through an 18-in. packed column gave unchanged tetramethylcyclobutanedione and 263 g. (61%) of 2,2,4,4-tetramethyl-3-phenyliminocyclobutanone (X), b.p. 124–125° (7 mm.), n_D^{20} 1.5165.

Anal. Calcd. for $C_{14}H_{17}NO$: C, 78.1; H, 8.0; N, 6.5. Found: C, 77.8; H, 7.9; N, 6.4.

The infrared spectrum had bands at 5.55 μ (cyclobutanone) and 5.9 μ (C=N, where carbon is part of strained ring).

The distillation residue (98 g.) crystallized on cooling. After recrystallization from ethyl alcohol, 81 g. (28%) of 2,2,4,4-tetramethyl-*N,N'*-diphenyl-1,3-cyclobutanediimine, m.p. 140–142°, was recovered.

2,2,4,4-Tetramethyl-N,N'-diphenyl-1,3-cyclobutanediimine (XI). A solution of 140 g. of tetramethyl-1,3-cyclobutanedione, 232.5 g. of aniline, and 5 g. of *p*-toluenesulfonic acid in 700 ml. of toluene was refluxed through a 10-in. packed column equipped with a Dean-Stark trap. The theoretical amount of water (36 ml.) was collected in 8 hr. The reaction solution was washed with sodium bicarbonate solution and with water, dried over magnesium sulfate, filtered, and evaporated on the steam bath. The residual slurry of crystals was filtered and the crystals were washed with cold hexane. The crude product, 221 g. (76%), melted at 137–140°. An analytical sample, prepared by two successive recrystallizations from ethyl alcohol, melted at 141–142°.

Anal. Calcd. for $C_{20}H_{22}N_2$: C, 82.7; H, 7.6; N, 9.7. Found: C, 82.6, H, 7.4; N, 9.6.

The infrared spectrum contained a doublet at 5.9 and 5.95 μ indicative of C=N (carbon in strained ring).

3-Anilino-2,2,4,4-tetramethylcyclobutanol (XII). A solution of 100 g. of 2,2,4,4-tetramethyl-3-phenyliminocyclobutanone (X) in 300 ml. of ethyl alcohol was hydrogenated over 20 g. of copper chromite (Harshaw Chemical Company Cu-1106 P) catalyst in a rocking autoclave for 4 hr. at 175° and under 5000 p.s.i. pressure of hydrogen. The hydrogenation mixture was filtered to remove the catalyst, and the filtrate was distilled through an 18-in. packed column to give 9.4 g. of forerun, b.p. 122–139° (3 mm.), and 76.0 g. (75%) of 3-anilino-2,2,4,4-tetramethylcyclobutanol, b.p. 131–132° (1.5 mm.). The material solidified slowly on standing at room temperature.

Anal. Calcd. for $C_{14}H_{21}NO$: C, 76.7; H, 9.7; N, 6.4; neut. equiv., 219. Found: C, 76.7; H, 9.8; N, 6.4; neut. equiv., 219.

The infrared spectrum of this product, compared with that of the starting material, showed complete removal of absorption at 5.55 μ (C=O) and 5.9 μ (C=N). A new doublet (N—H and —OH) appeared at 2.8 and 2.9 μ.

2,2,4,4-Tetramethyl-N,N'-diphenyl-1,3-cyclobutanediamine (XIII). A solution of 30 g. of 2,2,4,4-tetramethyl-*N,N'*-diphenyl-1,3-cyclobutanediimine (XI) in 75 ml. of benzene was hydrogenated in a rocking autoclave over 5 g. of Raney nickel catalyst at 100° and under 1500 p.s.i. pressure of hydrogen for 2 hr. The product was filtered and evaporated on the steam bath to 30 g. of viscous residue, which slowly crystallized. The infrared spectrum of this crude 2,2,4,4-tetramethyl-*N,N'*-diphenyl-1,3-cyclobutanediamine showed complete disappearance of the doublet at 5.9 and 5.95 μ (C=N) and appearance of a new band at 2.9 μ (N—H). The crude product was purified by recrystallization from petroleum ether and then from ethyl alcohol; 10.7 g. was recovered, m.p. 109–111°.

