is formed from its bicylic precursor and the *trans* double bond is introduced stereospecifically.[2]

Treatment of 8β-benzoyloxy-9β-methyl-Δ^4-3-octalone (I)[3] with alkaline hydrogen peroxide yielded 8β-benzoyloxy-9β-methyl-4,10ξ-epoxy-3-decalone (IV), m.p. 158–158.5° (found: C, 71.98; H, 6.66). Addition of hydrazine hydrate to a methanolic solution of IV containing a trace of acetic acid converted[4] IV to 8β-benzoyloxy-9β-methyl-Δ^3-10ξ-octalol (V), m.p. 116–117° (found: C, 75.18; H, 7.74), and subsequent hydrogenation gave 8β-benzoyloxy-9β-methyl-10ξ-decalol (VI), m.p. 119-120° (found: C, 75.31; H, 8.15). Without isolation of intermediate compounds VI was converted to III by successively (a) saponifying, (b) treating the crude decalindiol with one equivalent of methanesulfonyl chloride in pyridine, and (c) warming the crude monomesylate II with a solution of potassium *t*-butoxide in *t*-butanol.[5] The product was distilled at 0.1 mm. from an oil bath at 100° and yielded a colorless liquid which solidified on cooling, m.p. 18–21°. Analysis by gas chromatography[6] showed that a single sharp peak accounted for 97% of the total area corresponding to effluent. The preparation of an oxime, m.p. 132–134° (found: C, 72.92; H, 10.52; N, 7.80), confirmed the presence of the ketonic function observed in the infrared spectrum, $\lambda_{\max}^{\mathrm{CCl_4}}$ 5.86 μ. The formation of an unsaturated ten-membered ring was demonstrated by hydrogenation with platinum oxide in ethanol–acetic acid: oximation of the product yielded an oxime, m.p. 70–75°, in 25% yield, which, after several crystallizations from hexane, proved to be identical with the oxime prepared from authentic 6-methylcyclodecanone,[7] m.p. 82–83° (found: C, 72.10; H, 11.42). The NMR spectrum[8] of the unsaturated ketone confirmed the presence of the trisubstituted double bond —CH═CCH$_3$— (bands with an area ratio of *ca.* 3:1 centered at 8.31 and 5.05 τ, respectively), the *trans* nature of which was evident from the photodesmotic transition[9] observed in the ultraviolet spectrum[10]; in 2,2,3,3-tetrafluoropropanol,[11] $\lambda_{\max}$ 227 mμ (ϵ 2750) and in methanol, $\lambda_{\max}$ 221 mμ (ϵ 3050).

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[2] For a review of fragmentation reactions see C. A. Grob, *I.U.P.A.C. Kékulé Symposium*, Butterworths, London, 1959, p. 114. The fragmentation of 1,3-diol monotosylates is described by R. B. Clayton, H. B. Henbest, and M. Smith, *J. Chem. Soc.*, 1982 (1957), and implies a stereospecific relation of product to reactant. The observed formation of III (*trans* double bond) implies the stereochemistry of I as drawn, in agreement with that reasonably assumed on the basis of reduction of the corresponding 3,8-dione with lithium aluminum hydride and sodium borohydride. See ref. 3 and C. B. C. Boyce and J. S. Whitehurst, *J. Chem. Soc.*, 2680 (1960). It is interesting to consider the possibility that fragmentation is of significance in the biogenesis of medium-sized ring sesquiterpenes. At least, this is an attractive speculation to add to two others which are widely held: that medium-sized ring sesquiterpenes (1) arise by direct cyclization of a farnesol-type precursor, and (2) are of significance in general sesquiterpene biogenesis. See L. Ruzicka, *Proc. Chem. Soc.*, 341 (1959) and *Experientia*, **9**, 357 (1953); J. B. Hendrickson, *Tetrahedron*, **7**, 82 (1959); D. H. R. Barton and P. de Mayo, *Quart. Rev.*, **11**, 189 (1957).

[3] F. Sondheimer and D. Elad, *J. Am. Chem. Soc.*, **79**, 5542 (1957).

[4] This is a further example of a new synthetic method described by P. S. Wharton and D. H. Bohlen, *J. Org. Chem.*, **26**, 3615 (1961).

