The **semicarbazone** recrystallized from acetic acid melted at 212–213° (dec.).

Anal. Calcd. for $C_{15}H_{17}O_2N_3$: C, 66.40; H, 6.32. Found: C, 66.43; H, 6.37.

Attempted Cyclization of Henze's Ketol, 3-Hydroxy-2,5-hexanedione.—Fifteen grams of II g. was dissolved in 300 ml. of 2% sodium hydroxide solution with the addition of 0.1 g. of hydroquinone. The flask was filled with nitrogen and allowed to stand for four hours. After saturation with sodium chloride, the reaction mixture was extracted with ether in a continuous extractor for twenty-four hours. The ether was distilled off and the residue dried by refluxing with benzene by use of a Dean–Stark trap. The benzene was removed with a water pump, and the residue fractionated in a high vacuum to give three fractions as follows: (1) 0.90 g., b. p. 39–41° at 0.3 mm., $n^{25}\text{D}$ 1.4387; (2) 0.65 g., b. p. 92–103° at 0.3 mm., $n^{25}\text{D}$ 1.5104; (3) 1.75 g., b. p. 118–128° at 0.3 mm., $n^{25}\text{D}$ 1.5342. Only fraction (1) gave a semicarbazone (it precipitated immediately), but the amount was too small to characterize. It was evident from the distillation that the reaction was not clear cut and that cyclization had not taken place. By analogy with the other cyclopentenolones, which have a little higher boiling point than the respective hydroxydiketones from which they are prepared, the cyclized product from 3-hydroxy-2,5-hexanedione, if any were formed, would have an estimated boiling point in the region of 70–85° at 0.3 mm. No such fraction was obtained. If any cyclized product were formed, its detection would require a more rigorous search. The degradation of Henze's ketol by alkali apparently leads to a complex mixture of products.

Acknowledgment.—We wish to express our appreciation for samples of methallyl chloride received from the Shell Chemical Corp., for pyruvaldehyde from the Carbide & Carbon Chemicals Corp., for selenium dioxide from C. Tennant, Sons & Co., and for sodium hydride from E I. du Pont de Nemours and Co.

Summary

The reaction between substituted glyoxals of the type R′COCHO and salts of substituted acetoacetic acids of the type RCH_2COCH_2COOH, yields 2-hydroxy-1,4-diketones, which cyclize upon treatment with alkali to 2,3-disubstituted-4-hydroxy-2-cyclopenten-1-ones. The chrysanthemum monocarboxylic acid esters of certain of these cyclopentenolones exceed the pyrethrins in insecticidal activity to house flies.

Synthetic 2-(2-butenyl)-4-hydroxy-3-methyl-2-cyclopenten-1-one appears to be a geometric isomer of natural *dl*-cinerolone.

BELTSVILLE, MD. RECEIVED APRIL 4, 1949

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, TULANE UNIVERSITY]

The Nitration of 1,1,1-Trichloro-2,2-bis-(*p*-methoxyphenyl)-ethane

BY DAVID A. SHIRLEY, THEODORE N. GOREAU AND FRED S. EISEMAN, JR.

1,1,1 - Trichloro - 2,2 - bis - (*p* - methoxyphenyl)-ethane (methoxychlor) has recently become available commercially because of its favorable properties as an insecticide. We have investigated the nitration of methoxychlor because of the usefulness of this reaction as a route to various derivatives whose biological properties are of interest. We were primarily interested in the possible activity of methoxychlor derivatives, particularly the amino derivatives, as anti-tubercular chemotherapeutic agents in view of the observation reported by Kirkwood and Phillips[1] of the high anti-tubercular activity *in vitro* of 1,1,1 - trichloro - 2,2 - bis - (*p* - aminophenyl)-ethane and 1,1-dichloro-2,2-bis-(*p*-aminophenyl)-ethylene.

Nitration of methoxychlor (I in Fig. 1) with concentrated nitric acid in glacial acetic acid solution produced a dinitro derivative. This dinitro compound was shown to be 1,1,1-trichloro-2,2-bis-(3-nitro-4-methoxyphenyl)-ethane (II in Fig. 1) by the methods indicated below.

