unsaturated ketone, the ketonic portion of an aliquot of each reaction product was separated from the unsaturated alcohol by the use of Girard reagent (T)[12] and tested with 2% aqueous potassium permanganate. None of the ketonic portions so obtained gave positive tests. All of the unsaturated ketones employed did so immediately.

Discussion

In Table I are summarized the results of our experiments along with those of earlier investigators for comparison. It can be seen that except for the addition of ethylmagnesium bromide, the amount of conjugate addition to 2-cyclohexenone is comparable to the amount of conjugate addition to its open chain analogs. Since a cyclic intramolecular transition state (equation 1) is impossible for 2-cyclohexenone, these results imply that if one possible path for conjugate addition involves such an intermediate, the path is of relatively little importance with the compounds studied. The significance of the relatively low value with ethylmagnesium bromide and 2-cyclohexenone is not yet clear.

There is considerable disagreement among previous workers as to the amount of conjugate addition a given ketone undergoes. The analytical procedures which yielded these widely divergent values were investigated in connection with this study. It was found that fractionation[18,20] is unsatisfactory because of the tendency of the carbinols to dehydrate. Girard reagent[12] proved not to be quantitative; the separated non-ketonic portion gave a positive test with 2,4-dinitrophenylhydrazine.[22] The sodium bisulfite method[5] gave results which agree reasonably well with those obtained by the method of Bryant and Smith.[16] The bisulfite method, however, involves a large number of manipulations and it is limited to those ketones which will form bisulfite addition compounds. The method of Bryant and Smith was found to be the most accurate (±2%), the simplest and the most general of those yet reported.

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[22] One other reason that our results differ so much from those which were determined by the use of Girard reagent is that the earlier workers apparently used too little reagent. Thus from 10 g. of the product obtained from the reaction of ispropylmagnesium bromide and 3-hepten-2-one there was separated 4.63 g. (0.03 mole) of saturated ketone. This is all that could have been separated with the 5 g. (0.03 mole) of Girard reagent used. A similar situation appears to have been true in the analysis of the product from ethylmagnesium bromide and 3-hepten-2-one.

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[CONTRIBUTION FROM THE WEIZMANN INSTITUTE OF SCIENCE]

The Action of *t*-Butyl Hypochlorite on Organic Compounds. III. Phenols[1]

BY DAVID GINSBURG

The action of *t*-butyl hypochlorite on a series of phenols is reported. In most cases, chlorine enters the nucleus ortho to the phenolic hydroxyl group. Possible mechanisms of the reaction are discussed.

In continuation of previous experiments, the action of *t*-butyl hypochlorite on phenols was investigated. According to a brief report by Clark[2] this reagent acts on phenols with almost explosive violence, necessitating the use of diluents to moderate the reaction. Even so, the yields in many cases leave much to be desired, and mixtures of mono- and poly-chlorinated derivatives are often obtained, involving inevitable losses in the course of separation. Therefore, in contradistinction to aromatic aldehydes, the chlorination of phenols with *t*-butyl hypochlorite is not always worthwhile from the preparative point of view. Nevertheless, in certain cases the yields are high and compounds can easily be prepared which are not accessible by other chlorination methods.[3]

With one apparent exception (thymol), *t*-butyl hypochlorite introduces the chlorine atom *ortho* to the hydroxyl group of monohydric phenols. Thus, phenol gives *o*-chlorophenol, and *o*-chlorophenol yields 2,6-dichlorophenol, when treated with one mole of *t*-butyl hypochlorite. Clark's statement[2] that dichlorination of phenol leads to the 2,4-dichloro derivative, could not be substantiated. Also, when dichloro-substitution takes place with mono-*o*-substituted phenols, one of the chlorine atoms enters the free ortho-, the other the para position. In the heretofore unknown dichloro derivative, obtained from carvacrol, the ortho position of one of the chlorine atoms was proven by infrared analysis.

In the case of guaiacol, the para-directing influence of the methoxyl group outweighs the ortho-directing influence of the phenolic hydroxyl group, and 5-chloro-2-methoxyphenol results. Similar effects have been observed in the chlorination of aromatic aldehydes with *t*-butyl hypochlorite.[1]

As in the aldehyde series, nitro groups deactivate the ring: *o*- and *p*-nitrophenols do not react. The previously noted[1,2] deactivating effect of the carboxyl group is outweighed by the activating influence of the hydroxyl group: salicylic acid is attacked ortho to the phenolic group, yielding 3-chloro-2-hydroxybenzoic acid[2] (see also Table I).