Anal. Calcd. for $C_{20}H_{26}N_2$: C, 81.6; H, 8.9; N, 9.5; neut. equiv., 147. Found: C, 81.4; H, 9.0; N, 9.5; neut. equiv. (titration with perchloric acid), 146.

The residue from the recrystallizations was a viscous oil that continued to crystallize very slowly. Presumably, the hydrogenation product was a mixture of *cis* and *trans* isomers.

Acknowledgment. We are indebted to J. H. Chaudet,[12] R. D. Clark, W. Goodlett, R. G. Nations, and A. L. Thompson, of these laboratories, for contributions to these investigations.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, L. S. COLLEGE, BIHAR UNIVERSITY]

Dihydroisocoumarins. I. Synthesis of 3,4-Dihydro-7,8-dimethoxyisocoumarin

PRATUL KUMAR BANERJEE AND D. N. CHAUDHURY

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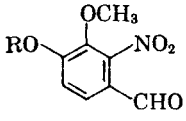
3,4-Dimethoxy-2-aminophenethyl alcohol (IV) was prepared by the reduction of methyl 2-nitrohomoveratrate successively with lithium aluminum hydride and sodium dithionite. In an alternative procedure, the reduction of 2-nitrohomoveratroyl chloride with sodium borohydride followed by sodium dithionite gave IV. On diazotization, Sandmeyer reaction and hydrolysis, IV afforded 3,4-dihydro-7,8-dimethoxyisocoumarin (V).

Interest in the chemistry of the dihydroisocoumarins, without any substituent in the lactone ring, stems from the studies in this laboratory, of the naturally occurring glucoside, blepherin,[1] which has been shown to be the first dihydrofuranodihydroisocoumarin to be detected in nature. Before attempting to synthesize the natural product it was thought desirable to synthesize a series of dimethoxydihydroisocoumarins having no substituent in the lactone ring and to compare their properties with those of the blepherigenin dimethyl ether.[1] The limited number of synthetic dihydroisocoumarins reported in the literature have substituents in the lactone ring. However, an obvious analogy with the use of 1-(2-amino-3-methoxyphenyl)propan-2-ol by Blair and Newbold[2] in the synthesis of 3,4-dihydro-8-methoxy-3-methylisocoumarin suggested 3,4-dimethoxy-2-aminophenethyl alcohol (IV) as an intermediate from which it was possible to achieve the synthesis of 3,4-dihydro-7,8-dimethoxyisocoumarin (V).

(1) D. N. Chaudhury, *J. Indian. Chem. Soc.*, **35**, 612 (1958).

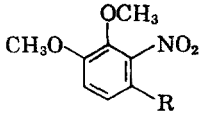
(2) J. Blair and G. T. Newbold, *J. Chem. Soc.*, 2871 (1955).

2-Nitrohomoveratric acid[3-5] (IId), the starting material for this work, was prepared from *O*-acetyl-2-nitrovanillin (Ia), through the



I

Ia. R = CH_3CO
b. R = H

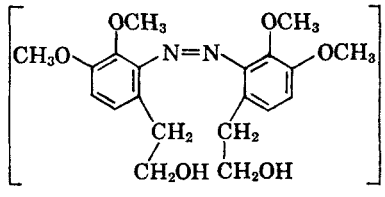


II

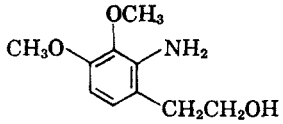
IIa. R = CHO
b. R = COOH
c. R = CH_2CONH_2
d. R = CH_2COOH
e. R = CH_2COOCH_3
f. R = CH_2CH_2OH

intermediates Ib, IIa, IIb and IIc, in improved yields by modifying the procedure of Hay and Lobo[5] at *three* stages: (a) the deacetylation of Ia was done with 50% hydrochloric acid to cut down the two-hour time period of hydrolysis to one-half hour, (b) the Wolff rearrangement of ω-diazo-3,4-dimethoxy-2-nitroacetophenone[5] was effected in a way to raise the 22.9% yield of IIc to 52%, and (c) the interaction of IIc with nitrous acid was carried out in 50% sulfuric acid, instead of concentrated acid, to afford IId in 94% yield as against 69.7%.

