sulfur and fluorine. This gas had a density which corresponded to molecular weight 107. The theoretical molecular weight of sulfur tetrafluoride is 108. The percentage of sulfur by weight was found to be 29.2, 29.7 and 29.3 for three determinations. The theoretical value for sulfur tetrafluoride is 29.6%. The percentage of fluorine by weight was found to be 67.2 and 67.4 for two determinations. The theoretical value for SF_4 is 70.4%.

A sample of $CSHF_7$ was decomposed by spark-over discharge in order to learn the nature of the decomposition products. No voltage measurements were taken. Boiling point measurements made on the mixture of decomposition products indicated the presence of carbon tetrafluoride, fluoroform and sulfur tetrafluoride. A considerable amount of free sulfur was deposited on the walls of the glass reaction flask.

Carbon disulfide was allowed to react with cobalt trifluoride at 200–250° in the manner described above for methyl mercaptan. As was the case with the mercaptan, a mixture of products was obtained. A 40% yield of CF_3SF_5 was obtained by this method. Sulfur hexafluoride and carbon tetrafluoride were the only other compounds present in sufficient quantities for separation and identification. Traces of the lower sulfur fluorides were thought to be present because of the odor of the mixture of reaction products.

Acknowledgment.—The authors wish to thank Drs. L. L. Burger, E. J. Barber and Mr. K. B. Kellogg for the use of apparatus constructed by them. Gratitude is also expressed to Mr. F. S. Linn and Dr. R. Geballe for electrical breakdown measurements made on CF_3SF_5. This work was performed under contract with the Office of Naval Research, U. S. Navy Department.

Summary

Methyl mercaptan was fluorinated by cobalt trifluoride at 250° and by the action of an excess of fluorine, diluted with nitrogen, in the presence of copper turnings coated with silver fluorides, at 200°. Both methods produced trifluoromethylsulfur pentafluoride, CF_3SF_5, as one of the products. The second method produced what is regarded as a mono-hydrogen derivative, $CSHF_7$. A preparative method which gave the highest yield of trifluoromethylsulfur pentafluoride was the reaction of carbon disulfide with cobalt trifluoride at approximately 250°.

Trifluoromethylsulfur pentafluoride boils at $-20.4°$, melts at $-86.9 \pm 0.2°$ and has a transition point at $-153.3 \pm 0.3°$. No evidence was found for the reaction of the gas with 6 N sodium hydroxide at room temperature. This gas reacts rapidly with alkali metals only at dull red heat. It is a very good gaseous insulator at low pressure, but is decomposed by spark-over discharge, yielding carbon tetrafluoride and sulfur tetrafluoride.

$CSHF_7$ boils at 5.1° and melts at approximately $-87°$. It reacts rapidly with 6 N sodium hydroxide at room temperature, all the fluorine atoms being removed.

SEATTLE 5, WASH. RECEIVED JANUARY 13, 1950

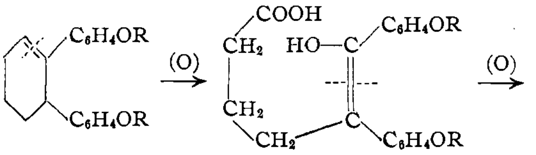
[CONTRIBUTION NO. 73 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TENNESSEE]

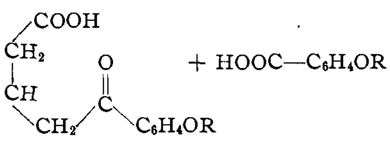
1,2- and 2,3-Bis-(*p*-methoxyphenyl)-cyclohexene

BY GEORGE P. MUELLER AND DONALD PICKENS

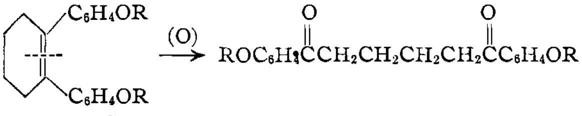
The reaction of *p*-methoxyphenylmagnesium bromide with either 2-chlorocyclohexanone or 2-*p*-methoxyphenylcyclohexanone followed by mild acid hydrolysis of the magnesium salts has yielded two disubstituted cyclohexenes directly. These were designated as isomers Ia and IIa in the order of their isolation and tentatively assigned the formulas 1,2- and 2,3-bis-(*p*-methoxyphenyl)-cyclohexene, respectively.[1] The true structures of these isomers are exactly opposite to this assignment.

