[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OREGON STATE COLLEGE]

The Dienone–Phenol Rearrangement. III. Rearrangement of 6,6-Dimethyl-2,4-cyclohexadienone[1]

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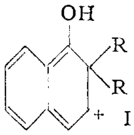
A new dienone, 6,6-dimethyl-2,4-cyclohexadienone, has been prepared, characterized and rearranged. A phenolic product was isolated in 75% yield and 2,3-dimethylphenol was identified in that product by preparation of a phenylurethan. The formation of 2,3-dimethylphenol is in accord with the Arnold mechanism for the dienone–phenol rearrangement.

It has been shown in earlier papers of this series[2] that the rearrangement of 1-oxo-2,2-dialkyl-1,2-dihydronaphthalenes does not proceed in complete accord with the Arnold mechanism[3] for the dienone–phenol rearrangement. Failure to follow the normal (Arnold) course for the dienone–phenol rearrangement in such cases was accounted for by the suggestion[2a] that one of the intermediates in that path is an *o*-quinoid structure (I) of high energy. The mechanism for the alternate path[2b] explains the means by which the rearrangement may occur without passing such an energy barrier. However, this energy barrier will be present only as long as the dienone ring is fused to an aromatic system so that one bond of the diene is also a part of the aromatic system. Accordingly if the sole reason for failure to follow the Arnold path lies in the high-energy *o*-quinoid intermediate, then an *ortho*-blocked dienone of the cyclohexane ring system might be expected to follow that path.



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Since all of the dimethylphenols are known 6,6-dimethyl-2,4-cyclohexadienone was considered the ideal case for study. Although 6-dichloromethyl-6-methyl-2,4-cyclohexadienone has been prepared and studied[4] there appears in the literature no record of the preparation of 6,6-dialkyl-2,4-cyclohexadienones. The straightforward approach to the synthesis of this system has been studied in part by Bennet and Burger[5] who prepared 6,6-diphenyl-4-bromo-2-cyclohexenone. Although one of the possible products of rearrangement of 6,6-diphenyl-2,4-cyclohexadienone is not known, the advantage of dealing with a previously studied series appeared sufficient to warrant the preparation of that dienone. Accordingly we repeated the work of Bennet and Burger, but found that the 4-bromo compound could not be dehydrohalogenated to the desired product by treatment with either γ-collidine or quinaldine.

Discouraging as this failure to dehydrohalogenate was, it seemed possible to attribute this reluctance to steric hindrance. According to this assumption the smaller methyl substituent might permit the reaction to proceed. Therefore, 2,2-dimethylcyclohexanone was prepared by two methods: first by the unequivocal procedure employed originally by Meerwein,[6] in order to obtain comparison samples. Later large-scale production was carried out by direct methylation of 2-methylcyclohexanone. The product reacted normally with elementary bromine giving 2-bromo-6,6-dimethylcyclohexanone as a light gray solid. Introduction of a double bond in the α,β-position was effected smoothly by treatment with γ-collidine at 135–140°. The yield of 6,6-dimethyl-2-cyclohexenone fell off considerably when the reaction was carried out at the boiling point of the collidine solution. The product was identified as 6,6-dimethyl-2-cyclohexenone since it absorbed one mole of hydrogen when treated with Adams catalyst and hydrogen at atmospheric pressure to give 2,2-dimethylcyclohexanone, identified as the 2,4-dinitrophenylhydrazone. According to Woodward's rules[7] an α,β-unsaturated ketone of this type should exhibit maximum absorption in the ultraviolet at 225 mμ. This ketone exhibited a maximum at 225.8 mμ.

