A blank run containing allyl chloride and sulfuric acid under the same experimental conditions did not yield a precipitate of silver chloride.

**More Rapid Condensation.**—It is possible to carry out the condensation at more elevated temperatures and so greatly decrease the reaction time. The method allows the isolation of the intermediate phenoxy compound in good yields where this is desired. If the reaction mixture be heated for a short time, the primary reaction product will be the ether; further heating increases the amount of the substituted phenol and decreases the relative amount of ether. The substituted phenol alone may be obtained as the final product. The condensation agent is again sulfuric acid; however, where heat is employed it is necessary to use a diluent to prevent sulfonation. Glacial acetic acid is used in this capacity. Equimolar quantities of allyl chloride, *m*-cresol and sulfuric acid (present as 33% of a glacial acetic acid solution) when refluxed for eight hours yielded approximately equal parts of the ether and the substituted phenol with about 30% of the *m*-cresol having reacted. It is advisable to use an excess of allyl chloride as there is some loss due to volatilization. After refluxing, the reactants were thrown upon water; the organic layer which separated was water washed and extracted with ten per cent. caustic potash. The alkali-insoluble portion was dried with anhydrous sodium sulfate and distilled. Analysis indicated the loss of water on distillation.

The alkaline extract was neutralized with 15% hydrochloric acid, the resulting organic liquid layer water washed and dried with anhydrous sodium sulfate. Distillation yielded isopropenyl-*m*-cresol. The hexa- and pentabromo derivatives were made from samples of this compound prepared by both the slow and rapid condensation. The procedure has been given in a former publication.[3]

## Summary

The condensation of phenolic type compounds with the ethylenic linkage has been extended to unsaturated halides and the resulting condensation products were identified.

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# The Common Basis of Intramolecular Rearrangements. II.[1] The Dehydration of Di-*tert*-butylcarbinol and the Conversion of the Resulting Nonenes to Trimethylethylene and Isobutylene

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The older conception of molecular rearrangements as involving primarily the migration of groups (positive, negative or neutral free radicals) has been superseded in this Laboratory by the hypothesis that the metathetical and elimination reactions[1] of organic chemistry which give rise to most rearrangements, involve the following steps: (1) removal of a group with a complete octet of electrons, leaving an atom with six electrons. The ensuing changes may include the following: (2a) union with

[1] Whitmore, THIS JOURNAL, **54**, 3274 (1932).

[2] Presented in partial fulfilment of the requirements for the Ph.D. degree.

a negative ion to form the "normal" metathetical product; (b) The loss of a proton with the formation of a double bond. (c) The atom with only a sextet of electrons may take an electron pair from an adjacent atom, leaving that atom with only six electrons. The group originally held by the electron pair migrates with it. This hypothesis does not assume that a group leaves one part of the molecule and later attaches itself to a different part.[3] The important process is the transfer of an electron pair from an adjacent atom. (3) The *rearranged* fragment from 2c may undergo the processes in 2a, b, c.

*Since the important process is the satisfying of the electronically deficient atom, change (2c) might consist of the shift of an electron pair without carrying along its organic group.* The latter would thus leave as a positive fragment in much the way that a positive proton leaves the molecule in (2b). The type of organic group most likely to part with an electron pair and become positive would be a tertiary group as evidenced by the striking difference in the action of acids on tertiary alcohols as contrasted with primary and secondary alcohols.

The compounds most likely to give such a splitting of the C–C linkage would thus be those capable of forming a fragment, $R_3C—C—C^{\oplus}$. Substances of this type are practically unknown and their synthesis is difficult. For some time, however, experiments along this line have been in progress in this Laboratory. The results have been complex in the extreme.[4] We have now found one case which gives definite results. It is the dehydration of di-*tert*-butylcarbinol at 180° to give a 77% yield of trimethylethylene. The other products are a small amount of isobutylene and a complex mixture containing some nonenes, a large amount of diisobutylenes and smaller amounts of diamylenes, triisobutylenes and tetraisobutylenes. Dehydration of the carbinol at 155° gives nonenes in 71% yield. Treatment of the nonenes with the dehydrating agent at 200° produces isobutylene, trimethylethylene, and polymers in yields of 50, 68 and 39%, respectively, thus accounting for 98% of the nonenes used.

