[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, THE DOW CHEMICAL CO.]

The Halogenation of *meta-tert*-Butylphenol

WARREN W. KAEDING

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Steric factors appear to control the course of aromatic ring halogenation of *m-t*-butylphenol according to the following sequence: 6 > 4 > 2. Iodine would not react at the positions adjacent to the *t*-butyl group. Bromine would not substitute at the position between the hydroxyl and *t*-butyl groups.

In connection with some work on a process for the catalytic air oxidation of carboxylic acids to phenols,[1] a supply of pure *m-tert*-butylphenol was obtained directly from *p-tert*-butylbenzoic acid. Small amounts of the phenol were previously prepared by multistep syntheses starting with *p-tert*-butylacetanilide[2a] or *tert*-butylbenzene.[2b]

m-tert-Butylphenol was of interest because a number of new derivatives could be prepared, characterized, and evaluated in various screening programs. Furthermore, this material was an interesting model compound which was used to determine certain steric characteristics of the bulky tertiary butyl group. The positions adjacent to this group on the aromatic ring were highly activated by virtue of the directing influence of the hydroxyl group, reinforced by that of the tertiary butyl group itself. Consequently, with electrophilic replacement reactions, the tendency for substitution at carbon atoms adjacent to the one holding the *t*-butyl group should have been similar to or greater than the analogous positions in phenol itself. Therefore, failure of reagents to react at the *ortho* and *para* positions of *m-tert*-butylphenol, especially those which ordinarily would react rapidly with phenol itself, may be attributed strictly to steric effects, rather than to low reactivity.

The relative size and directive influence of the substituents in *m-tert*-butylphenol make it possible to readily predict the favored positions for replacement reactions.

$$6 > 4 > 2 \gg 5$$

Models have indicated that large atoms like bromine and iodine would not be able to approach the 2-position closely enough to replace the hydrogen. On the other hand, chlorine should be able to substitute at the *ortho* and *para* positions. These predictions were verified experimentally.

With all of the halogenation reactions, it was assumed that the powerful directing influence of the hydroxyl and alkyl groups in *m-tert*-butylphenol would make it very unlikely that substitution would occur at the 5-position. With phenol itself, the *meta* positions were chlorinated only after the *ortho* and *para* positions were filled and only then by using vigorous conditions and the aid of a halogen carrier.[3] Smith[4] has shown that out of fifty-seven representative phenols tested, all but two compounds were brominated only in the positions *ortho* and *para* to the hydroxyl group, in aqueous acetic acid solution.

Bromination. The same general procedure was used for all of the bromination reactions. The *m-tert*-butylphenol was dissolved in three parts of carbon tetrachloride and treated with the required amount of bromine diluted with an equal volume of solvent. The halogen solution was slowly added to the phenol in the temperature range of 20–40°. Under these conditions, virtually no halogen exchange with the solvent occurred.

When equal molar amounts of bromine and *m-tert*-butylphenol were used, substitution occurred exclusively at the 6-position (I). The infrared spectra of the first and last distillation fractions were identical and no other products were isolated. The position of entry was determined by the alkaline hydrolysis of the product to produce 4-*tert*-butylcatechol (II) by the method of Hale and Britton.[5]

Under similar conditions, careful studies have shown that the bromination of phenol itself occurred at the *para* position first (98–99%) and that polybromophenols were made from a *p*-bromophenol intermediate.[6] The *t*-butyl group was large enough to completely reverse this tendency by effectively shielding the *para* position.

When two moles of bromine per mole of *m-tert*-butylphenol were used, only *one* dibromo isomer was produced. The work above clearly indicates that the first mole of bromine reacted to give 2-bromo-5-*t*-butyl phenol as an intermediate. A choice must be made between the remaining *ortho* and *para* positions for entry of the second bromine atom. As the *para* position is the less hindered by adjacent groups, it seems reasonable to conclude that the second bromine atom entered the ring to give 5-*t*-butyl-2,4-dibromophenol (III). This conclu-

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[1] W. W. Kaeding, *J. Org. Chem.*, 26, 3144 (1961).

