Table I. ^{13}C Chemical Shift Assignments[a]

C	1	2	3	C	1	2	3
1	119.5	119.6	119.5	12a	134.0	134.0	134.0
2	135.3	135.3	135.3	4a	120.2	122.2	120.5
3	118.2	118.3	118.1	5a	110.5	110.3	111.0
4	160.8	160.9	160.7	11a	110.7	110.4	111.5
5	186.0	186.0	186.0	10a	133.9	133.5	135.5
6	155.0	155.0	155.0	6a	133.6	133.3	135.0
7	69.0	61.9	69.0	15	56.6	56.6	56.5
8	34.8	34.3	34.7	1′	100.7		100.2
9	78.8	78.5	73.5	2′	32.3		29.9
10	33.4	33.1	32.4	3′	46.2		45.4
11	156.4	156.0	156.0	4′	70.5		70.2
12	186.0	186.0	186.0	5′	66.0		66.0
13	211.6	211.6	71.6	6′	17.0		16.9
14	24.7	24.5	16.6	NHC(=O)CH$_3$			169.0
				NHC(=O)CH$_3$			24.0

[a] In parts per million (δ), obtained from (0.03 M) CDCl$_3$ solutions containing Me$_4$Si as internal standard.

compounds,[9] permit us to assign all the carbons in the amino sugar in **1**.

Using the assignments of **1** and **2**, we were able to attribute all the carbons in our biotransformed molecule, *N*-acetyldaunorubicinol (**3**). The assignments are summarized in Table I. As expected, the ^{13}C NMR of **3** is similar to that of **1**, except at C-13 where the carbonyl (211.6 ppm) was reduced to the alcohol (71.6 ppm); carbons 9 and 14, which are adjacent to C-13, were slightly shifted upfield; two new peaks, which belong to the *N*-acetyl, appeared at 169.0 [HNC(=O)CH$_3$] and 24.0 ppm [HNC(=O)CH$_3$]. Thus ^{13}C NMR confirmed that the structure of one of the biotransformed molecules is **3**. Structure assignments have been made previously for this biotransformed molecule.[11]

The 4–10 ppm differences in chemical shift for carbons 5, 6, 11, 12, and 13 between daunorubicinone and that of the recently reported data[10] on daunorubicin tetraacetate could be attributed to the absence of hydrogen bonding in the latter. In addition, there is disagreement in the assignment of carbons 8 and 10, but single-frequency experiments clearly place C-10 upfield from C-8. However, the above assignments are in good agreement with recently published results[12] with the expected minor shift differences. These differences are due to the fact that Mondelli[12] et al. used Me$_2$SO as solvent whereas CDCl$_3$ was used in the present study.

Registry No.—**1,** 20830-81-3; **2,** 21794-55-8; **3,** 62133-95-3.

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Communications

Reaction between Dithioacetic Acid and Dicyclohexylcarbodiimide—Structure of Products. Crystal and Molecular Structure of *trans*-2,4-Dimethyl-2,4-bis(thioacetylthio)-1,3-dithietane

Summary: The reaction between dithioacetic acid and dicyclohexylcarbodiimide gives the unstable bis(thioacetyl) sulfide (**1**) which dimerizes to the hexathiaadamantane (**2**) and both isomers of 2,4-dimethyl-2,4-bis(thioacethylthio)-1,3-dithietane (**3**); **4** is a minor product.

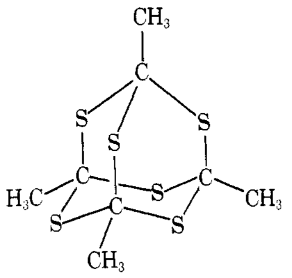
Sir: The reaction between monothioacetic acid and dicyclohexylcarbodiimide (DCC) has recently been shown to give dicyclohexylthiourea and bisacetyl sulfide—a symmetrical monothioanhydride.[1] The analogous reaction with dithioacetic acid should produce the hitherto unknown bis(thioacetyl) sulfide (**1**). In this context it is worthy of note that 1,3,5,7-tetramethyl-2,4,6,8,9,10-hexathiaadamantane (**2**)[2–4] may be considered as a dimeric form of **1**. Although this view is in accord with the mass spectral fragmentation of **2**,[4] there is no direct experimental evidence supporting **1** → **2** conversion.

We have now treated DCC with 2 mol of dithioacetic acid in acetonitrile or ether at temperatures between −20 and 20 °C. In addition to the expected dicyclohexylthiourea (~90% yield), a complicated mixture of products derived from dithioacid was obtained. By preparative TLC using a CCl$_4$/hexane/benzene (20:6:1) we have isolated three products, **2**, **3**, and **4**.