Oxidation of the isomer Ia has now yielded anisic acid together with γ-*p*-methoxybenzoylbutyric acid; the isomer IIa has given 1,4-bis-(*p*-methoxybenzoyl)-butane.





Ia, R = CH_3
Ib, R = H



IIa, R = CH_3
IIb, R = H

It seems helpful to summarize here the compounds reported in the previous paper about which any confusion could exist.

The mixture of cyclohexenes was obtained in 20% yield, of which about 95% was Ia and 3% IIa. The suggestion that alkaline demethylation of the former gave rise to IIb, in addition to Ib,

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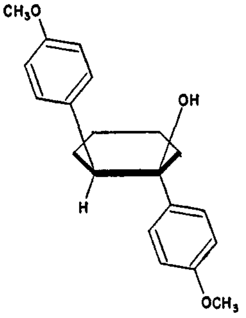
[1] Mueller and May, THIS JOURNAL, **71**, 3313 (1949).

	M. p., °C.	95% alc. max.	*E* (× 10⁻³)
Series I			
2,3-Bis-(*p*-methoxyphenyl)-cyclohexene	88.8–89.8	230 256	16.05 16.05
2,3-Bis-(*p*-hydroxyphenyl)-cyclohexene	171.0–173.5	231 260	11.86 13.61
2,3-Bis-(*p*-acetoxyphenyl)-cyclohexene	140.5–141.5	...	...
Series II			
1,2-Bis-(*p*-methoxyphenyl)-cyclohexene	90.8–91.4	226 277	18.20 3.30
1,2-Bis-(*p*-hydroxyphenyl)-cyclohexene	226.6–228.6	227 280	13.79 3.19
1,2-Bis-(*p*-acetoxyphenyl)-cyclohexene	149.0–150.4	...	...

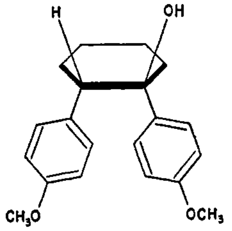
through isomerization of the double bond into the symmetrical and more fully conjugated position is now substantiated by the proof of these structures. It was this suspected isomerization that led us first to ozonize the less obtainable IIa.

Isolation of satisfactory oxidation products of Ia followed only after oxidation with potassium permanganate at room temperature, keeping the *p*H near 8 and using purified dioxane as solvent. Separation of the carbonyl components[2] and partition of the acids between ether and saturated sodium bicarbonate finally yielded two of the expected acids, although no δ-*p*-methoxyphenyl-δ-*p*-methoxybenzoylvaleric acid was isolated. Previous attempts employing various oxidizing agents[3] were all without success, for anisic acid and the original compound were the only pure products isolated from any of these experiments. Difficulty in degrading cyclohexenes has been encountered before where cleavage of the double bond results in an enolic system which itself may be oxidized, etc.[4] Therefore, after observing that permanganate oxidation of allyldesoxyanisoin yielded 4,4′-dimethoxydesylacetic acid and anisic acid,[5] we surmised from our isolation of the latter that the other product ought to be γ-*p*-methoxybenzoylbutyric acid, but that this keto acid was in turn being degraded in the alkaline medium to water-soluble acids. We therefore adopted a modified procedure with success.

