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Dimethylenedihydroheteroaromatic Compounds and Heterocyclophanes by 1,6-Hofmann Elimination Reactions

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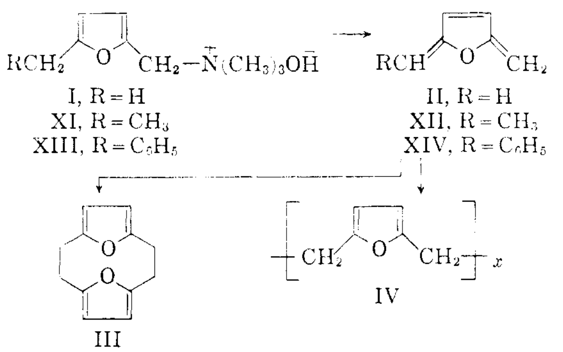
The pyrolysis of appropriately substituted quaternary ammonium hydroxides, involving the loss of trimethylamine and the elimination of the elements of water across a furan or thiophene ring system, has been investigated as a route to unusual cyclic conjugated trienes, their dimers and polymers. An example is the thermal decomposition of 5-methyl-2-furfuryltrimethylammonium hydroxide leading to the very reactive 2,5-dimethylene-2,5-dihydrofuran (II). This unusual triene polymerized readily or, in the presence of stabilizers, formed a crystalline dimer III, a heterocyclophane. Similar results were obtained with the thiophene analog of the furan quaternary hydroxide, and extensions of this chemistry to other furan and thiophene systems are reported. [2.2]Paracyclophane (XXVII) was synthesized in 17% yield by the low-temperature decomposition of p-methylbenzyltrimethylammonium hydroxide.

Furans.—Pyrolysis of 5-methyl-2-furfuryltrimethylammonium hydroxide (I) has been found to give 2,5-dimethylene-2,5-dihydrofuran (II); II was isolated at −78°, and when warmed in the presence of polymerization inhibitors it dimerized in high yield to form the heterocyclophane III. In the absence of inhibitors, polymerization occurred through the exocyclic methylene groups with reversion of the rings to the stable furan structure IV.[1] The formation of II presumably occurs by



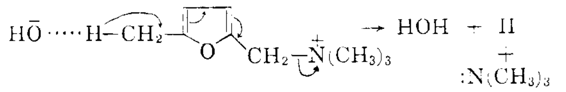
I, R = H
XI, R = CH$_3$
XIII, R = C$_6$H$_5$

II, R = H
XII, R = CH$_3$
XIV, R = C$_6$H$_5$

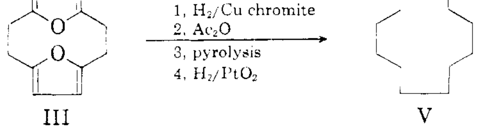
III

IV

a 1,6-elimination reaction of the Hofmann type involving removal of a proton from the methyl group of I and elimination of trimethylamine according to the scheme



The structure of the dimer 5,5′-ethylene-1,2-di-(2-furyl)-ethane (III), the furan analog of [2.2]-paracyclophane,[2,3] di-m-xylylene[4] and di-(pyridine-2,6-dimethylene),[5] was determined by means of elemental analysis and physical and chemical properties. Crystalline III, m.p. 189–190°, was obtained in 73% yield based on the starting quaternary halide. It possessed the molecular formula $C_{12}H_{12}O_2$. Quantitative hydrogenation[6] in 95% ethanol with PtO_2 catalyst showed the presence of four double bonds. The ultraviolet spectrum had λ_{max} 222 mμ (ϵ 14,650) compared with λ_{max} 218 mμ (ϵ 7,370) for 2,5-dimethylfuran, indicating the presence of two furan rings in the dimer. The infrared spectrum of III showed no absorption indicative of non-aromatic double bonds and it was similar in structure, although shifted in position,[7] to the spectrum of 2,5-dimethylfuran.[8] The proton magnetic resonance spectrum of III showed two peaks with areas in the ratio of 2:1. The weaker peak at +54.4 c.p.s. was due to the furan ring protons, while the stronger peak at −80 c.p.s. was assignable to the methylene protons. Finally, III was degraded to cyclododecane (V) by the sequence of reactions involving



III

V

hydrogenolysis of III at 3000 lb./sq. in. and 250° in the presence of barium-activated copper chromite and acetylation of the product to a mixture of acetates. Pyrolysis of the mixed acetates at 500° gave a cycloölefin mixture which on hydrogenation at 25 lb./sq. in. in the presence of PtO_2 gave cyclododecane. The latter was characterized by its elemental analysis, melting point,[9] infrared spectrum and X-ray diffraction pattern.[10]

In order to determine the geometrical form of the dimer 5,5′-ethylene-1,2-di-(2-furyl)-ethane (III), Dr. R. E. Merrifield of this Laboratory examined the vibrational spectra of the molecule. The following three models of III were considered, wherein the symbols denote the symmetry group to which

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(1) 2,5-Dimethylene-2,5-dihydrofuran (II) is the furan analog of p-xylylene (p-quinodimethane) whose structure and reactivity have been extensively investigated (see, for example, L. A. Errede and M. Szwarc, *Quart. Revs.* (*London*), **12**, 301 (1958), and C. A. Coulson, D. P. Craig, A. Maccoll and A. Pullman, *Disc. Faraday Soc.*, **2**, 36 (1947)). p-Xylylene undergoes addition reactions at the terminal methylene carbon atoms in forming poly-p-xylylene and various 1,6-adducts. The analog II also reacts at its terminal methylene positions with iodine to form IX and with aryloxy radicals derived from 2,4,6-tri-t-butylphenol (see W. R. Hatchard, R. D. Lipscomb and F. W. Stacey, This Journal, **80**, 3636 (1958)).

(2) C. J. Brown and A. C. Farthing, *Nature*, **164**, 915 (1949).

(3) D. J. Cram and H. Steinberg, This Journal, **73**, 5691 (1951).

(4) W. Baker, J. F. W. McOmie and J. M. Norman, *J. Chem. Soc.*, 1114 (1951); C. J. Brown, *ibid.*, 3278 (1953).

(5) W. Baker, K. M. Buggle, J. F. W. McOmie and D. A. M. Watkins, *ibid.*, 3594 (1958).

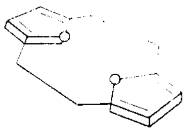
(6) E. C. Dunlop, *Ann. N. Y. Acad. Sci.*, **53**, 1087 (1951).

(7) Detailed spectral comparison of the dimer with its open-chain analogs, as made by Cram (ref. 3) for the paracyclophanes, would be expected to show shifts due to π-orbital overlap.

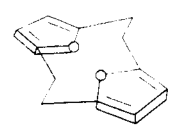
(8) M. Fétizon and P. Baranger, *Bull. soc. chim. France*, 1311 (1957).

(9) L. Ruzicka, M. Stoll, H. W. Huyser and H. A. Boekenoogen, *Helv. Chim. Acta*, **13**, 1169 (1930).

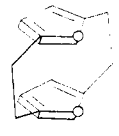
(10) A. Müller, *ibid.*, **16**, 155 (1933).



D_{2h}



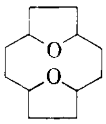
C_{2h}



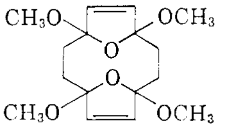
C_{2v}

each belongs. No coincidences were found in the fundamentals of the infrared and Raman spectra of III, and thus the molecule possesses a center of symmetry which allows rejection of the *cis* (symmetry C_{2v}) structure. The spectroscopic differences between the coplanar (symmetry D_{2h}) and the *trans* or step-like (symmetry C_{2h}) structures were too small to permit distinguishing between them. The *trans* or step-like (C_{2h}) structure for III appears to be the correct one, however, on the basis of bond angle considerations.[11] Di-*m*-xylylene also has been found from X-ray measurements to have the centro-symmetric, step-like structure.[4]

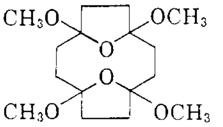
In examining other reactions of the dimer III, it was converted to the octahydro derivative VI on a preparative scale in 46% yield by low-pressure hydrogenation with PtO_2 catalyst in glacial acetic acid. Under these conditions furan and 2,5-dimethylfuran are cleaved almost quantitatively to butanol and 2-hexanol, respectively.[12] Reaction of III in methanol with bromine by the procedure of Clauson-Kaas[13] involved both furan rings and gave tetramethoxytetrahydro-5,5′-ethylene-1,2-di-(2-furyl)-ethane (VII). This ketal was readily soluble in water that contained a trace of mineral acid and the resulting aqueous solution gave a strong carbonyl test. Hydrogenation of VII at 2000 lb./sq. in. with Raney nickel catalyst at room temperature in dioxane gave the tetramethoxyoctahydro derivative VIII, a possible source of tetraketocyclododecane.



