termediate for the preparation of 2-bromo-4-(trifluoromethyl)-anisole, was not depressed. Acetyl and benzoyl derivatives of both the reaction product and the authentic sample were prepared and were identical. The acetyl derivative melted at 105°, the benzoyl derivative at 145°.

LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ROCHESTER]

Maleic and Fumaric Dialdehydes, Δ^4-Tetrahydrophthalaldehyde and Related Compounds[1]

BY DUANE L. HUFFORD, D. S. TARBELL AND THOMAS R. KOSZALKA

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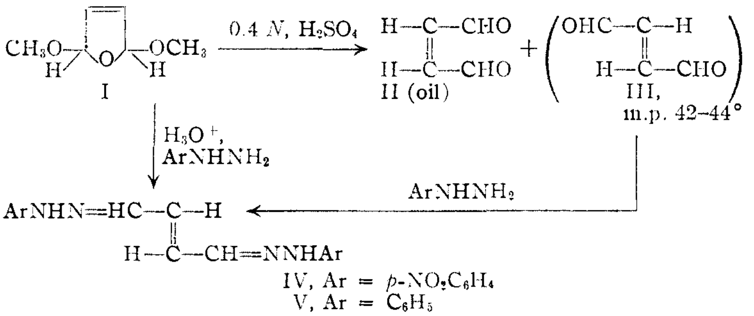
A crystalline dialdehyde, believed to be fumaric dialdehyde, has been isolated from the acid hydrolysis of dimethoxydihydrofuran, and its infrared and ultraviolet absorption spectra have been determined; the compound yields the same carbonyl derivatives as the oily maleic dialdehyde, and both unsaturated dialdehydes add butadiene to form Δ^4-tetrahydrophthalaldehyde. The latter has been reduced to hexahydrophthalaldehyde, and has been obtained in both the *cis*- and *trans*-form. Butadiene reacts with dimethoxydihydrofuran at 200° in the presence of a mole of water to form Δ^4-tetrahydrophthalaldehyde. Maleic dialdehyde could not be condensed with methoxy- or hydroxyacetone to form tropolone, although small amounts of *m*-hydroxybenzaldehyde were isolated.

Recent work[2,3] on the synthesis of 4,5-benztropolone and its methyl ether, by the condensation of phthalaldehyde with hydroxyacetone and methoxyacetone, respectively, suggested an investigation of the general adaptibility of the reaction of 1,2-dialdehydes with methoxyacetone to form tropolones. We have therefore made a fairly detailed study of the preparation and properties of maleic dialdehyde.

The preparation of aqueous solutions of maleic dialdehyde has been mentioned several times,[4-7] and several derivatives have been prepared, but the compound itself has been isolated only as an impure yellow oil.[8,9]

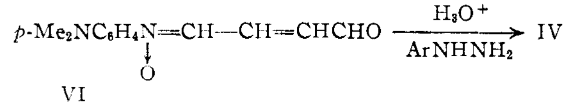
We have found it convenient to isolate maleic dialdehyde (II) from the acid hydrolysis mixture of 2,5-dimethoxy-2,5-dihydrofuran (I) by partition chromatography of the mixture on silicic acid. These mild conditions minimized decomposition of the aldehyde, and resulted, after vacuum distillation, in a yellow oil, consisting of maleic dialdehyde mixed with unchanged dimethoxydihydrofuran. From this oil could be isolated, in some runs, up to 27% of yellow crystalline solid, m.p. 42–44°, which had the composition of maleic dialdehyde, and which formed the same carbonyl derivatives which were obtained directly from the dimethoxydihydrofuran by the action of aqueous acid and arylhydrazines. This yellow solid was first regarded[10] as crystalline maleic dialdehyde, but further work has brought us to the view that it is fumaric dialdehyde, formed from the oily maleic form in some runs by isomerization. Since the same arylhydrazones IV and V are formed from the furan I and the solid III, it must be concluded that isomerization has occurred in the first case, either during preparation or purification of the derivatives; identity of the derivatives was established by infrared spectra and mixed m.ps.



IV, Ar = p-$NO_2C_6H_4$
V, Ar = C_6H_5

The reasons for regarding the crystalline dialdehyde as the *trans*-form are as follows. Treatment of the crystalline dialdehyde with hydrazine yielded only about 1% of pyridazine. The latter, identified as the chloroaurate, was formed in about 38% yield when the furan I was hydrolyzed with 0.4 N sulfuric acid and the resulting oily maleic dialdehyde was treated with hydrazine. Various modified procedures designed to decrease polymerization and favor the intramolecular reaction failed to form more than a trace of pyridazine from the crystalline dialdehyde.

