of the alteration products was made. Initial studies were made in an aprotic, inert solvent in order to identify all alteration products that were formed from DBSC in an acidic environment. This paper is concerned with the isolation and identification of these products, along with

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a kinetic analysis of the breakdown of DBSC and formation of alteration products.

MATERIALS AND METHODS

Chemicals. [*carbonyl*-^{14}C]DBSC (sp act. 25.20 mCi/mmol) and [*dibutylamino*-^{14}C]DBSC (sp act. 19.8 mCi/mmol) were available from previous studies (Umetsu et al., 1979; Clay et al., 1980). Biscarbofuran *N,N'*-disulfide also was available from an earlier study (Umetsu et al., 1980), and bis(di-*n*-butylamino) sulfide, bis(di-*n*-butylamino) disulfide, and bis(di-*n*-butylamino) trisulfide (Hatch, 1978) were obtained from the FMC Corp., Princeton, NJ. Other chemicals were analytical reagent grade, and redistilled solvents were used.

Stability of DBSC in Acidic, Neutral, and Basic Solvent Mixtures. In a preliminary examination of the stability of DBSC, samples of [*carbonyl*-^{14}C]DBSC (4.0 mg; 0.532 μCi) were dissolved in 0.4 mL of the following solvent mixtures and kept at 23 °C: dichloromethane, dichloromethane–acetic acid (9:1), and dichloromethane–triethylamine (9:1). At different time intervals, duplicate 5-μL samples were removed and the contents were examined by thin-layer chromatography (TLC).

Acid-Catalyzed Alteration of DBSC. [*carbonyl*-^{14}C]DBSC was repurified by Florisil column chromatography using the hexane–ether solvent as previously described (Umetsu et al., 1979), giving a product which was 94.7% DBSC, 4.2% carbofuran, and 0.9% CFS_nNBu_2 (see Table I for the structure). A mixture of 20 mg of purified DBSC (nonradioactive) and 40.2 μg of [*carbonyl*-^{14}C]DBSC (2.66 μCi) in 200 μL of dichloromethane was added to 200 μL of a 4:1 dichloromethane–acetic acid mixture. At predetermined time intervals, duplicate 2-μL samples were taken and examined by TLC. Similar experiments were carried out with [*dibutylamino*-^{14}C]DBSC. This material was also purified by Florisil column chromatography using a hexane–ether solvent, and TLC analysis showed it to be 93% DBSC, 5.0% $CF–S_nNBu_2$, 0.3% dibutylamine, and 2.2% unknown (four components).

The structures of the different alteration products formed in dichloromethane–acetic acid (9:1) were determined by using larger quantities of nonradioactive DBSC. Weighed amounts (1.6–2 g) of DBSC were dissolved in the 9:1 dichloromethane–acetic acid solvent (40 mL), and the mixtures were stirred at room temperature for the following time intervals: (1) 22 h, (2) 48 h under a nitrogen atmosphere, and (3) 96 h. Each reaction mixture was washed with water (2 times), and the dichloromethane phase was dried and concentrated. The residual oil was dissolved in ether and subjected to TLC analysis. Each mixture showed the presence of at least six different products (compounds I–VI; Figure 1) in varying amounts. These compounds were separated and purified by repeated preparative TLC, and their structures were determined by NMR, mass spectroscopy, and cochromatography with authentic standards.

Analyses. Precoated silica gel GHLF plates (0.25 mm; Analtech, Inc.) were used for analytical TLC and silica gel 60 PF-254 plates (1.0 mm; EM Laboratories) for preparative TLC. Location of spots on the plates was by use of iodine vapor or by ultraviolet detection. The location of radioactive spots was accomplished by means of a Berthold (Varian-Aerograph) thin-layer radioscanner (Model LB 2723) equipped with a dot printer and confirmed by autoradiography using Kodak X-ray film (BB-5) exposed for 7–15 days.

Radioactivity was quantitated with a Beckman Model LS-230 liquid scintillation counter using 10 mL of a scintillation cocktail consisting of 6 g of PPO, 0.2 g of POPOP, 333 mL of Triton X-100, and 666 mL of toluene. Radioactivity in each spot on TLC plates was determined by scraping the spot from the plate and placing the silica gel in counting vials with the scintillation cocktail.

