

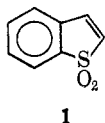
Photodimerization of Thianaphthene 1,1-Dioxide. Structure

DAVID N. HARPP AND CYRIL HEITNER¹*Department of Chemistry, McGill University, Montreal, Canada*

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Thianaphthene 1,1-dioxide (1) forms two isomeric cyclobutane dimers, 2 and 3, on uv irradiation. Reduction and Raney nickel desulfurization of 2 and 3 afforded products which allowed structural assignment of the dimers as *anti* head to head (2) and *anti* head to tail (3). The assignment of dimer 3 was confirmed by Raman and infrared spectroscopy.

The photodimerization of thianaphthene 1,1-dioxide (1) has been observed by Davies and James^{2a} and



Mustafa.^{2b} The structure and stereochemistry of the product(s),³ however, were not elucidated. We would like to report the isolation and structure elucidation of the two isomeric photodimers of thianaphthene 1,1-dioxide (1).

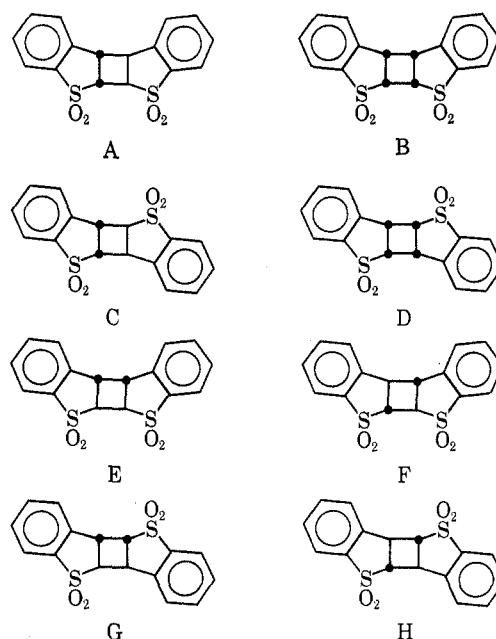
The photodimerization of indene⁴ and 1,1-dimethylindene,⁵ analogs of 1, have been studied. In both cases, photodimerization could be effected only in the presence of triplet sensitizers benzophenone ($E_T = 69$ kcal)⁴ and acetophenone ($E_T = 73.6$ kcal).⁵ In contrast, thianaphthene 1,1-dioxide (1) does not require the presence of a triplet sensitizer for photodimerization.

In a typical run, a benzene solution of 1 (4.0 g/l.), previously flushed with dry nitrogen, was irradiated with a type L 450-W Hanovia mercury vapor lamp (filtered by Pyrex) for 20 hr at room temperature. A white precipitate crystallized on the walls of the reaction flask. Examination of the solid as well as the residue from the benzene solution by tlc and glpc revealed that two photoproducts had formed, one being a major constituent of the insoluble material (2) and the other being a major constituent of the benzene solution (3). The total yield of the two photoproducts was 75% (21% of starting material was recovered). The ratio of compound 2 to compound 3 was 2.7 (73:27, glpc).

Elementary analysis and exact mass measurement of the molecular ion of both 2 (332.0192) and 3 (332.0179) agreed with the formula $C_{16}H_{12}S_2O_4$ (m/e , M^+ required 332.0177). This indicates the formation of two isomeric dimers. The ir⁶ and nmr spectra (AA'BB') for nonaromatic protons are in agreement with any one of the following structures (Chart I).

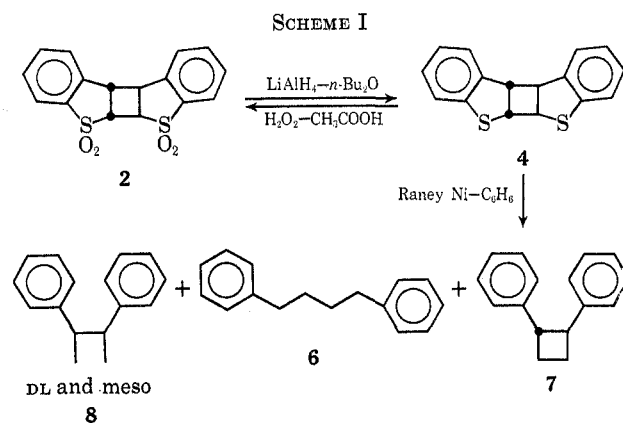
Structures E, F, G, and H, are highly strained and would be expected to epimerize readily on treatment with base.⁷ When 2 and 3 were refluxed with sodium

CHART I



methoxide in methanol, no change in the dimers was observed thus ruling out E-H as structures for 2 and 3.