Less convincing evidence for the configuration of the crystalline dialdehyde was afforded by the fact that the bis-*p*-nitrophenylhydrazone obtained from the nitrone VII, to which has been assigned the *trans*-configuration,[11] was found to be identical with the derivative IV obtained from the crystalline



$$p\text{-Me}_2\text{NC}_6\text{H}_4\underset{\substack{\downarrow\\ \text{O}}}{\text{N}}\text{=CH—CH=CHCHO} \xrightarrow[\text{ArNHNH}_2]{\text{H}_3\text{O}^+} \text{IV}$$

VI

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(1) Aided by a grant from the National Cancer Institute.

(2) D. S. Tarbell, G. P. Scott and A. D. Kemp, THIS JOURNAL, **72**, 379 (1950).

(3) D. S. Tarbell and J. C. Bill, *ibid.*, **74**, 1234 (1951).

(4) A. Wohl and E. Bernreuther, *Ann.*, **481**, 10 (1930).

(5) N. A. Preobrazhenskii, *et al.*, *J. Gen. Chem.* (*U. S. S. R.*), **15**, 952 (1945); *C. A.*, **40**, 6488 (1946).

(6) (a) N. Clauson-Kaas, *et al.*, *Kgl. Danske Videnskab. Selskab. Math.-Fys. Medd.*, **24**, (6) (1947); *C. A.*, **42**, 1930 (1948); (b) *Acta Chem. Scand.*, **1**, 216, 379, 415 (1947); (c) *ibid.*, **2**, 109 (1948).

(7) C. Schöpf and W. Arnold, *Ann.*, **558**, 117 (1947).

(8) A. Wohl and B. Mylo, *Ber.*, **45**, 1746 (1912).

(9) D. G. Jones and Imperial Chemical Industries, British Patent, 603,422 (*C. A.*, **43**, 1808 (1949)), have reported the isolation of the compound as an oil, but give no analysis or description.

(10) D. L. Hufford and D. S. Tarbell, Abstracts of Papers, 119th Meeting of the American Chemical Society, April, 1951, p. 39 M.

(11) H. Schmid and E. Grob, *Helv. Chim. Acta*, **32**, 79 (1949).

dialdehyde III. Attempts to prove the configuration of III by oxidation to maleic or fumaric acids, were unsuccessful.[12]

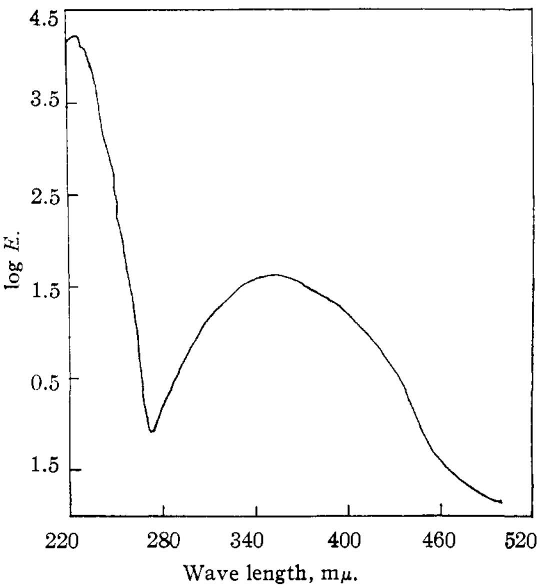


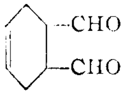
Fig. 1.—Absorption curve of fumaric dialdehyde in isooctane.

The ultraviolet absorption spectrum of the crystalline fumaric dialdehyde, III in isoöctane solution[13] (Fig. 1) is comparable to analogous compounds in showing two absorption peaks,[14] 225 mμ (E 17,000) and 354 mμ (E 70).

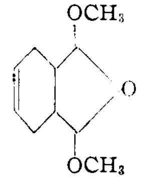
The infrared curve of fumaric dialdehyde in ethylene dichloride (Fig. 2A) shows a band at 1690 cm.$^{-1}$, doubtless the conjugated carbonyl stretching frequency, and additional bands at 1111, 1056 and 988 cm.$^{-1}$. No additional bands were observed in dioxane as solvent, except for a small peak at 1614 cm.$^{-1}$.

Attempts to prepare tropolone through the condensation of hydroxyacetone or methoxyacetone with maleic dialdehyde (II) in alkaline aqueous or methanolic media, in aqueous solutions buffered at slightly alkaline and acidic *p*H, in benzene with pyridine–acetate catalyst and in *t*-butyl alcohol with benzyltrimethylammonium hydroxide catalyst were unsuccessful. Small quantities of *m*-hydroxybenzaldehyde were isolated from the reactions in which sodium hydroxide was the condensing agent and either hydroxyacetone or methoxyacetone were reactants.[15]

Butadiene was found to add readily[16] to the oily maleic dialdehyde and to the crystalline fumaric dialdehyde, to yield Δ^4-tetrahydrophthalaldehyde (VII) which was characterized by preparation of derivatives, by dehydrogenation with chloranil[17] to phthalaldehyde, and by its infrared spectrum. The latter (Fig. 2B) is very similar to that of cyclohexene,[18] but contains several additional bands, including that for the normal carbonyl stretching at 1706 cm.$^{-1}$.