[2] (a) M. S. Carpenter, W. M. Easter, and T. F. Wood, *J. Org. Chem.*, 16, 586 (1951). (b) R. S. Bowman, D. R. Stevens, and W. E. Baldwin, *J. Am. Chem. Soc.*, 79, 87 (1957).

[3] V. Migrdichian, *Org. Synthesis*, II, 1544 (1957).

[4] B. Smith, *Acta Chemica Scand.*, 11, 839 (1957).

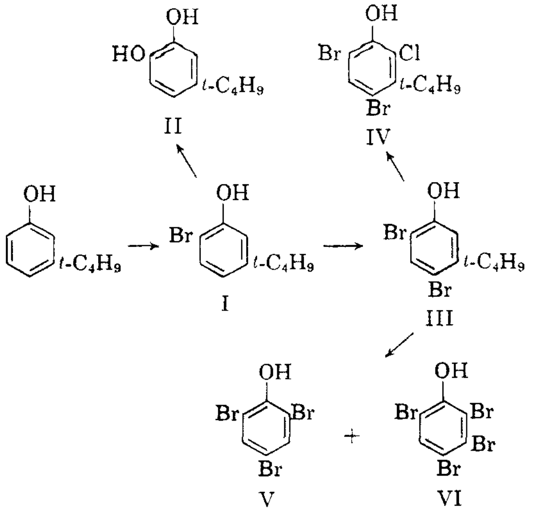
[5] W. J. Hale and F. G. Britton, *Ind. Eng. Chem.*, 20, 114 (1928).

[6] E. Podall and W. Foster, *J. Org. Chem.*, 23, 280 (1958).

sion was substantiated by measurement of the hydroxyl stretching frequency in the near infrared region at concentrations low enough to prevent intermolecular association. The value for the dibromo derivative described above was 3536 cm.$^{-1}$ and it was identical with that found for 2-bromo-5-*t*-butylphenol (I). *para*-Halogens are known to have little effect on this absorption band,[7a] in direct contrast with *ortho* halogen substituents.[7] A second *ortho* bromine atom would be expected to lower the frequency. For example, the absorption frequency for 2,4-dibromo-6-chloro-5-*t*-butyl phenol (IV) has shifted to 3517 cm.$^{-1}$

When three or more moles of bromine per mole of *m-tert*-butylphenol was used, under conditions of reaction similar to those described above, only the dibromo derivative mentioned above could be isolated. When powdered iron was used as a catalyst, under vigorous conditions of reaction, 2,4,6-tribromo (V) and 2,3,4,6-tetrabromophenol (VI) were the only new compounds isolated. It would appear from this that the position between the hydroxyl and *t*-butyl groups was effectively shielded from attack by bromine. Further halogenation occurred only by the replacement of the *t*-butyl group itself.

The data preceding this indicates that the position adjacent to the *t*-butyl group could not be brominated because of steric hindrance. If failure to react was strictly a steric effect, a similar reagent of sufficiently small size should substitute at this position under mild conditions of reaction. To verify this, an equimolar amount of chlorine was added to 5-*t*-butyl-2,4-dibromophenol. A rapid reaction occurred at room temperature with the production of a single product. Elementary analysis indicated that monochlorination occurred. This compound could only be 5-*t*-butyl-6-chloro-2,4-dibromophenol (IV).



Chlorination. A similar procedure was used with all chlorination reactions. The required amount of gaseous chlorine was slowly bubbled into a solution of the phenol in carbon tetrachloride.