VI

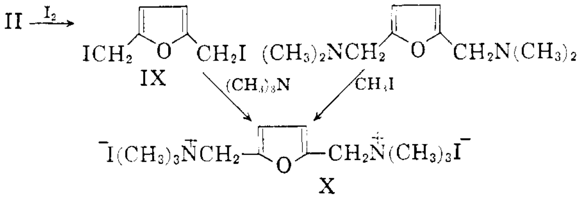


VII



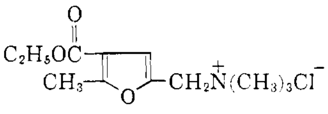
VIII

2,5-Dimethylene-2,5-dihydrofuran (II) was isolated as a white solid at −78° when the thermal decomposition of I was carried out at 150° under reduced pressure; II was found to be stable indefinitely at −78°. It reacted rapidly and quantitatively with one mole of iodine at this temperature to give 2,5-bis-(iodomethyl)-furan (IX) which, since it was unstable at room temperature, was isolated as the bis-quaternary salt, 2,5-furandimethylenebis-(trimethylammonium iodide) (X) by reaction with trimethylamine. Authentic X, prepared by quaternization of 2,5-bis-(dimethylaminomethyl)-furan[14] with methyl iodide, showed no depression in melting point when mixed with the quaternary salt derived from II, and a comparison of the ultraviolet and infrared spectra of the two salts showed them to be the same compound.



Trienes or their derivatives were obtained similarly from certain other substituted furans. 5-Ethylidene-2-methylene-2,5-dihydrofuran (XII) was isolated from the decomposition of 5-ethyl-2-furfuryltrimethylammonium hydroxide (XI) at 50–100° under reduced pressure. The triene on heating to 100° formed polymer and a mixture of dimers of structure analogous to III. Dimerization of XII would be expected to result in an isomeric mixture since two molecules of the monomer can combine by 1,6-addition in two ways and, in addition, two asymmetric carbon atoms are formed. Thermal decomposition of 5-benzyl-2-furfuryltrimethylammonium hydroxide (XIII) gave a 70% yield of polymer together with a 6% yield of a mixture of cyclic dimers derived from 1,6-dimerization of the expected intermediate 5-benzylidene-2-methylene-2,5-dihydrofuran (XIV). Monomeric XIV was not isolated, although one would expect it to be more stable than the unsubstituted triene II. Compound XIII decomposed at 30°, presumably because of the activating effect of the phenyl group on the adjacent methylene hydrogens, and at this temperature XIV is evidently unstable and yet insufficiently volatile to escape from the reaction zone.

The quaternary hydroxide route did not yield conjugated trienes of the above type from ester-containing intermediates. The facile self-catalyzed hydrolysis of the ester group evidently leads to the relatively stable betaine which does not undergo decomposition. For example, attempts to convert 5-methyl-4-ethoxycarbonyl-2-furfuryltrimethylammonium chloride (XV) to the hydroxide in aqueous or alcoholic medium at room temperature led only to the formation of the betaine.



XV

The possibility of obtaining 2,3-dimethylene-2,3-dihydrofuran (XVII) through the decomposition of 2-methyl-3-furylmethyltrimethylammonium hydroxide (XVI) was investigated. In this instance, a difurocycloöctadiene, m.p. 54–55°, was obtained in 53% yield as a result of dimerization of the uniso-

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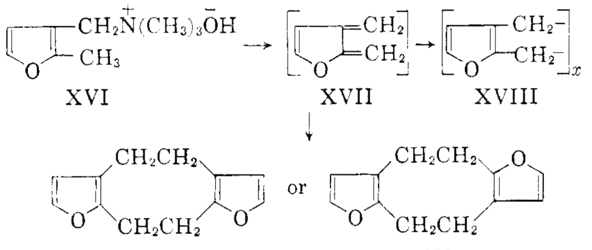
[11] Calculations by Dr. Merrifield show that coupling between the π-electron systems of the two furan rings of III presumably would take place through the 2p π-orbitals of the oxygen atoms. If the D_{2h} (coplanar, centro-symmetric) model for III is assumed, the O–O distance is estimated at 1.68 Å. For such a configuration the calculated value of the overlap integral between the two oxygen 2p π-orbitals is 0.071 or about one-fourth of the overlap integral between two adjacent carbon 2p π-orbitals in benzene. Deviation of the molecule from coplanarity, *i.e.*, to the C_{2h} structure, would not greatly alter this value.

[12] H. A. Smith and J. F. Fuzek, THIS JOURNAL, **71**, 415 (1949).

[13] N. Clauson-Kaas, *Kgl. Danske Videnskab. Selskab. Mat.-fys. Medd.*, **24** [6], 18 (1947); *C. A.*, **42**, 1930e (1948).

[14] E. L. Eliel and P. E. Peckham, THIS JOURNAL, **72**, 1209 (1950).

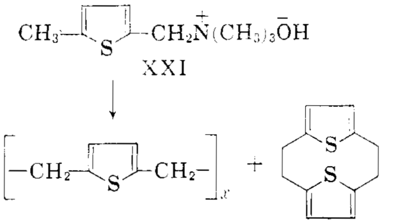
lated XVII. In addition to the dimer, the furan polymer XVIII was formed in low yield. The structure and stereochemistry of the single dimer which was isolated was not elucidated. Each of the two possible position isomers XIX and XX should be capable of existing in *cis* and *trans* conformations in a manner analogous to that of 1,2,5,6-dibenzocycloöctadiene.[15]



XVI XVII XVIII

XIX XX

Thiophenes.—In exploring analogous reactions in the thiophene series, the pyrolysis of 5-methyl-2-thenyltrimethylammonium hydroxide (XXI) in bulk at 150° was found to give the thiophene polymer XXII[16] along with traces of the heterocyclophane XXIII. Polymer XXII, the thiophene analog of poly-*p*-xylylene, softened at 140° and was rubbery at 220°, temperatures considerably below the softening point of poly-*p*-xylylene. Azeotropic removal of water from XXI in the presence of phenothiazine afforded the dimer XXIII in 19% yield.



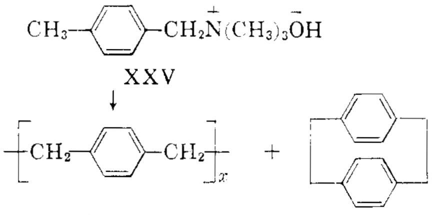
XXI

XXII XXIII

In neither method of quaternary hydroxide decomposition was the intermediate compound, 2,5-dimethylene-2,5-dihydrothiophene,[16] isolated. Its reactivity should approach closely that of *p*-xylylene which has been isolated only in solution at low temperature.[17] The dimer, m.p. 194.5–196°, has been assigned the structure 5,5′-ethylene-1,2-di-(2-thienyl)-ethane (XXIII) on the basis of its elemental composition, molecular weight and spectral characteristics. The infrared, ultraviolet and proton magnetic resonance spectra were consistent with the proposed structure. Although the geometrical form of XXIII has not been determined, by analogy with its furan analog III it probably exists in the "stepped" or *trans* (symmetry C_{2h}) configuration. Because the sulfur atom is larger than oxygen, the thiophene rings in XXIII should be somewhat more distorted than are the furan rings in III.