Evidence for the structures of 2 and 3 has been obtained (Schemes I and II) by converting the sulfone to



the corresponding sulfide followed by Raney nickel desulfurization to various diphenylcyclobutane derivatives.⁸

Compounds 2 and 3 were reduced by $LiAlH_4$ in *n*-butyl ether to give sulfides 4 and 5 respectively. These compounds (4 and 5) were oxidized (35% H_2O_2 -HOAc) in over 90% yield to compounds 2 and 3, respec-

(8) A \rightarrow *trans*-1,2-diphenylcyclobutane; B \rightarrow *cis*-1,2-diphenylcyclobutane; C \rightarrow *trans*-1,3-diphenylcyclobutane; D \rightarrow *cis*-1,3-diphenylcyclobutane.

(1) NRCC Bursary holder 1968-1970.

(2) (a) W. Davies and F. C. James, *J. Chem. Soc.*, 314 (1955); (b) A. Mustafa, *Nature*, **175**, 992 (1955); A. Mustafa, *J. Amer. Chem. Soc.*, **78**, 6174 (1956).

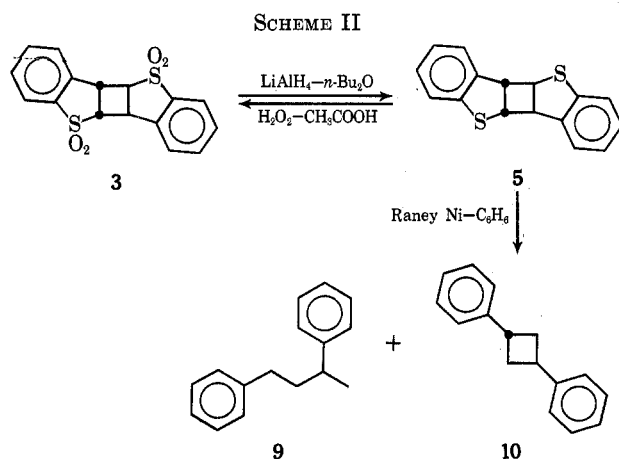
(3) Only one product was reported by Davies and James^{2a} and Mustafa.^{2b}

(4) (a) G. O. Schenck, W. Hartmann, S.-P. Mannsfeld, and C. H. Krauch, *Ber.*, **95**, 1642 (1962). (b) A. G. Anastassiou and G. W. Griffin, *J. Org. Chem.*, **33**, 3441 (1968).

(5) J. J. McCullough, *Can. J. Chem.*, **46**, 43 (1968).

(6) The infrared spectra of 2 and 3 showed marked differences in the 850- and 450- cm^{-1} regions.

(7) E. J. Corey, J. D. Bass, R. LeMahier, and R. B. Mitra, *J. Amer. Chem. Soc.*, **86**, 5570 (1964).



tively (ir and mixture melting point were identical with those of the original photodimers). Hence, no rearrangement occurred during reduction of the photodimers with LiAlH_4 .

Compound 4 was treated with Raney Ni W2 and afforded a mixture of *DL*- and *meso*-2,3-diphenylbutane⁹ (8) (27%), 1,4-diphenylbutane (6) (11%), and *trans*-1,2-diphenylcyclobutane (7) (62%). The identity of this mixture was verified with three different glpc columns (see Experimental Section). In addition, *trans*-1,2-diphenylcyclobutane (7) was collected and the nmr spectrum was found to be identical with that of an authentic sample.¹⁴ In order to exclude the possibility of isomerization of *cis*- to *trans*-1,2-diphenylcyclobutane during desulfurization, the *cis* isomer¹⁴ was refluxed in benzene under the same conditions as that of compound 4. Only a small amount of 1,4-diphenylbutane (6) was produced [no *DL*- or *meso*-2,3-diphenylbutane (8)] and no isomerization to *trans*-1,2-diphenylcyclobutane (7) was observed. Further, it was shown that no interconversion between *DL* and *meso* 8 occurred under the conditions of the desulfurization. Based upon the above results, we assign structure A to compound 2 (head to head, *anti*).