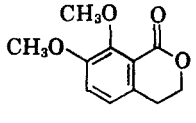
IId was converted to 3,4-dimethoxy-2-aminophenethyl alcohol (IV) by two different methods:



III



IV



V

Method (*a*). IId was transformed to methyl 2-nitrohomoveratrate (IIe) by treatment with excess ethereal diazomethane. The selective reduction of the nitro group of IIe to yield the corresponding amino ester was not undertaken to avoid the formation of oxindole. Since aromatic nitro compounds are reduced by lithium aluminum hydride to the azo compounds,[6] we decided to reduce both the nitro and the ester groups of IIe with lithium aluminum hydride in one step with a view to obtaining 2,3,2′-3′-tetramethoxy-6,6′-dihydroxyethylazobenzene (III), the azo group of which could subsequently be subjected to reductive cleavage by sodium dithionite to give the amino alcohol (IV). The reduction of IIe, however, gave a dark red syrup which could not be induced to crystallize. Chromatography of the syrup in benzene solution over a column of alumina yielded two fractions—a pale yellow oil and a deep red gum. The red gum, presumably the azo alcohol (III), which failed to crystallize, was next treated with sodium dithionite when the azo group was cleaved to form 3,4-dimethoxy-2-aminophenethyl alcohol (IV), isolated as its hydrochloride, m.p. 205–206° and characterized as 3,4-dimethoxy-2-*p*-nitrobenzamidophenethyl *p*-nitrobenzoate, m.p. 226°.

The pale yellow oil was identified as 2-nitrohomoveratryl alcohol (IIf) by comparison with a specimen prepared by an independent route as described in method (b). It was characterized as its *p*-nitrobenzoate, m.p. 191°. IIf has obviously been formed from a portion of IIe by the reduction of the ester group with lithium aluminum hydride while the nitro group remained unaffected.

Method (*b*). The acid chloride, obtained by the interaction of 2-nitrohomoveratric acid (IId) with thionyl chloride, was reduced with sodium borohydride in accordance with the method of Chaikin and Brown[7] to give 2-nitrohomoveratryl alcohol (IIf). Its *p*-nitrobenzoate, m.p. 190°, undepressed on admixture with the specimen prepared by the method (a). IIf was reduced with sodium dithionite to the amino alcohol (IV), isolated as its hydrochloride and characterized as 3,4-dimethoxy-2-*p*-nitrobenzamidophenethyl *p*-nitrobenzoate, m.p. 226°, undepressed on admixture with the sample prepared by method (a).

As IIf and III were separately reduced by sodium dithionite to the amino alcohol (IV), the lithium aluminum hydride reduction product of IIe, which has been shown to be a mixture of IIf and III was, in another experiment, directly reduced with sodium dithionite without separation, to yield IV.

Finally, diazotization of IV, conversion into the nitrile (which was not purified) and subsequent alkaline hydrolysis followed by acidification gave 3,4-dihydro-7,8-dimethoxyisocoumarin (V), m.p. 92°, in 50.6% yield.

EXPERIMENTAL[8]

2-Nitrovanillin (Ib). Deacetylation of Ia (15 g.) was effected by boiling with 50% hydrochloric acid (150 ml.) for 0.5 hr. when a clear solution was obtained. On cooling, Ib (10 g., 81%) separated as yellow needles, m.p. 137–138° (lit.[5] m.p. 137°).

3,4-Dimethoxy-2-nitrophenylacetamide (IIc). A solution of *ω-diazo-3,4-dimethoxy-2-nitroacetophenone*[5] (3 g.) in dioxane (40 ml.) was treated successively with ammonia (30 ml.; *d*, 0.88), 10% aqueous silver nitrate (6 ml.) and methanol

(3) F. W. Kay and A. Pictet, *J. Chem. Soc.*, 947 (1913).
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(5) D. H. Hay and L. C. Lobo, *J. Chem. Soc.*, 2246 (1954).
(6) R. F. Nystrom and W. G. Brown, *J. Amer. Chem. Soc.*, **70**, 3738 (1948).
(7) S. W. Chaikin and W. G. Brown, *J. Amer. Chem. Soc.*, **71**, 122 (1949).
(8) All melting points are uncorrected; microanalyses by Dr. Gore, University of Bombay.