3-Methyl-2-thenyltrimethylammonium hydroxide (XXIV) was pyrolyzed at 150° under 3–6 mm. pressure to give, in low yields, an intralinear polymer attached through the 2,3-positions of the thiophene ring. 2,3-Dimethylene-2,3-dihydrothiophene was apparently the transitory volatile intermediate to the polymer since the latter was formed at some distance from the decomposition zone. The nonformation of a dithenocycloöctadiene in this reaction is reminiscent of the failure of *o*-methylbenzyltrimethylammonium hydroxide to yield dibenzocycloöctadiene on Hofmann degradation.[18]

Synthesis of [2.2]Paracyclophane by Hofmann Degradation.—Thermal decomposition of *p*-methylbenzyltrimethylammonium hydroxide (XXV) occurred at 60–100° under reduced pressure and gave, in addition to poly-*p*-xylylene (XXVI),[19] a small amount of [2.2]paracyclophane (XXVII). The latter could be readily extracted from the reaction mixture with hot toluene. Polymer XXVI was formed in the apparatus a considerable distance from the decomposition zone, which indicates that *p*-xylylene was probably formed as a volatile transitory intermediate. Both dimer and polymer were formed also when the quaternary base was azeotropically dried and decomposed in boiling toluene. Although no extensive effort was made to develop this route to XXVII, it was observed that the addition of a polymerization inhibitor prior to decomposition of XXV appeared to increase the amount of XXVII formed, permitting its isolation in 17% yield. A more convenient method which does not require preparation of the quaternary base *per se* has been developed by Drs. F. D. Marsh and T. E. Young of this Laboratory. In this procedure, the quaternary halide is decomposed in hot concentrated aqueous alkali to give again a mixture of polymer and dimer. Since *p*-methylbenzyltrimethylammonium halides are readily available, this method provides a simple and convenient synthesis of [2.2]paracyclophane.



XXV

XXVI XXVII

Application of the quaternary hydroxide method to the synthesis of dibenzocycloöctadiene from *o*-methylbenzyltrimethylammonium hydroxide gave at best only traces of the dimer, in agreement with the work of Bersch.[18] The decomposition of *o*-benzylbenzyltrimethylammonium hydroxide, how-

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[15] W. Baker, R. Banks, D. R. Lyon and F. G. Mann, *J. Chem. Soc.*, 27 (1945). 1,2,5,6-Dibenzocycloöctadiene was prepared by the action of sodium on α,α′-dibromo-*o*-xylene. On crystallographic examination by E. M. Davidson it was found to have a center of symmetry and hence to have the *trans* form in the solid state. E. W. Randall and L. E. Sutton, *ibid.*, 1266 (1958), found the dipole moment of 1,2,5,6-dibenzocycloöctadiene at 25° in benzene solution to indicate 25–35% of the solute was in the polar C_{2v} (*cis*) conformation.

[16] J. L. Anderson, U. S. Patent 2,756,239 (1956), obtained 2,5-dimethylene-2,5-dihydrothiophene by pyrolyzing 5-ethyl-2-methylthiophene at 825° and collecting the monomer in a liquid nitrogen-cooled trap. The compound spontaneously polymerized on warming to room temperature.

[17] L. A. Errede and B. F. Landrum, THIS JOURNAL, **79**, 4952 (1957); L. A. Errede and S. L. Hopwood, Jr., *ibid.*, **79**, 6507 (1957); L. A. Errede and B. F. Landrum, U. S. Patent 2,777,005 (1957).

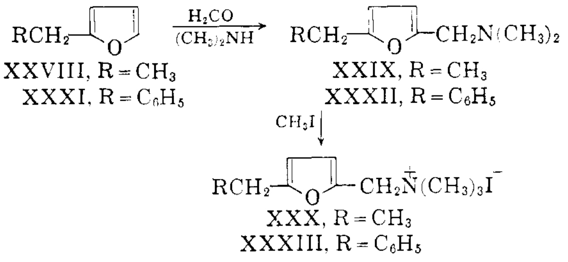
[18] H. W. Bersch, K. H. Fischer and A. v. Mletzko, *Arch. Pharm.*, **290**, 353 (1957).

[19] F. S. Fawcett, U. S. Patent 2,757,146 (1956).

ever, is reported to give diphenyldibenzocycloöctadiene in 7% yield.[18]

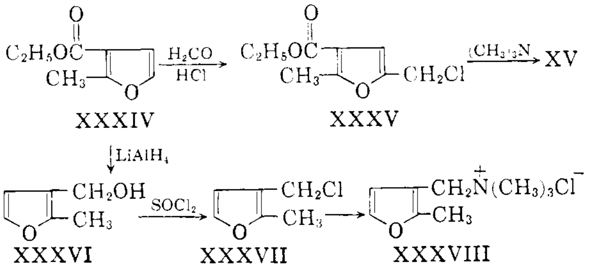
Intermediates.—The syntheses of the intermediates to the above quaternary compounds are summarized in the following paragraphs.

The starting material for the synthesis of 5-ethyl-2-furfuryltrimethylammonium hydroxide (XI) was 2-ethylfuran (XXVIII),[8,20] which was treated with formaldehyde and dimethylamine under the conditions of the Mannich reaction to give a 74% yield of 5-ethyl-2-furfuryldimethylamine (XXIX). This tertiary amine was quaternized with methyl iodide in 99% yield to the quaternary salt XXX.[20] Conversion of the quaternary iodide to the quaternary hydroxide XI was carried out with silver oxide in the usual manner. 2-Benzylfuran[21] (XXXI), carried through the same sequence of reactions, led to 5-benzyl-2-furfuryldimethylamine (XXXII, 61.5%), 5-benzyl-2-furfuryltrimethylammonium iodide (XXXIII, 93%) and 5-benzyl-2-furfuryltrimethylammonium hydroxide (XIII).



XXVIII, R = CH_3
XXXI, R = C_6H_5
XXIX, R = CH_3
XXXII, R = C_6H_5
XXX, R = CH_3
XXXIII, R = C_6H_5

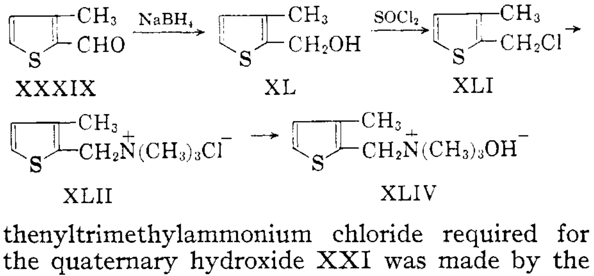
Ethyl 2-methyl-3-furoate (XXXIV)[22] provided the starting point for both the quaternary chloride XV and the quaternary hydroxide XVI. Chloromethylation of XXXIV gave a 29% yield of the chloromethyl derivative XXXV as a solid, m.p. 38–39.5°, which reacted readily with trimethylamine to give the quaternary chloride XV.



XXXIV
XXXV
XXXVI
XXXVII
XXXVIII

Reduction of XXXIV with lithium aluminum hydride gave 83% of 2-methyl-3-hydroxymethylfuran (XXXVI) which was converted to 2-methyl-3-chloromethylfuran (XXXVII) by treatment with thionyl chloride in pyridine. Since XXXVII was quite unstable at room temperature it was quaternized with trimethylamine immediately after its preparation, giving the hygroscopic quaternary chloride XXXVIII which, with silver oxide, formed the quaternary hydroxide XVI.

The synthesis of 3-methyl-2-thenyltrimethylammonium hydroxide (XXIV) followed a pattern similar to that used in preparing the quaternary salt XXXVIII. 3-Methyl-2-thenaldehyde[23] (XXXIX) was reduced with sodium borohydride to 3-methyl-2-hydroxymethylthiophene (XL). On treatment with thionyl chloride XL was converted in 79% yield to the unstable chloride XLI[24] which, on reaction with trimethylamine, gave the quaternary chloride XLII. The precursor 5-methyl-2-thenyltrimethylammonium chloride required for the quaternary hydroxide XXI was made by the quaternization of 5-methyl-2-thenyl chloride[25] with trimethylamine.