VII a and b



VIII

It was found that heating dimethoxydihydrofuran I with one mole of water in the presence of butadiene yielded tetrahydrophthalaldehyde directly; the product was, however, contaminated with the acetal VIII from which it could be separated only with difficulty. The structure of VIII was apparent from its composition, methoxyl content and the fact that it yielded the same bis-*p*-nitrophenylhydrazone as VII.

Evidence was obtained that both *cis*- and *trans*-forms of VII were formed, depending on the procedure employed. The same bis-*p*-nitrophenylhydrazone was obtained from VII, regardless of whether the *cis*-dialdehyde II or the *trans*-form III

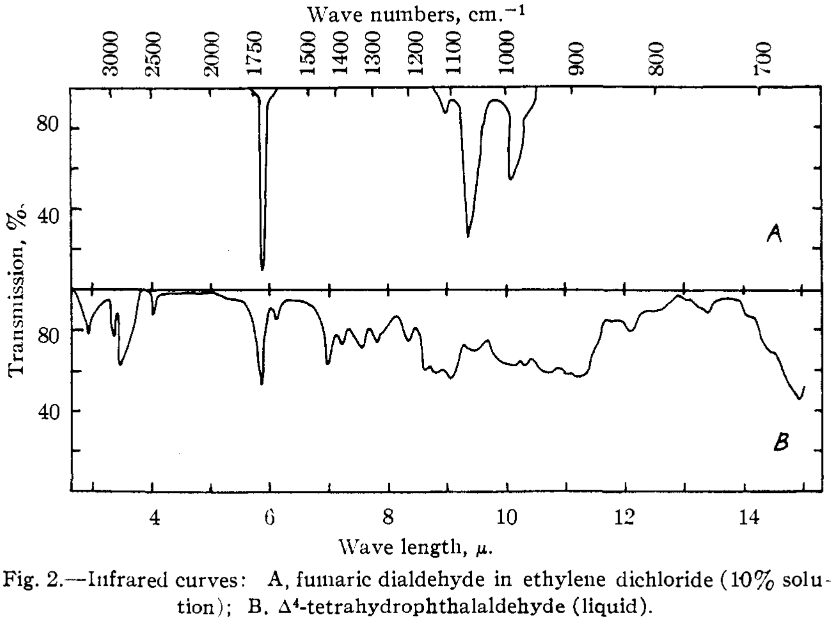


Fig. 2.—Infrared curves: A, fumaric dialdehyde in ethylene dichloride (10% solution); B. Δ^4-tetrahydrophthalaldehyde (liquid).

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[12] Consideration of models of II and III showed that dipole moment measurements would not offer any conclusive evidence about configuration.

[13] The spectrum was not determined in alcohol because the compound appears to react rapidly with alcohol, with a fading of the yellow color (*cf.* ref. 8).

[14] Diacetylethylene, which is also believed to be *trans* (G. D. Schenk, *Ber.*, **77**, 741 (1944)) shows (in alcohol) peaks at 226 mμ (*E* 14,600) and 338 mμ (*E* 70) (E. Braude, *J. Chem. Soc.*, 490 (1945)).

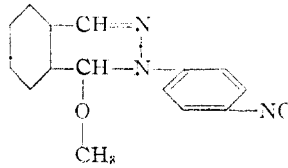
[15] For methods of synthesizing tropolones, see the review by J. W. Cook and J. D. Loudon, *Quarterly Revs.*, **5**, 99 (1951); also J. D. Knight and D. J. Cram, THIS JOURNAL, **73**, 4136 (1951).

[16] Using the conditions recommended by C. E. Boord, *et al.*, *ibid.*, **70**, 946 (1948), for the reaction of butadiene and acrolein.

[17] R. T. Arnold and C. Collins, *ibid.*, **61**, 1407 (1939).

[18] (a) American Petroleum Institute Res. Proj. 44, Serial No. 201, 1945; (b) *ibid.*, Serial No. 697, 1948; (c) C. W. Beckett, N. K. Freeman and K. S. Pitzer, THIS JOURNAL, **70**, 4227 (1948).

was used, suggesting that there was isomerization either during the Diels–Alder reaction or during the formation of the derivative. The dialdehyde VIIb prepared from the furan I, water and butadiene, was reduced with hydrogen and palladium–charcoal to hexahydrophthalaldehyde. This, when treated with *p*-nitrophenylhydrazine hydrochloride formed the derivative IX. Oxidation of the hexahydrophthalaldehyde with silver oxide in alkali yielded *trans*-hexahydrophthalic acid, which was identical with a known sample.[19]



IX

The tetrahydrophthalaldehyde VIIa, prepared from the oily maleic dialdehyde and butadiene, yielded on oxidation an impure acid, from which *cis*-Δ^4-tetrahydrophthalic acid[20] was isolated.