(4 ml.) at 55–60°. After 1.5 hr. when the evolution of nitrogen subsided, 10% aqueous silver nitrate (2 ml.) was added, the bath temperature being maintained for an additional period of 1.5 hr. The reaction mixture was again treated with 10% aqueous silver nitrate (2 ml.) and ammonia (2 ml.; *d*, 0.88) and refluxed for 10 min., filtered hot, and the red-colored filtrate evaporated to dryness on a water bath. The dark solid residue was extracted with boiling water (2 × 100 ml.) and filtered. The filtrate immediately deposited IIc as colorless needles which were collected on cooling; yield 1.5 g. (52%), m.p. 152° (lit.[5] yield 22.9%; m.p. 150–151°).

2-Nitrohomoveratric acid (IId). An ice-cooled solution of IIc (3 g.) in 50% sulfuric acid (300 g.) was treated dropwise with 5% aqueous sodium nitrite (60 ml.) with stirring. On adding more than half the nitrite solution, *2-nitrohomoveratric acid* (IId) started separating from the reaction mixture, as a white precipitate. Stirring of the cooled reaction mixture was continued for 15 min. after the addition of the nitrite solution was completed. At the end of this period, the white precipitate was filtered, washed with ice cold water, and dried at 110° to give the crude acid IId (2.56 g.). An additional amount of IId (0.3 g.) was recovered by ether extraction of the filtrate. The combined crude product (2.86 g.; yield, 94%; lit.[5] yield 69.7%) on crystallization from water gave IId (2.61 g; yield 87%) in glistening flakes, m.p. 145–146° (lit.[5] m.p. 144–146°).

2-Nitrohomoveratryl alcohol (IIf). A mixture of IId (1 g.), dry chloroform (10 ml.) and redistilled thionyl chloride (6 ml.) was refluxed at 70° on the water bath for 2 hr. The chloroform was removed by distillation under reduced pressure at 30° and the excess thionyl chloride removed by repeated codistillation with benzene, under reduced pressure. The red viscous liquid thus obtained was kept overnight *in vacuo* over caustic pellets.

The solution of the acid chloride in dry tetrahydrofuran (10 ml.) was added dropwise to a stirred ice cold suspension of sodium borohydride (0.1 g.) in dry tetrahydrofuran (10 ml.). The mixture was kept at room temperature for 0.5 hr. and then refluxed on water bath for 0.5 hr., cooled and then decomposed with water. The reaction solution was repeatedly extracted with ether and the ether extract washed thoroughly with aqueous sodium carbonate and dried over anhydrous sodium sulfate. Evaporation of the ether left a red oil which on vacuum distillation gave IIf as a pale yellow oil (0.76 g., 81%), b.p. 147°/0.05 mm.; n_D^{25} 1.5158.

Anal. Calcd. for $C_{10}H_{13}O_5N$: C, 52.8; H, 5.7; Found: C, 52.3; H, 5.4.

2-Nitrohomoveratryl p-nitrobenzoate was obtained in the usual way by treating IIf with *p*-nitrobenzoyl chloride in presence of pyridine. It crystallized from ethyl acetate–petroleum ether (b.p. 60–80°) as irregular plates, m.p. 191°.

Anal. Calcd. for $C_{17}H_{16}O_8N_2$: C, 54.2; H, 4.2; Found: C, 53.6; H, 3.8.

Methyl 2-nitrohomoveratrate (IIe). To a solution of IId (4.8 g.) in methanol (50 ml.) excess ethereal diazomethane (prepared from 6 g. of nitrosomethylurea) was added until the solution assumed a deep yellow coloration; it was kept overnight at room temperature. The solution on evaporation left a yellow oily residue which when purified by vacuum distillation yielded IIf as a pale yellow oil (4 g., 80%), b.p. 154°/0.05 mm.; n_D^{25} 1.5230.

Anal. Calcd. for $C_{11}H_{13}O_6N$: C, 51.7; H, 5.1; Found: C, 51.5; H, 5.0.