XXXIX
XL
XLI
XLII
XLIV

Experimental

Infrared spectra were determined on a Perkin–Elmer model 21 double-beam spectrometer. In addition to the assigned group frequencies, major unassigned bands useful for characterization purposes have been cited. The ultraviolet spectra were determined on a Cary model 11 spectrometer. The proton magnetic resonance spectra were obtained using a Varian high-resolution n. m. r. spectrometer and electromagnet at frequencies of 40 Mc. and fields of 10,000 gauss, respectively. The spectra were calibrated in terms of displacements in cycles per second (c.p.s.) from the proton resonance of water. Positive values are on the low field side of water and negative values are on the high field side. Calibration was accomplished by superimposing an audiofrequency on the sweep field to produce side band peaks to the water resonance. We are indebted to Dr. Harlan Foster for determining and interpreting the n. m. r. spectra.

2,5-Dimethylene-2,5-dihydrofuran (II) and Its Polymer (IV).—A solution of 11.7 g. (0.05 mole) of 5-methyl-2-furfuryltrimethylammonium bromide[26] in 30 ml. of distilled water was stirred for 1.5 hours with 16 g. of silver oxide. The mixture was filtered under nitrogen and the precipitate washed with a few ml. of water. The water was removed from the filtrate under oil-pump vacuum at 30°. The solid residue was then decomposed at 150° (3–4 mm.) over a period of 20 minutes. When pyrolysis was complete, only traces of char remained in the decomposition flask, and a receiver at room temperature contained no distillate. An attached solid carbon dioxide–acetone-cooled trap contained 2,5-dimethylene-2,5-dihydrofuran as a white solid. On warming, the solid melted to a light yellow liquid. The liquid was taken up in ether and superficially dried with magnesium sulfate. When the ether solution was warmed, the compound polymerized exothermically. The polymer, which softened to a viscous melt at 120–125°, was swollen by boiling benzene and dimethylformamide.

Anal. Calcd. for $(C_6H_6O)_x$: C, 76.57; H, 6.43. Found: C, 75.74; H, 6.30.

Reaction of 2,5-Dimethylene-2,5-dihydrofuran (II) with Iodine.—The pyrolysis of 5-methyl-2-furfuryltrimethylammonium hydroxide, prepared from 13.4 g. (0.0476 mole) of 5-methyl-2-furfuryltrimethylammonium iodide[26] and silver

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(20) A. K. Armitage and H. R. Ing, *Brit. J. Pharmacol.*, **9**, 376 (1954).

(21) R. Paul, *Compt. rend.*, **202**, 1444 (1936).

(22) E. Benary, *Ber.*, **44**, 493 (1911).

(23) E. Campaigne and W. L. Archer, THIS JOURNAL, **75**, 989 (1953).

(24) A. W. Weston, U. S. Patent 2,556,566 (1951).

(25) W. S. Emerson and T. M. Patrick, Jr., *J. Org. Chem.*, **14**, 790 (1949).

(26) The bromide was obtained by treating the free tertiary amine (R. F. Holdren and R. M. Hixon, THIS JOURNAL, **68**, 1198 (1946)) with methyl bromide in methanol-ether, recrystallized from acetonitrile, m. p. 185–186°C.; *anal.* Calcd. for $C_9H_{16}BrNO$: N, 5.98; Br, 34.13; found: N, 6.27, 6.20; Br, 34.17, 34.24. The iodide was obtained similarly using methyl iodide in ether, recrystallized from n-propyl alcohol, m.p. 159–160°; *anal.* Calcd. for $C_9H_{16}INO$: N, 4.98; I, 45.14; found: N, 5.09, 4.95; I, 44.49, 44.12, 44.42.

oxide, was carried out as above with the exception that the solid carbon dioxide–acetone-cooled receiver contained 12 g. (0.0474 mole) of iodine in 100 ml. of ether. After completion of the pyrolysis, the iodine color was completely discharged. The product was a light yellow solid insoluble in ether at −78°. On warming to room temperature the solid dissolved, and the solution rapidly discolored due to the formation of free iodine. The solution was again cooled and was saturated with trimethylamine. After 2 hours the precipitated salt was filtered and extracted twice with boiling acetone. The light tan 2,5-furandimethylenebis-(trimethylammonium iodide) (X) was taken up in methanol and treated twice with activated carbon. The filtrate was evaporated to a small volume and diluted with acetone, causing the salt to precipitate as needles. After crystallization from absolute alcohol the white needles darkened above 210° and melted at 229–231° dec.

Anal. Calcd. for $C_{12}H_{24}I_2N_2O$: C, 30.92; H, 5.19; N, 6.01. Found: C, 30.55; H, 5.28; N, 5.90.

Authentic X was prepared by quaternization of 2,5-bis-(dimethylaminomethyl)-furan[14] with excess methyl iodide. After three crystallizations from alcohol, the quaternary salt melted at 227–229° dec. A mixture melting point with the quaternary salt derived from 2,5-dimethylene-2,5-dihydrofuran was not depressed, and a comparison of the ultraviolet and infrared spectra of the two salts showed them to be the same compound.

5,5′-Ethylene-1,2-di-(2-furyl)-ethane (III).—Decomposition of the quaternary hydroxide from 40 g. (0.142 mole) of 5-methyl-2-furfuryltrimethylammonium iodide was carried out as above with the solid carbon dioxide–acetone-cooled trap containing 0.2 g. of hydroquinone and 15 ml. of absolute alcohol. On completion of the pyrolysis, an additional 25 ml. of absolute alcohol was added to the contents of the solid carbon dioxide trap. The resulting clear solution was gently refluxed, causing the 2,5-dimethylene-2,5-dihydrofuran to react exothermically with precipitation of a mixture of dimer and polymer. After 2 hours heating, the mixture was cooled, filtered, and the solid extracted with hexane in a Soxhlet extractor. The insoluble polymer weighed 0.54 g. From the hexane solution there was deposited 8.66 g. of white glossy dimer, m.p. 188–190° (sealed capillary). On concentrating the mother liquor to 20 ml., an additional 0.92 g. was obtained, this giving a 72% over-all yield of the dimer III from the quaternary iodide. After crystallization from ether the dimer melted at 189–190° (sealed capillary). The compound sublimed readily.

Anal. Calcd. for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43; mol. wt., 188.2; quant. hydrogenation, 0.043 g. H_2/g. (4 double bonds). Found: C, 76.69; H, 6.43; mol. wt., 190 (ebull. benzene); quant. hydrogenation (PtO_2),[6] 0.043 g. H_2/g.

The infrared spectrum (Nujol mull) of III showed bands at 5.96, 6.15, 6.27, 6.32 and 6.49 μ assigned to carbon–carbon double bonds along with strong unassigned bands at 8.60, 8.85, 9.95, 10.35, 10.47, 12.52 and 12.57 μ. The ultraviolet spectrum had $\lambda_{\max}^{\text{ethanol}}$ 222 mμ (ϵ 14,650). The proton magnetic resonance spectrum showed two types of hydrogen in the ratio of 2:1. The weaker peak at +54.4 c.p.s. was due to the ring protons while the stronger peak at −80 c.p.s. was assignable to the methylene protons.

Degradation of 5,5′-Ethylene-1,2-di-(2-furyl)-ethane (III) to Cyclododecane (V). A. Hydrogenolysis and Acetylation.—A mixture comprising 18.8 g. (0.1 mole) of the dimer, 75 ml. of dioxane and 10 g. of barium-activated copper chromite[27] was treated with hydrogen at 200 atm. pressure and 250° for 4 hours. After filtration, the solvent was removed under vacuum. Acetic anhydride (30 ml.) and a few drops of concentrated sulfuric acid were added to the residue and the mixture was then heated for 3 hours on a steam-bath. The resulting solution was poured into water and, after the excess acetic anhydride had been hydrolyzed, it was extracted with ether. The ether extract was washed with aqueous sodium carbonate solution and dried with anhydrous potassium carbonate. Removal of the ether and distillation of the residue gave a 9.6-g. fraction boiling over the range 75–120° (0.3–0.5 mm.).