A bromine was introduced onto the 4(?)-position with N-bromosuccinimide. No attempt was made to identify this product but it was dehydrogenated directly with either γ-collidine or quinaldine. Best results were obtained by working in an atmosphere of nitrogen, using quinaldine at 140°. The pressure was reduced to 40 mm. and the dienone distilled from the reaction mixture as fast as it was formed. The 6,6-dimethyl-2,4-cyclohexadienone is a clear mobile liquid when first isolated. On storage, even in the cold and dark, for short periods of time it changes to a thick viscous substance which eventually deposits some solid material. It is possible that the cyclohexadienone reacts with itself in a Diels–Alder condensation. This is a characteristic behavior of cyclohexadiene[8] and cyclopentadiene[9] and appears to occur with extreme ease with phenyl and chloro-substituted cyclopentadienones.[10]

The mobile liquid first isolated absorbs two moles of hydrogen forming 2,2-dimethylcyclohexanone. It gives a bright red 2,4-dinitrophenylhydrazone which melts with decomposition at 275°. The bright red color of the original 2,4-dinitrophenylhydrazone contrasts beautifully with the orange derivative of 6,6-dimethyl-2-cyclohexenone and the yellow one from 2,2-dimethylcyclohexanone. The liquid product also shows an absorption peak in the ultraviolet

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(1) Published with the approval of the Monographs Publications Committee, Oregon State College, as Research Paper No. 268, School of Science, Department of Chemistry.

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(5) W. B. Bennet and A. Burger, THIS JOURNAL, **75**, 84 (1953).

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(7) R. B. Woodward, THIS JOURNAL, **63**, 1123 (1941).

(8) K. Alder and G. Stein, *Ann.*, **496**, 197 (1932).

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(10) C. F. H. Allen and E. W. Spanagel, THIS JOURNAL, **55**, 3773 (1933); T. Zincke, *et al.*, *Ann.*, **394**, 7 (1912), and recent articles.

at 228.5 mμ. These facts provide a reasonable basis for assigning this compound the structure of 6,6-dimethyl-2,4-cyclohexadienone.

If the liquid product is treated with acetic anhydride and sulfuric acid immediately after isolation, it rearranges readily to give presumably an acetate which was not isolated. The initial product was hydrolyzed directly giving a liquid phenolic material which could not be induced to crystallize. If the 6,6-dimethyl-2,4-cyclohexadienone was allowed to stand for six to twelve hours after isolation the rearrangement would not proceed as described.

The hydrolysis product was a dark-colored oil with a strong phenolic odor. Treatment of a portion of this oil with phenyl isocyanate gave in low yield (9%), a phenylurethan melting at 179.5–181°. An authentic sample of the phenylurethan of 2,3-dimethylphenol melted at 180–181° and a mixture of the two urethans melted at 178.5–180°. No other phenylurethan was isolated from the rearrangement product. Analysis of this phenolic oil was attempted using paper chromatography according to the procedure of Freeman.[11] Although the results were not entirely satisfactory since the R_f values for the oil (0.90), 2,3-dimethylphenol (0.90) and 3,4-dimethylphenol (0.88) were nearly identical, certain conclusions may be reached. Thus the oil definitely contains at least one phenol; 2,3-dimethylphenol is a possible constituent in the oil; the presence of other phenols is not ruled out. Since 2,6-dimethylphenol did not give a color with the developing method employed it can be stated that if that phenol is present in the oil it cannot be the only one since the oil definitely gives a colored spot on development.

Identification of 2,3-dimethylphenol shows that 6,6-dimethyl-2,4-cyclohexadienone can rearrange, at least in part, in accord with the Arnold mechanism. This is in agreement with the suggestion made earlier that the rearrangement of analogous compounds in the naphthalenone series is forced into an alternate path by the presence of an *o*-quinoid intermediate of high energy in the normal sequence.

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Experimental

6,6-Dimethyl-2-cyclohexenone.—A solution containing 27.5 g. (0.135 mole) of the 2-bromo-6,6-dimethylcyclohexanone[12] in 53 ml. of γ-collidine was heated at 135–140° for 40 minutes. The reaction mixture containing precipitated collidine hydrobromide was poured into 500 ml. of water, neutralized with acetic acid and extracted with ether. The extracts were combined and washed with water, then dried. The product was isolated by distillation, b.p. 73–76° (21 mm.), coming over as a yellow oil weighing 9.3 g. (56%), n^{20}_{D} 1.4988, D^{20} 0.9808.

Anal. Calcd. for $C_8H_{12}O$: C, 77.4; H, 9.74. Found: C, 76.9; H, 9.49.

A 2,4-dinitrophenylhydrazone was prepared with Brady reagent. It melted at 167–168° and has been reported[13] to melt at 171–172°.