[5] The fragmentation of II to III could also be effected under solvolytic conditions in aqueous pyridine containing acetic acid.

[6] A four-foot column of 0.5% polyethylene glycol (average m. wt. 4000) on 60–80 mesh glass beads was used in conjunction with an ionization detector.

[7] V. Prelog and W. Küng, *Helv. Chim. Acta*, **39**, 1394 (1956).

[8] The spectrum of a solution *ca.* 10% in carbon tetrachloride containing tetramethylsilane was recorded on a Varian 60 mc. spectrometer.

[9] E. M. Kosower, W. D. Closson, H. L. Goering, and J. C. Gross, *J. Am. Chem. Soc.*, **83**, 2013 (1961).

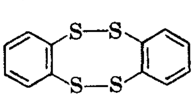
[10] The ultraviolet spectra were recorded on a Cary spectrophotometer, Model 14M, using 1 mm. cells.

[11] We are grateful to Dr. Kosower for supplying this spectroscopic-grade reagent.

Organic Disulfides and Related Substances. V. The Eight-Membered Ring System Bis(*o*-phenylene) Tetrasulfide[1,2]

Sir:

Bis(*o*-phenylene) tetrasulfide (I) is of interest for several reasons: (a) Two forms are possible,



I

a rigid *anti* form ($\mathrm{I_A}$) with the benzene rings on opposite sides of the plane of the sulfur atoms and a *syn* form ($\mathrm{I_{s1}}$) with the rings on the same side; $\mathrm{I_{s1}}$ may exist in a conformation ($\mathrm{I_{s2}}$) with mutually perpendicular benzene rings. The stereoisomerism of I is interesting *per se*, but particularly in its probable connection with orbital dispositions about the sulfur atoms. (b) Both the isosterism of sulfur with carbon-carbon double bonds and the electron swarm about the sulfur atoms imply interesting properties. (c) Ring-ring interactions are possible in $\mathrm{I_{s1}}$.

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[1] Dibenzo[c,g][1,2,5,6]tetrathiocin.

[2] Research supported by the Office of Ordnance Research, U. S. Army. Taken mainly from the Ph.D. dissertation of W.D.S., Vanderbilt University, 1960. Paper IV, L. Field, T. C. Owen, R. R. Crenshaw, and A. W. Bryan, *J. Am. Chem. Soc.*, *in press*.

Iodine oxidation of *o*-benzenedithiol reportedly yields a disulfide "$C_6H_4S_2$,"[3] but the product "was insoluble in ordinary organic solvents" and evidently was polymeric. At high dilution, we have obtained I and have established its identity by molecular weights (cryoscopic, ebullioscopic, x-ray), analysis, and absence of thiol.

o-Benzenedithiol[4] (12.50 g.) in 2.5 l. of benzene was added (68 hr.) with stirring under nitrogen to iodine (24.00 g.) in benzene (7.5 l.)-water (1 l.). Evaporation[5] of the mixture to 3 l. gave crop A (2.85 g., largely insoluble in molten camphor).

Concentration of the washed (aqueous bisulfite, water) and dried filtrate to 600 ml. gave 2.10 g. (17%) of crop B. Molecular weights of B were concentration-dependent; extrapolation to zero concentration gave 288 (Rast, camphor)[6] and 340 (ebullioscopic,[7] carbon disulfide); calcd., 280.4. When heated for 10 min. at 180° or for 12 hr. near 146°, I became insoluble in camphor; in contrast, it had a molecular weight (Rast) of 313–351 after 1–12 hr. at 120° and of 311 after irradiation for 1 hr. with ultraviolet light. The possibility of a rather specific temperature for polymerization seems unlikely, since differential thermal analysis[8] showed endotherms only at *ca.* 216° (probably the m.p.) and at 380°. Crop B when recrystallized from benzene (73%), carbon disulfide (47%), and chloroform (68%) gave I as small lemon yellow prisms of ill-defined m.p. (immersion at 145° and heating at 6°/min. gave m.p. *ca.* 215–230°). (*Anal.* Calcd. for $C_{12}H_8S_4$: C, 51.39; H, 2.88; S, 45.74. Found: C, 51.58; H, 3.05; S, 45.90.)