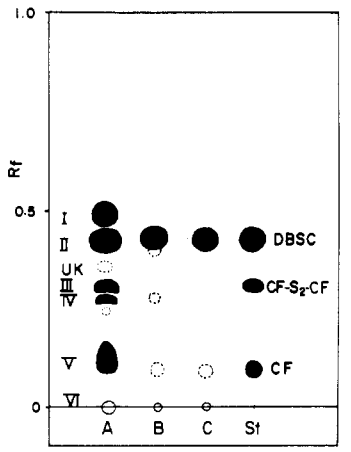


Figure 1. Thin-layer chromatograms of [*carbonyl*-^{14}C]DBSC incubated in dichloromethane–acetic acid (9:1) (A), dichloromethane (B), and dichloromethane–triethylamine (9:1) (C) at 23 °C for 24 h; the solvent was hexane–ether (7:3). St = standard; Uk = unknown.

NMR spectra were recorded on a Varian EM 390 spectrometer using Me_4Si as the lock signal and chloroform-*d* as the solvent. Mass spectral data were obtained by direct insertion probe in a Finnigan Model 1015 mass spectrometer interfaced with a data acquisition and reduction system (Systems Industries, System 150). An electron energy of 70 eV was used.

RESULTS

DBSC Stability in Dichloromethane Containing Acetic Acid or Triethylamine. Preliminary experiments were carried out to determine the stability of DBSC in dichloromethane in the presence of an acid (acetic) and organic base (triethylamine). In the dichloromethane–triethylamine mixture (9:1), and also in dichloromethane alone, DBSC was stable and most of the radioactivity was recovered as unchanged DBSC, although trace amounts of several alteration products were detected. For example, after 48 h, 93.0% of the charged radioactivity was recovered as DBSC from dichloromethane and 93.1% was recovered from the dichloromethane–triethylamine mixture. Recovery of DBSC was virtually the same from the same two solvents after 96 h.

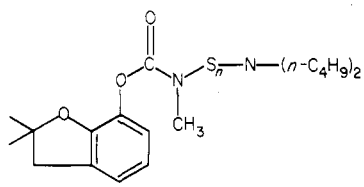
In contrast, DBSC was highly unstable in dichloromethane–acetic acid, being converted into at least five other materials within 24 h (see Figure 1). TLC analysis (cochromatography with available standards) showed that two of the products were biscarbofuran *N,N'*-disulfide (III) and carbofuran (V). After 24 h, only 34% of the radioactivity was returned as DBSC, 32% as carbofuran, and 34% as other products (I, III, IV, and VI). Recovery of DBSC was 10.7% after 48 h and 1.3% after 96 h. Thus, after 96 h in dichloromethane–acetic acid, DBSC was almost completely transformed into other compounds.

Isolation and Identification of the DBSC Alteration Products Formed in Dichloromethane–Acetic Acid. Three separate experiments were carried out to isolate and characterize the different alteration products formed in the presence of acetic acid. These are described as follows.

Experiment 1. DBSC (1.6 g) in the dichloromethane–acetic acid solvent was stirred for 96 h at 23 °C. TLC analysis of the products using hexane–ether (7:3) as the developing solvent showed the presence of six different

products (I–VI). The individual products were separated by preparative TLC (20 plates) according to the following R_f values: 169 mg of I, R_f 0.50–0.60 (light yellow gum); 155 mg of II, R_f 0.41–0.5 (DBSC); 107 mg of III, R_f 0.24–0.29 (white solid); 114 mg of IV, R_f 0.18–0.24 (white solid); 393 mg of V and VI, R_f 0–0.14 (light yellow solid).

I (89 mg) was further purified by TLC using hexane–ether (3:1) as the developing solvent. The TLC plate showed the presence of two other minor components, formed either during storage or during the purification procedure, i.e., I-a, R_f 0.30–0.46, and I-b, R_f 0.07–0.15. Reextraction of each zone with ether gave 78 mg of I, 2.8 mg of I-a, and 7 mg of I-b. The NMR spectrum of I, δ ($CDCl_3$), showed the following signals: 6.65–7.08 (m, 3 H, aromatic protons), 3.30–3.42 (m, 3 H, N–CH_3), 2.98 (s, 2 H, CH_2), 2.92 (t, 4 H, two N–$CH_2C_3H_7$, J = 6 Hz), 1.05–1.72 (m, 8 H, two N–$CH_2CH_2CH_2CH_3$), 1.49 (s, 6 H, *gem*-di-CH_3), 0.89 [t, 6 H, two N–$(CH_2)_3CH_3$]. This spectrum was very similar to that of DBSC except for the upfield shift of the N–CH_2 signals and the appearance of the N–CH_3 protons as a multiplet instead of as a singlet in DBSC. The mass spectrum of I showed three different molecular ion peaks at m/e 412 (CFS_2NBu_2), 444 (CFS_3NBu_2), and 476 (CFS_4NBu_2) along with peaks at 285 (CFS^+SH) and 192 ($S{=}S^+NBu_2$). These results, combined with the multiplet observed for the NMR signals for the N–CH_3 protons, suggest I to have the structure



