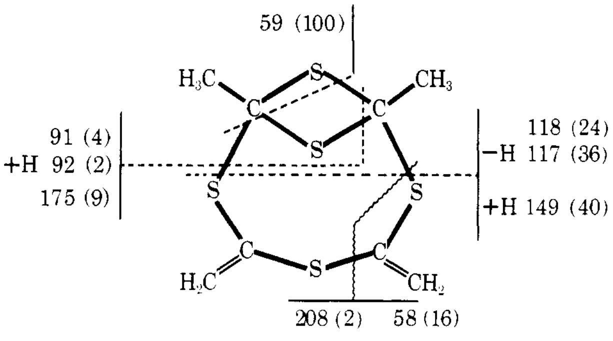
Table II. Bond Angles

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 ($J_{^{13}C-^{1}H}$ = 137 Hz), 55.6, 126 ($J_{^{13}C-^{1}H}$ = 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]

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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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(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,

Table I. Preparative Photoelectrochemical Oxidations [a]

Substrate	Product[b]	Oxidn time, h	Initial current, mA	Product isold, mmol	Current yield,[c] %
Toluene	Bibenzyl	20	35	3.5	90
p-Xylene	1,2-Di-*p*-xylylethane	24	76	10	60
Ethylbenzene	2,3-Diphenylbutane (meso and *RR*–*SS*)	20	17	2.9	~100
2-Propanol	Acetone	6	80	6.3	75[d]

[a] The yields based upon catalyst were from 300 to 1000%. [b] The hydrocarbon products were isolated in a pure form, and their properties agreed with literature values. [c] Current yield is calculated as product formed per coulomb of electricity passed (two electrons per mole of product). The starting material was present in excess. [d] Acetone was isolated as a 2,4-dinitrophenylhydrazone.

Shelepin, and Vasil'ev[8] with the same equations for 1, 2, and 3. No products were reported. The preparative data are summarized in Table I.

$$Q \xrightarrow{h\gamma} Q^* \qquad (1)$$

$$Q^* + 2RH \rightarrow 2R\cdot + QH_2 \qquad (2)$$

$$QH_2 - 2e - 2H^+ \rightarrow Q \qquad (3)$$

$$2R\cdot \rightarrow RR \qquad (4)$$

The cell used was essentially a 450-W Hanovia source enclosed in a Pyrex cooling sleeve placed in a tall glass cell containing a graphite felt[9] anode (75 cm^2) and a similar graphite cathode (22 cm^2 placed in a small sack made of Du Pont Nafion membrane).[10] A standard calomel reference electrode was placed close to the anode, and the potential was controlled at the anodic peak of the quinone (as deduced from a cyclic voltammogram; generally about +0.6 V with a PAR Model 170 electrochemical system).[11] Several quinones were investigated: anthraquinone, anthraquinone-2-sulfonic acid, and anthraquinone-2,6-disulfonic acid. The data in Table I were obtained using anthraquinone-2-sulfonic acid. The reaction mixture consisted of 800 mL of CH_3CN–H_2O (4:1), containing $LiClO_4$ (0.1 M) and 0.2–2 g of quinone. The cell was deoxygenated with N_2, and the reaction was carried out under N_2. About 20 mL of substrate was added. Yields are based upon the current observed to flow through the cell.

All of the reactions, 1–4, are known to occur under various conditions. However, the combined system as described in this paper offers at least one unique feature. The benzyl radicals formed from arylalkanes are produced in an environment containing *no* oxidizing agent strong enough to oxidize them to carbonium ions.[12] Thus, they dimerize, and the reaction appears to be without by-products. When the reaction is carried out in the presence of air or oxygen, the products are, as expected, benzoic acids. In the oxidation of 2-propanol, the initially formed ketyl radical $CH_3\dot{C}OHCH_3$ is apparently more easily oxidized than the benzyl radical and is converted to acetone, either electrochemically or by another molecule of quinone.

The reaction is being further explored.

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