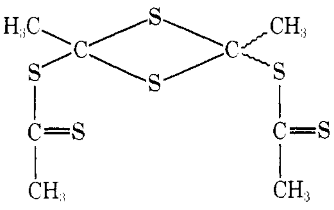
The first compound (R_f 0.06–0.13) has been identified as

$CH_3\underset{\displaystyle S}{\overset{}{\underset{\|}{C}}}S\underset{\displaystyle S}{\underset{\|}{C}}CH_3$

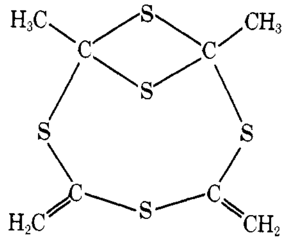
1



2



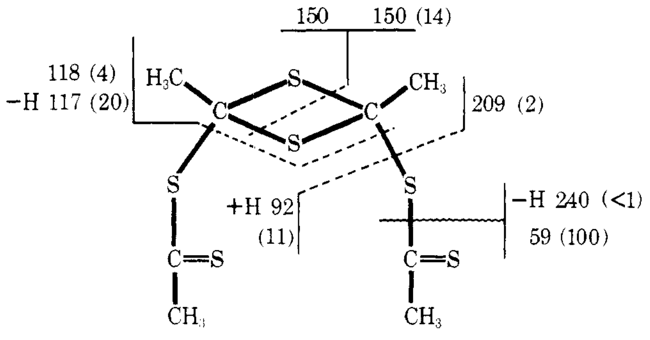
3



4

hexathiaadamantane **2** by NMR[5] [^{1}H NMR 2.1 ppm (s, CH_3); ^{13}C NMR 29.2 (CH_3), 58.5 ppm (>C<)], mass spectra[4] (*m/e* 300), and comparison with an authentic sample of **2**.[2] It is formed in ~40% yield in acetonitrile at room temperature. However, in ether at −20 °C **2** is formed in a trace amounts only.

The second isolated product (R_f 0.3–0.42) with a broad melting point, 120–135 °C, when crystallized from ethanol or hexane gave yellow crystals, $C_8H_{12}S_6$, mp 145–147 °C. The spectral data agree with structure **3** which is a new dimeric form of **1**. The ^{1}H NMR spectrum shows two singlets of equal intensity at 2.27 and 2.8 ppm. The ^{13}C NMR spectrum showed four signals at 34.4 and 38.0 ($J_{^{13}C-^{1}H}$ = 137 ± 2 Hz) corresponding to the methyl carbons, at 60.6 belonging to the dithietane ring carbon, and at 229.5 ppm (C=S). The IR spectrum showed thiocarbonyl absorption at 1180 cm^{-1}. The mass spectrum of **3** is very similar to that of **2**.



3, M^{+} 300 (<1)

Since dithietane **3** may exist in two geometrical forms and the ^{1}H and ^{13}C NMR spectra of the product having mp 120–135 °C showed two distinct sets of the above-discussed signals, it was obvious that a mixture of both isomers was obtained. This mixture is formed as a major product in 50–65% yield when the reaction between dithioacetic acid and DCC is carried out in ether. The spectral differences permitted an easy estimation of isomeric ratio as 1:1 and permitted assignment of the spectral data to the second isomer [^{1}H NMR 2.3 and 2.8 ppm (2 s, CH_3); ^{13}C NMR 35 and 38 (CH_3), 61 (ring carbon), 230 ppm (C=S)]. An attempt to isolate the more soluble isomer of **3** from the hexane mother liquor gave a sample of 75% diastereomeric purity.

