erts, *et al.*, for benzoic acid.[24] Insertion of the electrodes into 0.02 *N* potassium acid phthalate buffer in 50% ethanol gave a reading of 5.51 ± 0.01 for three titrations and duplicate buffer preparations. In subsequent runs the meter was standardized directly against phthalate buffer.[25]

All titrations were carried out in a 100-ml. three-neck flask maintained at 25.0 ± 0.1°. The two electrodes, fitted through rubber stoppers, were inserted into two of the necks and a 5-ml. buret (graduated in 0.01 ml.), into the third. The solutions were stirred with a magnetic stirring bar under a nitrogen atmosphere. While a pH reading was being taken, the stirrer and all current in the vicinity of the meter was shut off temporarily to avoid interference from a.c. fields.

Except for terephthalic acid, 100 ml. of 6.2×10^{-5} *M* stock solutions of the different acids in absolute alcohol were prepared; 25 ml. of this solution was titrated into the three-neck flask followed by addition of 25 ml. of water and 2.2 ml. of 50% ethanol (the latter to compensate for the contraction on mixing). For each acid duplicate stock solutions were used in the titrations. The base used in all titrations was 0.05 *N* sodium hydroxide in 50% ethanol and was prepared from carbonate-free water and base. Terephthalic acid precipitated on preparation of a 50% ethanol solution; so a partially neutralized solution was prepared by adding 10.0 ml. of the 0.050 *N* sodium hydroxide to a 1-l. flask followed by 200 ml. of 50% ethanol and 0.1024 g. of terephthalic acid. A glass stopper was wired on and the solution was stirred magnetically at 50° for 2 hr. This partially neutralized acid remained in solution when the flask was cooled to 25°. A 52.5-ml. sample of this solution was titrated as before; the initial pH corresponded to the addition of 2.5 ml. of base.

Calculation of p*K* Values.—The dissociation constants of the dicarboxylic acids were evaluated by the method of Speakman which takes into account explicitly the activity coefficients of the various species present as the solution is progressively neutralized. The activity coefficients of the species H_2A, HA^-, and A^{-2} are f_0, f_1, and f_2, respectively; f_0 was taken as unity; f_1 and f_2 were estimated from the Debye–Hückel limiting law using the value of 52.5 for the dielectric constant of 50% ethanol. The Speakman plots were drawn for measurements between 25% and 75% neutralization which in general represented about 14 different pH readings.

The dissociation constants of the monocarboxylic acids were evaluated in a similar fashion using a reduced Speakman expression in which the K_2 term had been set equal to zero. The activity coefficients of the zwitterions were evaluated by the simple[26] Ingold expression

$$-\log f_{\pm} = \frac{4\pi N e^4 z^2 d I}{2303 k^2 (DT)^2}$$

where *d* is the separation of the changes, *I* is the ionic strength, and the remaining symbols have their conventional meaning.

---

[24] After the original work Roberts and Regan reported a value of 5.80 using different apparatus and materials.

[25] It should be emphasized that 5.51 is only a relative, apparent value that places the meter on the same scale used by Roberts. The work of Grunwald with benzoic acid suggests that our p*K*'s and those of Roberts may be high on an absolute scale by as much as 0.1 p*K* unit.

[26] Two other much more complicated equations have been presented by Kirkwood and Westheimer.[8] It can be shown that with reasonable values for their parameters appropriate to the present molecules that the Kirkwood–Westheimer expressions are, in fact, very nearly the same as the simpler Ingold expression. Numerically, the p*K* obtained using activity coefficients calculated from any of the three expressions would not vary by more than 0.01 units.

Medium-Ring Thiacycloalkanes. II.[1,2]

Long-Chain Dibromides and *gem*-Dimethyl-Substituted Dibromides

PAUL FRIEDMAN AND PAUL ALLEN, JR.[3]

Stevens Institute of Technology, Hoboken, New Jersey

Received August 11, 1964

A versatile synthesis of long-chain *gem*-dimethyl-substituted dibromides has been developed. The preparation of 6,6-dimethylundecanedioic acid (VI), a key intermediate in the preparation of several of these dihalides, has been substantially improved. Cristol and Firth's modification of the Hunsdiecker reaction has been extended to the synthesis of dibromides including 1,9-dibromo-5,5-dimethylnonane (XII). 1,11-Dibromo-6,6-dimethylundecane (IX) and 1,10-dibromo-5,5-dimethyldecane (XIII) were prepared and cyclized to 7,7-dimethylthiacyclododecane (XVIII) and 6,6-dimethylthiacycloundecane (XXI) in 23 and 22% yield, respectively. Identical procedures applied to 1,11-dibromoundecane and 1,10-dibromodecane yielded less than 3% of crude product in the former case and 13% of thiacycloundecane in the latter. Comparison of yields of the substituted and unsubstituted 10-, 11-, and 12-membered ring sulfides strongly implies operation of the *gem*-dimethyl effect in these ring closures. Certain cyclic sulfides were oxidized to sulfoxides and sulfones.