When equimolar amounts of chlorine and *m-tert*-butylphenol were combined, a number of liquid products were formed. Distillation gave three major fractions, each composed of a mixture of compounds. The low boiling fraction (75% by weight) was a mixture of two monochloro isomers. The strong, sharp absorption band at 2.85 μ was typical for hydrogen bonding with an ortho chlorine atom. Redistillation of this fraction partially separated the two *o*-chloro isomers which were distinguished by absorption bands at 12.78 μ (lower boiling fraction) and 12.43 μ. The latter was tentatively assigned the structure 2-chloro-5-*t*-butylphenol (VII) and the former 2-chloro-3-*t*-butylphenol (IX). These bands are typical of 1,2,4- and 1,2,3-trisubstituted aromatic rings.[8]

As will be shown later, only the 6-position of *m-tert*-butylphenol is available for iodination. Therefore, only one of the isomers in the mixture should react to give a high boiling iodophenol. When the mixture was iodinated, a volatile monochloro *m-tert*-butylphenol derivative was distilled from the reaction mixture. A strong absorption peak appeared at 12.43 μ while the band at 12.78 μ, found in the original mixture was completely eliminated. Relatively pure 5-*t*-butyl-2-chlorophenol was removed from the mixture by this method. A solid derivative was isolated from the nonvolatile portion. Analysis confirmed that this compound was 3-*t*-butyl-2-chloro-6-iodophenol (X). Pure 2-chloro-3-*t*-butyl phenol was never isolated from this mixture.

The intermediate fraction (14%) of the original chlorination product, was a mixture of various mono- and dichloro-*m-tert*-butylphenol isomers. The high boiling fraction (11%) was a relatively pure monochloro isomer. The infrared spectrum, in a dilute carbon tetrachloride solution, revealed a sharp absorption band at 2.79 μ which is typical of an unassociated phenolic OH group. This positively eliminated a chloro substituent in either the 2 or 6 position and, therefore, the structure assigned was 3-*t*-butyl-4-chlorophenol (VIII).

When two moles of chlorine were used per mole of *m-tert*-butylphenol, a mixture of dichloro *m-tert*-butylphenol isomers was formed. In this case, however, one of the isomers slowly separated by crystallization. A sample of this material was treated with excess bromine in carbon tetrachloride solution. Hydrogen bromide evolution did not occur and only unchanged starting material was recovered. As it was shown previously that the *ortho* position adjacent to the *t*-butyl group can not be brominated, the structure assigned was 2,4-dichloro-5-*t*-

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[7] (a) A. W. Baker, *J. Am. Chem. Soc.*, **80**, 3598 (1958). (b) A. W. Baker and W. W. Kaeding, *J. Am. Chem. Soc.*, **81**, 5904 (1959).

[8] L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Wiley, New York, p. 66–67 (1954).

butylphenol (XII). This is the predicted most abundant isomer. The other two isomers would brominate with ease under the conditions of reaction used.

The liquid portion which remained after the separation of 2,4-dichloro-5-*t*-butylphenol was distilled. Two distinct fractions were obtained, a mobile liquid and a crystalline solid both of which gave an analysis corresponding to dichloro-*m-tert*-butylphenol and which were different from the 2,4-dichloro-5-*t*-butylphenol described previously. Each of the new compounds had a chlorine atom in the 2-position. This was verified by the unusually low γ_{OH} frequency which is a result of the OH bonding to an adjacent chlorine atom crowded by a neighboring *t*-butyl group. The remaining chlorine atom could then be at the 6-position for one compound and at the 4-position for the other.

The assignment of isomers was verified by iodination reactions. Because of steric factors, only 3-*t*-butyl-2,4-dichlorophenol (XIII) had a position available for iodination. The liquid isomer reacted with iodine under alkaline conditions to give a monoiodo derivative. The latter could only be 3-*t*-butyl-2,4-dichloro-6-iodophenol (XIV). The other isomer failed to iodinate and was designated then as 3-*t*-butyl-2,6-dichlorophenol (XI) by a process of elimination.

When three moles of chlorine was added per mole of *m-tert*-butylphenol, under similar mild conditions of reaction, 3-*t*-butyl-2,4,6-trichlorophenol (XV) was produced. This indicated that the *ortho* and *para* positions of *m-tert*-butylphenol could be easily substituted with chlorine in a manner similar to that of phenol itself.