Formation of the two olefins in the relative amounts actually obtained was contrary to expectations. The assumption that both carbinols III and IV were present as intermediates and that each was dehydrated to a different cyclohexene explains the nature of the products but requires predominance of the one carbinol yielding the major product, 2,3-bis-(*p*-methoxyphenyl)-cyclohexene. The reasonable view that *p*-methoxyphenylmagnesium bromide adds preferentially to the unhindered side of the ketone suggests III as the principal carbinol which, however, should yield 1,2-bis-(*p*-methoxylphenyl)-cyclohexene because the hydrogen atom and hydroxyl group are both *trans* and tertiary. Since the latter was in fact observed only as the minor product, another explanation is required, for even though we grant that the adjacent secondary hydrogen atom is also available for elimination, such a reaction is less probable. Formation of the more highly substituted olefin seems, for example, to be the preferred course of dehydration of the acyclic analog, 3,4-bis-(*p*-methoxyphenyl)-hexan-3-ol.[6] If in seeking another explanation we continue to assume *trans* elimination of water,[4b,4c] then the carbinol must have had the *cis* structure, IV. This explanation is not entirely satisfactory and the problem is still under study.



III



IV

Ultraviolet absorption spectra of the various cyclohexenes and derivatives confirm the structures shown by oxidation. For example, 2,3-bis-(*p*-methoxyphenyl)-cyclohexene, Fig. 1, shows the styrene[7] type of spectrum with due allowance for the bathochromic effect of substituents. Thus, the maximum is almost identical with that of anethole.[8] Again comparing, in Fig. 2, 1,2-bis-(*p*-methoxyphenyl)-cyclohexene with *cis*-stilbene[9] we find in both cases the same broad peaks lying at longer wave lengths. Although *cis*-stilbene lies toward the visible region with respect to styrene, its broad peak is at shorter wave lengths than that of *trans*-stilbene due to the non-coplanarity of the two phenyl groups.[10] The bathochromic shift of the 1,2-isomer with respect to the 2,3-bis-(*p*-methoxyphenyl)-cyclohexene is much smaller than found in the styrene–*cis*-stilbene comparison. This is probably due to the greater constraint offered by the cyclohexene ring so that the aryl groups are more crowded in 1,2-bis-(*p*-methoxyphenyl)-cyclohexene, for example, than in *cis*-stilbene.

Figure 3 shows the spectra of cyclohexestrol[1] and its dimethyl ether. These curves have maxima at wave lengths nearly identical with those

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(2) Girard and Sandulesco, *Helv. Chim. Acta*, **19**, 1095 (1936).

(3) *Cf.* Campbell, Dodds and Lawson, *Proc. Roy. Soc.* (*London*), **B128**, 253 (1940); Milas and Sussman, THIS JOURNAL, **59**, 2347 (1937); Meisenheimer, *Ber.*, **54**, 3206 (1921).

(4) *Cf.* (a) Huckel, Neunhoeffer, Gercke and Frank, *Ann.*, **477**, 99 (1929); (b) Price, THIS JOURNAL, **61**, 1847 (1939); (c) Price and Karabinos, *ibid.*, **62**, 1159 (1940).

(5) Golberg and Robinson, *J. Chem. Soc.*, 575 (1941).

(6) Wessely, Kerchbaum, Kleedorfer, Prillinger and Zajic *Monatsh.*, **73**, 127 (1940).

(7) Rodebush and Feldman, THIS JOURNAL, **68**, 896 (1946).

(8) Kharasch and Kleiman, *ibid.*, **65**, 11 (1943).

(9) Solmssen, *ibid.*, **65**, 2373 (1943).

(10) Jones, *ibid.*, **65**, 1818 (1943).

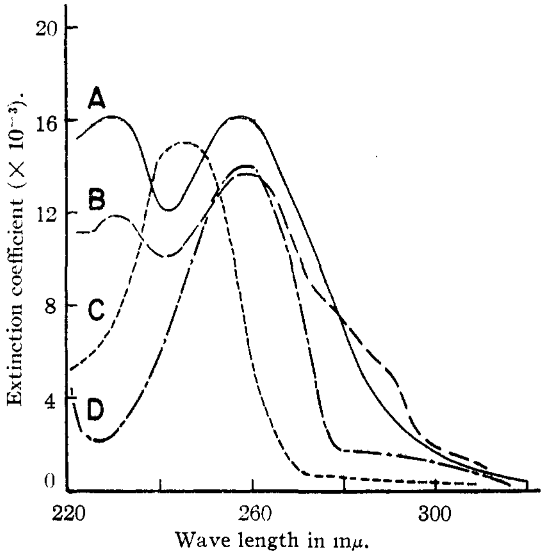

Fig. 1.—Ultraviolet absorption spectra of 2,3-bis-(*p*-methoxyphenyl)-cyclohexene, A; 2,3-bis-(*p*-hydroxyphenyl)-cyclohexene, B; styrene, C; anethole, D.