Earlier work[2] showed that 1,9-dibromononane and sodium sulfide in very dilute alcohol yield only 5.7% of thiacyclodecane, whereas the 5,5-dimethyl-substituted dibromide yields 34.5% of 6,6-dimethylthiacyclodecane. These results confirmed our belief that the *gem*-dimethyl effect would obtain in ring closures ininvolving sulfide ion nucleophilic substitution at a saturated carbon atom. However, we needed an improved synthesis of the *gem*-dimethyl dihalides required for the study of other medium ring thiacycloalkanes, the bishomologization procedure used for 1,9-dibromo-5,5-dimethylnonane[1,4] being prohibitively laborious for the preparation of higher homologs.

$(C_2H_5O_2C)_2C(C_4H_8OCH_3)_2$ I $(HOCH_2)_2C(C_4H_8OCH_3)_2$ II

The preparation of dihalides *via* malonic ester failed; although I was prepared and reduced to II, the latter could not be converted to a dibromide completely nor could the two hydroxymethyl groups be changed to methyl groups *via* the ditosylate. However, we modified the ingenious work of Badger[5] (Scheme I). Badger's conversion of 2,2-bis(2-thienyl) propane (III) to V *via* 2,2-bis(5-acetyl-2-thienyl) propane (IV) was unsuitable for large-scale preparation as IV is difficult to isolate and oxidize, but III could be easily converted

---

[1] Paper I in this series: P. Friedman and P. Allen, Jr., *J. Org. Chem.*, **27**, 1095 (1962).

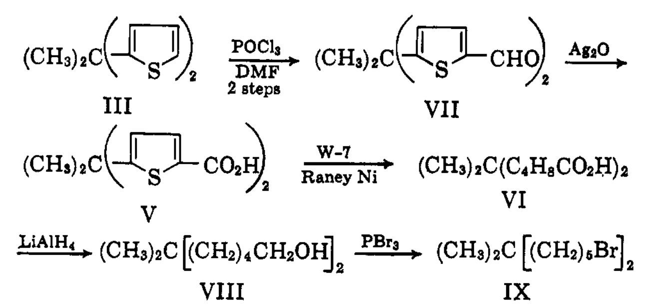
[2] (a) Presented in part at the 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 1962; Abstracts, p. 70. (b) From a portion of the Doctoral Dissertation of P. Friedman, Stevens Institute of Technology, June 1963. (c) This work was supported by a grant from the U. S. Public Health Service, National Institutes of Health, Am-03649.

[3] Author to whom inquiries should be addressed.

[4] A. T. Blomquist, E. S. Wheeler, and Y. Chu, *J. Am. Chem. Soc.*, **77**, 6307 (1955). Thirteen steps were required in adapting this synthesis to the preparation of XII from δ,δ-dimethylglutaric acid.

[5] G. M. Badger, H. J. Rodda, and W. H. F. Sasse, *J. Chem. Soc.*, 4162 (1954).

Scheme I



to V *via* the diformyl derivative VII. A monoaldehyde was formed when III was treated with phosphorus oxychloride and dimethylformamide. Treating the crude monoaldehyde with a 100% excess of the reagents or, more conveniently, cooling the reaction mixture after monosubstitution and then adding 100% excess of the reagents gave 80–86% of VII. The diformylation of III could not be accomplished by a single treatment regardless of the quantity of the reagents or the time of reaction.

Silver oxide oxidized VII to V in good yield.[6] Reduction of VI and bromination of VIII yielded the desired dibromide IX.

Heptamethylene and octamethylene dibromides were needed for exploratory work in developing our high-dilution ring closure procedures. Although glutaric acid, the only dicarboxylic acid tried by Cristol and Firth,[7] gave a low yield of dibromide in reaction with mercuric oxide and bromine, we assumed that intramolecular interaction between carboxyl groups was responsible, but would be substantially diminished in higher dicarboxylic acids. The reaction of azelaic and sebacic acids with mercuric oxide and bromine gave yields of better than 60% of the dibromides. The simplicity and rapidity of this reaction should make it a preferred synthetic method for higher dibromides.

The application of this method to VI made possible an elegant synthesis of 1,9-dibromo-5,5-dimethylnonane (XII) in 58% yield. The over-all yield from dithienylpropane (four steps) was 35–40% compared with 10–15% from the original 13-step procedure.

Table I summarizes our applications of the Cristol-Firth reaction.

Table I

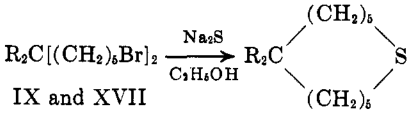
Carboxylic acid	Product (yield, %)
Azelaic	1,7-Dibromoheptane (59)
Sebacic	1,8-Dibromooctane (62)
6,6-Dimethylundecanedioic (VI)	1,9-Dibromo-5,5-dimethylnonane, XII (58)
Monomethyl ester of VI (XIV)	Methyl 10-bromo-6,6-dimethyldecanoate (57%, crude)
11-Bromo-6,6-dimethylundecanoic (XI)	1,10-Dibromo-5,5-dimethyldecane, XIII (34%)[a]
11-Hydroxy-6,6-dimethylundecanoic	Ester or lactone (?)