The chlorination of *o*-cresol with *t*-butyl hypochlorite gave a mono- and a dichlorinated product. The latter was the known 4,6-dichloro-2-methylphenol, the former, therefore, presumably either 4- or 6-chloro-2-methylphenol. As its condensation product with chloroacetic acid was not identical with Synerholm and Zimmerman's[4] 4-chloro-2-methylphenoxyacetic acid (m.p. 119–120°), it must have been the 6-chloro-isomer[5] and the monochlorinated *o*-cresol, 6-chloro-2-methylphenol.

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[1] Paper II in this series: D. Ginsburg, THIS JOURNAL, **73**, 702 (1951).

[2] B. F. Clark, *Chem. News*, **143**, 265 (1931).

[3] For example, treatment of phenol with chlorine gives mainly *p*-chlorophenol, with *t*-butyl hypochlorite the *o*-isomer.[2]

[4] M. E. Synerholm and P. W. Zimmerman, *Contrib. Boyce Thompson Inst.*, **14**, 91 (1945); *C. A.*, **40**, 1473 (1946).

[5] It proved identical with the product obtained by Haskelberg (*J. Org. Chem.*, **12**, 426 (1947)) upon chlorination of 2-methylphenoxyacetic acid.

TABLE I

CHLORINATION OF PHENOLS WITH *t*-BUTYL HYPOCHLORITE

A = See experimental section.

Compound	Product	Yield, %	*Anal.* Cl, %		Proof of structure
			Calcd.	Found	
o-Cresol	6-Cl-2-CH_3-phenol	31	17.7[a]	17.9	A
	4,6-di-Cl-2-CH_3-phenol	18	40.1	39.9	A
m-Cresol	2-Cl-3-CH_3-phenol	44	17.7[a]	17.9	M.p. 55–56.5°[b]
p-Cresol	2-Cl-4-CH_3-phenol	69	17.7[a]	17.5	B.p. 196°[c]
Pyrogallol	4-Cl-pyrogallol	79	22.1	21.8	M.p. 143°[d]
Carvacrol	2-CH_3-4(?),6-di-Cl-5-*i*-C_3H_7-phenol	21	32.4	32.7	A
Thymol	4-Cl-3-CH_3-6-*i*-C_3H_7-phenol	48	19.2	19.4	M.p. 61°[e]
Guaiacol	5-Cl-2-CH_3O-phenol	68	16.4[a]	16.3	A
o-Cl-Phenol	2,6-di-Cl-phenol	73	43.5	43.2	A
p-Cl-Phenol	2,4-di-Cl-phenol	80			A
o-NO_2-Phenol	No reaction				
p-NO_2-Phenol	No reaction				
Methyl salicylate	Methyl 2-OH-3,5-di-Cl-benzoate	35			A
Salicylic acid	2-OH-3-Cl-benzoic acid	73			M.p. 180°,[f] methylation yielded 2 CH_3O-3-Cl-benzoic acid, m.p. 118°[g]
α-Naphthol	2-Cl-1-naphthol	77	19.9	20.1	M.p. 64–65°,[h] 2-Cl-1,4-naphthoquinone-4-anil, m.p. 110°[i]
β-Naphthol	1-Cl-2-naphthol	67	19.9	19.5	M.p. 71°,[j] methyl ether, m.p. 71°[k]

[a] *Anal.* of corresponding aryloxyacetic acid. [b] G. P. Gibson, *J. Chem. Soc.*, 1425 (1926) reports m.p. 55–56° for this compound; 6-chloro-3-methylphenol melts at 45–46° (H. H. Hodgson and F. H. Moore, *ibid.*, 2038 (1926)); 4-Cl-3-methylphenol melts at 66° (Beilstein, "Handbuch," Vol. 6, 2nd supplement, p. 355). [c] G. T. Morgan and F. H. Burstall, *J. Chem. Soc.*, 3268 (1928) report b.p. 196°; 3-chloro-4-methylphenol melts at 55° (F. Ullmann and C. Wagner, *Ann.*, **355**, 367 (1907). [d] C. Graebe and M. Suter, *ibid.*, **340**, 228 (1905) report m.p. 143°. [e] The reported m.p. is 61° (German Patent 431,513; *Chem. Zentr.*, **97**, II, 1462 (1926)). [f] R. Anschütz and R. Anspach, *Ann.*, **346**, 312 (1906) report m.p. 180°. [g] W. Davies and L. Rubenstein, *J. Chem. Soc.*, **123**, 2851 (1923), report m.p. 117°. [h] R. Lesser and G. Gad, *Ber.*, **56**, 972 (1923) report m.p. 64–65°. [i] P. Friedländer and L. Sander, *ibid.*, **57**, 646 (1924) report m.p. 112°. [j] G. T. Morgan and F. H. Burstall (ref. *c*, p. 3269) report m.p. 70°. [k] H. Franzen and G. Stäuble, *J. prakt. Chem.*, [2] **103**, 379 (1921), report m.p. 70–71°.