Treatment of the dinitro derivative II with alcoholic base effected dehydrohalogenation to 1,1 - dichloro - 2,2 - bis - (3 - nitro - 4 - methoxyphenyl)-ethylene (III). Oxidation of this compound with chromic anhydride in glacial acetic acid gave 3,3′-dinitro-4,4′-dimethoxybenzophenone (VII). This ketone has been reported by several workers[2] and its melting point reported as 205°,[2a] 193°,[2d] 190°[2c] and 189–190°.[2b] Our product VII reached a maximum melting point of 187–187.5°[3] after a total of eight recrystallizations from a variety of solvents.

Conclusive proof of the structure of II was given by two independent methods. The first of these was by the condensation of chloral hydrate and *o*-nitroanisole to a product identical with II, indicating that the nitro groups in II were ortho to the methoxyl groups. In addition the nitration product (VI) of DDT (V), shown by Backeberg and Morris[4] to be 1,1,1-trichloro-2,2-bis-(3-nitro-4-chlorophenyl)-ethane, on treatment with alcoholic sodium methoxide caused dehydrohalogenation and replacement of the para chlorine atoms by methoxyl groups giving a product identical with III.

Reduction of the nitro groups in III gave the corresponding diamine, 1,1-dichloro-2,2-bis-(3-amino-4-methoxyphenyl)-ethylene, IV.

Preliminary *in vitro* tests were carried out on compounds II, III and IV by the Parke, Davis

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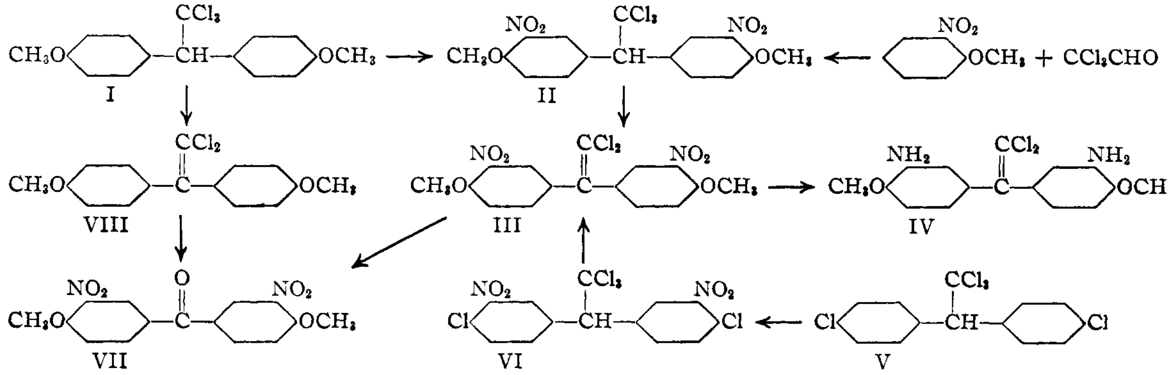
[1] Kirkwood and Phillips, THIS JOURNAL, **69**, 934 (1947).

[2] (a) Consonno, *Gazz. chim. ital.*, **34**, 376, 381 (1904); (b) van Alphen, *Rec. trav. chim.*, **49**, 153 (1930); (c) Quelet, *Compt. rend.*, **196**, 1411 (1933); (d) Matsumura, THIS JOURNAL, **57**, 128 (1935).

[3] All melting points are uncorrected and determined with a Fisher–Johns apparatus.

[4] Backeberg and Morris, *J. Chem. Soc.*, 803 (1945).

Fig. 1.—Summary of reactions.



Co. for activity against the H37Rv strain of human tuberculosis bacillus.[5] None of the compounds was active.