The possible changes,[1] starting with di-*tert*-butylcarbinol, are as follows: (1) removal of the hydroxyl to give a positive di-*tert*-butylcarbinyl group. This is doubly a positive neopentyl system and consequently most susceptible to rearrangement.[5] No other change is probable.

(2) The transfer of an electron pair with any one of the six methyl groups to give the fragment, $(CH_3)_3C—CH(CH_3)—C^{\oplus}(CH_3)_2$. (A.)

(3*a*) Fragment A would be expected to lose a proton from the tertiary hydrogen or from one of the two methyl groups. The expected nonenes are formed in only small amounts, however, unless dehydration is carried out under the mildest possible conditions.

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[3] *Cf.* Wallis, THIS JOURNAL, **55**, 1702 (1933).

[4] Unpublished work of A. H. Homeyer, S. N. Wrenn, E. E. Stahly, A. L. Houk and J. W. Heyd.

[5] *Cf.* Whitmore and Rothrock, THIS JOURNAL, **54**, 3431 (1932); **55**, 1106 (1933).

(*b*) Another possible change would result in the transfer of the tertiary butyl group to give the fragment, $^{\oplus}CH(CH_3)—C(CH_3)_2—C(CH_3)_3$. No product corresponding to this fragment has been found.

(*c*) The change in fragment A, formed either from the carbinol or *by the addition of a proton to one of the nonenes,* which agrees with the experimental facts is *the transfer of the electron pair from the tertiary butyl group but without the transfer of that group*

$$(CH_3)_3C—CH(CH_3)—C^{\oplus}(CH_3)_2 \longrightarrow (CH_3)_3C^{\oplus} + CH_3CH{=}C(CH_3)_2$$

The positive tertiary butyl fragment gives isobutylene and its polymers. Part of the trimethylethylene is polymerized.

The significance of the apparent instability of the grouping, $R_3C—C—C^{\oplus}$, is being further studied especially in relation to the depolymerization of polymerized olefins.

## Experimental

**Distillation Equipment.**—All of the columns were of the total condensation, adjustable take-off, adiabatic type.[6] The packed sections were as follows: column A, 73 × 2.3 cm.; column B, 65 × 2.5 cm.; column C, 40 × 1.3 cm.; column D, 40 × 1.3 cm.; column E, 25 × 1.0 cm. A, B and C were packed with glass tubes, 5 × 5 mm., and D and E were packed with glass helices.[7]

**General.**—Di-*tert*-butylcarbinol was prepared by reducing hexamethylacetone which was made by the sodamide synthesis[8] from diisopropyl ketone.

**Preparation of Diisopropyl Ketone.**—Oxidation of diisopropylcarbinol with sulfuric acid–sodium dichromate mixture below 35° gave a 74% yield of diisopropyl ketone,[9] b. p. 120–125° (742 mm.), $n^{20}_{D}$ 1.4001.

**Hexamethylacetone.**—A typical preparation will be described.[9] Toluene was distilled through Column A and the fraction distilling at 110–110.5° (740 mm.) was dried over sodium. Three liters of this toluene was placed in a 5-liter 3-necked flask equipped with a mechanical stirrer, reflux condenser, and dropping funnel. Commercial sodamide (about 50%) was pulverized under toluene and 160 g. (2 moles) was suspended in the toluene. To this suspension was added 228 g. (2 moles) of diisopropyl ketone. The mixture was stirred vigorously while heating to brisk reflux in an oil-bath. When the evolution of ammonia ceased the solution was cooled and 270 g. of methyl sulfate (2.14 moles) was added during one hour. When the refluxing again ceased the mixture was heated to boiling for fifteen minutes and then allowed to cool. To the cold solution 400 cc. of water and 200 cc. of ammonium hydroxide were added during two hours and stirring continued for twelve hours. Vigorous stirring was necessary throughout the whole process. The upper layer was then separated and washed with 5% hydrochloric acid and 5% sodium carbonate solution successively. The main portion of toluene was distilled off and the remainder used in the next step. Some of the pentamethylacetone was purified by distillation through Column A: b. p. 132–134.5° (730 mm.); $n^{20}_{D}$ 1.4073.