[a] Our first synthesis of XIII employed the selective reduction of methyl 10-bromo-5,5-dimethyldecanoate by addition to lithium aluminum hydride. Even at low temperatures there was loss of bromine and lengthy separation was needed to isolate pure XIII.

XI was prepared in two ways: (a) XV, the monoethyl ester of VI, was reduced by the Bouveault–Blanc procedure, and the crude ω-hydroxy acid XVI was brominated with 48% hydrobromic acid or phosphorus tribromide to XI and purified by chromatography on silica gel; (b) VIII was converted to its bromohydrin X, $Br(CH_2)_5C(CH_3)_2(CH_2)_4CH_2OH$, in a cyclic reactor[8] and X was oxidized with nitric acid[8] or with potassium dichromate–sulfuric acid[9] to XI.

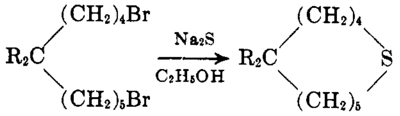
The nitric acid oxidation of X produced a substantial amount of a bromine-free olefinic side product. The dehydrobromination was shown to occur during the oxidation reaction itself, the crude reaction mixture exhibiting absorption at 1625 cm.$^{-1}$. Since the olefinic material was base soluble, it was assumed to be the ω-olefinic acid. The infrared spectrum of the mixed products was identical with that of XI made by method a except for the band at 1625 cm.$^{-1}$. The intensity of the band was decreased by oxidizing under milder conditions but enough olefinic contaminant was still present to make purification difficult. However, oxidation by dichromate–sulfuric acid mixture did not cause formation of the olefinic material and gave XI with an infrared spectrum identical with that from method a.

Ring Formation.—By a technique of high dilution in alcohol and slow addition, dibromides were treated with sodium sulfide to form thiacycloalkanes. IX yielded 7,7-dimethylthiacyclododecane (XVIII) in 23.4% yield, whereas 1,11-dibromoundecane (X) gave, under identical conditions, in two trials, less than 3% of crude product, presumably XIX, isolated by the same methods used with XVIII. Similarly, ring closure of XIII and of 1,10-dibromodecane (XX) yielded 22 and 13% of the respective thiacycloundecanes. The larger yields of the substituted sulfides confirm the operation of the *gem*-dimethyl effect in this cyclization reaction (Table II).



IX and XVII XVIII and XIX

IX and XVIII, R = CH_3
XVII and XIX, R = H



XIII and XX XXI and XXII

XIII and XXI, R = CH_3
XX and XXII, R = H

Table II

Yield of Cyclic Sulfides

Atoms in ring	Unsubstituted, %	Dimethyl substituted, %
8	34[a]	
9	6.6[a]	
10	5.7[b]	34.5[b]
11	13	22
12	3	23.4

[a] See ref. 15. [b] See ref. 1.

---

(6) E. Campaigne and W. M. Le Seur, *J. Am. Chem. Soc.*, **75**, 1555 (1953).

(7) S. J. Cristol and W. C. Firth, *J. Org. Chem.*, **26**, 280 (1961).

(8) Adapted from a procedure for hexamethylene bromohydrin and 6-bromohexanoic acid: E. F. Degering and L. G. Boatright, *J. Am. Chem. Soc.*, **72**, 5137 (1950).

(9) P. Chuit and J. Hauser, *Helv. Chim. Acta*, **12**, 481 (1929).

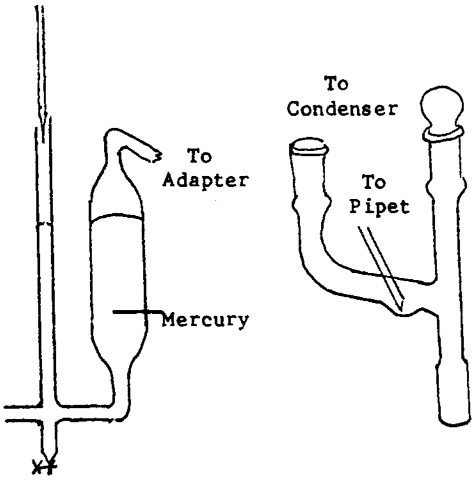


Figure 1.—The apparatus on the left is part of an addition device; the bottom opening in the apparatus on the right leads to a 5-l. three-neck flask with two adapters and a stirrer.

Certain cyclic sulfides were oxidized to the corresponding sulfoxides and sulfones (Table III).

TABLE III

Sulfide	Sulfoxide, m.p., °C.	Sulfone, m.p., °C.
Thiacyclooctane	61–62	55–56, 74–75
Thiacyclononane	40 (dihydrate)	79.5–80 (81.5–82)
6,6-Dimethylthiacyclodecane		86.5–87
7,7-Dimethylthiacyclododecane	107–108	147–148

Experimental[10]

Description of High-Dilution Apparatus.—A simple, effective device for obtaining very slow addition of equivalent quantities of two solutions was adapted from a design by Ziegler.[11] Our dropping device was conveniently assembled from two 100-ml. pipets, a glass tee, and tygon tubing. The addition rate was controlled by dropping mercury through capillaries of varying bore into the center tube. As the mercury was added both solutions overflowed at the same rate. Each solution was led directly into a depression in the bottom of the arm of a "Y" adapter so that the solution was washed into the reaction vessel by condensate which then flowed down the side of the flask, avoiding drop formation and high local concentrations (see Figure 1).