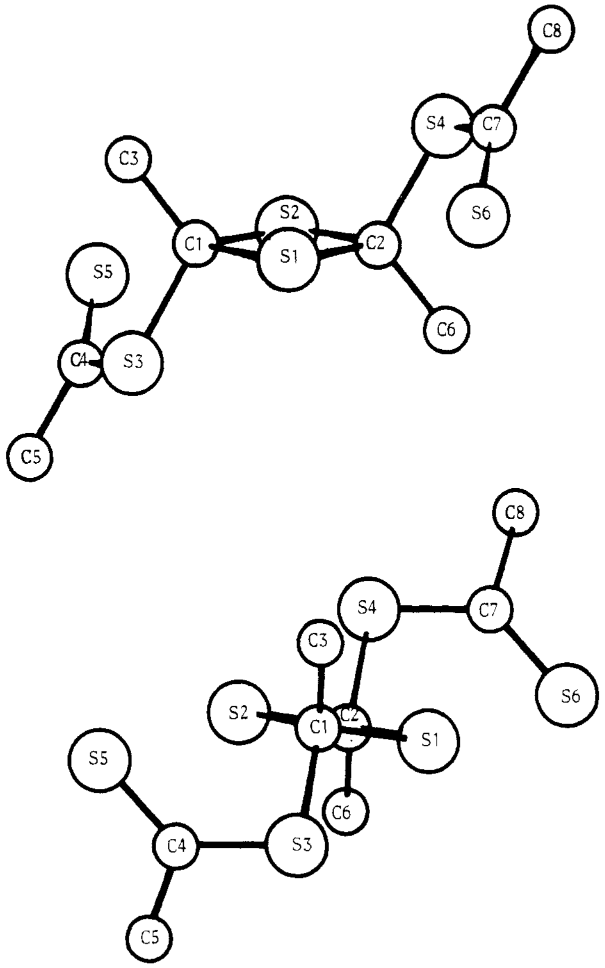


Figure 1. A view of *trans*-2,4-dimethyl-2,4-bis(thioacetylthio)-1,3-dithietane (**3**) along the S(1)–S(2) (upper) and C(1)–C(2) (bottom) axis.

To obtain further information concerning the geometry of the less soluble, diastereomerically pure dithietane **3**, mp 145–147 °C, we determined its structure by x-ray analysis.[6]

Crystal Data. $C_8H_{12}S_6$, M = 300; orthorhombic, a = 11.15 (7), b = 5.945 (17), c = 19.91 (5) Å, U = 1319.6 Å^3, Z = 4, d_{measd} = 1.506 g cm^{-3}, d_{calcd} = 1.51 g cm^{-3}; space group $Pna2$; 1399 reflections with $I < 3\sigma(I)$ have refined to R = 0.0289. The geometry of the molecule is shown in Figure 1. Bond lengths and angles are listed in Table I and II.[7] Crystallographic analysis revealed the trans geometry of the isomer investigated. From the drawings and coordinates the molecule can be seen to be almost perfectly centrosymmetric. An exception is the greater length of the C(1)–S(1)[8] compared to the remaining ring C–S distances. This appears to be genuine as an idealized centrosymmetric set of coordinates returned to the values given on further refinement. A consequence of the approximate center of symmetry is the planarity of the four-membered ring. Thus, dihedral angles between the two pairs of planes—S(1), C(1), S(2) and S(1), C(2), S(2); and C(1), S(1), C(2) and C(1), S(2), C(2)—are 0.85 and 0.79°, respectively.

Table I. Bond Lengths

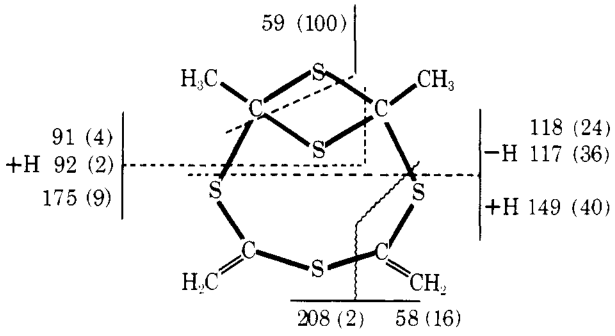
Bond	Length, Å (esd)	Bond	Length, Å (esd)
C(1)–S(1)	1.851 (4)	C(2)–S(1)	1.815 (4)
C(1)–S(2)	1.816 (4)	C(2)–S(2)	1.819 (4)
C(1)–S(3)	1.815 (4)	C(2)–S(4)	1.835 (4)
C(1)–C(3)	1.501 (6)	C(2)–C(6)	1.512 (6)
C(4)–S(3)	1.705 (5)	C(7)–S(4)	1.722 (5)
C(4)–S(5)	1.631 (5)	C(7)–S(6)	1.609 (5)
C(4)–C(5)	1.495 (8)	C(7)–C(8)	1.540 (8)

Table II. Bond Angles

Bonds	Angle, degree (esd)	Bonds	Angle, degree (esd)
C(1)-S(1)-C(2)	85.4 (2)	C(1)-S(2)-C(2)	86.3 (2)
S(1)-C(1)-S(2)	93.6 (2)	S(1)-C(2)-S(2)	94.7 (2)
S(1)-C(1)-S(3)	106.4 (2)	S(1)-C(2)-S(4)	111.8 (2)
S(1)-C(1)-C(3)	112.8 (3)	S(1)-C(2)-C(6)	116.7 (3)
S(2)-C(1)-S(3)	112.7 (2)	S(2)-C(2)-S(4)	106.8 (2)
S(2)-C(1)-C(3)	116.5 (3)	S(2)-C(2)-C(6)	115.1 (3)
S(3)-C(1)-C(3)	112.9 (3)	S(4)-C(2)-C(6)	110.6 (3)
C(1)-S(3)-C(4)	104.9 (2)	C(2)-S(4)-C(7)	105.2 (2)
S(3)-C(4)-S(5)	125.4 (3)	S(4)-C(7)-S(6)	125.6 (3)
S(3)-C(4)-C(5)	111.9 (4)	S(4)-C(7)-C(8)	109.9 (4)
S(5)-C(4)-C(5)	122.5 (4)	S(6)-C(7)-C(8)	124.5 (4)

It is interesting to note that the nonbonded S· · ·S and C· · ·C distances of the four-atom ring of trans-**3** are 2.672 and 2.488 Å, respectively.