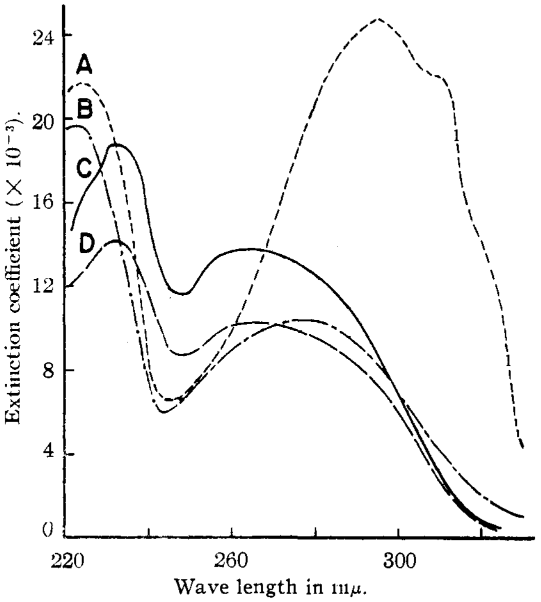

Fig. 2.—Ultraviolet absorption spectra of *trans*-stilbene, A; *cis*-stilbene, B; 1,2-bis-(*p*-methoxyphenyl)-cyclohexene, C; 1,2-bis-(*p*-hydroxyphenyl)-cyclohexene, D.

given for hexestrol[8] and its dimethyl ether.[11] Also compared were the spectra, Fig. 4, of 4′,4″-dimethoxy-*o*-terphenyl and 4′,4″-dihydroxy-*o*-terphenyl,[12] used earlier in proving the structures of the cyclohexestrol intermediates, with *o*-terphenyl[13] itself. Again, allowing for bathochromic effects, the curves have essentially the same form.

[11] Kaiser and Koenig, This Journal, **68**, 740 (1946).

[12] Price and Mueller, *ibid.*, **66**, 632 (1944).

[13] Pickett, Walter and France, *ibid.*, **58**, 2296 (1936). The curve shown in Fig. 4 was reproduced from unpublished results kindly made available by Dr. C. E. Crompton.

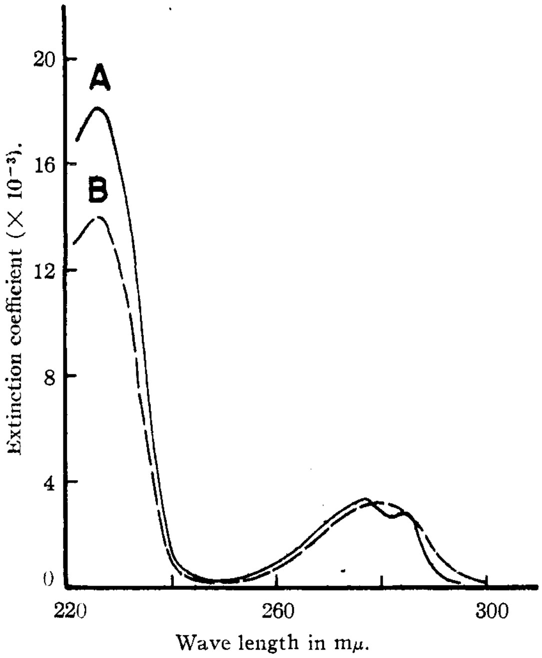

Fig. 3.—Ultraviolet absorption spectra of 1,2-bis-(*p*-methoxyphenyl)-cyclohexane, A; 1,2-bis-(*p*-hydroxyphenyl)-cyclohexane B.