Diethyl Di(4-methoxybutyl)malonate (I).—A solution of sodium *t*-butoxide was prepared from 1.2 g. (0.052 g.-atom) of sodium and 50 ml. of anhydrous *t*-butyl alcohol in a nitrogen atmosphere. After 4.5 hr. of refluxing to dissolve the sodium completely, 12.8 g. (0.052 mole) of 4-methoxybutylmalonic acid diethyl ester[12] was added dropwise with stirring and under reflux. The reaction mixture was cooled to 30° and 9.2 g. (0.055 mole) of 1-bromo-4-methoxybutane[12] was added dropwise with stirring. The mixture was then heated at reflux for 3 hr. and the *t*-butyl alcohol was distilled at reduced pressure. Water (50 ml.) was added to the residue and after thorough shaking the mixture was poured into a separatory funnel and extracted with ether. The ether extract was washed consecutively with 50 ml. of water, 1 *N* hydrochloric acid, and water and dried overnight with Molecular Sieves (4A).

The ether was distilled at atmospheric pressure and some *t*-butyl alcohol was removed at 25 mm. The residue was distilled through a Vigreux column. The main fraction, 9.8 g. (53.4%), was collected at 164–167° (2 mm.).

Anal. Calcd. for $C_{17}H_{32}O_6$: C, 61.42; H, 9.70. Found: C, 61.58; H, 9.85.

1,9-Dimethoxy-5,5-di(hydroxymethyl)nonane (II).—In a 250-ml. flask fitted with a pressure-equalizing dropping funnel, a well-stirred slurry of 1.3 g. (0.034 mole) of lithium aluminum hydride in 100 ml. of anhydrous ether was treated with 9.7 g. (0.03 mole) of the dialkylmalonic ester in 10 ml. of anhydrous ether over a 25-min. period. After stirring for an additional hour, 14 ml. of water was cautiously added and the mixture was stirred for 20 min.

The resulting white precipitate was filtered with light suction, and subsequently triturated with two portions of ether. The ethereal portions were filtered, dried (4A Molecular Sieves), and concentrated. The residue was distilled and 5.8 g. of product (78%) was collected at 156–158° (0.5 mm.), $n^{25}D$ 1.4655.

Anal. Calcd. for $C_{13}H_{28}O_4$: C, 62.87; H, 11.37. Found: C, 62.74; H, 11.29.

2,2-Bis(5-carboxy-2-thienyl)propane (V).—Crude dialdehyde VII, 13 g. (0.049 mole), was added over a 20-min. interval to a well-stirred silver oxide suspension prepared from 18.7 g. (0.11 mole) of silver nitrate and 8.8 g. (0.22 mole) of sodium hydroxide. Stirring was continued for 1 hr. The reaction mixture was filtered; the filtrate, diluted to 500 ml. with water, was added to a mixture of 25 g. of concentrated hydrochloric acid, 100 ml. of water, and 100 g. of ice with stirring. After filtering and drying the yield of the diacid was 12.2 g. (83.6%), m.p. 272–274°, lit.[5] m.p. 275–277°.

6,6-Dimethylundecanedioic acid (VI).—This compound was prepared by the desulfurization of V with W-7 Raney nickel using Badger's procedure.[5]

2,2-Bis(5-formyl-2-thienyl)propane (VII).—A mixture of 20.8 g. (0.1 mole) of dithienylpropane and 9.2 g. (0.126 mole) of dimethylformamide was intermittently shaken and cooled, while 19.2 g. (0.125 mole) of phosphorus oxychloride was slowly added. The mixture was heated for 1 hr. at 80–90°, then cooled to room temperature. The same quantities of, first, dimethylformamide and then, slowly, phosphorus oxychloride were added. An exothermic reaction set in yielding a homogeneous black solution. After the reaction subsided the solution was heated for 2 hr. at 80° with occasional shaking. The solution was cooled and poured onto 200 g. of crushed ice. When the excess phosphorus oxychloride was completely hydrolyzed, sufficient sodium acetate solution was added to react with the acids formed. This mixture was stirred for 1 hr. while precipitation ensued. This ensured an even, granular precipitate of the dialdehyde. The mixture was filtered and the precipitate was dried yielding 22.0 g. (83.3%) of the dialdehyde.

Recrystallization from ethanol gave white flaky crystals, m.p. 87.5–88°.

Anal. Calcd. for $C_{13}H_{12}O_2S_2$: C, 59.06; H, 4.58. Found: C, 59.20; H, 4.28.