Experimental

1,1,1-Trichloro-2,2-bis-(3-nitro-4-methoxyphenyl)-ethane (II).—Five grams (0.0145 mole) of methoxychlor (I), prepared in essential accordance with the procedure of Schneller and Smith,[6] was dissolved in 50 ml. of glacial acetic acid and heated to reflux while a solution of 25 ml. of concentrated nitric acid was added dropwise over a period of thirty minutes. Reflux was continued for an additional hour, and the mixture allowed to stand for five hours. The reaction mixture was poured into excess water and the precipitated solid filtered off, dried, and recrystallized from alcohol. The product was 4.3 g. (68%) of small lemon yellow prisms, m. p. 166–167°. Another recrystallization from a mixture of alcohol and benzene gave 3.7 g. melting at 167–168°.

Anal. Calcd. for $C_{16}H_{13}Cl_3N_2O_6$: N, 6.43; Cl, 24.42. Found: N, 6.27 and 6.48; Cl, 24.45 and 24.40.

A mixture of 75.5 g. (0.50 mole) of *o*-nitroanisole, 37 g. (0.25 mole) of chloral hydrate, and 50 g. of concentrated sulfuric acid was stirred while 100 g. of 20% fuming sulfuric acid was added over a thirty-minute period. The temperature of the mixture increased to 65–70°. The mixture was stirred for one and one-half hours longer and then poured into excess water. The precipitated brown semi-solid mass was filtered off, washed with water, and recrystallized from glacial acetic acid and then from alcohol–benzene mixture to give 12.5 g. (12%) of yellow prisms, m. p. 168°. A mixed melting point between this material and that formed above by nitration of methoxychlor showed no depression.

1,1-Dichloro-2,2-bis-(3-nitro-4-methoxyphenyl)-ethylene (III).—A solution of 44 g. (0.10 mole) of II in a mixture of 250 ml. of alcohol and 75 ml. of benzene was heated to reflux and stirred while a solution of 8.6 g. (0.15 mole) of potassium hydroxide in 80 ml. of alcohol was added slowly. After a ten-minute reflux period, the hot mixture was filtered to remove the precipitated potassium chloride. Cooling the filtrate precipitated 31 g. (78%) of yellow prisms, m. p. 160–161°.

Anal. Calcd. for $C_{16}H_{12}Cl_2N_2O_6$: N, 7.03; Cl, 17.8. Found: N, 7.07 and 7.09; Cl, 17.4 and 17.4.

1,1-Dichloro-2,2-bis-(3-amino-4-methoxyphenyl)-ethylene (IV).—Raney nickel catalyst[7] suspended in alcohol was added to a hot solution of 8.0 g. (0.02 mole) of III in 100 ml. of alcohol. The mixture was agitated under a hydrogen pressure of 40 lb. until absorption of hydrogen was complete (about thirty minutes). The catalyst was removed by filtration, and the filtrate evaporated to a volume of 30–40 ml. Cooling precipitated 3.4 g. (50%) of the amine, m. p. 108.5°.

Anal. Calcd. for $C_{16}H_{16}Cl_2N_2O_2$: N, 8.26. Found: N, 8.39.

Oxidation of 1,1-Dichloro-2,2-bis-(3-nitro-4-methoxyphenyl)-ethylene (III).—The ethylene derivative III (2.0 g.) was oxidized with chromium trioxide in glacial acetic acid in general accordance with a procedure used by other workers[1,8] to give 1.1 g. of crude 3,3′-dinitro-4,4′-dimethoxybenzophenone, m. p. 178–180°. Eight recrystallizations utilizing ethanol, benzene, ethyl acetate, methanol and acetophenone as solvents gave a product with a constant and maximum melting point of 187–187.5°.[2]

Anal. Calcd. for $C_{15}H_{12}N_2O_7$: N, 8.43. Found: N, 8.38 and 8.42.

Treatment of 17 g. (0.055 mole) of 1,1-dichloro-2,2-bis-(*p*-methoxyphenyl)-ethylene (VIII), prepared by dehydrohalogenation of methoxychlor,[8b] with concentrated nitric acid (75 ml.) in glacial acetic acid (200 ml.) at the reflux temperature (one hour) gave 8 g. of 3,3′-dinitro-4,4′-dimethoxybenzophenone (VII) which was shown to be identical by the method of mixed melting points with the material isolated above. This indicated that both dinitration and oxidation to the ketone had occurred.