Lithium aluminum hydride reduction of (IIf). A solution of the *nitro ester* IIf (3.6 g.) in dry ether (50 ml.) was added dropwise to a stirred suspension of lithium aluminum hydride (0.9 g.) in dry ether (50 ml.), cooled to −15°, and left overnight at room temperature. Unchanged lithium aluminum hydride and the complex were decomposed by careful portionwise addition of ice water (30 ml.) followed by 2*N* sulfuric acid (85 ml.). The deep red ether layer was separated and the aqueous layer was extracted with ether (4 × 25 ml.). The ether extracts were combined, dried over anhydrous sodium sulfate, and evaporated to a deep red gum (3 g.). It was dissolved in a few milliliters of benzene and chromatographed by passage through a column of Brockmann alumina (35 g.). The column was eluted with benzene and a pale yellow fraction was collected. The fraction was cut with the appearance of a reddish tinge in the washing and a second fraction which was colored red, was subsequently collected till the washing became almost colorless.

The pale yellow first fraction, on evaporation, afforded a yellow oil (1.7 g.), identified as *2-nitrohomoveratryl alcohol* (IIf) by preparing *2-nitrohomoveratryl p-nitrobenzoate*, in the usual way. It was crystallized from ethyl acetate–petroleum ether (b.p. 60–80°) as irregular plates, m.p. 191°, undepressed on admixture with sample prepared as under IIf.

The deep red gum (III 1 g.) from the second fraction, which failed to crystallize, was reduced with sodium dithionite as described below in method (a).

3,4-Dimethoxy-2-aminophenethyl alcohol (IV). *Method (a).* To the solution of III (1 g.) in methanol (25 ml.) and water (10 ml.), sodium dithionite (2 g.) was added in portions. The deep red color was immediately discharged to a pale yellow solution. It was refluxed on a water bath for 15 min. After distilling most of the methanol, the solution was repeatedly extracted with ether, the yellow ether solution then extracted with 50% hydrochloric acid (100 ml.) and separated. The acid solution was cooled, overlaid with ether (100 ml.), made basic carefully with ammonia (*d*, 0.88), and vigorously shaken. The ether layer was separated and the aqueous layer further extracted with ether (3 × 50 ml.). The combined ether extracts were dried over anhydrous sodium sulfate and the ether distilled to yield IV as a red oil (0.6 g.). The oil was dissolved in dry ether (25 ml.), chilled to −15° and dry hydrogen chloride bubbled through. The *amine hydrochloride* (0.5 g., 45%) separating as dark needles, was crystallized from methanol-ether. It was further purified by vacuum sublimation (bath temp. 140°/0.05 mm.) as white needles, m.p. 205–206° dec. with previous darkening at 200°.

Anal. Calcd. for $C_{10}H_{16}O_3NCl$: C, 51.4; H, 6.9. Found: C, 50.7; H, 7.0.

Interaction of IV in ether with a benzene solution of *p*-nitrobenzoyl chloride in presence of pyridine afforded *3,4-dimethoxy-2-p-nitrobenzamidophenethyl p-nitrobenzoate*, needles from ethyl acetate, m.p. 226°.

Anal. Calcd. for $C_{24}H_{21}O_9N_3$: C, 58.2; H, 4.2. Found: C, 57.9; H, 4.6.

Method (b). 2-Nitrohomoveratryl alcohol (IIf) (1 g.) in methanol (25 ml.) and water (10 ml.) was refluxed with sodium dithionite (3.5 g.) for 0.5 hr. During this period, water (10 ml.) was added in installments to dissolve the sodium dithionite when a clear solution was obtained. It was cooled, the methanol distilled and the aqueous solution extracted with ether (3 × 50 ml.). The ether solution was treated as in method (a) to isolate the amino alcohol IV as its hydrochloride (0.7 g., 70%).

IV was characterized as *3,4-dimethoxy-2-p-nitrobenzamidophenethyl p-nitrobenzoate*, m.p. and mixed m.p. 225°, prepared as in method (a).

In one experiment, the nitro ester (IIf) (1 g.) was treated with lithium aluminum hydride (0.25 g.) in dry ether and worked up in accordance with the procedure described earlier. The red gummy product was next dissolved in methanol (25 ml.) and reduced with sodium dithionite (3.0 g.) and the hydrochloride of IV (0.5 g.) was isolated as detailed in method (b).