6,6-Dimethyl-1,11-undecanediol (VIII).—A solution of 4.9 g. (0.02 mole) of VI in 25 ml. of anhydrous ethyl ether was added over a 15-min. period to a well-stirred ether suspension of 1.6 g. (0.042 mole) of lithium aluminum hydride. The mixture was refluxed with stirring for an additional 3 hr. and cooled. Water (10 ml.) was cautiously added to destroy the excess hydride. After 1 hr. of stirring the mixture was filtered. The dried precipitate was triturated with four 15-ml. portions of dry ether and these washings were combined with the original filtrate. After drying with magnesium sulfate, the ether solution was concentrated, and the residue was freed of the last traces of solvent. The yield of diol was 3.5 g. (82%), b.p. 135–137° (1 mm.), $n^{29}D$ 1.4629.

Anal. Calcd. for $C_{13}H_{28}O_2$: C, 72.16; H, 13.04. Found: C, 72.25; H, 13.16.

1,11-Dibromo-6,6-dimethylundecane (IX).—This was prepared in 74% yield from VIII by the procedure employed for 1,9-dibromo-5,5-dimethylnonane,[1] b.p. 125–127° (0.3 mm.), $n^{24}D$ 1.4893.

Anal. Calcd. for $C_{13}H_{26}Br_2$: C, 45.62; H, 7.68. Found: C, 45.68; H, 8.01.

11-Bromo-6,6-dimethylundecanol (X).—A mixture of 8.6 g. (0.04 mole) of diol VIII and 7.5 ml. (0.06 mole) of 48% hydrobromic acid in a liquid–liquid extraction assembly containing an extraction tube with a fritted-glass bubbler was extracted at 70° with *n*-heptane during an 18-hr. period.

Distillation of the *n*-heptane yielded 8.4 g. of crude product which was estimated to be 80–85% bromohydrin by thin layer and gas–liquid chromatography. Distillation of the crude residue yielded 6.4 g. (57.0%) of product, b.p. 120–123° (0.1 mm.). Its structure was proved by oxidation to XI.

11-Bromo-6,6-Dimethylundecanoic Acid (XI). A.—Oxidation of X with Nitric Acid.[8]—In an 8-in. test tube equipped with a

---

[10] Melting and boiling points are uncorrected. Elemental analyses were by Schwartzkopf Microanalytical Laboratory, Woodside 77, N. Y.

[11] K. Ziegler, H. Eberle, and H. Ohlinger, *Ann.*, **504**, 94 (1933).

[12] H. Schmid, *Helv. Chim. Acta*, **27**, 134 (1944).

magnetic stirrer, 3 g. (0.011 mole) of bromohydrin X was added during 0.5 hr. to 4.2 ml. (0.066 mole) of concentrated nitric acid at 25°. The mixture was stirred for 3 hr. at room temperature, then heated in a boiling water bath. The vigorous evolution of nitric oxide that occurred was allowed to subside before reapplying heat for a 40-min. period. The reaction mixture was treated with 10 ml. of water and then with an excess of 10% sodium carbonate solution. The mixture was extracted with two 10-ml. portions of ether and the extract was set aside. The sodium carbonate solution was added with stirring to a mixture of 6 *N* hydrochloric acid and crushed ice. The liberated oil was extracted with three 10-ml. portions of ether. The ether extracts were combined, washed twice with water, and dried (magnesium sulfate). The residual oil (1.9 g.) left by distillation (100 mm.) of the ether assayed 89% by titration (based on diacid as impurity). The infrared spectrum showed a strong band at 1625 cm.$^{-1}$ (apparently due to C=C). Repetition of this reaction indicated that olefin formation occurred before treatment with sodium carbonate solution. Considerable dehydrobromination occurred in each case.

B. **Oxidation of X by Dichromate.**[9]—A solution of 2.8 g. (0.01 mole) of X in 7 ml. of benzene was treated with a mixture of 4 g. (0.013 mole) of potassium dichromate, 5.6 g. of concentrated sulfuric acid, and 11 ml. of water. The mixture was stirred and heated for 4 hr. at 80°. The benzene layer was separated and the benzene was distilled, leaving a residue which was stirred with cold sodium carbonate solution. After ether extraction, the carbonate solution was poured onto crushed ice and 10% sulfuric acid, liberating the bromo acid. The crude bromo acid weighed 1.7 g. (58.2%). The infrared spectrum showed no band at or near 1625 cm.$^{-1}$ (indicating the absence of C=C). The acid was purified by chromatography on silica gel using chloroform to elute the bromo acid.

Anal. Calcd. for $C_{13}H_{25}BrO_2$: C, 53.24; H, 8.59. Found: C, 52.75; H, 8.59.

Dibromides from Diacids. (1) **Conversion of Azelaic Acid to 1,7-Dibromoheptane.**—A mixture of 18.8 g. (0.1 mole) of azelaic acid (technical), 33.0 g. (0.15 mole) of red mercuric oxide, and 200 ml. of carbon tetrachloride was gently refluxed with vigorous stirring. The flask and condenser were wrapped in aluminum foil to exclude light. Thirty-two grams (0.2 mole) of bromine was added during 15 min., and stirring and heating were continued for an additional hour.