Similarly, compound 5 when treated with Raney Ni W2 gave 1,3-diphenylbutane (9) (38%) and *trans*-1,3-diphenylcyclobutane (10) (62%). *trans*-1,3-diphenyl-

(9) The formation of *meso* 8 was unexpected. If the photodimer 2 had head to head, *syn* stereochemistry (structure B), then not only *meso* 8 but *cis*-1,2-diphenylcyclobutane would be expected from Raney nickel treatment. Since there is ample evidence¹⁰ that racemization or *cis-trans* interconversions of centers α to sulfur are not observed, *DL* and *meso* 8 must arise from fragmentation processes on the catalyst surface.¹¹ At least two explanations for *DL* and *meso* 8 formation are possible and have literature precedent. Simultaneous removal of two sulfur atoms from 4 after α C-C bond reduction would give a 1,4 diradical¹² which would give 2,3-diphenyl-1-butene on disproportionation.^{10a,13} Reduction of this molecule would provide *DL* and *meso* 8. Also, cleavage of the C-C bond α to each sulfur atom would give a different 1,4 diradical which on disproportionation,^{10a,13} desulfurization, and reduction would give *DL* and *meso* 8.

(10) (a) S. F. Birch and R. A. Dean, *Ann.*, **585**, 234 (1954); (b) S. F. Birch, R. A. Dean and E. V. Whitehead, *J. Org. Chem.*, **19**, 1449 (1954); (c) A. F. Hussey, H. P. Liao, and R. H. Baker, *J. Amer. Chem. Soc.*, **75**, 4727 (1953); (d) G. Stork, E. E. van Tamselen, L. J. Fredman and A. W. Burgstahler, *ibid.*, **75**, 384 (1953); (e) J. F. Ford, R. C. P. Kethly, and V. O. Young, *Tetrahedron*, **4**, 325 (1958); (f) for an authoritative review on Raney nickel desulfurizations, see W. A. Bonner and R. A. Grimm, in "Organic Sulfur Compounds," Vol. II, N. Kharasch and C. Y. Meyers, Ed., Pergamon Press, N. Y. and London, pp 35-71, 1966, pp 35-71.

(11) H. R. Snyder and G. W. Cannon, *J. Amer. Chem. Soc.*, **66**, 155 (1944).

(12) (a) W. Baker, A. S. El-Nawawy, and W. D. Ollis, *J. Chem. Soc.*, 3163 (1952); (b) C. Djerassi, M. Shamma, and T. Y. Kan, *J. Amer. Chem. Soc.*, **80**, 4723 (1958).

(13) A. W. Weitkamp, *ibid.*, **81**, 3434 (1959).

(14) R. M. Dodson and A. G. Zielske, *J. Org. Chem.*, **32**, 23 (1967).

cyclobutane (10) was isolated by preparative glpc. The nmr spectrum¹⁵ of 10 (aromatic, τ 2.82, 10 H, s; methine, τ 6.56, 2 H, p, $J = 8.0$ Hz; methylene, τ 7.60, 4 H, t, $J = 8.0$ Hz) in CDCl_3 is indicative of *trans* stereochemistry. Changing the solvents to acetone- d_6 or benzene- d_6 did not change the multiplicity or symmetry of the nmr signals. In the *trans* isomer the methylene protons would be symmetrically equivalent hence, a triplet methylene for this *trans*-1,3-disubstituted cyclobutane would be expected. The methylene protons in the *cis* isomer are not equivalent; thus a more complex pattern would likely occur.