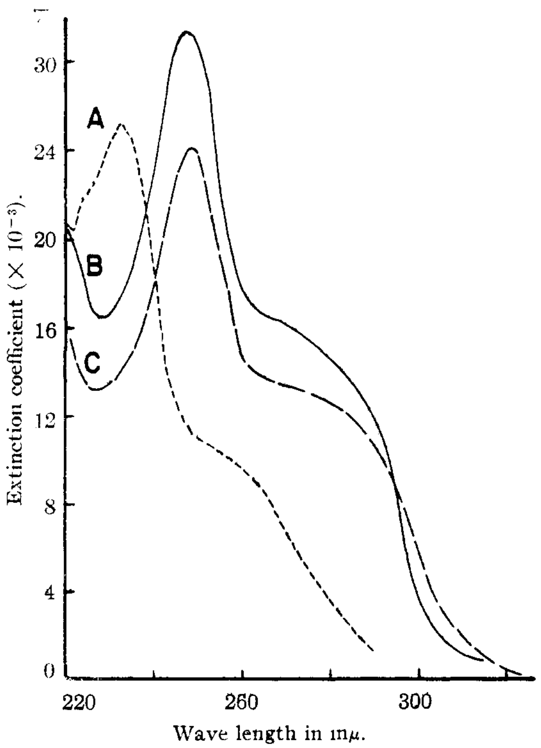

Fig. 4.—Ultraviolet absorption spectra of *o*-terphenyl, A; 4′,4″-dimethoxy-*o*-terphenyl, B; 4′,4″-dihydroxy-*o*-terphenyl, C.

Experimental

Oxidation of Bis-(*p*-methoxyphenyl)-cyclohexene, I.—The cyclohexene, m.p. 86.5–88°, 2.98 g., was dissolved in 100 ml. of dioxane. The solvent had been purified by refluxing over sodium metal during forty-eight hours and distilling; it was stable toward dilute potassium permanganate. A saturated aqueous solution containing 6.32 g. of potassium permanganate was added in small portions. The solution was stirred and the *p*H measured with glass and calomel electrodes. As oxidation proceeded 1 *N* hydrochloric acid was added as necessary to maintain *p*H within the limits 7.0–8.5. An additional 50 ml. of dioxane was added at the half-way point to keep the organic material in solution. When the last permanganate had been added the purple color persisted for an hour during which the *p*H was constant. The solution was acidified, sufficient sodium metabisulfite added just to clear the solution; it was extracted six times with ether. The ethereal concentrate was dried by distilling benzene from it and treated with 60 ml. of absolute alcohol, 6.0 ml. of glacial acetic acid and 6 g. of Girard reagent "T." After two hours at reflux the solution was poured into 100 ml. of ice water and 9.54 g. of sodium bicarbonate and the mixture extracted with ether. Removal of ether left 1.45 g. of oily needles; partition of this material between saturated sodium bicarbonate and ether yielded 0.43 g. of an acid which was crystallized three times from benzene, m. p. 182.5–184.0°; m. p., with recrystallized anisic acid, 182.6–184.5° (micro).

The aqueous solution containing the carbonyl derivatives was made about one-half normal with hydrochloric acid and extracted with ether after standing eight hours. Back extraction of the ether layer with sodium bicarbonate solution, acidifying and extracting again with ether yielded 0.25 g. of crude acid which was recrystallized several times from benzene, with decolorization, to yield colorless plates, m. p. 141.2–142.0° (micro): m. m. p. 141.2–142.2° (micro) with purified synthetic γ-*p*-methoxybenzoylbutyric acid.[14]

p-Bromophenacyl γ-*p*-methoxybenzoylbutyrate was prepared with 9 mg. of the keto acid from oxidation. It was washed with dilute sodium hydroxide and recrystallized three times from alcohol–water, m. p. 106.3–107.5°. The same derivative prepared from the synthetic acid on a large scale melted at 108.1–108.9°; melting point of mixture, 106.8–108.0° (micro).