The reaction mixture was filtered, with light suction, after cooling. The filtrate was washed with dilute sodium bicarbonate to remove any unchanged bromine and azelaic acid. The carbon tetrachloride solution was dried (magnesium sulfate) and evaporated under vacuum. The residue, a clear, pale light yellow oil (18–20 g.), was chromatographed on 100 g. alumina using 400 ml. of petroleum ether. This was necessary to remove a side product detected by its absorption at 1690 cm.$^{-1}$, for repeated washings with both sodium carbonate and dilute sodium hydroxide solutions diminished but did not completely eliminate this absorption band (probably due to lactone or ester). Evaporation of the petroleum ether followed by fractional distillation gave 15.2 g. (59%) of 1,7-dibromoheptane, b.p. 82–85° (0.5 mm.), lit.[13] b.p. 125° (2 mm.).

(2) **Conversion of Sebacic Acid to 1,8-Dibromooctane.**—1,8-Dibromooctane was prepared in 62% yield by the procedure used for 1,7-dibromoheptane; b.p. 118–120° (1.5 mm.), lit.[13] b.p. 140° (5 mm.).

1,9-Dibromo-5,5-dimethylnonane[1] **(XII).**—A mixture of 5.1 g. (0.021 mole) of VI and 7.5 g. of red mercuric oxide in 55 ml. of dry carbon tetrachloride was refluxed with stirring. Light was excluded by wrapping the apparatus with aluminum foil. A solution of 6.6 g. (0.041 mole) of bromine in 20 ml. of carbon tetrachloride was added over a 20-min. period. Heating and stirring were continued for an additional 45 min. The light orange solution was separated by filtration. The precipitate was washed several times with carbon tetrachloride and the washings were combined with the main filtrate. After washing with dilute potassium carbonate and drying, the carbon tetrachloride was evaporated under reduced pressure. The residue showed some absorption at 5.8 μ in the infrared, probably due to an ester. The pure dibromide was obtained by chromatography on alumina, eluting it with ligroin and the more polar bromo acid with benzene. The yield of dibromide was 3.8 g. (58%). It had the same refractive index and infrared spectrum as the dibromide prepared by our initial method.[1]

1,10-Dibromo-5,5-dimethyldecane (XIII).—A mixture of 1.5 g. (0.005 mole) of XI, 0.87 g. (0.004 mole) of red mercuric oxide, and 25 ml. of carbon tetrachloride was treated with 0.8 g. (0.005 mole) of bromine following the procedure for the synthesis of 1,7-dibromoheptane.

The crude dibromide was partially purified by chromatography on alumina using petroleum ether as the eluent. The product had the simple infrared spectrum characteristic of polymethylene bromides. The yield of still somewhat impure dibromide was 0.55 g. (33.6%). Its structure was confirmed by cyclization to 6,6-dimethylthiacycloundecane (XXI).

6,6-Dimethylundecanedioic Acid Monomethyl Ester (XIV).—A mixture of 7.3 g. (0.03 mole) of VI, 10 ml. of acetic anhydride, and 8 drops of acetyl chloride was refluxed for 15 hr. After cooling, the homogeneous solution was treated with 25 ml. of anhydrous methanol and refluxed for 1 hr. The solution was concentrated on a rotary evaporator; the residue was distilled. After a 1.6-g. forerun (substantially all dimethyl ester) at 120–130° at 0.5 mm., 2.9 g. of the half-ester was collected at 165–172° (0.35 mm.). Redistillation through a packed column at 168–170° (0.3 mm.) gave 3.1 g. (40%); the equivalent weight, determined by neutralization, was 253 (calcd. for $C_{14}H_{26}O_4$, 258).

On treatment with mercuric oxide and bromine, XIV yielded 57% of a bromo compound which appeared to be methyl 10-bromo-6,6-dimethyldecanoate (94% pure), as determined by saponification and titration of the liberated bromo acid.

6,6-Dimethylundecanedioic Acid Monoethyl Ester (XV).—This monoester was prepared most readily from a mixture of diacid VI and its diethyl ester. It boiled at 152–160° (0.2 mm.); the equivalent weight, determined by neutralization, was 264 (calcd. for $C_{15}H_{28}O_4$, 272).

11-Hydroxy-6,6-dimethylundecanoic Acid (XVI).—A solution of 8.3 g. (0.03 mole) of half-ethyl ester XV in 150 ml. of ethanol was treated with 7 g. of sodium. After refluxing for 1.5 hr. the mixture was allowed to stand overnight and then concentrated. Water was added and the solution was extracted with ether to remove 2 g. of diol VIII. The basic aqueous solution was acidified by pouring onto ice and 6 *N* hydrochloric acid. The liberated acid was taken up in ether. After drying, the ether gave 5 g. (71%) of light amber-colored viscous oil. The infrared spectrum had a distinct band at 2.9 μ; the equivalent weight of oil, determined by neutralization, was 226 (calcd. for $C_{13}H_{26}O_3$, 230).

Bromination of XVI to XI.—Three grams (13 mmoles) of XVI was added in portions during 20 min. to 2 g. (7.4 mmoles) of phosphorus tribromide stirred at 0°. The mixture was slowly warmed to 80° and stirred overnight. On cautious addition of water, an orange glossy solid precipitated. The solid and water were extracted with methylene chloride. Evaporation of the methylene chloride left 1.2 g. of residue which was purified by chromatography on silica gel to yield material identical with that produced by oxidation of X.