Similar arguments have been used in assigning the stereochemistry of *trans*- and *cis*-1,3-dihalocyclobutane,¹⁶ *trans*- and *cis*-1,3-dihalo-1,3-dimethylcyclobutane,^{17,18} *trans*- and *cis*-2,4-diphenylthietane,¹⁹ *trans*- and *cis*-2,4-dimethylthietane,²⁰ and *trans*-1,3-dimethylcyclobutane.¹⁷

Further evidence as to the structure of 5 was obtained by Raman spectroscopy. It has been established that molecules possessing a symmetry center give fewer coincident vibrational bands (Raman *vs.* infrared spectrum) than do noncentrosymmetric molecules (C_1 symmetry).²¹ This concept has been utilized to define a number of centrosymmetric photodimers.²¹

Raman and infrared comparisons were made for compounds 4 and 5 scanning from 250 to 3200 cm^{-1} (Tables I and II). Transitions within 10 cm^{-1} for these comparisons were considered coincidences²² (Table II). The observation of 14 fewer coincident bands (25-39, Table II) for 5 *vs.* 4 strongly indicate that 5 is centrosymmetric.

Based on the above considerations, we assign structure C to compound 2.

Experimental Section

Materials and apparatus:—Benzene (Fisher Certified reagent) was used as photodimerization solvent. Melting points were taken on a Gallenkamp apparatus and are not corrected. The glpc data were obtained on a Hewlett-Packard F & M series 5670 research chromatograph using three columns (A, B, C). Column A was a $\frac{1}{8}$ in. \times 6 ft 20% Apiezon L on Chromosorb W, AW, DMCS (acid-washed, dimethyldichlorosilane treated); column B was a $\frac{1}{8}$ in. \times 6 ft 10% UC-W98 (silicone gum rubber) on Diatoport S; and column C was a $\frac{1}{8}$ in. \times 6 ft 10% LAC-728 on Chromosorb W, AW, DMCS treated. Infrared spectra were measured on Perkin-Elmer 225 spectrometer, nmr spectra were obtained from Varian Associates A-60 and T-60 spectrometers, mass spectra were recorded on an AEI MS 902 spectrometer, and Raman spectra were recorded as solid samples (several milligrams) on a Jarrel-Ash 25-300 Raman spectrometer.

Thianaphthene 1,1-Dioxide (1).—Sulfone 1 was obtained by the oxidation of thianaphthene with H_2O_2 in glacial acetic acid according to the method of Davies and James.² This sulfone was further purified by recrystallization from ethanol-activated charcoal (mp 142.5-143; lit.² mp 142°) yield 76%.

The Photodimerization of Thianaphthene 1,1-Dioxide.—Two liters of a benzene solution of 1 (8.0 g, 2.4×10^{-2} M), previously

(15) Chemicals shifts for nmr given in parts per million with tetramethylsilane as τ 10; m = multiplet; s = singlet; t = triplet; p = pentuplet.

(16) K. B. Wiberg and G. M. Lampman, *J. Amer. Chem. Soc.*, **88**, 4429 (1966).

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(18) K. Griesbaum, W. Naegle, and G. G. Wanless, *J. Amer. Chem. Soc.*, **87**, 3151 (1965).

(19) R. M. Dodson and G. Klose, *Chem. Ind. (London)*, 540 (1963).

(20) B. M. Trost, W. L. Sohinski, and I. B. Mantz, *J. Amer. Chem. Soc.*, **91**, 4320 (1969).

(21) H. Ziffer and I. W. Levin, *J. Org. Chem.*, **34**, 4056 (1969).

(22) This is 5 cm^{-1} outside the range utilized by previous workers (ref 21) and should easily allow for crystal perturbations.