The combined crude products from methylation of 5 moles of diisopropyl ketone were methylated in 3 liters of toluene as above. Distillation of the final toluene solution through Column B gave 374 g. of hexamethylacetone, b. p. 144–50° (740 mm.) $n^{20}_{D}$ 1.4191–1.4197; yield, based on diisopropyl ketone, 52%. It was identified by con-

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[6] Whitmore and Lux, THIS JOURNAL, **54**, 3451 (1932).

[7] Wilson, Laughlin and Parker, *ibid.*, **55**, 2795 (1933).

[8] Haller and Bauer, *Ann. chim.*, [8] **29**, 313 (1913).

[9] Whitmore and Laughlin, THIS JOURNAL, **54**, 4392 (1932).

version to methyl-di-*tert*-butylcarbinol by reaction with methylmagnesium chloride;[10] m. p. of carbinol, 42°.

**Reduction of Hexamethylacetone.**—The reduction was by the method of Krueger.[11] From 4 half-mole runs, 220 g. (76% yield) of solid carbinol, b. p. 108–113° (150 mm.), was obtained. Redistillation through Column D gave 198 g., b. p. 117–118° (166 mm.), m. p. 50–51°.

**Dehydration of Di-*tert*-butylcarbinol.**—In a typical dehydration 57.7 g. (1 mol) of carbinol and 2 g. (0.02 mol) of 1-chloro-4-naphthalenesulfonic acid[12] were placed in a 200-cc. flask attached to Column D. The take-off tube was attached to a copper coil condenser cooled with water at 10°. The receiver was cooled in an ice-bath and its outlet was connected to a gas collector containing saturated salt solution. The flask was heated in an oil-bath at 180°. Dehydration proceeded without *evolution of gas* until almost the theoretical amount of water had been drawn off (three hours). At this point the distillation temperature dropped from 88 to 34° (733 mm.), trimethylethylene distilled, and gas was evolved. After one and one-half hours the distillation temperature rose and the evolution of gas ceased. The receiver was changed and distillation was continued under reduced pressure to give 16.1 g. of material, b. p. 43° (737 mm.) to 132° (113 mm.) and a residue consisting of 6 g. of liquid and 2 g. of solid material. A total of 90% of the starting material was accounted for as follows: water, 6.2 g. (theory, 7.2); gas, 1.2 liters, trimethylethylene 21.4 g. (calcd. 28 g., yield 77%) 22.1 g. of high boiling material (polymers).

**Identification of Trimethylethylene.**—The above volatile olefin, b. p. 34° (733 mm.), $n_D^{20}$ 1.3815, was identified by conversion to the dibromide and hydrolysis to methyl isopropyl ketone by refluxing with water.[13] After the small bromide layer had disappeared and an upper one formed, the ketone was distilled through Column E and the 2,4-dinitrophenylhydrazone prepared, m. p. 116–118°. Two crystallizations raised the m. p. to 117–118°. Starting with pure trimethylethylene obtained by fractionation of the olefins from pure *tert*-amyl alcohol, a similar series of transformations yielded a 2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 117–118°, thus proving the olefin from di-*tert*-butylcarbinol to be trimethylethylene.

**Higher-Boiling Olefins.**—The olefins obtained from three similar dehydrations were combined and distilled through Column D; 21 cuts (0.5–2.0 g. each) were taken from 82° (742 mm.) to 161° (730 mm.) and sixteen similar cuts between 116° (182 mm.) and 141° (75 mm.). All fractions decolorized dilute carbon tetrachloride solutions of bromine. A curve obtained by plotting $n_D^{20}$ against total distillate gave six small breaks in an otherwise steadily rising curve. A molecular weight determination was made for the fraction corresponding to each of these breaks. For the four higher boiling fractions Solty's modification of Rast's camphor method was used.[14] It was not satisfactory for the two more volatile samples because vaporization caused a serious error. The lowering of the freezing point of benzene was used in the usual manner for the latter two.