1,1-Dichloro-2,2-bis-(3-nitro-4-methoxyphenyl)-ethylene (III) from 1,1,1-Trichloro-2,2-bis-(3-nitro-4-chlorophenyl)-ethane (VI).—DDT (V) (10 g.) was nitrated in essential accordance with the procedure of Forrest, Stephenson and Waters[8a] to form 1,1,1-trichloro-2,2-bis-(3-nitro-4-chlorophenyl)-ethane (VI) in 91% yield. The product melted at 143–144°.[8a,9]

To a solution of 2.3 g. (0.0052 mole) of the nitration product (VI) in 100 ml. of methanol was added a solution of 0.6 g. (0.026 g. atom) of sodium in 60 ml. of methanol. The mixture was refluxed for two hours and then filtered to remove the precipitated sodium chloride. The solvent was removed from the filtrate by distillation to one-half volume, and upon cooling yellow prisms precipitated. These were recrystallized from ethanol to give 0.6 g. (27%) of 1,1-dichloro-2,2-bis-(3-nitro-4-methoxyphenyl)-ethylene (III), m. p. 161–162°. A mixed melting point with a sample of III prepared as described above by dehydrohalogenation of the nitration product of methoxychlor showed no depression.

Acknowledgment.—The authors wish to express appreciation to the Research Corporation of New York for a grant which supported a portion of this work, and to Mr. G. A. Schmidt for analytical assistance.

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[5] We are indebted to Dr. L. A. Sweet of the Parke, Davis Co. or arranging the pharmacological tests.

[6] Schneller and Smith, This Journal, **70**, 4059 (1948).

[7] *Org. Syntheses*, **21**, 15 (1940).

[8] (a) Forrest, Stephenson and Waters, *J. Chem. Soc.*, 338 (1946); (b) Harris and Frankforter, This Journal, **48**, 3149 (1926); (c) Haller, *et al.*, *ibid.*, **67**, 1596 (1945).

[9] Zeidler, *Ber.*, **7**, 1181 (1874).

Summary

Nitration of 1,1,1-trichloro-2,2-bis-(*p*-methoxyphenyl)-ethane (methoxychlor) forms 1,1,1-trichloro-2,2-bis-(3-nitro-4-methoxyphenyl)-ethane.

Two independent methods of proof showed that the structure of the nitration product is that indicated in the above name.

1,1-Dichloro-2,2-bis-(3-amino-4-methoxyphenyl)-ethylene and its precursors showed no activity *in vitro* when tested against *M. tuberculosis.*

NEW ORLEANS 15, LOUISIANA RECEIVED APRIL 18, 1949

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE OHIO STATE UNIVERSITY]

Racemic Glucose

BY M. L. WOLFROM AND H. B. WOOD

Racemic glucose was described as a sirup by Fischer.[1] Its purported occurrence in jute leaf[2] requires further experimental substantiation. The excellent synthesis of Sowden and Fischer[3] now makes L-glucose a readily available substance. We have succeeded in crystallizing a racemic form of this sugar. Hudson[4] has discussed the possible anomeric forms of a racemic mutarotating sugar and Fletcher and Hudson[5] have shown how these may be distinguished by acylative and crystallographic technics. Applying these criteria to our substance, we find that the X-ray powder diffraction pattern (Table I) for the racemic form of glucose isolated by us, is sensibly identical with the data reported by Sponsler and Dore[6] for anhydrous α-D-glucose. Since enantiomorphs exhibit like patterns, this is definitive proof that the racemic glucose is α-D,α-L-glucose and that it is a racemic mixture and not a true racemic compound. Supporting indirect evidence for this deduction is obtainable by acetylation technics. The racemic glucose was acetylated at low temperature with acetic anhydride and pyridine[7] and the crystalline product was characterized. L-Glucose was employed to prepare its hitherto unknown α and β pyranoid pentaacetates. These were admixed with equal quantities of their enantiomorphs and the crystalline racemic substances were characterized by melting point and X-ray powder diffraction pattern. The data of Table I show that the two racemic pentaacetates have a different crystal structure than is exhibited by either enantiomorph. Therefore α-D,α-L-glucopyranose pentaacetate (m. p. 140.5–141°) and β-D,β-L-glucopyranose pentaacetate (m. p. 125–126°) are true racemic compounds. The former was identical with the product obtained by the low temperature acetylation of the racemic glucose. This is further evidence that the racemic glucose is α-D,α-L-glucopyranose. The required assumption that the ring or anomeric structure of the sugar did not change on acetylation, while eminently probable, is not rigorous and this evidence is therefore equivocal.