TABLE I
COMPARISON OF THE RAMAN DISPLACEMENTS
AND INFRARED FREQUENCIES FOR THE
BENZOTHIOPHENE 1,1-DIOXIDE PHOTODIMERS^a

5			4		
Head to tail		Raman, cm ⁻¹	Head to head		Raman, cm ⁻¹
Infrared, cm ⁻¹			Infrared, cm ⁻¹		
252	1100	252	979	232	
292	1122	1115	252 ^a	992	252 992
		330 1130	265	1020	
363	1148		275 ^a	1025 ^a	1028
	1150	410 1155	282	1055 ^a	288
430 ^a	1160			1060	340 1060
432	1181		368	1070	370 1070
445	1190	440 1190	415		415 1035
481	1205	475			430 1048
488		1230	448	1152	450 1155
528		528 1248	470	1188 ^a	478 1188
605	1260	605	495	1190	495 1190
692		690 1270	510	1198 ^a	1198
711	1282	710 1280	525	1240	520 1240
745		740 1310	535	1248	540
750	1440		575	1262	1260
768	1458	760 1460	620	1275	621 1282
	1568	785 1565	694	1360	694
	1580	841 1580	718	1320	720 1320
863		860 2925	728	1400	
871	2950	2950	745	1420 ^a	743
902	2989	2980	753	1460	753
	3010	928 3010	770 ^a	1462 ^a	770
938		942 3020	800	1570	1570
960	3050	3050	833	1579 ^a	832
971	3060	970	855	1582	1582
990		990 3130	862	2932	2930
1022		1020 3160		2960 ^a	2955
1055		1055	904	2980	904 2975
			935	3000	930
			970	3040	3038
				3060	3060

^a sh denotes shoulder.

TABLE II
COMPARISON OF THE RAMAN AND INFRARED
FREQUENCY COINCIDENCES^a

Head-to-tail photodimer			Head-to-head photodimer				
Compd	ir	R	Compd	ir	R	C	
5	42	39	25 ^b	4	60	42	39 ^b
	42	39	19 ^c		60	42	29 ^c

^a ir, R, and C denote infrared peaks, Raman peaks, and coincidences respectively. ^b Coincidences within 10 cm⁻¹. ^c Coincidences within 5 cm⁻¹.

purged with dry nitrogen for 45 min, was irradiated with a type L 450-W Hanovia mercury vapor lamp in the usual quartz water-cooled immersion apparatus with Pyrex filter for 20 hr at room temperature. A white precipitate (3.0 g) crystallized on the walls of the reaction flask; in addition, 4.7 g of material was recovered from the benzene solution. Examination, by tlc (silica gel eluted with CHCl₃:acetone, 85:15) and glpc on column A, of the precipitate and the benzene solution revealed the presence of two compounds, compounds 2 being a major constituent of the insoluble material and compound 3 being a major constituent of the benzene solution. In a typical run the residue from the benzene solution was combined with the precipitate and the total mixture analyzed with glpc on column A. The ratio of 2 to 3 was found to be 73:27. The total yield of the dimers was 6.0 g (75% yield). Recrystallization of the fraction precipitating from benzene with DMSO gave 2.6 g of 2 (mp 329–330° dec): ir 1320 cm⁻¹ and 1160 cm⁻¹ (SO₂ stretching); nmr τ 1.83–2.15 (8 H m), 5.20–5.80 (4 H AA'BB').

Anal. Calcd for C₁₆H₈S₂O₄: C, 57.83; H, 3.62; S, 19.27; exact mass of molecular ion, 332.0177. Found: C, 57.80; H, 3.70; S, 19.18; exact mass of molecular ion, 332.0192.

The residue was obtained by evaporation of the benzene and was extracted with boiling water until 1 no longer crystallized from the water (1.7 g, 21%, of 1 was recovered). The resulting mixture was recrystallized twice from DMSO (crystallizing mixture allowed to stand overnight), resulting in 1.1 g of 3 (mp 334–335° dec): ir 1320 and 1160 cm⁻¹ (SO₂ stretching); nmr τ 1.85–2.15 (8 H m), 4.90–5.80 (4 H AA'BB').

Anal. Calcd for C₁₆H₈S₂O₄: C, 57.83; H, 3.62; S, 19.27; exact mass measurement of molecular ion, 332.0177. Found: C, 58.22; H, 3.92; S, 19.06; exact mass measurement of molecular ion, 332.0179.