The cuts corresponding to the breaks and the b. p., $n_D^{20}$, and molecular weight of each follow: 5–8, 4.6 g., 101–119° (740), 1.415, 118; 11–13, 5.1 g., 125–132° (742), 1.423, 124; 18–20, 2.3 g., 142–151° (738), 1.430, 1.40; 23–26, 5.0 g., 159° (736)–122° (130), 1.436, 147; 30–31, 1.8 g., 127–131° (102), 1.440, 172; 32–33, 2.6 g., 131–132° (102), 1.441, 172. The fractions thus correspond in properties and molecular weights to nonenes, diamylenes, and triisobutylenes. Although there was no break in the curve

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(10) Whitmore and Laughlin, THIS JOURNAL, **55**, 3736 (1933).

(11) *Cf.* Whitmore and Krueger, *ibid.*, **55**, 1531 (1933).

(12) Prepared by F. A. Karnatz of this Laboratory.

(13) Whitmore and co-workers, THIS JOURNAL, **55**, 1136 (1933).

(14) "Quant. Org. Micro. Analysis," P. Blakiston's Son and Co., New York, 1930, p. 219.

for 35–36, the refractive index corresponded to that for the ordinary mixture of the tetraisobutylenes, $n^{20}_{D}$ 1.452.[15]

**Analysis of the Gases.**—An Orsat apparatus was used with 100-cc. samples of the gas (25°). Carbon dioxide was absorbed by 40% potassium hydroxide, oxygen by potassium pyrogallate solution, and isobutylene by 68% sulfuric acid,[16] other olefins by bromine water, and carbon monoxide by cuprous chloride in hydrochloric acid solution. Remaining gas was considered to be nitrogen as it was nearly four times the amount of oxygen. The average of three analyses gave the composition of the gas as 1% carbon dioxide, 29.7% isobutylene, 0.2% other olefins, 0.2% carbon monoxide and 69% air. Thus the total volume of gas, 1200 cc., corresponded to 0.9 g. of isobutylene, a yield of 4%.

**Summary of Products.**—The dehydration of 57.7 g. of di-*tert*-butylcarbinol at 180° gave the following: water, 6.2 g. (86%), trimethylethylene, 21.4 g. (77%), isobutylene, 0.9 g. (4%) and polymers, 22.1 g. (42%).

**Dehydration of the Carbinol at Lower Temperature without Splitting.**—The dehydration of 43 g. of di-*tert*-butylcarbinol by 1.5 g. of 1-chloro-4-naphthalenesulfonic acid was conducted below 155°. The water formed was not drawn off but allowed to reflux in the column. After two and one-half hours the bath was removed and the pot cooled. The olefins were shaken with 30 cc. of 10% sodium hydroxide solution and extracted with ether. The ether solution after drying over sodium was distilled through Column D. The main fractions of the olefins, 18.6 g., 71% yield, distilled 123–140° (733 mm.) and had $n^{20}_{D}$ 1.4230–1.4262. A residue of unchanged carbinol of 13 g. remained, m. p. and mixed m. p. 42–45°.

**Splitting of the Nonenes Obtained from Di-*tert*-butylcarbinol.**—To 18.5 g. of the nonenes was added 0.4 g. of 1-chloro-4-naphthalenesulfonic acid and the flask attached to Column D and heated as in the dehydration. Upon heating the bath to 145–205°, gas was evolved and trimethylethylene distilled. The total products obtained were: 2300 cc. of gas (27°), 7.0 g. of trimethylethylene, b. p. 34–36°, $n^{20}_{D}$ 1.3800, 7.2 g. of yellow liquid residue, $n^{20}_{D}$ 1.4350; total products recovered, 18.3 g. (98%). Analysis of the gas with an Orsat apparatus showed it to contain 73.1% isobutylene and 3% trimethylethylene or 3.9 g. and 0.2 g., respectively. The nonenes were thus split to yield 68% trimethylethylene, 50% isobutylene and 39% polymers.

## Summary

1. Di-*tert*-butylcarbinol has been dehydrated to give a 77% yield of trimethylethylene together with isobutylene and its polymers.

2. The dehydration has been shown to proceed by way of nonenes which are unstable at 180–200° in the presence of the dehydrating agent.

3. These unusual reactions are interpreted in terms of the current theory of molecular rearrangements.

4. This type of reaction is being further studied.

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(15) Unpublished results of S. N. Wrenn of this Laboratory.

(16) Marcowitch and Moore, *Nat. Pet. News*, Oct. 14 and 21, 1931.