Attempted condensation of VIIb with methoxyacetone in the presence of piperidine acetate or of sodium hydroxide yielded a small amount of Δ^4-tetrahydrophthalide as the only crystalline product. Condensation products derived from VIIa and acetone dicarboxylic ester, and from methoxyacetone, are under investigation at present.

Experimental[21]

2,5-Dimethoxy-2,5-dihydrofuran (I).—The procedure outlined by Fakstorp[22] for the preparation of 2,5-diethoxydihydrofuran was employed. Freshly distilled furan (72 cc., 1 mole), 200 cc. of absolute ether and 250 cc. of anhydrous methanol dried over magnesium were placed in a 2-l. three-necked flask equipped with thermometer, stirrer, dropping funnel and soda lime tube, and cooled in a bath of Dry Ice in acetone. Bromine (56 cc., 1 mole) dissolved in 650 cc. of anhydrous methanol and cooled in an acetone–Dry Ice-bath, was added rapidly with stirring at such a rate that the temperature did not exceed −25°. Dimethoxydihydrofuran (100 g., 77%) b.p. (1 mm.) 42°, n^{20}D 1.4296, was obtained in a manner similar to that used in the isolation of the diethoxydihydrofuran.[22]

Maleic Dialdehyde (II).—2,5-Dimethoxydihydrofuran (30 g.) and 40 cc. of 0.35 *N* sulfuric acid saturated with sodium sulfate were heated for 20 minutes (80–85°) on a steam-bath. The reaction mixture was added in one operation to 140 g. of Baker C.P. silicic acid, and thoroughly mixed by stirring, yielding a uniform light yellow dry powder. The resulting silica gel was packed into a large chromatographic column (diameter, 40 mm.) by suspending the gel in chloroform containing 2% of *t*-butyl alcohol and then allowing the chloroform to flow out of the bottom of the tube. After the silica gel had been packed in the column, more chloroform containing 2% of *t*-butyl alcohol was passed through the column until the yellow color had been removed. The eluate (600–700 cc.) was cooled during collection by an ice-bath and dried over anhydrous sodium sulfate.

After the solvent had been removed at reduced pressure, the residual oil was rapidly distilled *in vacuo* through a 20-cm. Vigreux column from an oil-bath previously heated to 115°, b.p. 54–61° (10 mm.); yield 13 g., n^{20}D 1.4575.[23] The distillate was collected in receivers immersed in Dry Ice–acetone-baths.[24]

Fumaric Dialdehyde (III).—In a similar run starting with 27 g. of the furan I, the residue from the chloroform eluate was distilled at 30 mm. in a von Braun flask, with the collecting bulb immersed in a Dry Ice–acetone freezing mixture. The yellow solid distillate was dissolved in 25 cc. of benzene; the yield was 4.7 g. (27%), m.p. 40–43°. The analytical sample, prepared in another run, melted at 42–44°.

Anal. Calcd. for $C_4H_4O_2$: C, 57.14; H, 4.80. Found: C, 56.84; H, 4.69.

It was not always possible to obtain the crystalline dialdehyde; very frequently the product remained an oil. The reason for the variation in different runs could not be determined.

The Bis-phenylhydrazone V and the Monophenylhydrazone.—Phenylhydrazine (0.2 cc.) in 10 cc. of 10% acetic acid was mixed with 118 mg. of crystalline dialdehyde dissolved in 2 cc. of methanol and 0.3 cc. of 0.01 *N* sulfuric acid. A red-orange powder (0.2 g.) precipitated immediately, melting at 170–175° with decomposition (darkening from 135°). Recrystallization of this material from benzene–acetone yielded two types of crystals, yellow clusters and brown prisms. These were separated and recrystallized separately. The yellow crystals melted at 173–175° with decomposition (darkening from 160°). A sample of the bis-phenylhydrazone V prepared directly from the furan I following Clauson-Kaas[6a] showed the same behavior on mixed m.p. The infrared spectra of the two samples were identical.

The brown prisms melted, after two recrystallizations from benzene, at 126–127°, and were shown by analysis to be the **monophenylhydrazone.**

Anal. Calcd. for $C_{10}H_{10}N_2O$: C, 68.55; H, 5.75. Found: C, 68.76; H, 5.77.

The Bis-*p*-nitrophenylhydrazone IV. A. From the Crystalline Dialdehyde III.—Crystalline fumaric dialdehyde (III, 75 mg.) was heated for several minutes with 270 mg. of *p*-nitrophenylhydrazine in 25 cc. of methanol; water (20 cc.) and methanol (50 cc.) were added, the mixture was digested on a steam-bath for 20 minutes, filtered and washed with boiling methanol. A red brick powder (50 mg.), m.p. 224–225° (with decomposition), was obtained; recrystallization gave material decomposing at 235–236°. Additional material (50 mg.) was obtained from the original filtrate.