3,4-Dihydro-7,8-dimethoxyisocoumarin. (V). In a manner similar to the procedure of Blair and Newbold,[2] the hydrochloride of IV (0.380 g.) in hydrochloric acid (0.38 ml.; *d*, 1.16) and water (9 ml.) was diazotized with sodium nitrite (0.120 g.) in water (1 ml.) at 0°. After neutralization with anhydrous sodium carbonate, the diazonium solution was

added to a solution of potassium cyanide (0.380 g.), nickel chloride (0.300 g.), and anhydrous sodium carbonate (0.1 g.) in water (10 ml.) at 15° with stirring. The mixture allowed to stand for 2 hr. and then heated at 70° for 0.5 hr. The cooled reaction solution was extracted with ether (4 × 25 ml.); the combined ether extract dried over anhydrous sodium sulfate and ether removed by distillation to give a gum. The gum was refluxed with aqueous caustic potash (20 ml.; 10%) for 5 hr., cooled, and acidified with concentrated hydrochloric acid (Congo red). The acidified solution was filtered from insoluble matter and repeatedly extracted with chloroform; the combined extracts were dried over anhydrous sodium sulfate. Evaporation of the solvent gave a gum which slowly solidified in an ice chest, m.p. 65–66°. Vacuum sublimation at 110–115°/0.05 mm. yielded a white solid, m.p. 86–88°. It was crystallized from petroleum ether (b.p. 40–60°) with a few drops of chloroform (ice chest) when *3,4-dihydro-7,8-dimethoxyisocoumarin* (V) was obtained as rectangular prisms (0.130 g.; 50.6%), m.p. 92°.

Anal. Calcd. for $C_{11}H_{12}O_4$: C, 63.4; H, 5.8. Found: C, 63.2; H, 5.8.

The infrared spectrum (chloroform solvent) had a band at 5.88 μ (conjugated δ-lactone.).

Acknowledgment. We are grateful to Dr. Tapan. K. Mukherjee, Retina Foundation, Boston 14, Mass., for the infrared data of the dihydroisocoumarin (V).

MUZAFFARPUR, INDIA

[CONTRIBUTION FROM THE RESEARCH AND ENGINEERING DIVISION, MONSANTO CHEMICAL CO.]

Chlorination of Biphenyl

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Biphenyl was chlorinated under a wide range of conditions. The *ortho-para* ratios were observed to rise sharply with increasing *meta-para* ratio. Explanations are discussed.

Although the halogenation of biphenyl has received only moderate attention in the past thirty years,[1–3] we felt it would be a convenient system with which to study the chlorination process. In this paper we report the results of a detailed examination of the chlorination of biphenyl, 2-chlorobiphenyl, and 4-chlorobiphenyl. These results have permitted us further insights into the electrophilic aromatic substitution process.

RESULTS AND DISCUSSION

Biphenyl, 2-chlorobiphenyl, and 4-chlorobiphenyl were chlorinated under a wide range of conditions and the results are recorded in Tables I, II, and III, respectively.

Table I is arranged in descending order of $^1/_2$ *m/p* ratios and represents, therefore, a scale of chlorinating agent reactivity[4] and Lewis acid strength. The order of Lewis acid strength is in good agreement with previous reports.[5–7] Attention should be called to the sulfuric acid–silver sulfate system which falls in the middle portion of the scale. This system has been reported to involve a positive specie as chlorinating agent[8] and seems to be similar, at least in $^1/_2$ *m/p* ratio, to acid-catalyzed halogenation by hypohalous acids.[2,9] Since the $^1/_2$ *m/p* ratios in Table I continue to increase, it is unlikely that chloronium ion is involved in this system or in any of the examples. Some form of complexing between chlorine molecule and acid is probably involved in each case.

Changes in $^1/_2$ *m/p* ratio can be correlated with $^1/_2$ *o/p* ratio changes. As the $^1/_2$ *m/p* ratio increases, the $^1/_2$ *o/p* ratio increases precipitously, then levels out just below unity (Fig. I). This relationship can be rationalized in several ways. One explanation is based on the arguments of Ingold,[10] Waters,[11] Remick,[12] and DeLaMare,[13] suggesting that the transition state for substitution *para* to an *ortho-para*-directing conjugative substituent is more stable than the *ortho* transition state as a result of conjugative effects. The magnitude of this *para* preference would be approximated by the examples at the bottom of Table I where conjugative effects are expected to be large. If the above assumption is correct the $^1/_2$ *o/p* ratio should gradually rise with increasingly reactive chlorinating agents, and this

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