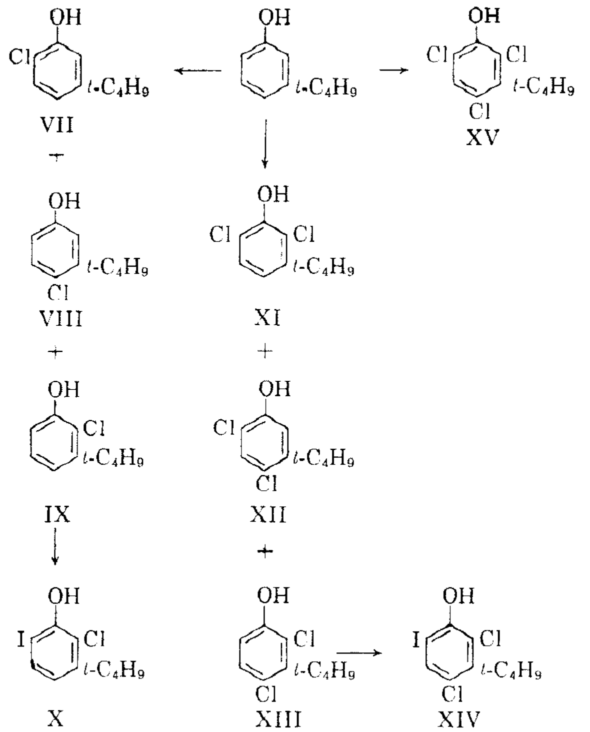
Iodination. When *m-tert*-butylphenol was treated with an equimolar amount of iodine under alkaline conditions of reaction, 5-*t*-butyl-2-iodophenol was the exclusive product formed. The use of a large excess of iodinating agent failed to produce a diiodo derivative. The *t*-butyl group completely shielded the adjacent positions from attack by iodine.

The assigned structure of the iodination was proven conclusively by the frequency of the OH group. This frequency is 2.851 μ and is nearly identical with that of *o*-iodophenol (2.857 μ). Moreover, the presence of a small band at 2.795 μ, which has about 1/10 the intensity of the lower frequency band is compatible with the *cis-trans* isomerism expected for this compound.[7a]

As it has been demonstrated that only the 6-position of *m-tert*-butylphenol can be iodinated, this provided a method for the confirmation of the structure of isomers which had this position vacant.

EXPERIMENTAL

2-Bromo-5-t-butylphenol (I). Five hundred twelve grams (3.2 moles) of bromine, dissolved in 500 ml. of carbon tetrachloride, was added dropwise to a solution of 480 g. of *m-t*-butylphenol in 1 l. of carbon tetrachloride. An ice



bath was needed to keep the temperature in the 20–40° range. Copious amounts of hydrogen bromide were evolved immediately and absorbed in an aqueous caustic solution. The crude product was distilled through a 15 tray, 1-in. Oldershaw column to give 660 g. of colorless oil, b.p. 138°/13 mm. (91% yield).

Anal. Calcd. for $C_{10}H_{13}BrO$: Br, 34.88. Found: Br, 34.8.

4-t-Butylcatechol (II). Thirty-five grams of 2-bromo-5-*t*-butylphenol (the product obtained above), 24 g. of sodium hydroxide and 250 ml. of water were placed in a Parr bomb and heated at 225° for 20 min. After cooling, the solution was neutralized and the dark oil released was extracted with methylene chloride. Vacuum distillation of the product after removal of the solvent gave unchanged starting material and a tan crystalline solid which melted at 50–53° when recrystallized from pentane. The infrared spectra was identical with that of an authentic sample of 4-*t*-butylcatechol.