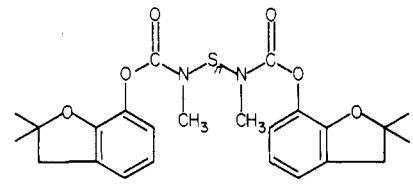
where n = 2–4. Elemental analysis of I gave C, 55.60%, H, 6.84%, and S, 20.9%, indicating that the average value for n is close to 3. The percentage of sulfur in CFS_3NBu_2 is 21.6.

I-a cochromatographed with authentic samples of bis(di-*n*-butylamino) *N,N'*-disulfide ($Bu_2NS_2NBu_2$) and bis(di-*n*-butylamino) *N,N'*-trisulfide ($Bu_2NS_3NBu_2$), these two compounds having the exact same R_f values on silica gel plates with a variety of different solvent systems. The mass spectrum of I-a showed at least four different molecular ion peaks at m/e 288 (Bu_2NSNBu_2), 320 ($Bu_2NS_2NBu_2$), 352 ($Bu_2NS_3NBu_2$) and 384 ($Bu_2NS_4NBu_2$). I-a is probably $Bu_2NS_nNBu_2$ where n is 1–4.

I-b cochromatographed with IV on silica gel plates using several different solvent systems. The mass spectrum of I-b showed at least three molecular ion peaks at m/e 504 (CFS_2CF), 536 (CFS_3CF), and 568 (CFS_4CF). I-b is therefore a mixture of biscarbofuran *N,N'*-polysulfides (see discussion on IV for structure identification).

III (54 mg) was subjected to further purification by TLC, using two migrations of hexane–ether (7:3). Extraction of the zone at R_f 0.28–0.34 with ether gave 38 mg of a white crystalline solid, mp 133–134 °C. NMR and mass spectral data reveal III to be a biscarbofuran *N,N'*-disulfide, in agreement with spectroscopic data obtained from an authentic sample of this compound (Umetsu et al., 1980).

IV (114 mg) was subjected to further purification by TLC using two migrations with 7:3 hexane–ether as the developing solvent. Extraction of the zone at R_f 0.20–0.27 gave 113 mg of an off-white gum which gave the following NMR spectrum: δ 6.70–7.0 (m, 3 H, aromatic protons), three singlets at 3.37–3.44 (3 H, NCH_3), 2.98 (s, 2 H, CH_2), and 1.45 (s, 6 H, *gem*-di-CH_3). This spectrum was almost identical with that of III except for the three singlets for the N–CH_3 protons (δ 3.38, 3.40, and 3.42). The mass spectrum of IV showed four molecular ion peaks at m/e 504 (CFS_2CF), 536 (CFS_3CF), 568 (CFS_4CF), and 600 (CFS_5CF). While it is possible that IV was still contaminated with a small amount of III, it is also possible that the molecular ion peak at 504 was the result of desulfurization by electron impact of a higher polysulfide. On the basis of NMR and mass spectral data, IV was concluded to have the structure



where n is 3–5.

The mixture containing V and VI (50 mg) was resubjected to TLC using hexane–ether (1:1) as the developing solvent. Extraction of the zone at R_f 0.11 to ~0.22 gave 40 mg of V, mp 150–151 °C, which proved to be identical with an authentic sample of carbofuran.

VI stayed at the origin after development with 1:1 hexanes–ether and was not characterized owing to its small amount.

Structures and TLC properties of the individual alteration products of DBSC formed in dichloromethane–acetic acid are given in Table I.