B. Pyrolysis of Mixed Acetates.—The above mixture of acetates was added dropwise over 1 hour into a 25-mm. i.d. Vycor tube having a 300-mm. section packed with short pieces of Vycor tubing and heated to 500°. A slow stream of nitrogen was simultaneously passed through the pyrolysis tube. The condensed product was dissolved in ether and the solution washed with water, followed by aqueous sodium carbonate, and was dried over anhydrous sodium sulfate. Removal of the solvent and distillation of the residue gave 3.35 g. of colorless liquid, b.p. 99–111° (10 mm.). The infrared spectrum of an intermediate fraction, b.p. 99–104° (10 mm.), showed no absorption in the hydroxyl or carbonyl regions. The material appeared to be solely hydrocarbon possessing a *trans* double bond as suggested by a band at 10.35 μ. Gas chromatography on a Silicone 200–firebrick column at 200° employing a fairly fast flow rate showed a small sharp peak at 2.5 minutes followed by the main sharp peak at 10.5 minutes. The main component appeared to be about 95% of the charge.

C. Hydrogenation of Cycloölefins.—A 2.47-g. sample of the above cycloölefin mixture was dissolved in 100 ml. of 90% ethanol, 100 mg. of PtO_2 was added, and the mixture was hydrogenated in a modified low-pressure Parr apparatus at an initial pressure of 1.7 atm. When hydrogenation was complete, the mixture was filtered and the filtrate distilled to give 2.15 g. of colorless distillate, b.p. 104–109° (9 mm.). Repeated crystallization of the distillate from methanol–ethyl acetate gave cyclododecane as fine white needles, m.p. 61.5–62.5° (lit.[9] b.p. 104° (9 mm.), m.p. 61°). The infrared spectrum (KBr wafer) of the solid was that of a saturated hydrocarbon, and the lack of absorption at 7.25 μ indicated the absence of methyl groups. When sealed in glass, the compound gave an X-ray diffraction pattern with the longest spacing in the crystal of 7.02 Å. compared with the reported value of 7.05 Å. for cyclododecane.[10]

Anal. Calcd. for $C_{12}H_{24}$: C, 85.63; H, 14.37. Found: C, 85.68; H, 14.48.

Octahydro-5,5′-ethylene-1,2-di-(2-furyl)-ethane (VI).—A low-pressure Parr hydrogenation apparatus was charged with 9.4 g. (0.05 mole) of 5,5′-ethylene-1,2-di-(2-furyl)-ethane, 200 ml. of glacial acetic acid and 0.1 g. of PtO_2 and the mixture was hydrogenated at an initial pressure of 2 atm. After 1 hour absorption ceased and the accumulated pressure drop was 17 lb. corresponding to the absorption of 4 moles of hydrogen per mole of compound. The mixture was filtered and the solvent removed under vacuum. The soft residue of the crude octahydro derivative after washing with water and drying weighed 4.55 g. (46%). It was crystallized first from alcohol, then from hexane to give glossy white plates, m.p. 147.5–149°. The infrared spectrum (Nujol mull) was consistent with the expected structure. It possessed bands at 8.90 9.06 and 9.67 μ probably associated with –C–O–C– and medium unassigned bands at 10.18, 10.52, 11.25 and 12.6 μ. There was no absorption in the carbonyl or hydroxyl region nor in the ultraviolet.

Anal. Calcd. for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.00; H, 10.26.

Tetramethoxytetrahydro-5,5′-ethylene-1,2-di-(2-furyl)-ethane (VII).—A mixture of 1.88 g. (0.01 mole) of 5,5′-ethylene-1,2-di-(2-furyl)-ethane, 4.6 g. of freshly-fused potassium acetate and 50 ml. of reagent methanol was vigorously stirred and cooled to −5°. Over 15 minutes a cold solution of 3.60 g. of bromine in 25 ml. of reagent methanol was added through the dropping funnel. When the addition was complete, the cold mixture was filtered and the solid was triturated with 50 ml. of warm water containing a trace of sodium carbonate. After filtering and drying, the ketal weighed 2.66 g. (85%), m.p. 154–158.5°. When crystallized from ethyl acetate, it formed colorless needles, which melted at 159–160°.

Anal. Calcd. for $C_{16}H_{24}O_6$: C, 61.52; H, 7.75. Found: C, 61.74; H, 7.64.

The infrared spectrum (KBr wafer) of VII possessed bands at 3.25 (unsaturated CH), 3.39 and 3.52 (saturated CH), 6.17 (C=C), 8.63 and 8.92 (C–O–C) and strong unassigned bands at 9.98 and 10.13 μ. The ketal was insoluble in water, but on the addition of a trace of mineral acid the solid dissolved readily and the solution gave a strong carbonyl test with 2,4-dinitrophenylhydrazine reagent.

Tetramethoxyoctahydro-5,5′-ethylene-1,2-di-(2-furyl)-ethane (VIII).—Tetramethoxytetrahydro-5,5′-ethylene-1,2-di-(2-furyl)-ethane (19 g., 0.061 mole) dissolved in 100 ml. of dry dioxane was hydrogenated over 5 g. of Raney nickel at

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(27) W. A. Lazier and H. R. Arnold, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York. N. Y., 1943, p. 142.

136 atm. hydrogen pressure and room temperature. After 2 hours, hydrogen absorption ceased. The catalyst was separated by filtration, and the solvent was removed under reduced pressure, leaving 18 g. of crude product. After crystallization from methanol the octahydro derivative melted at 132–135°. The infrared spectrum (KBr wafer) had absorption bands at 3.39 and 3.53 (saturated CH), 9.30, 9.49 and 9.95 μ (C–O–C) and unassigned bands at 8.24, 10.37, 11.60 and 12.30 μ. There was no absorption in the double bond region.

Anal. Calcd. for $C_{16}H_{25}O_6$: C, 60.74; H, 8.92. Found: C, 61.48; H, 9.15.

5-Ethylidene-2-methylene-2,5-dihydrofuran (XII). Its Dimer and Polymer. A. 5-Ethyl-2-furfuryldimethylamine (XXIX).—A mixture of 39 g. (0.406 mole) of 2-ethylfuran,[8,20] 16.5 g. (0.55 mole) of paraformaldehyde, 44.8 g. (0.55 mole) of dimethylamine hydrochloride and 200 ml. of ethyl alcohol was refluxed for 4 hours with stirring. The alcohol was then removed under water-pump vacuum, the residue cooled and made basic with a solution of 24 g. of sodium hydroxide in 100 ml. of water. The organic layer was taken up in ether, the ether extract was washed with water and dried over anhydrous magnesium sulfate. Distillation gave 46 g. (74%) of the amine, b.p. 84–84.5° (25 mm.), $n^{25}D$ 1.4611.

Anal. Calcd. for $C_9H_{15}NO$: N, 9.14. Found: N, 8.84.

B. 5-Ethyl-2-furfuryltrimethylammonium Iodide (XXX).—To a solution of 44 g. (0.274 mole) of 5-ethyl-2-furfuryldimethylamine in 400 ml. of dry ether was slowly added excess methyl iodide. The quaternary salt precipitated quite rapidly. After stirring for 3 hours, the mixture was filtered and the salt washed with ether and dried at 70° under vacuum. It weighed 84 g. (99%) and melted at 102–103°.[20] Crystallization from ethyl acetate–ethanol did not change the melting point.

Anal. Calcd. for $C_{10}H_{18}INO$: C, 40.69; H, 6.15; N, 4.75. Found: C, 40.55; H, 6.11; N, 4.75.

C. Decomposition of 5-Ethyl-2-furfuryltrimethylammonium Hydroxide (XI). Formation of 5-Ethylidene-2-methylene-2,5-dihydrofuran (XII) and Its Dimer.—A solution of 29.5 g. (0.1 mole) of 5-ethyl-2-furfuryltrimethylammonium iodide and 50 ml. of water was shaken with 23 g. (100% excess) of silver oxide for 1 hour. The mixture was then filtered under nitrogen and the water removed from the filtrate at a maximum temperature of 30° under oil-pump vacuum. The residue was subjected to decomposition at 50–100° under 150 to 3 mm. pressure; excessive foaming caused difficulty in controlling the vacuum. When decomposition was complete, the 5-ethylidene-2-methylene-2,5-dihydrofuran contained in the solid carbon dioxide-cooled receiver was extracted with ether and the extract dried with anhydrous magnesium sulfate. Upon removal of the ether and heating to approximately 100°, the residue polymerized to a semi-solid mixture. This was extracted with absolute alcohol leaving a somewhat rubbery polymeric material which formed a viscous melt above 70° and turned light yellow in air.