The products obtained in this investigation are listed in Table I.

An obvious similarity exists between the reaction of phenols with *t*-butyl hypochlorite and their benzyloxylation by means of benzoyl peroxide, which also usually attacks the position ortho to the hydroxyl group.[6] It seems, therefore, possible that the chlorinating species in the present reaction are chlorine atoms. However, it is not excluded that (positive) chloronium ions may lead to substitution regularities similar to those observed here. The reaction with *t*-butyl hypochlorite would then be parallel to the nitration of organic compounds with the positive nitronium ion.[7] Such a hypothesis has been proposed before for the reaction of hypochlorite with olefinic double bonds.[8]

A kinetic investigation now in hand is expected to lead to a decision between the two alternatives.

Experimental[9]

General Chlorination Procedure.—The phenol (0.5 mole) was dissolved or suspended in carbon tetrachloride (150–300 ml.) and *t*-butyl hypochlorite (0.5 mole) was added dropwise with stirring. The temperature of the reaction mixture was allowed to rise, usually reaching the boiling point of the solvent. The mixture was then refluxed for two hours, the carbon tetrachloride and *t*-butanol removed under slightly diminished pressure and the residue fractionated through a Todd (15 plate) column.

2,6-Dichlorophenol.—From *o*-chlorophenol (64.3 g.) in carbon tetrachloride (150 ml.) and *t*-butyl hypochlorite (55 g.), 2,6-dichlorophenol (60 g., yield 73%) was obtained after fractionation. It melted at 67° (petroleum ether).[10]

2,6-Dichlorophenoxyacetic acid was prepared by the procedure of Koelsch[11] and melted at 135°, while 2,4-dichlorophenoxyacetic acid melts at 140–141°. An authentic sample of 2,4-D depressed the m.p. of the above acid.

2,4-Dichlorophenol.—This product was formed in 80% yield by chlorination of *p*-chlorophenol. It melted at 43°.[10] Condensation with chloroacetic acid gave authentic 2,4-D.

Chlorination of *o*-Cresol.—From *o*-cresol (56 g. of which 21 g. was recovered), there was obtained a fraction weighing 40 g. which partially solidified on cooling. When this fraction was condensed with chloroacetic acid, a compound was obtained which, after several crystallizations from aqueous ethanol, sintered at 118° and melted at 130°. It showed no m.p. depression on admixture with Haskelberg's[5] x-chloro-2-methylphenoxyacetic acid; it depressed, however, the m.p. of Synerholm and Zimmerman's[4] 4-chloro-2-methylphenoxyacetic acid.

Filtration of the original partly crystalline chlorination product and recrystallization from petroleum ether yielded 4,6-dichloro-2-methylphenol, m.p. 54–55°[11a] (see Table I for analysis).

2-Methyl-4-(?),6-dichloro-5-isopropylphenol.—Chlorination of carvacrol with one mole of *t*-butyl hypochlorite gave no monochloro derivative, and about 50% of the starting material was recovered. A heretofore unreported dichlorocarvacrol, m.p. 82°, was obtained by crystallization (petroleum ether) of the fraction boiling at 155–160° (56 mm.). Its structure has not been completely elucidated but the infrared absorption at 3520 cm.$^{-1}$ (2.84 μ) (0.13 g. in 1 ml. carbon tetrachloride)[12] excludes the possibility of 2-methyl-

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[6] S. L. Cosgrove and W. A. Waters, *J. Chem. Soc.*, 3189 (1949). Compare also the action of potassium persulfate on phenols, *e.g.*, *p*-cresol yields 3,4-dihydroxytoluene; *p*-hydroxybenzoic acid yields protocatechuic acid (Schering, German Patent 81,068, German Patent 81,298 (1895)).