2,4-Dibromo-5-t-butylphenol (III). One thousand ten grams of bromine (6.32 moles) dissolved in 300 ml. of carbon tetrachloride was added dropwise to a solution of 475 g. (3.16 moles) of *m-tert*-butylphenol dissolved in 750 ml. of carbon tetrachloride. The addition was complete after 2 hr. At this point, the solution was slowly heated and gently refluxed for 30 min. The solvent was removed by distillation until the temperature of the boiling liquid reached 120°. The remaining oil was cooled and diluted with an equal volume of pentane. After standing overnight, 784 g. of coarse, colorless crystals (80% yield) was obtained which melted at 62–63° after one recrystallization from pentane. Distillation of the mother liquor gave an additional quantity of the product which increased the over-all yield to 96%.

Anal. Calcd. for $C_{10}H_{12}Br_2O$: Br, 51.89; C, 38.99; H, 3.93. Found: Br, 51.8; C, 38.99; H, 4.00.

3-t-Butyl-2-chloro-4,6-dibromophenol (IV). Thirteen and two-tenths grams of liquid chlorine (0.186 mole) was allowed to evaporate into a solution of 50 g. of 5-*t*-butyl-2,4-dibromophenol (0.162 mole) and 150 ml. of carbon tetrachloride. Quantities of hydrogen chloride were evolved immediately. The temperature was maintained at 25–35°. Ten minutes after the addition was complete, the solvent was evaporated to give about 58 g. of crude oil. The material was crystallized from pentane (cooled to Dry Ice temperature) to give about 40 g. of white needles, m.p. 30–31°.

Anal. Calcd. for $C_{10}H_{11}Br_2ClO$: C, 35.07; H, 3.24; equiv. wt., 342. Found: C, 34.75; H, 3.42; equiv. wt., 337.

Polybromination. A. A solution of 15 g. of *m-tert*-butylphenol (0.10 mole) and 48 g. of bromine (0.30 mole) in glacial acetic acid was heated and eventually refluxed for 30 min. Only 2,4-dibromo-5-*t*-butylphenol was isolated.

B. Over a period of 2 hr., 250 g. of bromine (1.55 mole) dissolved in 100 ml. of carbon tetrachloride was added to a solution of 75 g. of *m-tert*-butylphenol (0.5 mole) in 150 ml. of carbon tetrachloride in the presence of 10 g. of powdered iron. The temperature was kept below 50° during the addition. The temperature was then slowly increased to reflux at which time 25 g. of bromine in 25 ml. of carbon tetrachloride was added. Work-up of the product gave about 25 g. of crystalline product from pentane which melted at 111–112° after recrystallization from hexane. This was identified as 2,3,4,6-tetrabromophenol (lit. m.p., 114°).

Anal. Calcd. for $C_6H_2Br_4O$: Br, 78.0; equiv. wt., 410. Found: Br, 77.5; equiv. wt., 407.

Distillation of the mother liquor gave 2,4,6-tribromophenol; m.p., 95°, with an infrared spectrum identical with an authentic sample.

Monochlorination. One hundred eighteen grams of chlorine (1.66 moles) was bubbled into a solution of 240 g. of *m-tert*-butylphenol in 500 ml. of carbon tetrachloride, at 30–40°, over a 2-hr. period. The product was distilled from a 30 tray Oldershaw column to give three major fractions. The low-boiling fraction was redistilled from the same column. However, only a partial separation of the two isomers, 5-*t*-butyl-2-chlorophenol (VII) and 3-*t*-butyl-2-chlorophenol (IX), was achieved. The mixture was a colorless liquid, b.p. 109–111°/10 mm., η_D^{25} 1.5297–1.5286.

B.P.[a]	Press	Reflux Ratio	Wt.	Cl, %
110–112	10 mm.	0.8	205 g.	18.1–18.2
138–141	10	0.9	38 g.	24.2–28.8
142	10	0.9	32 g.	20.0–21.3

[a] Temperature where most of the fraction distilled.

Anal. Calcd. for $C_{10}H_{13}ClO$: Cl, 19.22. Found: Cl, 19.03, 18.88.