The above alcoholic extract on cooling deposited white, fluffy needles that softened below 100° and melted over the range 110–140°. After crystallization from absolute alcohol, with considerable loss, the resulting needles of the dimer melted over the range 132–143° with softening beforehand. The material was soluble in benzene and in ethyl acetate.

Anal. Calcd. for $C_{14}H_{16}O_2$: C, 77.72; H, 7.45; mol. wt., 216. Found: C, 77.51; H, 7.53; mol. wt., 209 (ebull. benzene).

The dimer mixture sublimed readily at 100° (0.1 mm.), and the sublimate melted at 138–144° with shrinking above 100°. By repeated crystallization from alcohol the melting point was raised to 146–148°. The infrared spectrum (Nujol mull) of the material melting over the range 138–144° had bands at 3.27 (unsaturated CH), 6.00, 6.27 and 6.47 μ (C=C), with the remaining major bands being essentially identical to those of 5,5′-ethylene-1,2-di-(2-furyl)-ethane. The ultraviolet spectrum had $\lambda_{\max}^{\text{ethanol}}$ 222 mμ (ε 14,880).

5-Benzylidene-2-methylene-2,5-dihydrofuran Dimer and Polymer. A. 5-Benzyl-2-furfuryldimethylamine (XXXII).—A mixture of 7 g. (0.0443 mole) of 2-benzylfuran,[21] 5 g. (0.0613 mole) of dimethylamine hydrochloride, 2 g. (0.0667 mole) of paraformaldehyde and 25 ml. of alcohol was refluxed with stirring for 3 hours. The solvent was then removed from the clear solution, and the residue was treated with a solution of 2 g. of sodium hydroxide in 10 ml. of water. The resulting oil was extracted with ether, the extract washed twice with water and dried with anhydrous magnesium sulfate. After removal of the solvent the residue was distilled to give 5.87 g. (61.5%) of colorless product boiling largely at 115–117° (1.5 mm.). On redistillation the compound boiled at 121° (2.1 mm.), $n^{25}D$ 1.5298.

Anal. Calcd. for $C_{14}H_{17}NO$: C, 78.10; H, 7.96; N, 6.51. Found: C, 77.82; H, 8.00; N, 6.78.

The infrared spectrum of this compound indicated it to be a 2,5-disubstituted furan.[8] It showed absorption at 3.26 and 3.30 (unsaturated CH), 3.41, 3.50 3.56 and 3.60 (saturated CH), 6.23, 6.30, 6.44 and 6.74 (conjugated C=C) and 9.85 μ (C–O–C), as well as strong bands at 12.71 and 14.20 μ.

B. 5-Benzyl-2-furfuryltrimethylammonium Iodide (XXXIII).—A solution of 5.87 g. (0.0273 mole) of 5-benzyl-2-furfuryldimethylamine in 100 ml. of absolute ether was treated with excess methyl iodide while cooling in an ice-bath. The quaternary iodide precipitated rapidly. After 3 hours it was filtered, washed with ether and dried. The salt weighed 9 g. (93%) and when crystallized from absolute alcohol melted at 140–141°.

Anal. Calcd. for $C_{15}H_{20}INO$: C, 50.43; H, 5.64; N, 3.92. Found: C, 50.38; H, 5.81; N, 3.98.

C. Decomposition of 5-Benzyl-2-furfuryltrimethylammonium Hydroxide (XIII). Formation of Dimer and Polymer.—A warm solution of 9 g. of 5-benzyl-2-furfuryltrimethylammonium iodide in 40 ml. of water was agitated for 1 hour with 5.8 g. (100% excess) of silver oxide. The mixture was then filtered under nitrogen and the precipitate washed with water. The filtrate, which was free of iodide ion, was concentrated under oil-pump pressure at a maximum temperature of 30°. When the last of the water had been removed, the residue decomposed with the evolution of trimethylamine and the formation of a solid residue. This residue was heated in an oil-bath up to 150°, but there was no further evidence of decomposition. Extraction, first with water at 60° and then with methanol in a Soxhlet extractor, left 3 g. (70%) of insoluble polymer which softened above 75° to a viscous melt.

The methanol extract was evaporated to dryness and the semi-solid residue crystallized from alcohol to give 0.25 g. (6%) of dimer as brown needles, m.p. 182–186°. Recrystallization from absolute alcohol using decolorizing carbon gave white needles, m.p. 182–186°.

Anal. Calcd. for $C_{24}H_{20}O_2$: C, 84.68; H, 5.92; mol. wt., 340.4. Found: C, 84.68; H, 6.07; mol. wt., 339.

5-Methyl-4-ethoxycarbonyl-2-furfuryltrimethylammonium Chloride (XV). A. Ethyl 2-Methyl-3-furoate (XXXIV) was prepared by modification of the procedure of Benary.[22] A mixture of 250 ml. of pyridine and 130 g. (1 mole) of ethyl acetoacetate was stirred while 185 g. (*ca.* 1 mole) of 40–45% aqueous chloroacetaldehyde was added over about a 10-minute period. The mixture was stirred for 4 hours, during which time the temperature rose to 50° then slowly subsided. After standing overnight, the layers were separated and the organic layer was washed twice with water, dried with calcium chloride and distilled. There was obtained 97 g. (63%) of crude ester boiling at 80–85° (16 mm.), $n^{25}D$ 1.4600. This material was contaminated with ethyl acetoacetate but was satisfactory for subsequent reaction. Material purified by treatment with formaldehyde was found to be analytically pure, b.p. 81–84° (18 mm.), $n^{25}D$ 1.4620.

B. Ethyl 5-Chloromethyl-2-methyl-3-furoate (XXXV).—Dry hydrogen chloride was passed into a stirred mixture of 44.5 g. (0.288 mole) of ethyl 2-methyl-3-furoate, 9 g. (0.30 mole) of paraformaldehyde and 150 ml. of methylene chloride at room temperature. There was a slight exothermic reaction, and the temperature was maintained at 25–30° by intermittent cooling. After 45 minutes, the paraformaldehyde had dissolved and the reaction mixture was then poured into ice-water. The organic layer was separated, washed with water and dried with anhydrous sodium carbonate. Distillation gave a forerun of unreacted starting material followed by 17 g. (29%) of the chloromethyl derivative, b.p. 105–108° (1.2–1.8 mm.). The colorless liquid crystallized on cooling, m.p. 38–39.5°.

Anal. Calcd. for $C_9H_{11}ClO_3$: Cl, 17.50. Found: Cl, 17.40.

The thiouronium salt was obtained by refluxing 0.5 g. of the chloromethyl compound with 0.2 g. of thiourea in 15 ml. of absolute alcohol for 3 hours. The reaction mixture was diluted with five volumes of ether and cooled in ice. The precipitated thiouronium salt weighed 0.5 g. and melted at 168–170°.

Anal. Calcd. for $C_{10}H_{15}ClN_2O_3S$: N, 10.05. Found: N, 10.37.

C. 5-Methyl-4-ethoxycarbonyl-2-furfuryltrimethylammonium Chloride (XV) and the Corresponding Betaine.—A solution of 16 g. (0.079 mole) of the above chloromethyl compound in 200 ml. of dry ether was saturated with trimethylamine. After standing overnight the mixture was filtered, the solid washed with ether and dried at 70° under vacuum. The quaternary chloride weighed 17 g. (83%) and on crystallization from methyl ethyl ketone melted at 160–165°.

Anal. Calcd. for $C_{12}H_{20}ClNO_3$: N, 5.35. Found: N, 4.88.

A solution of 9.63 g. (0.0368 mole) of the above quaternary chloride in 40 ml. of methanol was treated with the calculated quantity of a 3.32 molar solution of potassium hydroxide in methanol. The precipitated potassium chloride was removed by filtration and the solvent was distilled from the filtrate at a temperature below 20°. The residue was then heated at 140° for 30 minutes while under 3 mm. pressure. There was no evidence of decomposition. The dark residue was still completely water soluble and hygroscopic. It weighed 6.0 g. and melted over the range of 160–200°. This product appeared to be largely the betaine resulting from hydrolysis of the ester.