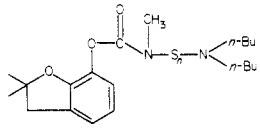
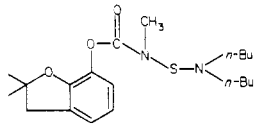
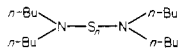
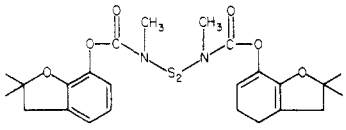
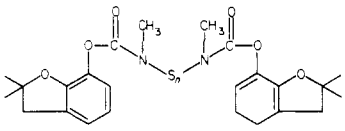
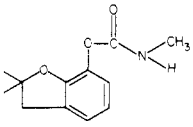
Experiment 2. DBSC (2.0 g) in dichloromethane–acetic acid solvent was stirred for 48 h at 23 °C under a nitrogen atmosphere. TLC analysis showed the same alteration products (I–VI) obtained under air (Experiment 1). Preparative TLC of the reaction mixture resulted in 200 mg of I, 95 mg of III and 258 mg of IV. NMR and mass spectral analysis showed that I was CFS_nNBu_2, where n = 2, 3, and 4. NMR and mass spectral analysis of IV showed it was CFS_nCF, where n = 3, 4, and 5.

Experiment 3. For determination of the effect of a shorter reaction time on the acid-catalyzed alteration of DBSC, a 1-g sample was stirred in dichloromethane–acetic acid for 22 h at 23 °C. Preparative TLC gave 135 mg of I and 98 mg of III and IV, along with 455 mg of DBSC. The NMR spectrum of I exhibited essentially only one N–CH_3 proton (δ 3.35), indicating it to be a single component, probably CFS_2NBu_2. Mass spectral analysis, however, showed that I also contained a trace of CFS_3NBu_2.

The mixture consisting of III and IV was resubjected to preparative TLC to give 48 mg of III (white crystalline solid) and 50 mg of IV (off-white gum). Both mass spectral analysis (molecular ion peak at m/e 536) and NMR spectrum (a singlet for the N–CH_3 signal at δ 3.42) indicated IV to be CFS_3CF.

Time Course for the Alteration of [*carbonyl*-^{14}C]-DBSC. The breakdown of DBSC and formation of alteration products in 9:1 dichloromethane-acetic acid were monitored at short time intervals over a period of 120 h in order to gain insight into the sequence of events taking place during the acid-catalyzed alteration of DBSC. Autoradiographs of thin-layer chromatograms after allowing [*carbonyl*-^{14}C]DBSC to stand in dichloromethane–acetic acid for 12 and 36 h are shown in parts A and B of Figure 2. The chromatograms indicate rapid alteration of DBSC, resulting in the formation of products I and III–IV. Recovered DBSC (II) was 45 and 33% of the original amount after 12 and 36 h, respectively. The chromatograms also showed two additional unknown spots in samples taken

Table I. Structure and TLC Properties of DBSC and Its Alteration Products

no.	abbreviated name	structure	solvent[a] A	solvent[a] B
I	CFS_nNBu_2	 n = 2-4	0.49	0.91
II	DBSC		0.43	
I-a	$Bu_2NS_nNBu_2$	 n = 1-4	0.71	
III	CFS_2CF		0.26	
IV	CFS_nCF	 n = 3-5	0.23	
V	carbofuran		0.10	0.90
VII	dibutylamine		0	0.52

[a] Solvent system: (A) hexane-ether (7:3); (B) ethyl acetate-methanol-ammonium hydroxide (15:4:1).

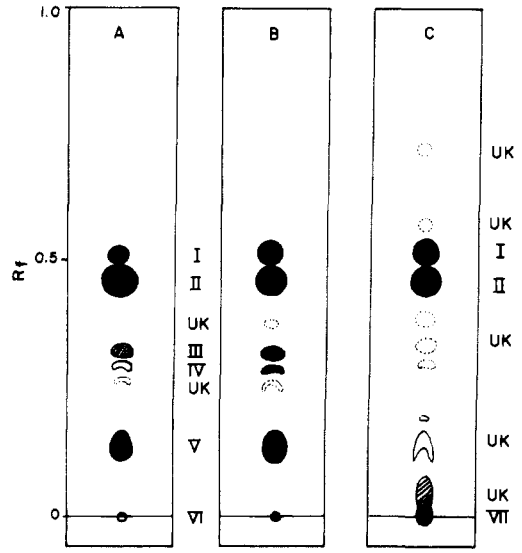


Figure 2. Thin-layer chromatograms of [*carbonyl*-^{14}C]DBSC and [*dibutylamino*-^{14}C]DBSC kept in dichloromethane–acetic acid (9:1). (A) [*carbonyl*-^{14}C]DBSC kept for 12 h; (B) [*carbonyl*-^{14}C]DBSD kept for 36 h; (C) [*dibutylamino*-^{14}C]DBSC kept for 36 h; the solvent was hexane–ether (7:3). Uk = unknown.