Evaporation of the filtrate from B to 75 ml. gave 1.21 g. of crop C, mol. wt. 513 (Rast). Molecular weights of recrystallized A, B, and C by x-ray diffraction were 280.1, assuming two molecules per unit cell of 586.4 Å^3.

Another oxidation gave crop B (7% yield, m.p. *ca.* 210–218°), mol. wt. 281.5 (x-ray); stability at *ca.* 25° for 21 months is evidenced by absence of apparent change in the x-ray pattern. Ebullioscopic molecular weights were 297 (chloroform, also carbon disulfide), 342 (benzene); 207 (benzene),[9] 192 (chloroform);[9] the Rast mol. wt. was 323. No infrared absorption characteristic of a thiol was seen. Feigl's test[10] was negative in dioxane, although 2-mercaptobenzothiazole gave a strong test at less than 1/300 the concentration. After 16 hr. in refluxing benzene, the molecular weight was 700, showing extensive polymerization.

All x-ray patterns are believed to represent only one substance. I showed no damage during x-ray studies, which are being continued.

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[3] P. C. Guha and M. N. Chakladar, *Quart. J. Ind. Chem. Soc.*, **2,** 318 (1925).

[4] Prepared essentially according to W. R. H. Hurtley and S. Smiles, *J. Chem. Soc.*, 1821 (1926).

[5] All evaporations effected below 25°.

[6] In high concentration, I polymerized readily. As the last crystal melted, solid began appearing and did not melt at 40° higher.

[7] Micro apparatus developed and kindly loaned by Prof. M. T. Bush.

[8] Kindly performed by W. R. Adams, Redstone Division, Thiokol Chemical Corp.

[9] Clark Microanalytical Laboratory, Urbana, Ill.

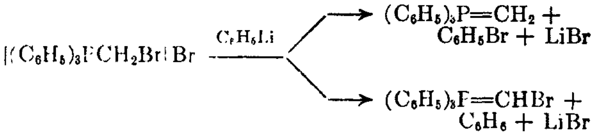
[10] F. Feigl, *Spot Tests. Vol. II. Organic Applications,* Elsevier Publishing Co., New York, 1954, p. 164.

The Action of Phenyllithium on Bromomethyl- and Iodomethyltriphenylphosphonium Halides[1]

Sir:

All known cases of triphenylphosphinealkylidene formation using organometallic reagents involve proton abstraction from the $[(C_6H_5)_3P{-}\overset{|}{\underset{|}{C}}{-}H]X$ system.[2] Such behavior was observed by us also in the case of chloromethyltriphenylphosphonium bromide, only triphenylphosphinechloromethylene being formed when the phosphonium salt was treated with phenyllithium.[3]

We have investigated the reaction of bromomethyltriphenylphosphonium bromide[4] and iodomethyltriphenylphosphonium iodide[5] with phenyllithium in ether and subsequent Wittig reactions of the triphenylphosphinealkylidenes formed. In both cases a mixture of triphenylphosphinemethylene and the respective triphenylphosphinehalomethylene was formed. Thus the action of one molar equivalent of ethereal phenyllithium on bromomethyltriphenylphosphonium bromide gave an orange solution to which cyclohexanone was added subsequently. The usual procedure[2] for carrying out such Wittig reactions was followed,



$$[(C_6H_5)_3PCH_2Br]Br \xrightarrow{C_6H_5Li} \begin{cases} (C_6H_5)_3P{=}CH_2 + C_6H_5Br + LiBr \\ (C_6H_5)_3P{=}CHBr + C_6H_6 + LiBr \end{cases}$$

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[1] Studies in Phosphinemethylene Chemistry, Part V. For Part IV see D. Seyferth and K. A. Brändle, *J. Am. Chem. Soc.*, **83,** 2055 (1961).

[2] For a review see U. Schöllkopf, *Angew. Chem.*, **71,** 260 (1959).

[3] D. Seyferth, S. O. Grim, and T. O. Read, *J. Am. Chem. Soc.*, **82,** 1510 (1960); *J. Am. Chem. Soc.*, **83,** 1617 (1961).

[4] Prepared by Dr. Erwin Hahn in these laboratories by the action of phosphorus tribromide in hot benzene on hydroxymethyltriphenylphosphonium bromide. An independent synthesis was reported recently by F. Ramirez *et al.*, *J. Am. Chem. Soc.*, **83,** 3539 (1961).