Wohl and Bernreuther[4] reported this derivative to melt with decomposition at 238–240° (darkening at 230°).

B. From the Nitrone VI.—The nitrone VI[11] was converted to the bis-*p*-nitrophenylhydrazone, and the derivative, after crystallization from pyridine–hexane, decomposed at 216–218° as reported.[11] Recrystallization from pyridine, however, raised the decomposition point to 230–231° and it was therefore analyzed.

Anal. Calcd. for $C_{16}H_{14}N_6O_4$: C, 54.23; H, 3.98. Found: C, 54.52; H, 4.07.

C. From the Furan I.—The derivative was prepared from the furan I by heating with *p*-nitrophenylhydrazine and mineral acid.

The derivatives obtained as described under A, B and C showed no depression in mixed decomposition point, and showed identical infrared spectra (in Nujol), after they had

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[19] This was readily prepared by the action of butadiene on fumaric acid in aqueous solution at 125° (L. C. Lane and C. H. Parker, Jr., U. S. Patent 2,444,263 (*C. A.*, **42**, 7102 (1948)), followed by reduction with palladium–charcoal. This is more convenient than the addition of butadiene to fumaryl chloride (K. Alder and M. Schumacher, *Ann.*, **564**, 107 (1949)).

[20] O. Diels and K. Alder, *ibid.*, **460**, 113 (1928).

[21] Melting points are uncorrected; analyses by Microtech Laboratories and Miss Claire King.

[22] J. Fakstorp, D. Raleigh and L. E. Schniepp, THIS JOURNAL, **72**, 869 (1950); this procedure is preferable to that of ref. 6c.

[23] The product prepared in this way contains a large amount of starting material. However, it can be used advantageously for the Diels–Alder reaction with butadiene. The highest refractive index observed for the crude maleic dialdehyde has been 1.4730.

[24] It is important that concentrated solutions of maleic dialdehyde be kept cold, because such samples maintained a few minutes at room temperature undergo rapidly polymerization accompanied by the evolution of heat and the formation of extremely viscous solutions. These samples can be partially depolymerized again by heating at 115° *in vacuo* and distilling the monomer formed through a Vigreux column. The use of small amounts of antioxidants such as methylene blue, hydroquinone or *t*-butylcatechol in the hydrolysis of dimethoxydihydrofuran, the removal of chloroform solvent, or the distillation of the maleic dialdehyde caused a marked decrease in the yield of distillable product, and an increase in the brown resin which remained behind in the distilling flask.

been recrystallized from pyridine. The derivative from A, however, showed some change in infrared spectrum after crystallization from pyridine, indicating either marked purification or isomerization.

Configuration of the Dialdehydes II and III; Pyridazine Formation.[4] **A. From Crystalline Fumaric Dialdehyde (III).**—The crystalline dialdehyde (m.p. 42–44°, 1.0 g.), was dissolved in 2 cc. of 0.4 *N* sulfuric acid, and 17 cc. of 4.4% hydrazine solution (in which the *p*H had been adjusted to 4.5) was added. Immediately a solid mass of brown product, probably a polymer, precipitated. After ten minutes, 50 cc. of water was added, the solution was saturated with potassium hydroxide, a few crystals of potassium dichromate were added, the mixture was extracted three times with ether and the extracts were dried. Distillation of the residue from the ether yielded nothing with a b.p. greater than 170°. Treatment of the distillate with about 0.2 g. of chloroauric acid trihydrate yielded 45 mg. (1%) of the gold chloride salt of pyridazine.[25]

B. From Maleic Dialdehyde.—2,5-Dimethoxy-2,5-dihydrofuran (I, 2.0 g.) was treated with 2 cc. of 0.4 *N* sulfuric acid on the steam-bath for 30 minutes; the mixture was then added to 17 cc. of the hydrazine solution described above, and the mixture allowed to stand for ten minutes. Although it turned brown, nothing precipitated. The reaction mixture was treated in the same manner as that from the crystalline dialdehyde above. Pyridazine (400 mg., b.p. 205°, $n^{20}\text{D}$ 1.5170) was isolated. From 150 mg. of this pyridazine in 10 cc. of water, a quantitative precipitation of the gold chloride salt, m.p. 111–112° with decomposition, was obtained.

Dimethoxydihydrofuran (2 g.) was mixed with 17 cc. of the hydrazine solution, allowed to stand for ten minutes and heated in the same manner as the two samples described above. Nothing distilled above 110°, and no pyridazine could be detected.