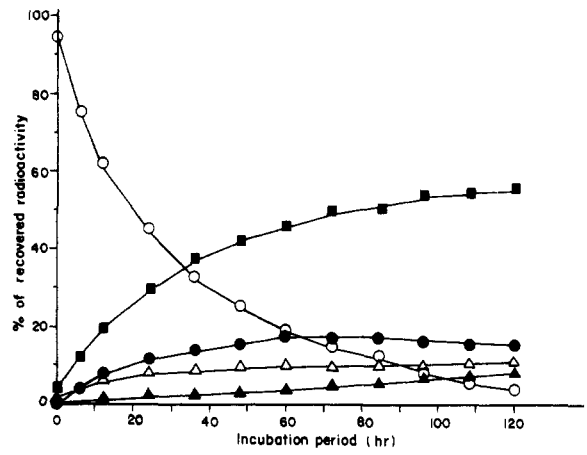


Figure 3. Plots showing the disappearance of [*carbonyl*-^{14}C]-DBSC and formation of alteration products in dichloromethane–acetic acid (9:1). (○) DBSC; (■) carbofuran; (●) CFS_nNBu_2 (n = 2-4); (△) CFS_2CF; (▲) CFS_nCF (n = 3-5).

at 24 h (see Figure 1) and 36 h but these were observed in trace amounts. Numerous unsuccessful attempts were made to separate each component in I and III by using silica gel TLC and a wide variety of solvents.

Plots showing the relative amounts of each alteration product formed in dichloromethane–acetic acid at different time intervals are presented in Figure 3. The gradual disappearance of DBSC and concomitant formation of CFS_nNBu_2 (I), CFS_2CF (III), CFS_nCF (IV) and carbofuran (V) are clearly indicated. The major product after 48 h was carbofuran (48%), followed by I (16%), III (10%), and IV (3.3%). During the first 84-h period, the combined amount of III and IV (biscarbofuran polysulfides) was slightly less than the amount of I at each time interval, but the relative amounts were reversed after 96 and 120 h. During the early period of the kinetic study, significantly less IV was formed compared to III, e.g., 2.1% IV

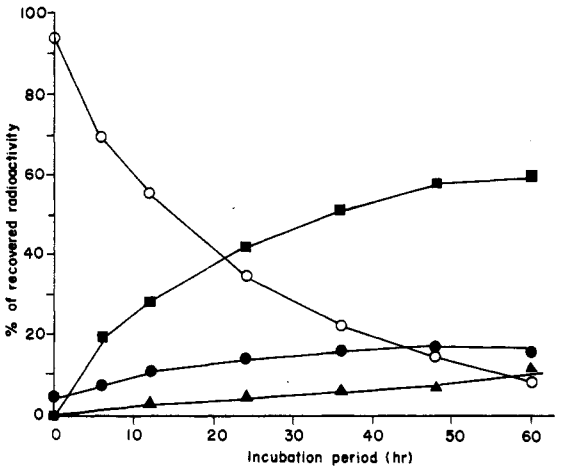


Figure 4. Plots showing the disappearance of [*dibutylamino*-^{14}C]DBSC and formation of alteration products in dichloromethane–acetic acid (9:1). (○) DBSC; (■) carbofuran; (●) CFS_nNBu_2 (n = 2–4); (▲) unknowns.

and 7.9% III after 24 h. However, the rate of formation of IV increased more rapidly than the rate of formation of III, and after 96 h 7.1% IV was present compared to 10.9% for III. These results suggest that I, formed initially from DBSC, was being converted into IV.

The rate of DBSC decomposition into the different alteration products was first order in DBSC with a first-order rate constant for the disappearance of DBSC of 0.027 h^{-1}.