3-t-Butyl-2-chloro-6-iodophenol (X). In order to isolate one of the isomers, 9.7 g. (.0525 mole) of the mixture was dissolved in a solution of 3.2 g. of potassium hydroxide in 100 ml. of water. A solution of 6.1 g. of iodine (0.024 mole) and 1.5 g. of potassium hydroxide in water was added. Dilute sulfuric acid was added till a *p*H of 7.3 was reached. A small amount of excess iodine was removed by the addition of sodium thiosulfate pellets. The oil which separated was extracted with pentane, dried with magnesium sulfate, filtered, and cooled to Dry Ice temperature. A white solid separated, 3.5 g., which melted at 70–72.5° after one recrystallization from pentane.

Anal. Calcd. for $C_{10}H_{12}CO$: C, 38.67; H, 3.90; Cl, 11.42; I, 40.87.Found: C, 39.13; H, 4.09; Cl, 11.2; I, 40.5.

5-t-Butyl-2-chlorophenol (VII). The solvent was evaporated from the mother liquor and the residue distilled from a Claisen flask with a 12-in. Vigreux column to give a colorless oil, η_D^{27} = 1.5279. Infrared analysis indicated a strong absorption band at 12.4 μ, typical of 1,2,4-substitution on the aromatic ring. The band at 12.8 μ, typical of 1,2,3-substitution, present in the original mixture was completely absent.

Anal. Calcd. for $C_{10}H_{13}ClO$: C, 64.04; H, 7.09; Cl, 19.20. Found: C, 64.98; H, 7.18; Cl, 19.02.

3-t-Butyl-4-chlorophenol. The high-boiling fraction, a colorless oil, b.p., 142°/10 mm., η_D^{25} 1.5430 was identified by means of its infrared spectra (see text).

Anal. Calcd. for $C_{10}H_{13}ClO$: Cl, 19.20. Found: Cl, 19.99.

Several years after the original work was performed, 60 g. of *m-tert*-butylphenol was monochlorinated in a similar manner and the crude product analyzed with a Model 154C Perkin Elmer Gas Chromatograph, operating at 170° utilizing a 4-ft. glass column with ground Teflon coated with a triphenyl phosphate derivative. The following distribution of products in mole % was observed: unchanged *m-tert*-butylphenol, 5.7%; 6-chloro, 52.8%; 2-chloro, 13.5%; 4-chloro, 19.3%; 4,6-dichloro, 4.1%; 2,6-dichloro, 4.6%.

Dichlorination. 5-t-Butyl-2,4-dichlorophenol (XII). One-hundred-five grams of liquid chlorine (1.48 moles) was allowed to evaporate into a solution of 100 g. of *m-tert*-butylphenol (0.67 mole) in 500 ml. of carbon-tetrachloride over a 2-hr. period. The solution was then gently refluxed for 1 hr. and the solvent distilled until a liquid temperature of 120° was reached. The resulting oil was cooled and diluted with 100 ml. of pentane and allowed to crystallize overnight. Colorless granular crystals were obtained, 56.5 g. (39% yield), m.p. 48–49.5° after several recrystallizations from pentane.

Anal. Calcd. for $C_{10}H_{12}Cl_2O$: Cl, 32.22. Found: Cl, 32.2.

3-t-Butyl-2,4-dichlorophenol (XIII). The mother liquor from several similar runs was combined (371 g. after removal of solvent) and distilled through a 45 tray, 1-in. Oldershaw column. A low-boiling fraction, b.p. 111–139°/8 mm., 81 g., was discarded. Five intermediate fractions of colorless oil were next obtained, b.p., 139–140°/8 mm., with a 3% take-off rate.