7,7-Dimethylthiacyclododecane (XVIII).—Solutions of 3.0 g. (0.00876 mole) of IX and sodium sulfide (0.018 mole), each in 80 ml. of absolute ethanol, were added simultaneously in the high-dilution apparatus over a 40-hr. period to 2.5 l. of refluxing alcohol; the solution was refluxed for 2 hr. after the addition. The product was isolated by the same procedure used with 6,6-dimethylthiacyclodecane[1] as 0.44 g. (23.4%) of yellow needles. Sublimation [35° (1 mm.)] and recrystallization from ethanol gave colorless needles, m.p. 41.5–42°.

Anal. Calcd. for $C_{13}H_{26}S$: C, 72.82; H, 12.22. Found: C, 72.60; H, 12.02.

Thiacyclododecane (XIX).—Following the procedure for XVIII, 3.14 g. (0.01 mole) of 1,11-dibromoundecane (XVII) (K and K Laboratories) was treated with sodium sulfide (0.02 mole) over a 50-hr. period. A viscous oil (50 mg.) was recovered. This represents less than 3% yield of the impure material. Attempts to prepare an analytical sample by chromatography on alumina and through the mercuric chloride adduct were unsuccessful.

6,6-Dimethylthiacycloundecane (XXI).—Solutions of 0.55 g. (1.7×10^{-4} mole) of XIII and sodium sulfide (about 3.5×10^{-4} mole), each in 70 ml. of absolute ethanol, were added simultaneously in the high-dilution apparatus, during 15 hr., to 2.5 l. of vigorously stirred, refluxing absolute ethanol.

---

[13] J. W. H. Oldham, *J. Chem. Soc.*, 100 (1958).

The solution was refluxed for 24 hr. and the sulfide was isolated in the manner described for XVIII; 76 mg. (22%) of light yellow oil which was about 95% pure (by gas-liquid chromatography) was obtained. Microfractionation yielded a colorless liquid.

Anal. Calcd. for $C_{12}H_{24}S$: C, 71.95; H, 12.08. Found: C, 72.08; H, 12.12.

Thiacycloundecane (XXII).—The above procedure duplicated with 11.5 g. (0.038 mole) of 1,10-dibromodecane (XX) (Fisher Scientific Corp.) yielded 850 mg. (13%) of 96+% pure (g.l.c.) thiacycloundecane, b.p. 66–68° (0.2 mm.).

Anal. Calcd. for $C_{10}H_{20}S$: C, 69.72; H, 11.70; S, 18.58. Found: C, 69.82; H, 11.74; S, 18.36.

Thiacyclooctane 1-Oxide[14] **(XXIII).**—A solution of 130 mg. (1 mmole) of thiacyclooctane in 2 ml. of methanol was treated at 0° with 2 ml. of a 0.52 *M* aqueous solution of sodium metaperiodate during a 10-min. period. The mixture was stirred overnight at 0° and filtered. The precipitate, sodium iodate, was washed with two 5-ml. portions of chloroform. The aqueous-methanol layer was extracted with chloroform and all chloroform portions were joined, dried (magnesium sulfate), and concentrated, first at 100 mm., and then at 0.1 mm., leaving colorless prisms (120 mg., 82%). The product was extremely hygroscopic, liquefying within minutes after exposure to the atmosphere. Sublimation of a portion of the sulfoxide (handled under nitrogen in a glove bag) at 50° (0.5 mm.) yielded fine needles, m.p. 61–62° (sealed capillary). The infrared spectrum of this material (neat) had an intense band at 1025 cm.$^{-1}$ characteristic of sulfoxides.

Anal. Calcd. for $C_7H_{14}OS$: S, 21.87. Found: S, 21.75.

Thiacyclononane 1-oxide (XXIV) was prepared in 89% yield by the procedure used for XXIII. It was much less hygroscopic than XXIII. Sublimation at 50° (0.05 mm.) gave fine colorless needles, melting below 40° apparently due to hydration. The infrared spectrum (Nujol) had an intense band at 1045 cm.$^{-1}$.

Anal. Calcd. for $C_8H_{16}OS$: S, 19.96. Calcd. for $C_8H_{16}OS\cdot 2H_2O$: S, 16.32. Found: S, 16.87.

7,7-Dimethylthiacyclododecane 1-oxide (XXV) was prepared from XVIII in 92% yield by the procedure used for XXIII. Recrystallization from petroleum ether followed by sublimation at 70° (0.05 mm.) gave fine white needles, m.p. 107–108°. The product was not appreciably hygroscopic. The infrared spectrum (carbon tetrachloride) had a strong band at 1047 cm.$^{-1}$.

Anal. Calcd. for $C_{13}H_{26}OS$: S, 13.89. Found: S, 14.40.