Condensation between Maleic Dialdehyde and Hydroxy- and Methoxyacetone.—Only the following are described out of a large number of runs. To hydroxyacetone[26] (13 g.) and 2,5-diacetoxydihydrofuran[6b] (23 g.) in 900 cc. of methanol, a solution of sodium hydroxide (16 g.) in 75 cc. of 80% methanol was added dropwise with stirring over 20 minutes, the color of the solution rapidly changing to a dark reddish-brown. After standing overnight, the solvent was removed *in vacuo*, water was added, the solution was acidified and filtered to remove an amorphous precipitate. Extraction of the filtrate with ether–chloroform, followed by vacuum sublimation, yielded a crystalline product, which melted, after crystallization from heptane, at 101–102°, and was shown to be *m*-hydroxybenzaldehyde by a mixed m.p. with an authentic sample.[27]

Condensation of I and methoxyacetone[28] in aqueous solution at *p*H 12 also gave a small amount of *m*-hydroxybenzaldehyde as the sole isolable product.

Δ⁴-Tetrahydrophthalaldehyde (VIIa).—Crude maleic dialdehyde (12.5 g.), $n^{20}\text{D}$ 1.4575, 12.5 cc. of butadiene and 0.2–0.3 g. of *t*-butylcatechol were placed in a 100-cc. glass liner immersed in a Dry Ice–acetone-bath. The liner and contents were transferred to a steel bomb cooled to 0°, the bomb was heated as rapidly as possible (30 minutes) to 190°, and was kept at this temperature for 30 minutes. The bomb was cooled with an air stream to room temperature (two hours) and the reaction mixture distilled *in vacuo* at 3 mm., yielding, after 1.4 g. of dimethoxydihydrofuran forerun, 7.7 g. of tetrahydrophthalaldehyde (42%, based on unrecovered starting material), b.p. 72–76°.[29]

The analytical sample had the following properties: b.p. 56° (0.3 mm.); $n^{20}\text{D}$ 1.4936; d_{20} 1.1053; *M*D obsd. 36.36, *M*D calcd. 36.51.

Anal. Calcd. for $C_8H_{10}O_2$: C, 69.54; H, 7.30. Found: C, 69.39; H, 7.08.

The bis-*p*-nitrophenylhydrazone was prepared by allowing the components to stand in methanol in the cold overnight. The resulting precipitate was recrystallized four times from methanol, forming golden yellow needles, m.p. 218–219°.

Anal. Calcd. for $C_{20}H_{20}N_6O_4$: C, 58.81; H, 4.99; N, 20.58. Found: C, 58.62; H, 4.78; N, 20.80.

The bis-2,4-dinitrophenylhydrazone was prepared in ethanol containing sulfuric acid and the precipitate which formed was filtered, washed, dried and chromatographed on alumina using benzene–ethyl acetate as eluant. The product thus obtained, after crystallization from ethyl acetate and then from xylene–pyridine, formed golden clusters, m.p. 230–232°.

Anal. Calcd. for $C_{20}H_{18}N_8O_8$: C, 48.19; H, 3.64; N, 22.48. Found: C, 48.33; H, 3.63; N, 22.36.

The reaction of butadiene and crystalline fumaric dialdehyde (4.6 g.) under conditions similar to those described above yielded 74% of product apparently identical with the above tetrahydrophthalaldehyde, as judged from its refractive index, and the identity of its bis-*p*-nitrophenylhydrazone with the one described above.

Dehydrogenation of Δ⁴-Tetrahydrophthalaldehyde (VIIa) to Phthalaldehyde.—About 1 g. of the aldehyde VIIa and 17 g. of chloranil[17] were heated at reflux in xylene for three hours. After cooling, the tetrachlorohydroquinone and unreacted chloranil were filtered from the mixture. The xylene was removed from the filtrate *in vacuo*, the residue was dissolved in methyl alcohol, several grams of sodium pyrophosphate was added and the mixture steam distilled, until a negative ammonia–acetic acid test[30] indicated that all of the phthalaldehyde had distilled. The distillate was saturated with sodium sulfate and extracted continuously with ethyl acetate until the aqueous phase gave a negative test for phthalaldehyde. The solution was dried, the solvent was removed and the residue was recrystallized several times from hexane. A mixed m.p. with authentic phthalaldehyde[31] gave no depression, m.p. 55–56°.

Δ⁴-Tetrahydrophthalaldehyde (VIIb) and Its Acetal (VIII).—Dimethoxydihydrofuran (8.2 g.), 10 cc. of butadiene, 10 cc. of dioxane, 5.5 cc. of water and about 0.2 g. of *t*-butylcatechol were placed in a glass liner (100 cc.) immersed in a Dry Ice–acetone-bath. The liner was transferred to a steel bomb, heated to 200° as fast as possible (30 minutes) and kept at this temperature for one hour. Distillation yielded 6.7 g. (78%) of product, $n^{20}\text{D}$ 1.4940. In later runs, there was always obtained, in addition to the tetrahydrophthalaldehyde, a lower boiling product with lower refractive index, which could be obtained only fairly pure by repeated distillation, and which was shown to be the acetal VIII.