Reduction of Photodimers 2 and 3.—Compound 2 (4.0 g, 0.012 mol) was refluxed with LiAlH₄ (2.8 g, 0.073 mol) in 200 ml of *n*-butyl ether (previously dried over sodium) for 5 hr. The excess LiAlH₄ was decomposed by carefully adding 3 ml of water, 3 ml of 15% NaOH, and 6 ml of water in succession. After filtration and evaporation of the solvent, the crude product was chromatographed over 50 g of neutral alumina with petroleum ether (bp 30–60°) and hexane to give 2.1 g of white crystals of 4, mp 217–218° (66% yield). Infrared analysis showed the absence of the two SO₂ stretching absorptions.

Anal. Calcd for C₁₆H₈S₂: C, 71.64; H, 4.47; S, 23.84. Found: C, 71.55; H, 4.61; S, 23.89.

Compound 3 was treated similarly except that the product 5 was purified by recrystallization from CHCl₃–ethanol; 1.8 g (56%) mp 180–180.5° was obtained. Infrared analysis showed the absence of the SO₂ stretching bands.

Anal. Calcd for C₁₆H₈S₂: C, 71.64; H, 4.47; S, 23.84. Found: C, 71.69; H, 4.16; S, 23.89.

Oxidation of Bis Sulfides 4 and 5.—After compound 4 (80 mg, 0.03 mmol) was dissolved in 10 ml of glacial acetic acid, 10 ml of 35% H₂O₂ was added and the resulting mixture heated on a steam bath for 1 hr. The solution was cooled and poured into 50 ml of cold water. The suspension was filtered and dried under vacuum. Compound 2 (75 mg, 73%, mp 329–330° dec) resulted. A mixture melting point with photoproduct 2 was not depressed. In addition, the ir spectrum was identical with that of photoproduct 2.

Similarly, 100 mg of 5 was oxidized to 80 mg (63% yield) of 3 (mp 334–335° dec). A mixture melting point with photoproduct 3 was not depressed and the ir spectrum was identical with that of photoproduct 3. The mixture melting point of 2 and 3 was 285–290°.

meso- and DL-2,3-Diphenylbutane.—These compounds were prepared from 37 g (0.2 mol) of 1-phenylethyl bromide according to the method of Conant and Blatt.²³ Recrystallization of the mixture in ethanol gave 10 g of *meso*-2,3-diphenylbutane (mp 126–128°; lit.²³ mp 124–126°; 25% yield). The mother liquor was evaporated and the residue distilled under vacuum to give 5 g of *DL*-2,3-diphenylbutane: bp 100–102° (1 mm); lit.²⁴ bp 103–104° (1 mm); *n*_D²⁰ = 1.5552; lit.²⁴ *n*_D²⁰ 1.55516; 13% yield.

1,2-Dibenzoylthane.—1,2-Dibenzoylthane was prepared in 95% yield by the method of Schaefer.²⁵

Bis(ethylene dithioacetal) of Dibenzoylthane.—This material was prepared by mixing 2.6 g (0.011 mol) of dibenzoylthane with 12 ml of ethylenedithiol and 2 ml of boron trifluoride etherate at room temperature for 1 hr. After recrystallization from dioxane, 3.6 g (85% yield) of white crystals, mp 197–198°, resulted.

Anal. Calcd for C₂₀H₂₂S₄: C, 61.28; H, 5.64. Found: C, 61.45; H, 5.65.

1,4-Diphenylbutane (6).—The above bis(ethylene dithioacetal) (3 g, 0.0079 mol) was refluxed in ethanol with about 3 g of Raney nickel W2 for 15 hr, affording 1.5 g (89% yield) of 1,4-diphenylbutane (mp 48–49°, lit.¹⁴ mp 50.5–51.5°).

1,2-Diphenylcyclobutene.—This compound was prepared in 40% yield as previously reported.¹⁴

cis-1,2-Diphenylcyclobutene.—This material was prepared by hydrogenation of 1,2-diphenylcyclobutene over a Pt catalyst in 95% yield.¹⁴ nmr¹⁵ (CDCl₃) τ 3.05 (10 H s), 5.88–6.20 (2 H m), and 7.45–7.55 (4 H m).

trans-1,2-Diphenylcyclobutene (7).—The *cis* isomer (0.2 g, 0.96 mmol) was mixed with 0.2 g of potassium *t*-butoxide in anhydrous DMSO at 70° for 22 hr. The solution was added to water, extracted with benzene, and chromatographed over silica gel with petroleum ether. The *trans* isomer (7) (0.18 g,

(23) J. B. Conant and A. H. Blatt, *J. Amer. Chem. Soc.*, **50**, 555 (1928).