[7] See P. B. D. de la Mare and P. W. Robertson, *ibid.*, 100 (1948); P. B. D. de la Mare, *ibid.*, 2871 (1949).

[8] J. J. Ritter and D. Ginsburg, THIS JOURNAL, **72**, 2381 (1950). and refs. 4, 5, 6 in that paper.

[9] All melting and boiling points are uncorrected.

[10] 2,4-Dichlorophenol melts at 43° (K. W. F. Kohlrausch, *et al.*, *Monatsh.*, **67**, 89 (1936)).

[11] C. F. Koelsch, THIS JOURNAL, **53**, 304 (1931).

[11a] T. Zincke, *Ann.*, **417**, 191 (1918), reports m.p. 55° for this compound.

[12] At a comparable concentration (0.048 g. in 1 ml. carbon tetrachloride), phenol showed an absorption band at *ca.* 3300 cm.$^{-1}$. The infrared absorption found for dichlorocarvacrol is in agreement with the figure given by Davies (*Trans. Faraday Soc.*, **34**, 1427 (1938)) for *o*-chlorophenol (2.825μ) at a different concentration (0.005 g./ml. carbon

3,4-dichloro-5-isopropylphenol. One of the chlorine atoms must have entered the free *o*-position of carvacrol (see Table I for analysis).

5-Chloro-2-methoxyphenol.—Chlorination of guaiacol gave a 68% yield of a mono-chloro derivative, b.p. 225–230°. It gave, by condensation with chloroacetic acid, a product of m.p. 134–135° (see Table I for analysis) and upon methylation 4-chloroveratrole. This was proven by nitration of the latter to the known 5-nitro-4-chloro-1,2-dimethoxybenzene, m.p. 118°.[13]

The chlorination product of guaiacol is 5-chloro-2-methoxyphenol; it was not identical with the other possible derivative **4-chloro-2-methoxyphenol**, which was prepared as follows: (a) *o*-anisidine was converted into *sym*-di-(2-methoxyphenyl)-urea, m.p. 190° (from petroleum ether), by treatment with phosgene in toluene in presence of dimethylaniline.

Anal. Calcd. for $C_{15}H_{16}O_3N_2$: N, 10.3. Found: N, 10.2.

Chlorination with sulfuryl chloride in tetrachloroethane gave *sym*-di-(4-chloro-2-methoxyphenyl)-urea, m.p. 232–234° (from ethanol).

Anal. Calcd. for $C_{15}H_{14}O_3N_2Cl_2$: Cl, 20.8. Found: Cl, 20.8.

The substituted urea was hydrolyzed by means of sodium hydroxide in ethylene glycol to 4-chloro-2-methoxyaniline which was purified by steam distillation and had m.p. 54°.[14]

(b) **4-Chloro-2-methoxyphenol.**—To a solution of 4-chloro-2-methoxyaniline (4 g.) in a mixture of sulfuric acid (4.5 ml.), water (12.5 ml.) and ice (11 g.), a solution of sodium nitrite (2 g.) in water (6 ml.) was added. The resulting diazonium solution was poured into a hot mixture of sulfuric acid (10 ml.) and water (6 ml.) and distilled with steam. 4-Chloro-2-methoxyphenol (1.4 g.) was isolated from the distillate. Its condensation product with chloroacetic acid, (4-chloro-2-methoxy)-phenoxyacetic acid, could not be induced to crystallize; nor did it crystallize when seeded with the chloroacetic acid derivative (m.p. 134–135°) of the monochloroguaiacol, obtained above.

Anal. Calcd. for $C_9H_9O_4Cl$: Cl, 16.4. Found: Cl, 16.2.

Methyl 2-Hydroxy-3,5-dichlorobenzoate.—Chlorination of methyl salicylate with one mole of *t*-butyl hypochlorite gave a 35% yield of the dichloro compound which crystallized from the reaction mixture after removal of the solvents. Distillation of the mother liquor yielded 45% of unreacted methyl salicylate. The dichloro-compound melted at 150°[15] and was hydrolyzed by means of ethanolic potassium hydroxide to 2-hydroxy-3,5-dichlorobenzoic acid, m.p. 216–218°.[16]

Anal. Calcd. for $C_7H_4O_3Cl_2$: Cl, 34.4. Found: Cl, 34.4.