The best sample of the acetal had the following properties: b.p. 64–65° (1.5 mm.); $n^{21}\text{D}$ 1.4775.

Anal. Calcd. for $C_{10}H_{16}O_3$: C, 65.19; H, 8.76; OCH_3, 33.7. Found: C, 65.87; H, 8.49; OCH_3, 27.1.

The acetal yielded the same bis-*p*-nitrophenylhydrazone as the tetrahydrophthalaldehyde VII.

Hexahydrophthalaldehyde.—Δ⁴-Tetrahydrophthalaldehyde (VIIb, 2.5 g.) prepared from the furan, was reduced with hydrogen and palladium–charcoal at atmospheric pressure in methanol. After removal of the catalyst and solvent, distillation yielded three fractions, of about 300 mg. each. The analytical sample boiled at 72° (1 mm.).

Anal. Calcd. for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.35; H, 8.93.

Treatment of the hexahydrophthalaldehyde in methanol with *p*-nitrophenylhydrazine hydrochloride and 0.2 *N* hydrochloric acid yielded a yellow product, which, after recrystallization from methanol–water, melted at 126–127°. This was shown by analysis to be, instead of the expected bis-*p*-nitrophenylhydrazone, **1-methoxy-2-*p*-nitrophenyl-1,2,5,6,7,8,9,10-octahydrophthalazine (IX)**. Several crystallizations were necessary for a satisfactory analytical sample.

Anal. Calcd. for $C_{15}H_{19}N_3O_3$ (IX): C, 62.27; H, 6.62. Found: C, 62.42; H, 6.64.

Oxidation of Hexahydrophthalaldehyde to *trans*-Hexahydrophthalic Acid.—To an ice-cold mixture of 0.3 g. of the

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[25] This salt melted with decomposition at 110° as reported (E. Tauber, *Ber.*, **28**, 455 (1895); also ref. 4).

[26] *Org. Syntheses*, Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 5.

[27] *Org. Syntheses*, **25**, 55 (1945).

[28] R. P. Mariella and J. L. Leech, THIS JOURNAL, **71**, 3558 (1949).

[29] A sizeable portion of dimethoxydihydrofuran forerun escaped into the cold trap. In another experiment, most of the unreacted dimethoxydihydrofuran was recovered, and the yield of Δ⁴-tetrahydrophthalaldehyde based on unrecovered starting material was practically quantitative.

[30] J. Thiele and E. Winter, *Ann.*, **311**, 360 (1900).

[31] Prepared by the method of J. Thiele and O. Gunther, *Ann.*, **347**, 106 (1906), by Dr. John Bill.

aldehyde, 5 cc. of water, 2.5 g. of silver nitrate and 1 cc. of methanol, was added dropwise over a 10-minute period a solution of 1.7 g. of potassium hydroxide in 5 cc. of water. The mixture was stirred for 2.5 hours at room temperature. The black silver precipitate which resulted on addition of base to the original solution was filtered, the residue was washed with water, and the water washings were combined with the filtrate. The aqueous basic filtrate was extracted three times with 100-cc. portions of ether to remove any traces of the dialdehyde. The filtrate was then acidified with 6 *N* sulfuric acid to a *p*H of 2–3 and again extracted with three 100-cc. portions of ether. The ether extract was evaporated to dryness at reduced pressure and the white crystalline residue was dissolved in 10 cc. of methanol. Crystallization from methanol yielded 0.1 g. of a white crystalline compound, m.p. 220–221°. A mixed m.p. with *trans*-hexahydrophthalic acid, prepared as described below, gave no depression.

***trans*-Hexahydrophthalic Acid.**[19]—Fumaric acid (5 g.), 25 cc. of water, a trace of *t*-butylcatechol and 5 cc. of butadiene were heated at 135° for 45 minutes in a bomb. The resulting solution was filtered hot through a Filteraid to remove any polymer, and 3.9 g. of product was obtained after the solution stood overnight; recrystallization from water gave material melting at 171–172°. (Alder and Schumacher[28] report a m.p. of 172°.) The product gave a large depression on mixed m.p. with *cis*-Δ^4-tetrahydrophthalic acid.[20,32]

Reduction of the tetrahydro acid with hydrogen and palladium–charcoal, followed by crystallization from hot water, yielded the *trans*-acid, of m.p. 217–221° (Diels and Alder[20] report 215–221°.)

Oxidation of Δ^4-Tetrahydrophthalaldehyde (VIIa) to *cis*-Δ^4-Tetrahydrophthalic Acid.—The oxidation of 1.3 g. of tetrahydrophthalaldehyde ($n^{22}\text{D}$ 1.4942, prepared from the oily maleic dialdehyde and butadiene) with silver oxide was carried out essentially as described above. The ether solution containing the acidic products of oxidation was concentrated, the residue was dissolved in 50 cc. of water and was treated with norite. Concentration to small volume yielded crystalline material, which, after three further crystallizations from water, melted at 169–171° (wt., 0.2 g.) and gave no depression on mixed m.p. with *cis*-Δ^4-tetrahydrophthalic acid; a large depression was observed on mixed m.p. with the *trans*-acid.