(24) "Dictionary of Organic Compounds," Vol. III Eyre & Spottiswoode Ltd., London, 1965, p 1274.

(25) J. P. Schaefer, *J. Org. Chem.*, **25**, 2027 (1960).

90% yield) was isolated: n_{D}^{20} (CDCl₃) τ 2.81 (10 H s), 6.27–6.61 (2 H m) and 7.52–8.05 (4 H m).

Desulfurization of Compound 4.—Compound 4 (1.7 g, 0.0063 mol) was refluxed with about 4 g of Raney Ni W2 slurry in benzene for 4 hr. After filtration and evaporation of the benzene, 1.1 g of an oil was isolated. Analysis by glpc on columns A, B and C, using internal standards, showed that the mixture contained *trans*-1,2-diphenylcyclobutane (7), *DL*- and *meso*-2,3-diphenylbutane, and 1,4-diphenylbutane (6) in 62%, 27%, and 11% yield respectively. Using column C, *trans*-1,2-diphenylcyclobutane (7) was collected and the nmr spectrum obtained was identical with that of authentic material.

1,3-Diphenyl-3-butanol.—This compound was prepared by adding 12 g (0.10 mol) of acetophenone to an ether solution of Grignard reagent made from 27.7 g (0.15 mol) of β -phenylthyl bromide and 5 g of magnesium. The reaction mixture was refluxed for 2 hr and worked up in the usual way. The crude alcohol was distilled at 136° (0.25 mm), giving on cooling an amorphous solid (12 g). The infrared spectrum showed the presence of an OH group and the absence of a carbonyl and bromide groups. This material was used without further purification.

1,3-Diphenylbutane (9).—1,3-Diphenyl-3-butanol (7.6 g, 0.034 mol) in 150 ml of glacial acetic acid was mixed with 0.1 g of 10% Pd–C at 45 psi of hydrogen for 15 hr. After filtration and evaporation of the acetic acid the mixture was chromatographed over silica gel with petroleum ether–CCl₄ (1:1) graduated slowly to CCl₄, affording 1,3-diphenylbutane (9) (3.5 g, 50% yield). The material was found to be glpc pure (column A, B, and C): n_{D}^{20} 1.5520; lit.²⁴ n_{D}^{20} 1.5525; n_{D}^{15} τ 2.80–2.91 (10 H, m), 7.18–7.69 (3 H, m), 7.98–8.40 (2 H, m), and 8.80 (3 H, d).

Desulfurization of Compound 5.—Compound 5 (1.0 g) was refluxed with ~3 g of Raney nickel W2 in benzene for 15 hr.

Filtration and evaporation gave 0.5 g (65%) of an oil and 0.3 g of 5. Analysis by glpc showed two compounds were present. The first fraction was identified as 1,3-diphenylbutane by comparing the retention times with an authentic sample on column A, B, and C. About 50 mg of the second fraction was collected from glpc column A and was identified as *trans*-1,3-diphenylcyclobutane: mass spectra (molecular ion) m/e 208; nmr τ 2.82 (10 H, s), 6.56 (2 H, p, $J = 8.0$ Hz), 7.60 (4 H, t, $J = 8.0$ Hz).

Anal. Calcd for C₁₆H₁₆: C, 92.26; H, 7.74; exact mass measurement of molecular ion, 208.1245. Found: C, 92.14; H, 7.55; exact mass measurement of molecular ion, 208.1252.

Attempted Epimerization of Dimers 2 and 3.—Compounds 2 and 3 (150 mg) were each refluxed 12 hr with 1.2 g of sodium methoxide in 25 ml of methanol. Dimers 2 and 3 were recovered unchanged (glpc, column A; melting point and mixture melting point).

Registry No.—1, 825-44-5; 2, 25558-18-3; 3, 25558-19-4; 4, 25558-20-7; 5, 25558-21-8; 7, 7694-31-7; 9 (*trans*), 25558-23-0; bis(ethylene dithioketal) of dibenzoylthane, 25557-76-0.