The unsaturated ketone absorbed 1.01 moles of hydrogen when treated with Adams catalyst and hydrogen at atmospheric pressure. The product was a ketone whose 2,4-dinitrophenylhydrazone melted at 140–141°. That derivative of 6,6-dimethylcyclohexanone has been reported[13] to melt at 140–142°.

4(?)-Bromo-6,6-dimethyl-2-cyclohexenone.—Eleven grams (0.09 mole) of 6,6-dimethyl-2-cyclohexenone was dissolved in 100 ml. of dry carbon tetrachloride and 17.4 g. (0.097 mole) of N-bromosuccinimide added. The mixture was heated under reflux for five hours using a 250-watt heat lamp. After separation from the succinimide the product was obtained as a clear oil, b.p. 111–116° (15 mm.), weight 11.0 g. (61%). The compound was not characterized but was used directly in the next step.

6,6-Dimethyl-2,4-cyclohexadienone.—A small distillation apparatus was fitted with a gas inlet tube (capillary) which reached to the bottom of the still-pot. After the apparatus had been swept with dry nitrogen, a solution of 10.1 g. (0.05 mole) of 6,6-dimethyl-4(?)-bromo-2-cyclohexenone in 45 g. of redistilled quinaldine was added. The pressure was maintained at 40 mm. during the reaction and nitrogen was allowed to bubble through the mixture. The still-pot was immersed in a wax bath maintained at 135–140°, and under these conditions the dienone distilled as rapidly as it was formed while the quinaldine remained undistilled. The product came over between 84 and 91° as a clear mobile liquid weighing 1.8 g. (30%).

The dienone formed a bright red 2,4-dinitrophenylhydrazone, m.p. 183°, when treated with Brady reagent. After melting it resolidified to a yellow solid, m.p. 275° dec.

Anal. Calcd. for $C_{14}H_{14}O_4N_4$: C, 55.6; H, 4.67. Found: C, 55.6; H, 4.55.

The dienone absorbed two moles of hydrogen when treated with Adams catalyst and hydrogen. This treatment gave a ketone whose 2,4-dinitrophenylhydrazone melted at 138–139° and did not depress the melting point of an authentic sample of 2,2-dimethylcyclohexanone 2,4-dinitrophenylhydrazone.

After being stored for four days under nitrogen in a refrigerator the dienone reacted with itself becoming more viscous, and the viscous material would not rearrange in the manner described below. After long periods of storage this viscous material deposited a clear solid substance which is being studied further.

Rearrangement of 6,6-Dimethyl-2,4-cyclohexadienone.—A solution containing 0.61 g (0.005 mole) of the dienone in 20 ml. of acetic anhydride with five drops of sulfuric acid was allowed to stand at room temperature for 6.5 hours. The solution was then stirred with ice-water for one hour, made strongly basic with sodium hydroxide and stirred for one hour longer. This solution was made acid with dilute hydrochloric acid and extracted continuously with ether for 24 hours. After being dried the ether solution was evaporated leaving 0.45 g. (75%) of an oil with a strong phenolic odor.

A 200-mg. sample of the above oil was heated for ten minutes with two drops of phenyl isocyanate. After several recrystallizations from benzene–heptane mixture, the phenylurethan, m.p. 179.5–181°, was obtained in 9% yield as fine white needles.

An authentic sample of 2,3-dimethylphenol was prepared from 2,3-dimethylaniline according to the procedure of Tohl.[14] The phenylurethan of this phenol prepared according to the directions above was obtained in 21% yield as white needles, m.p. 180–181°. Mixture of the two urethans melted at 178.5–180°. The phenylurethan of 2,3-dimethylphenol has been reported[15] to melt at 176°.

The phenolic oil from the rearrangement and a series of dimethylphenols were submitted to paper chromatographic analysis using a one-dimensional system and employing *sec*-butyl alcohol-29% ammonia as solvent system.[11] Of the three comparison samples tested 2,6-dimethylphenol failed to give a color on development, while 2,3-dimethylphenol and 3,4-dimethylphenol gave R_f values of 0.90 and 0.88, respectively. The oil gave a single spot with R_f value 0.90.

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