Condensation Reaction between Tetrahydrophthalaldehyde and Methoxyacetone; Tetrahydrophthalide.—Tetrahydrophthalaldehyde (6.0 g., VIIa, prepared from oily maleic dialdehyde) and 4.2 cc. of methoxyacetone in 300 cc. of absolute alcohol were treated with a solution of 6 g. of sodium hydroxide in aqueous alcohol. After standing for 36 hours, most of the alcohol was removed *in vacuo*, the residue was dissolved in 250 cc. of water and extracted four times with 200-cc. portions of chloroform. The aqueous layer was acidified and extracted with 250-cc. portions of chloroform. The chloroform from the extraction of the basic solutions was removed at reduced pressure and the residue was dissolved in benzene and chromatographed on alumina. None of the fractions showed a conjugated carbonyl absorption in the ultraviolet.

The chloroform from the extraction of the acidified solution was removed at reduced pressure and the residue was dissolved in benzene and chromatographed on magnesol. About 30 mg. of a greasy solid was obtained which was sublimed, recrystallized from heptane, and resublimed; it melted at 99–100°, and was tetrahydrophthalide.

Anal. Calcd. for $C_8H_{10}O_2$: C, 69.54; H, 7.30. Found: C, 69.40; H, 7.11.

The hydrazide[33] was formed from the lactone (90 mg.) by heating with 100% hydrazine hydrate on the steam-bath for three hours. The reaction mixture was dissolved in hot ethyl acetate; on cooling, 60 mg. of the hydrazide crystallized as thin white needles, m.p. 169–170°.

Anal. Calcd. for $C_8H_{14}N_2O_2$: C, 56.45; H, 8.29. Found: C, 56.78; H, 8.45.

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(32) A. C. Cope and E. C. Herrick, THIS JOURNAL, **72**, 983 (1950).

(33) *Cf.* S. L. Friess, *ibid.*, **71**, 2571 (1949).

[CONTRIBUTION FROM THE DEPARTMENT OF SCIENTIFIC AND INDUSTRIAL RESEARCH, GOVERNMENT OF PAKISTAN, KARACHI, PAKISTAN,[1] AND THE DEPARTMENT OF PHYSIOLOGICAL CHEMISTRY, THE OHIO STATE UNIVERSITY, COLUMBUS, OHIO[2]]

Preparation of Deuterized Raney Nickel and Selective Deuteration of the Triple Bond[2]

BY N. A. KHAN[3]

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A procedure is described for the preparation of deuterized Raney nickel for use in deuterating the triple bond selectively to the double bond with a view to obtaining dideutero-olefinic compounds. A comparative study of hydrogenation and deuteration has been made, and selective deuteration is shown to be as effective as hydrogenation. The composition of the crude products obtained by the selective deuteration of the triple bond has been determined by an analytical scheme. A plausible explanation for the unusual selectivity of reduction of symmetrical acetylenic compounds by deuterium or hydrogen is presented. Evidence has been put forward for no exchange of deuterium gas with the hydrogen of saturated C-chain of methyl stearate over deuterized Raney nickel during the short period needed for selective deuteration. A method of preparation of a Raney nickel catalyst, designated W-8, containing much less hydrogen than other varieties, and free of lighter variety of the catalyst containing alumina, is also reported.

In a previous paper,[4] methyl stearolate was selectively deuterated to the corresponding olefinic compound with an assumption that the deuteration follows the same pattern of reaction as hydrogenation. No critical consideration was given to the identification of the different products formed by deuteration, nor were any conditions set up for this process. Furthermore, the Raney nickel catalyst, W-1,[5] used was not freed from the hydrogen adsorbed on the surface during preparation. Such retained hydrogen (125–250 ml. per 4 g. of catalyst)[6] would introduce some error in the extent of deuteration. The deuterium content of the purified methyl 9,10-dideutero-oleate reported[4] (only 90% of theory) confirms this fact.

In the present investigation a special procedure was developed to prepare deuterized Raney nickel, having deuterium adsorbed on its surface rather

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(2) Most of the experimental work was completed at the Ohio State University. Paper presented by title to the XII^th^ International Congress, New York City, September, 1951.

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(4) N. A. Khan, F. E. Deatherage and J. B. Brown, *J. Am. Oil Chemists' Soc.*, **28**, 27 (1951).

(5) H. Adkins and L. W. Covert, THIS JOURNAL, **54**, 4116 (1932).

(6) R. Mozingo, D. E. Wolf, S. A. Harris and K. Folkers, *ibid.*, **65**, 1013 (943).