Thiacyclooctane 1,1-Dioxide.—Oxidation of thiacyclooctane (130 mg. in 2 ml. methanol) by 2.5 ml. of 1 *M* sodium metaperiodate[14] yielded colorless needles of sulfone. Recrystallization from petroleum ether gave crystals melting at 55–56° and 74–75° (microscope hot stage). These are dimorphic forms of the same compound, for their gas-liquid chromatograms were identical in shape and retention times; the infrared bands of both were at 1116 and 1285 and 1308 cm.$^{-1}$ (doublet). Müller,[15] who first made this compound, reported a melting point of 61° and apparently did not notice its dimorphism.

Thiacyclononane 1,1-Dioxide.—Thiacyclononane was oxidized by sodium metaperiodate.[14] The sulfone melted at 79.5–80°, lit.[15] 81.5–82°; its infrared spectrum had bands at 1112 and[15] 1280 and 1310 cm.$^{-1}$ (doublet).

6,6-Dimethylthiacyclodecane 1,1-Dioxide.—Oxidation of 6,6-dimethylthiacyclodecane[1] by hydrogen peroxide[16] produced the sulfone as colorless plates, m.p. 86.5–87°. Gas-liquid chromatography indicated a purity of 99+%; infrared absorption bands were at 1115, and 1271, 1287, and 1298 cm.$^{-1}$ (triplet).

7,7-Dimethylthiacyclododecane 1,1-Dioxide.—Oxidation of XVIII by hydrogen peroxide by the method of Tarbell and Weaver[16] yielded 89% of the crude sulfone. Recrystallization from petroleum ether and sublimation at 50° (0.05 mm.) gave colorless plates, m.p. 147–148°; infrared absorption bands were at 1118, and 1276 and 1292 cm.$^{-1}$ (doublet).

---

[14] N. J. Leonard and C. R. Johnson, *J. Org. Chem.*, **27**, 282 (1962).

[15] A. Müller, E. Funder-Fritzche, W. Konar, and E. Rintersbacher-Wlasak, *Monatsh.*, **84**, 1206 (1953).

[16] D. S. Tarbell and C. Weaver, *J. Am. Chem. Soc.*, **63**, 2941 (1941).

Ozonation of Substituted Diazomethanes[1]

ARTHUR M. READER, PHILIP S. BAILEY,[2] AND HAROLD M. WHITE

Department of Chemistry, The University of Texas, Austin, Texas 78712

Received July 27, 1964

Ozonation of diphenyldiazomethane, diazofluorene, and azibenzil resulted in cleavage of the carbon–nitrogen bond to give the corresponding ketones in high yield. Depending on the solvent, temperature, and solution concentration, the stoichiometry of the ozonation varied from 1:1 to nearly 2:1 in regard to moles of diazo compound reacting per mole of ozone. Two ozonation routes are proposed, one with 1:1 stoichiometry and resulting in the ketone, nitrogen, and oxygen, and the other involving 2:1 stoichiometry and yielding the ketone, nitrogen, and nitrous oxide.

In two previous papers we have reported the attack of ozone on the carbon–nitrogen double bonds of certain Schiff bases,[3] nitrones,[3] and 2,4-dinitrophenylhydrazones.[4] The major reaction was cleavage of the carbon–nitrogen double bond, although noncleavage products also were obtained in the case of Schiff bases.[3] The suggestion was made that the major type of ozone attack on the carbon–nitrogen double bonds of the substances was nucleophilic.[3,4]

Wibaut and Boon[5] recently reported the attack of ozone on azibenzil (Ic) to give benzil (Vc). Since we had independently discovered the same type of reaction and found a variable stoichiometry, we published a preliminary report concerning the ozonation of diphenyldiazomethane (Ia).[1] The present paper gives the experimental details of the ozonation of Ia, extends the study to azibenzil (Ic) and diazofluorene (Ib), and discusses possible mechanisms for the reaction.

Diphenyldiazomethane (Ia) and diazofluorene (Ib) absorbed ozone quantitatively and gave quantitative, or near quantitative, yields of benzophenone (Va) and fluorenone (Vb), respectively, in carbon tetrachloride, methylene chloride, or methanol solutions. In carbon tetrachloride solution, at the point where the starting material (Ia or Ib) had all reacted, as determined by the disappearance of the red color, the mole ratio of Ia and Ib to ozone reacting was 1.7–1.9 and 1.4–1.5, respectively. Changes in temperature and in concentration of the solution appeared to have little effect on the ratio. With methylene chloride solvent, however,

---

[1] For a preliminary report on a part of this work, see A. M. Reader and P. S. Bailey, *Chem. Ind.* (London), 1620 (1961). A major part of the work presented in the present paper came from the Ph.D. Dissertation of A. M. Reader, The University of Texas, June 1962.

[2] To whom inquiries should be directed.

[3] A. H. Riebel, R. E. Erickson, C. J. Abshire, and P. S. Bailey, *J. Am. Chem. Soc.*, **82**, 1801 (1960).

[4] R. E. Erickson, A. H. Riebel, A. M. Reader, and P. S. Bailey, *Ann.*, **653**, 129 (1962).

[5] J. P. Wibaut and J. W. P. Boon, *Helv. Chim. Acta*, **44**, 1171 (1961).