2,3-Dimethylene-2,3-dihydrofuran Dimer (XIX or XX) and Polymer XVIII. A. 2-Methyl-3-hydroxymethylfuran (XXXVI).—A mixture of 5 g. (0.132 mole) of lithium aluminum hydride and 200 ml. of anhydrous ether was stirred for 15 minutes, then a solution of 30.8 g. (0.20 mole) of ethyl 2-methyl-3-furoate in 200 ml. of anhydrous ether was added over a period of 1.5 hours. The mixture refluxed gently during the addition. After all of the ester had been added, stirring was continued for 1 hour, then 10 ml. of ethyl acetate was slowly added. When decomposition of the residual lithium aluminum hydride was complete, 180 ml. of 10% sulfuric acid was added with stirring and the two phases were separated. The ether layer was dried with anhydrous potassium carbonate and distilled. There was obtained 18.5 g. (83%) of colorless, pleasant-smelling liquid boiling largely at 70° (7 mm.), $n^{25}D$ 1.4840.

Anal. Calcd. for $C_6H_8O_2$: C, 64.27; H, 7.19. Found: C, 64.27; H, 7.32.

B. 2-Methyl-3-chloromethylfuran (XXXVII).—In a flask protected with a drying tube was charged 30 g. (0.268 mole) of 2-methyl-3-hydroxymethylfuran, 26 g. (0.33 mole) of pyridine and 75 ml. of anhydrous ether. Over a period of one hour, there was added dropwise to the reaction mixture a solution of 35 g. (0.294 mole) of thionyl chloride in 30 ml. of hexane while the temperature was maintained below 15°. The mixture was then permitted to warm to room temperature over a period of 1 hour, cooled to 0° and 50 ml. of water followed by 10 ml. of concentrated hydrochloric acid in 50 ml. of water were slowly added. The ether layer was separated and the aqueous layer extracted with ether. The combined ether solutions were washed with cold 10% aqueous sodium hydroxide and dried with anhydrous potassium carbonate. On distillation there was obtained 17 g. (48.5%) of colorless liquid, 2-methyl-3-chloromethylfuran, b.p. 57–59° (16 mm.), $n^{25}D$ 1.4850. This compound decomposed quite rapidly at room temperature; within 24 hours it had become a black viscous tar.

C. 2-Methyl-3-furylmethyltrimethylammonium Chloride (XXXVIII).—A solution of 8.8 g. (0.0676 mole) of freshly prepared 2-methyl-3-chloromethylfuran dissolved in 200 ml. of absolute ether was saturated with dry trimethylamine while being protected from moisture by a calcium chloride drying tube. The mixture was permitted to stand for 24 hours, after which the very hygroscopic quaternary salt was isolated by filtration in a dry-box and was washed with ether. There was obtained 8.8 g. (69%), m.p. 141–143°.

Anal. Calcd. for $C_9H_{16}ClNO$: N, 7.39. Found: N, 7.43.

D. Decomposition of 2-Methyl-3-furylmethyltrimethylammonium Hydroxide (XVI). Formation of Dimer XIX or XX and Polymer XVIII.—A solution of 8 g. (0.0422 mole) of 2-methyl-3-furylmethyltrimethylammonium chloride in 50 ml. of water was tumbled with 9.5 g. (100% excess) of silver oxide for 1 hour. The mixture was filtered under nitrogen and the filtrate charged to a flask along with 250 ml. of toluene and 0.2 g. of phenothiazine. With vigorous stirring, the water was removed by azeotropic distillation. When all of the water had been removed, the quaternary hydroxide decomposed with the elimination of trimethylamine and water. Refluxing was continued for 1 hour, then the mixture was filtered while hot to remove a trace of haziness and the solvent removed under water-pump vacuum. The solid residue was crystallized from absolute alcohol. There was obtained 1.50 g. of off-white product, m.p. 48–50°. A second crop, 0.60 g., m.p. 42–45°, was obtained by concentrating the mother liquor. This corresponds to a total yield of 2.10 g. (53%) of crude dimer. An analytical sample was obtained by sublimation at 100° (3 mm.). The sublimed material melted at 54–55° and crystallized from methanol as coarse needles with unchanged melting point. The infrared spectrum (Nujol mull) had bands at 6.17, 6.25, 6.41 and 6.61 μ for C=C, a band at 9.55 μ for C–O–C and unassigned strong bands at 11.18, 13.58 and 13.73 μ along with numerous weak bands. The ultraviolet spectrum had $\lambda_{max}^{ethanol}$ 220 mμ (ϵ 12,030).

Anal. Calcd. for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43; mol. wt., 188.2. Found: C, 76.61; H, 6.77; mol. wt. (ebull. C_6H_6), 164.

By decomposition of the quaternary ammonium hydroxide at 70° under a pressure of 3 mm., there was collected in a solid carbon dioxide–acetone-cooled receiver a mixture of the above dimer and a very small amount of polymer XVIII. The polymer was white in color, softened above 70°, but was viscous up to a temperature of 200°.

2,5-Dimethylene-2,5-dihydrothiophene Dimer (XXIII) and Polymer XXII.—Dry trimethylamine was slowly bubbled into a stirred solution of 20 g. (0.137 mole) of 5-methyl-2-thenyl chloride[25] in anhydrous ether. When saturated with trimethylamine, the mixture, protected from moisture with a drying tube, was allowed to stand for 24 hours. It was then filtered in a dry nitrogen atmosphere and the precipitate dried at 70° under vacuum. There was obtained 23 g. (82%) of 5-methyl-2-thenyltrimethylammonium chloride, m.p. 225–226° dec. The salt was soluble in water and in absolute alcohol but insoluble in acetone.

Anal. Calcd. for $C_9H_{16}ClNS$: Cl (ionic), 17.23. Found: Cl (ionic), 17.23.

The above 5-methyl-2-thenyltrimethylammonium chloride (23 g.) was converted to the quaternary hydroxide in the usual fashion employing 15.5 g. of silver oxide. After filtration, the water was removed from the aqueous solution at a maximum temperature of 30°. The residue was heated to 150° (3 mm.) for 10 minutes, during which time the quaternary hydroxide decomposed with the formation of polymer in the decomposition flask. The polymer softened about 140°, darkened above that temperature, and was soft and rubbery at 220°.

The distillate from the quaternary hydroxide decomposition was collected in a small solid carbon dioxide–acetone-cooled receiver containing 25 ml. of absolute alcohol and 0.1 g. of hydroquinone. It consisted of a liquid phase with a very small amount of white, insoluble film at the surface of the liquid. The entire contents of the receiver was heated to gentle reflux for 1 hour, cooled and filtered. Sublimation of the precipitate resulted in the isolation of a few milligrams of the dimer, whose preparation is described in the next paragraph. The unsublimable polymer softened at 140° and was rubbery at 220°. It was insoluble in boiling toluene and was light tan in color.

Anal. Calcd. for $(C_6H_6S)_x$: C, 65.44; H, 5.49; S, 29.06. Found: C, 64.98; H, 5.53; S, 28.49.

Isolation of the dimer XXIII was achieved by decomposition of the hydroxide in the presence of an inhibitor. An aqueous solution containing 0.141 mole of the quaternary hydroxide in approximately 100 ml. of water was charged to a flask containing 0.2 g. of phenothiazine and 400 ml. of toluene. Removal of the water from this solution by azeotropic distillation caused decomposition of the quaternary hydroxide. When the reaction was complete, the hot toluene solution was filtered to give a small amount of polymer. Evaporation of the filtrate under vacuum left the dimer as a white solid. This was crystallized from acetone to give 3.0

g. (19%) of white needles, m.p. 188–192° with softening beforehand. Crystallization from ether formed fine, white needles, m.p. 194.5–196°. The infrared spectrum (Nujol mull) contained a band at 6.32 μ assigned to C=C and strong unassigned bands at 8.15, 8.38, 9.16, 9.85, 12.34 and 12.54 μ. The ultraviolet spectrum had $\lambda_{\max}^{\text{ethanol}}$ 245 (7,700) and 275 mμ (ε 5,720). The proton magnetic resonance spectrum showed two types of hydrogen in the ratio of 2:1. The weaker peak at +73 c.p.s. resulted from the ring protons while the stronger peak at −66 c.p.s. was due to the methylene protons.