Fraction	Wt.	n_D^{25}	d^{25}	Cl, %
2	35.0 g.	1.5564	1.250	32.8
3	46.9	1.5569	1.251	32.2
4	29.6	1.5573	1.252	32.7
5	43.8	1.5572	1.253	32.7
6	14.3	1.5572	1.252	32.1

3-t-Butyl-2,4-dichloro-6-iodophenol (XIV). Iodination of a sample of fraction 5 in a manner similar to that described previously, produced a white, crystalline solid, m.p., 34–35° without recrystallization.

Anal. Calcd. for $C_{10}H_{11}Cl_2IO$: C, 34.81; H, 3.21; Cl, 20.55; I, 36.97. Found: C, 34.32; H, 3.22; Cl, 20.9; I, 35.6.

3-t-Butyl-2,6-dichlorophenol (XI). The distillation was continued to give 21 g. of an intermediate, higher-boiling fraction which was discarded. The remaining column inventory and flask residue was distilled from a Claisen flask with a 12-in. Vigreux column. A colorless oil, b.p. 90°/0.6 mm., 58 g., was obtained, which solidified on standing. Coarse, brilliant white, granular crystals were obtained from pentane, m.p. 64–64.5°. This material failed to iodinate under the conditions of reaction described above.

Anal. Calcd. for $C_{10}H_{12}Cl_2O$: Cl, 32.36. Found: 32.59.

Trichlorination. 3-t-Butyl-2,4,6-trichlorophenol (XV). Three hundred thirty grams of liquid chlorine (4.65 moles) was allowed to evaporate into a solution of 230 g. of *m-tert*-butylphenol (1.54 moles) dissolved in 500 ml. of carbon tetrachloride. The temperature was kept below 40°. When the addition was complete the solution was refluxed for 1 hr. and the solvent removed by distillation until the liquid temperature reached 130°. After cooling, 150 ml. of pentane was added to 350 g. of the crude product (yield 62%) and the solution allowed to crystallize overnight. Granular, colorless crystals, m.p. 41–42°, were obtained with an infrared spectra virtually identical with the crude material. The addition of more chlorine to the mother liquor increased the yield.

Anal. Calcd. for $C_{10}H_{11}Cl_3O$: Cl, 41.95. Found: Cl, 41.9.

Iodination. 5-t-Butyl-2-iodophenol. Seventy-five grams of *m-tert*-butylphenol (0.50 mole) and 28 g. of potassium hydroxide (0.5 mole) were dissolved in 200 ml. of water to give a solution with an initial *p*H of 12.3. In another beaker, 56 g. of potassium hydroxide (1 mole), and 127 g. of pulverized iodine (0.5 mole) were dissolved in 800 ml. of water.

The two solutions were combined immediately and agitated for 5 min. Then 300 ml. of methylene chloride was added. Vigorous agitation was supplied as dilute sulfuric acid was added to reduce the *p*H to about 8.0, where a permanent brown color appeared. The phases were separated and the organic layer was washed with water until the final wash was neutral. When the solvent was evaporated, 131 g. of crude oil (48% yield) was obtained. Crystallization was induced by the addition of pentane to give coarse white granular crystals, m.p. 48–49°.

Anal. Calcd. for $C_{10}H_{13}IO$: I, 45.96; C, 43.50; H, 4.74. Found: I, 46.4; C, 43.23; H, 4.69.

A second crop was obtained from the original aqueous phase by neutralization to a *p*H of 7.2.

Acknowledgment. I am indebted to Dr. A. W. Baker for assistance with the interpretation of infrared spectra and to Mrs. Veda M. Brink and Mrs. Lillian Troxell for assistance with the experimental work.

PITTSBURG, CALIF.

[CONTRIBUTION FROM THE ORGANIC BASIC RESEARCH LABORATORY, THE DOW CHEMICAL CO.]

Preparation of *alpha* Allyl Ketones from Allyl Alcohol and Ketones

N. B. LORETTE

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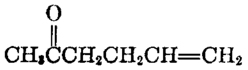
Various ketones and allyl alcohol were allowed to react at elevated temperatures to give *alpha* allyl-substituted ketones. The influence of the reaction time, temperature, reactant ratio, and catalysts on the course of the reaction was studied. The presence of an allyl group on an *alpha* carbon atom of a ketone inhibits further reaction at that atom. A reaction mechanism is proposed.