As mentioned above TLC revealed the presence of a third minor product (R_f 0.19–0.29). Although we did not succeed in purifying it to an analytical purity all of the spectral data point to the structure of 1,7-dimethyl-3,5-dimethylene-2,4,6,8,9-pentathiabicyclo[5.1.1]nonane (**4**). The mass spectrum showed molecular peak at *m/e* 266 and the number of the sulfur atoms present in the molecule was easily recognized from the pattern of isotopic peaks due to ^{34}S. The ^1H NMR spectrum showed two singlets at 2.08 and 5.84 ppm with the intensity ratio 3:2 which have been ascribed to the methyl and methylene protons, respectively. In ^{13}C NMR four signals appeared at 29 ($J_{^{13}C-^1H}$ = 137 Hz), 55.6, 126 ($J_{^{13}C-^1H}$ = 164 Hz), and 133.6 ppm attributed to the methyl, quaternary, methylene, and thiomethylene carbon, respectively.



4. M$^{+\cdot}$ 266 (6)

In summary, one may conclude that the reaction of dithioacetic acid with DCC results in the formation of trithioanhydride (**1**) which owing to its instability undergoes ready dimerization to give **2** and the mixture of *trans*-**3** and *cis*-**3**. The latter eliminates H_2S giving rise to **4**. Further experiments to stabilize the monomeric structure of aliphatic trithioanhydrides by steric hindrance are in progress.[9]

Acknowledgment. We thank Dr. D. J. H. Smith, the University of Leicester, for his interest in the present work.

Supplementary Material Available. A typical experimental procedure, Figure 2, showing the ^1H NMR spectrum of the crude reaction product, and the atomic coordinate and thermal parameter tables (5 pages). Ordering information is given on any current masthead page.

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(5) ^1H NMR spectra were measured with a Perkin-Elmer R-12B instrument and ^{13}C NMR spectra with a JEOL FX-60 F. T. NMR spectrometer, with deuteriochloroform as a solvent and tetramethylsilane as internal standard. Mass spectra were recorded with a GCMS-LKB-9000S instrument.

(6) For recent x-ray analysis of the 1,3-dithietane system and other references on dithietanes, see E. Block, E. R. Corey, R. E. Penn, T. L. Renkin, and P. F. Sherwin, *J. Am. Chem. Soc.*, **98**, 5717 (1976).

(7) Atomic coordinates and atomic thermal parameters will appear in Tables 3 and 4 following this article in the microfilm edition of this volume.

(8) This fact coincides well with our observation that *trans*-**3** is not configurationally stable and undergoes slow transformation into a mixture of *cis*- and *trans*-**3** on storage at room temperature or on heating. The mechanism of epimerization of dithietane **3** is currently under investigation.

(9) After completion of this work Kato et al.[10] reported the reaction of DCC with some para-substituted dithiobenzoic acids which gave relatively stable bis(thioaroyl) sulfides.

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Oxidation with Light and Electrochemistry. An Apparently Selective Radical Forming Reaction

Summary: Catalytic amounts of various quinones have been irradiated in the presence of a substrate and a graphite anode charged at the potential of the quinone–hydroquinone couple. The photochemical reaction yields hydroquinone (or quinhydrone) and an oxidized substrate. The hydroquinone is converted back to quinone electrochemically. With toluene and similar materials as substrates, the products are bibenzyls in clean high-yield reactions. With 2-propanol, the product is acetone.

Sir: Although photochemical oxidations have been known for a long time,[1] their preparative use has been limited since photochemical reactions in themselves do not involve any change in oxidation state. Thus, some sort of disproportionation (i.e., the benzophenone reactions[1]) must be involved, or an external oxidizing agent such as air, iodine, or more recently Cu(II)[2] must be used. Frequently these secondary oxidizing agents are not very specific. We have devised a method in which the oxidizing "agent" is a suitably charged graphite anode.[3]

The specific reactions involved are the photochemical reactions of quinones with alkylbenzenes to yield dehydrodimers (e.g., bibenzyl from toluene)[4] and the reaction of quinones with alcohols to yield carbonyl products.[5] Poor yields are reported in both cases. Since the quinone is regenerated electrochemically, it serves as a catalyst only and can be used in small amounts. There are two advantages in the system. First, the electrochemical potentials needed to regenerate quinone are quite low[6] and are therefore fairly specific. Second, the hydroquinone which is reported[7] to retard the photochemical reaction is rapidly removed.

In our system, reactions 1–4 appear to take place.[7] A similar system has been described for analytical work by Zolotova,