Anal. Calcd for $C_{12}H_{12}S_2$: C, 65.44; H, 5.49; S, 29.06; mol. wt., 220. Found: C, 65.54; H, 5.54; S, 29.05; mol. wt. (ebull. C_6H_6), 211.

2,3-Dimethylene-2,3-dihydrothiophene Polymer. A. 3-Methyl-2-hydroxymethylthiophene (XL).—A solution of 7.1 g. (0.188 mole, 50% excess) of sodium borohydride in 150 ml. of acetone-free methanol was treated dropwise over 45 minutes with 63 g. (0.5 mole) of 3-methyl-2-thenaldehyde.[23] The mixture was stirred and cooled during the addition to keep the temperature between 25 and 35°. After stirring for 2 hours at room temperature, 20 ml. of acetone was added and the mixture was stirred an additional 15 minutes. The solvent was then removed under vacuum, and a solution of 16.5 g. of sodium hydroxide in 75 ml. of water was added to the residue. The resulting mixture was stirred and heated to 60° for 30 minutes, cooled and the layers separated. The aqueous phase was extracted with ether and the extract added to the organic phase. The ether solution was washed two times with water, dried with magnesium sulfate and distilled. There was obtained 33 g. (51.5%) of the alcohol, b.p. 103–104° (13 mm.), $n^{25}D$ 1.5558.

Anal. Calcd. for C_6H_8OS: C, 56.24; H, 6.29. Found: C, 57.00; H, 6.45.

B. 3-Methyl-2-thenyl Chloride[24] (XLI).—A solution of 32 g. (0.25 mole) of 3-methyl-2-hydroxymethylthiophene in 150 ml. of reagent benzene was treated with 51 g. of thionyl chloride over a 20-minute period, during which time the temperature was kept below 30° by cooling. The mixture was stirred for 1 hour at room temperature, and the solvent was then removed under water-pump vacuum. The black residue was distilled in a small Vigreux still. There was obtained 29 g. (79%) of colorless liquid, b.p. 80–83° (12–13 mm.). This compound was quite unstable; on standing overnight at room temperature, it turned black and became largely solid. For the preparation of the quaternary salt, the compound was used immediately after distillation.

C. 3-Methyl-2-thenyltrimethylammonium Chloride (XLII).—A solution of 29 g. of freshly distilled 3-methyl-2-thenyl chloride in 300 ml. of anhydrous ether was saturated with dry trimethylamine and then permitted to stand for 2 days at room temperature. The hygroscopic quaternary chloride was isolated by filtration in a dry-box followed by washing with ether. After drying at 70° under vacuum there was obtained 38 g. (92.5%) of the salt melting at 163–168° dec. The salt was crystallized from acetonitrile, m.p. 167–169° dec.

Anal. Calcd. for $C_9H_{16}ClNS$: Cl, 17.23; N, 6.81; S, 15.58. Found: Cl, 18.04; N, 6.98; S, 15.22.

D. 2,3-Dimethylene-2,3-dihydrothiophene Polymer.—A solution of 20.6 g. (0.1 mole) of 3-methyl-2-thenyltrimethylammonium chloride in 50 ml. of water was tumbled with 23.1 g. (0.1 mole) of silver oxide for 1 hour. The solution was filtered under nitrogen through a sintered glass filter employing a filter aid. The water was then removed from the filtrate at a maximum temperature of 30° under oil-pump vacuum. The thick, black residue was subjected to decomposition at 3–6 mm. pressure and up to 150° bath temperature. When the decomposition was complete, a solid carbon dioxide–acetone-cooled trap connected to the decomposition flask contained a small amount of polymer deposited as a film along the edges of the trap. The white polymer became transparent above 70° and was viscous at 160°.

Anal. Calcd. for $(C_6H_6S)_x$: C, 65.44; H, 5.49. Found: C, 64.98; H, 5.54.

Decomposition of *p*-Methylbenzyltrimethylammonium Hydroxide (XXV). Formation of [2.2] Paracyclophane[2,3] (XXVII) and Poly-p-xylylene (XXVI).—*p*-Methylbenzyltrimethylammonium bromide was obtained by quaternization of *p*-methylbenzyl bromide[28] (m.p. 35.5–36°) in ether solution with excess trimethylamine. The non-hygroscopic salt was obtained in 94% yield, m.p. 198–200° dec. It can be crystallized from alcohol or acetonitrile but holds the latter solvent tenaciously.

Anal. Calcd. for $C_{11}H_{18}NBr$: N, 5.74; Br, 32.73. Found: N, 5.86, 5.57; Br, 32.64, 32.73.

The quaternary hydroxide solution prepared from 24.4 g. (0.1 mole) of *p*-methylbenzyltrimethylammonium bromide and 23 g. of silver oxide in 75 ml. of water was treated with 300 ml. of toluene and 0.5 g. of phenothiazine. The mixture was refluxed with stirring and the water was separated by azeotropic distillation. When all of the water had been removed, the quaternary hydroxide decomposed with formation of a solid. Heating was continued for an additional 15 minutes after evolution of trimethylamine had ceased, and the solid was then extracted in a Soxhlet extractor, employing the toluene used as the reaction medium. The insoluble poly-*p*-xylylene left from the extraction weighed 5.7 g. (55%). Concentration of the toluene extract to approximately 20 ml. and cooling gave 1.75 g. (17%) of acetone-washed dimer. When crystallized from glacial acetic acid, the [2.2] paracyclophane melted at 285–287° (sealed tube), and its X-ray diffraction pattern agreed with that of authentic material[29] prepared by the pyrolysis of *p*-xylene.

Alkaline Decomposition of *p*-Methylbenzyltrimethylammonium Chloride.[30]—A mixture of 212 g. of sodium hydroxide, 200 ml. of water and 100 ml. of xylene was heated to reflux. With vigorous stirring, a solution of 50 g. (0.25 mole) of *p*-methylbenzyltrimethylammonium chloride dissolved in 50 ml. of water was added dropwise during 45 minutes and the mixture was stirred at reflux for an additional 45 minutes. Solid separated throughout the addition. The slurry was cooled, filtered through a sintered glass filter, and the white solid was washed on the filter with water. The filtrate, which consisted of two layers, was extracted with toluene and the extract dried over sodium sulfate. The moist solid polymer was dried azeotropically with toluene and then extracted in a Soxhlet apparatus with this solvent for 12 hours. The undissolved polymer amounted to 17.5 g. (68%) of fluffy white solid. The combined extracts from this solid and from the filtrate were concentrated to dryness to give a white solid residue of [2.2] paracyclophane which after washing with acetone amounted to 2.50 g. (10%), m.p. 283–285° (sealed tube).

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(28) E. F. J. Atkinson and J. F. Thorpe, *J. Chem. Soc.*, **91**, 1697 (1907).

(29) C. J. Brown, *ibid.*, 3265 (1953).

(30) This method of preparing [2.2]paracyclophane was developed by Drs. F. D. Marsh and T. E. Young of this Laboratory, compare British Patent 807,196 (1959); treatment of refluxing *p*-xylene with a one-half molar quantity of chlorine in the presence of ultraviolet light gave *p*-methylbenzyl chloride in 61% yield, b.p. 91–92° (20 mm.), f.p. 4.97–5.57°. (*Anal.* Calcd. for C_8H_9Cl: C, 68.40; H, 6.45; Cl, 25.22. Found: C, 68.29, 68.19; H, 6.76, 6.53; Cl, 25.12) which with excess trimethylamine in methyl ethyl ketone at 20–30° gave the quaternary chloride in 98% yield, m.p. 224–225° (*Anal.* Calcd. for $C_{11}H_{18}NCl$: C, 66.14; H, 9.09; N, 7.02. Found: C, 66.50; H, 9.02; N, 7.01).