While carrying out experiments related to recent work[1] in which 5-hexen-2-one was being prepared by heating a solution of 2,2-dimethoxypropane and excess allyl alcohol, it was noted that 5-hexen-2-one (allylacetone) and 3-allyl-5-hexen-2-one continued to be formed after the 2,2-dimethoxypropane had disappeared. This indicated that the allyl alcohol was reacting directly with the ketones present. This was shown to be the case by the formation of 5-hexen-2-one when an acidified mixture of acetone and allyl alcohol was heated.

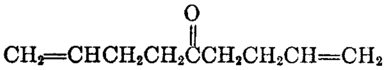
TABLE I

PRODUCT DISTRIBUTION FOR THE REACTION BETWEEN ALLYL ALCOHOL AND ACETONE AT 250–260°

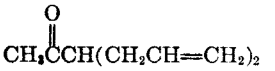
Moles Allyl Alcohol per Mole Acetone	Reaction Time (Hr.)	% Conversion of Acetone to Product		
		I	II	III
1	1	13	Trace	Trace
1	3	24	0.5	1.8
1	6	34	1.7	5.2
3	1	30	0.5	3.2
3	3	37	3.5	8.8
3	6	32	5.8	21.0[a]
5	1	34	1.0	5.7
5	3	39	4.0	21.0[a]
5	6	30	8.5	30.0[a]

I = 

$$CH_3\overset{\overset{O}{\|}}{C}CH_2CH_2CH{=}CH_2$$

II = 

$$CH_2{=}CHCH_2CH_2\overset{\overset{O}{\|}}{C}CH_2CH_2CH{=}CH_2$$

III = 

$$CH_3\overset{\overset{O}{\|}}{C}CH(CH_2CH{=}CH_2)_2$$

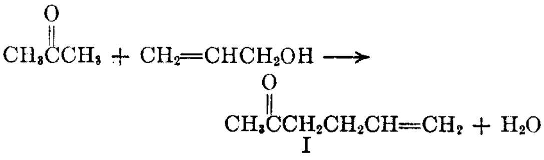
[a] Small amounts of triallylacetones present.

The reaction does not stop at the monoallyl product, however, but proceeds as shown.

The formation of the more substituted ketones was favored by increasing the ratio of allyl alcohol to ketone and by longer reaction time (Table I).

It is known[2] that diallyl ketals will crack and rearrange (Claisen rearrangement) to give *alpha* allyl-substituted ketones but the conditions of the experiments for the direct reaction between allyl alcohol and ketones are quite different from the conditions which favor the formation of ketals. The temperatures used for the direct reaction were 200° to 300°. At these temperatures it is doubtful that any diallyl ketal would be present. Generally, temperatures below 0° are preferred for ketal preparation because at 25° there is very little ketal present at equilibrium.[3]

K. C. Brannock[4] reported that *alpha* allyl aldehydes could be prepared by refluxing an acidified solution of an aldehyde, allyl alcohol, and an inert



$$CH_3\overset{\overset{O}{\|}}{C}CH_3 + CH_2{=}CHCH_2OH \longrightarrow \underset{\text{I}}{CH_3\overset{\overset{O}{\|}}{C}CH_2CH_2CH{=}CH_2} + H_2O \quad (1)$$

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[1] N. B. Lorette and W. L. Howard, *J. Org. Chem.*, **26**, 3112 (1961).

(2) C. D. Hurd and M. A. Pollack, *J. Am. Chem. Soc.*, **60**, 1909 (1938).

(3) N. B. Lorette, W. L. Howard, and J. H. Brown, Jr., *J. Org. Chem.*, **24**, 1731 (1959).

(4) K. C. Brannock, *J. Am. Chem. Soc.*, **81**, 3379 (1959).