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tetrachloride). However, it is reasonable to assume that concentration has only a minor effect in the infrared absorption of chelate compounds. It is worthy of note that the infrared absorption at 3520 cm.$^{-1}$ (2.84μ) is the fundamental band corresponding to the overtone at 7050 cm.$^{-1}$ as found by Wulf and Liddell for *o*-chlorophenol (THIS JOURNAL, **57**, 1464 (1935); see also L. Pauling, *ibid.*, **58**, 94 (1936)).

(13) C. A. Fetscher and M. T. Bogert, *J. Org. Chem.*, **4**, 77 (1939).

(14) W. Fitzky, U. S. Patent 1,792,156 (*C. A.*, **25**, 1844 (1931)).

(15) Lassar-Cohn and F. Schultze, *Ber.*, **38**, 3301 (1905), report m.p. 150°.

(16) R. Anschütz and H. Mehring, *Ann.*, **346**, 300 (1906), report m.p. 219°.

[CONTRIBUTION FROM THE NORTHERN REGIONAL RESEARCH LABORATORY][1]

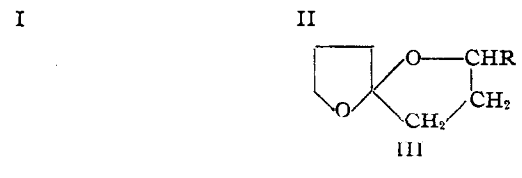
1,6-Dioxaspiro[4.4]nonanes from γ-(2-Furyl)-alkanols

BY KLIEM ALEXANDER, L. S. HAFNER AND L. E. SCHNIEPP

1,6-Dioxaspiro[4.4]nonane and 2-methyl-1,6-dioxaspiro[4.4]nonane were prepared in significant yield from 1-(2-furyl)-propanol-3 and 1-(2-furyl)-butanol-3, respectively. A mechanism for the formation of 1,6-dioxaspiro[4.4]nonanes from γ-(2-furyl)-alkanols is proposed.

The formation of 1,6-dioxaspiro[4.4]nonane[2] (III, R = H) on hydrogenation of β-(2-furyl)-acrolein was observed by Adkins and co-workers.[3,4] Furfuralacetone[5,6] and difurfuralacetone[6] were found to yield the same type of products.

The route of formation of these spiranes has not been adequately explained. Burdick and Adkins[3] concluded that β-(2-furyl)-propionaldehyde was an intermediate in the conversion of furylacrolein to 1,6-dioxaspiro[4.4]nonane and that 1-(2-furyl)-propanol-3 was not. Their tabulated experimental data show, however, that the furylpropanol was hydrogenated over Raney nickel whereas the best yields of spirane had been obtained with nickel-on-kieselguhr catalysts. Recent investigations with furfuralacetone and its hydrogenation products showed that Raney nickel promoted rapid and complete reductions to 1-tetrahydrofurylbutanol-3 and that copper chromite and nickel-on-kieselguhr always gave appreciable amounts of 2-methyl-1,6-dioxaspiro[4.4]nonane (III, R = CH_3). The observation that 1-furylbutanol-3 gave higher yields of the spirane than did 1-furylbutanone-3 prompted a reinvestigation of furylpropanol. It was found that reduction of furylpropanol over a nickel-on-kieselguhr catalyst gave a 38% yield of 1,6-dioxaspiro[4.4]nonane. It is, therefore, concluded that the γ-(2-furyl)-alkanol (I) structure is an intermediate in the formation of these spiranes. A mechanism for the ring closure, involving the intramolecular addition of the hydroxyl group into the double bond of a 4,5-dihydrofuryl intermediate (II), is proposed;



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[1] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

[2] A. M. Patterson and L. T. Capell, "The Ring Index," Reinhold Publishing Corp., New York, N. Y., 1940, p. 109; previously named 1,9-dioxa-5-spirononane, ref. 4.

[3] H. E. Burdick and H. Adkins, THIS JOURNAL, **56**, 438 (1934).

[4] M. Farlow, H. E. Burdick and H. Adkins, *ibid.*, **56**, 2498 (1934).

[5] A. Heinz, G. Meyer and G. Schucking, *Ber.*, **76B**, 676 (1943).

[6] K. Alexander, G. H. Smith, L. S. Hafner and L. E. Schniepp, THIS JOURNAL, **72**, 5506 (1950).