Anal. Calcd. for $C_{20}H_{19}O_5Br$: C, 57.29; H, 4.57. Found: C, 57.26; H, 4.58.

Oxidation of Bis-(*p*-methoxyphenyl)-cyclohexene, II.—Ozone in oxygen was passed through a solution of 70 mg. of the cyclohexene, m. p. 83–87°, in 80 ml. of ethyl acetate for two minutes, when absorption was complete as judged by iodine liberation in a potassium iodide solution beyond the absorption vessel. The ethyl acetate solution was shaken with water, dried and evaporated. The white, crystalline residue, 65 mg., was recrystallized twice from ethyl acetate; m. p. 145.0–146.5°. A mixture with synthetic 1,4-bis-(*p*-methoxybenzoyl)-butane,[15] m. p. 146.8°, was not depressed.

The dioxime was prepared from hydroxylamine hydrochloride in alcoholic potassium hydroxide with refluxing for ninety minutes, and purified from ethyl acetate; m. p. 201.5–202.5°. A sample of the synthetic diketone gave a dioxime, m. p. 205.5–206°. A mixture of the two melted in an intermediate range but showed no depression. Literature values for this dioxime vary from 201.5°[15] to 208°.[16]

Summary

The structures of 1,2-bis-(*p*-methoxyphenyl)-cyclohexene and 2,3-bis-(*p*-methoxyphenyl)-cyclohexene have been clarified through oxidation to known compounds. Ultraviolet absorption spectra of several derivatives are in agreement with the structures given.

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[14] Plant and Thomlinson, *J. Chem. Soc.*, 856 (1935).

[15] Fuson, Kuykendall and Wilhelm, THIS JOURNAL, **53**, 4187 (1931).

[16] Zanden, de Vries and Westerhof, *Rec. trav. chim.*, **62**, 283 (1943).

KNOXVILLE, TENNESSEE RECEIVED SEPTEMBER 23, 1949

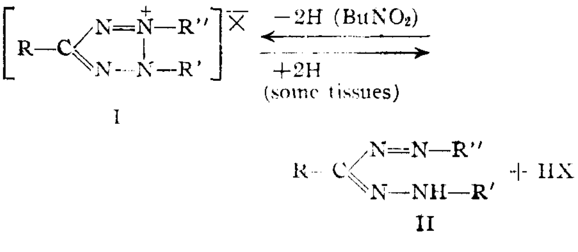
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Synthesis of Some Substituted Tetrazolium Chlorides[1,2]

BY SIDNEY W. FOX AND ELSIE HEMMINGSON ATKINSON

Although tetrazolium salts have been known to organic chemistry since 1894[3] and a variety of these compounds has since been synthesized, the biological properties of the tetrazolium salts have received attention only in the last decade.[4] The intrinsic characteristics responsible for the unique behavior of the tetrazolium series include the following:

1. They represent one of the few organic types colorless in the oxidized form, I, but colored in the reduced form (formazan, II).



I

II

2. The tetrazolium salt is frequently water-soluble, whereas the formazan is not, and the latter will, under proper circumstances, deposit as a colored material in the tissue which reduces it.

3. The oxidation-reduction potentials of many of the tetrazoles overlap values found in living systems.

4. The tetrazolium salts and formazans are sufficiently innocuous that their properties may be manifest directly in thriving cultures of micro-

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[1] This work was supported in part by the Industrial Science Research Institute of Iowa State College and in part by a research grant from the National Cancer Institute of the National Institutes of Health, U. S. Public Health Service. Journal Paper No. J1717 of the Iowa Agricultural Experiment Station, Project 1111.

[2] From a thesis submitted by Elsie Hemmingson Atkinson to the Graduate School of Iowa State College in partial fulfillment of the requirements for the degree of Master of Science, 1949.

[3] von Pechmann and Runge, *Ber.*, **27**, 2920 (1894).

[4] Kuhn and Jerchel, *ibid.*, **74B**, 941 (1941).