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The Chemistry of Small-Ring Sulfur Compounds. Thietanes and 1,2-Dithiolanes¹

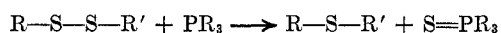
DAVID N. HARPP AND JOHN G. GLEASON²

Department of Chemistry, McGill University, Montreal, Canada

Received January 19, 1970

A variety of 1,2-dithiolanes undergo facile desulfurization with tris(diethylamino)phosphine (2) to give thietanes in good yield. By this method, the tetrahydropyranyl ester of α -lipoic acid afforded (after hydrolysis) thietane-2-valeric acid (3). 3H-1,2-Benzodithiole (17) did not give benzo[b]thiete (18) on desulfurization, but rather formed the dimeric sulfide (19). The tricyclic steroid 22 underwent rearrangement on desulfurization to afford the steroidal phosphine 25. The use of iodine–triethylamine in a new, modified procedure for the oxidation of propane-1,3-dithiols was found to be an excellent method for the preparation of 1,2-dithiolanes in high yield.

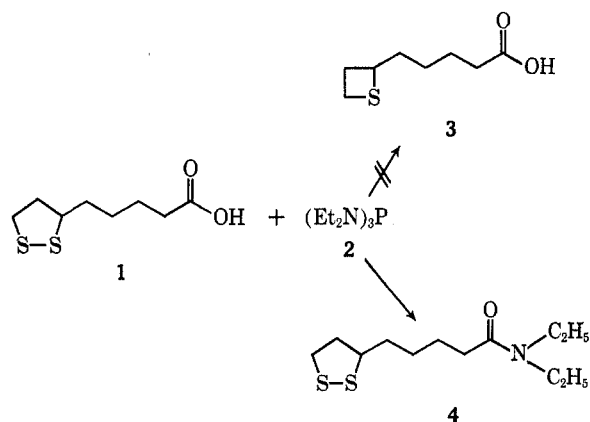
As part of our study on the selective desulfurization³ of disulfides and related compounds, it occurred to us



that the use of aminophosphines for the desulfurization of 5-membered disulfide rings (dithiolanes) could provide a new synthetic approach to thietanes.⁴ Accordingly, the desulfurization of several dithiolanes was attempted and the results are summarized in Table I.

While the dithiolane, α -lipoic acid (1), a coenzyme in the biological oxidation of pyruvic acid, is readily available from natural sources, the corresponding thietane derivative, thietane-2-valeric acid (3), has only recently been prepared *via* a multistep synthesis.⁵ However, attempts to obtain this derivative by the desul-

furization of α -lipoic acid were unsuccessful. When α -lipoic acid (1) was treated with tris(diethylamino)phosphine (2), no thietane derivative (3) was obtained. The main product, isolated in 78% yield, was the di-



(1) Organic Sulfur Chemistry. III. For part II, see D. N. Harpp and J. G. Gleason, *Tetrahedron Lett.*, 1447 (1969).

(2) Holder of an NRCC Studentship 1968–1969.

(3) D. N. Harpp, J. G. Gleason, and J. P. Snyder, *J. Amer. Chem. Soc.*, **90**, 4181 (1968).

(4) Although other methods for the synthesis of thietanes are available, the formation of polymer in these reactions is often competitive; see M. Sander, *Chem. Rev.*, **66**, 341 (1966); S. Ogawa, M. Morita, K. Donome, and K. Fujisawa, Japanese Patent 23937 (1967) [*Chem. Abstr.*, **69**, 35919 (1968)].

(5) (a) M. W. Bullock, U. S. Patent 2,788,355 (1957); *Chem. Abstr.*, **51**, 13909 (1957). (b) Sh. Yurugi, H. Yonemoto, and T. Fushimi, *Yakugaku Zasshi*, **80**, 169b (1960); *Chem. Abstr.*, **55**, 12288 (1961). (c) Sh. Yurugi and T. Fushimi, Japanese Patent 6532 (1962); *Chem. Abstr.*, **56**, 13916 (1963).