Time Course for the Alteration of [*dibutylamino*-^{14}C]DBSC. An analogous study was conducted to examine the acid-catalyzed breakdown and formation of alteration products of [*dibutylamino*-^{14}C]DBSC in dichloromethane–acetic acid (9:1). Thin-layer chromatograms showing the number of different products obtained from the dibutyl-labeled DBSC after 36 h are shown in Figure 2C. The principal products were dibutylamine (VII, 51%) and I (16%), along with 23% of the starting DBSC. At least six minor unknown products (total 8.4%) also were detected. Dibutylamine was identified by cochromatography with a standard (Aldrich) using ethyl acetate–methanol–ammonium hydroxide (15:4:1) and hexane–ether (7:3) as the solvents. A small amount of I-a ($Bu_2NS_nNBu_2$, 0.3–0.5%) and an unknown compound (1.3–1.4%) with a slightly higher R_f value than I-a were present in the original DBSC as contaminants, and the amount of these materials remained unchanged during the 60-h incubation period.

Plots showing the relative amounts of products formed from [*dibutylamino*-^{14}C]DBSC in dichloromethane–acetic acid at different time intervals are shown in Figure 4. The plots reveal the gradual disappearance of DBSC and appearance of dibutylamine and CFS_nNBu_2 (I). As expected, the degradation of DBSC was first order. It is noteworthy that evidence was not found for the conversion of the dibutylamino-labeled DBSC to $Bu_2NS_nNBu_2$. In contrast, CFS_2CF (III) and CFS_nCF (IV) were significant products from carbonyl-labeled DBSC under the same conditions.

DISCUSSION

Sulfenylated derivatives of methylcarbamate esters have recently gained prominence as useful insecticides having favorable properties of selectivity. Chief among the compounds of this type currently being developed are Larvin [bismethomyl *N,N'*-sulfide or *O*-[[*N*-[*N'*-(methylthioethylideneiminoxycarbonyl)-*N'*-methylaminosulfenyl]-*N*-methylcarbamoyl]]-*S*-methylacetothiohydroximate] (Sousa et al., 1977), Upjohn-47319 [methyl-*N*-[[[[(diethoxyphosphinothioyl)isopropylamino]thio]methylamino]-carbonyl]oxy]ethanimidothioate], and Marshal (DBSC). All three compounds contain the N–S–N linkage which is vulnerable to cleavage at one or both of the N–S bonds. Previous studies (Umetsu et al., 1980) revealed the facile cleavage of the carbamate N–S bond in DBSC in a variety of aqueous environments to yield carbofuran as the sole or major product.

In dichloromethane–acetic acid DBSC also experienced N–S bond cleavage, but in this case several other reaction products were observed in addition to carbofuran. These were the polysulfide derivatives of DBSC (I), biscarbofuran *N,N'*-disulfide (III) and polysulfides (IV), and dibutylamine. While spectroscopic evidence indicated the presence of several different polysulfide derivatives of I and IV, numerous attempts to separate the individual components by silica gel TLC proved to be unsuccessful.

Analysis of the individual products obtained from carbonyl- and dibutylamino-^{14}C labeled DBSC showed that the amount of CFS_nNBu_2 (I) gradually increased to a steady-state level after 60–72 h, while the amounts of CFS_2CF (III) and CFS_nCF (IV) continued to increase throughout the entire reaction period to 120 h (see Figure 3). This would suggest that CFS_nNBu_2 is an intermediate and is slowly transformed into CFS_2CF and CFS_nCF. Noteworthy also is the 3:2 ratio observed for carbofuran and total polysulfide products (CFS_nNBu_2 and CFS_nCF) during the reaction period.

It is not possible at this time to provide a mechanism which explains the formation of the various products obtained from DBSC in dichloromethane–acetic acid. However, the results indicate that the carbamate N–S and dibutylamino N–S bonds are both being broken since carbofuran, CFS_nNBu_2 (I), CFS_nCF (III and IV, n = 2–5), and dibutylamine were all observed in significant amounts. DBSC was stable in dichloromethane alone or when an organic base such as pyridine was present but was unstable when acetic acid was present. This suggests that protonation, probably on the dibutylamino nitrogen atom or possibly the carbamoyl nitrogen, is the first step in the alteration process. Because of the variety of products that are formed, it is difficult to propose the next step in the reaction process. It is likely that at some place in the sequence of reactions, a disproportionation reaction takes place to give the various polysulfide derivatives.

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