TABLE I

X-RAY POWDER DIFFRACTION PATTERNS[a] OF α-D,α-L-GLUCOSE AND OF SEVERAL GLUCOSE PENTAACETATES[b]

				Pyranose pentaacetates					
α-D,α-L-Glucose I-P-S,[c] Å.	I[d]	α-L-Gluco- I-P-S, Å.	I	α-D,α-L-Gluco- I-P-S, Å.	I	β-D,β-L-Gluco- I-P-S, Å.	I	β-L-Gluco- I-P-S, Å.	I
1.22	1	1.82	1	1.77	1	1.58	1	1.47	1
1.28	1	1.85	1	1.86	2	1.65	1	1.58	1
1.34	2	2.02	1	1.92	1	1.68	1	1.62	1
1.37	1	2.08	1	2.12	2	1.77	2	1.81	3
1.49	1	2.16	3	2.22	2	1.83	2	1.85	1
1.59	2	2.25	1	2.32	1	1.92	1	1.90	2
1.63	1	2.30	1	2.47	3	2.04	1	2.01	2
1.68	1	2.40	1	2.56	3	2.11	1	2.06	1
1.79	1	2.49	1	2.76	3	2.30	1	2.11	2
1.87	1	2.59	1	2.96	1	2.62	3	2.18	3
1.91	3	2.84	1	3.10	4	2.76	1	2.34	3
1.95	3	2.88	2	3.27	4	3.07	1	2.44	2
2.06	3	2.95	1	3.54	8	3.39	5	2.55	4
2.15	1	3.05	1	3.90	9	3.57	1	2.95	2
2.24	4	3.14	2	4.35	5	3.82	1	3.07	5
2.46	8	3.32	2	4.70	6	4.04	10	3.36	4
2.56	4	3.57	7	5.36	7	4.47	6	3.51	7
2.89	3	3.91	4	6.25	1	4.71	7	3.99	1
3.13	7	4.21	9	8.05	10	5.18	4	4.17	6
3.30	1	4.42	6			5.61	9	4.44	10
3.49	5	4.80	5			6.95	2	5.23	1
3.94	3	5.12	2			8.17	5	5.59	8
4.29	10	5.47	8			11.05	8	9.94	9
4.70	9	6.22	1						
5.21	4	7.09	1						
6.06	6	9.25	10						
7.40	3								
8.53	4								

[a] Filtered CuK$_\alpha$ radiation, effectively 1.5148 Å.; film exposure two hours; no back reflections observed. [b] Acknowledgment is made to Professor P. M. Harris and Mr. A. L. Foster for assistance in obtaining these data. [c] Interplanar spacings. [d] Relative intensity, estimated visually; 10, strongest band; 1, weakest band.

Experimental

α-D,α-L-Glucose.—Crystalline α-L-glucose (0.5000 g.) was prepared according to the method of Sowden and Fischer[3] and in admixture with a like amount of α-D-glu-

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(1) E. Fischer, *Ber.*, **23**, 2620 (1890).

(2) H. Saha and K. N. Choudhury, *J. Chem. Soc.*, **121**, 1044 (1922).

(3) J. C. Sowden and H. O. L. Fischer, THIS JOURNAL, **69**, 1963 (1947).

(4) C. S. Hudson, *ibid.*, **65**, 1239 (1943).

(5) H. G. Fletcher, Jr., and C. S. Hudson, *ibid.*, **69**, 1145 (1947).

(6) O. L. Sponsler and W. H. Dore, *ibid.*, **53**, 1639 (1931).

(7) R. Behrend and P. Roth, *Ann.*, **331**, 359 (1904).