HO—C ◄ - - - H₅IO₆ ⟶ H₂O + (II)

(II)

H⁺ / \ OH⁻

(I) + H₂O

of the chelate ring by either means would allow the molecule to assume a configuration more favorable for ring closure by inversion to form the cyclic diester. If pinacol is the only one of the four glycols sufficiently basic to chelate with the periodate group, the anomalous behavior of this glycol could be qualitatively accounted for since ring closure could occur more readily in strongly acidic or strongly basic solution than in the intermediate range. Actually one would predict that a tertiary hydroxyl group (as in pinacol) would be more basic than a primary (as in ethylene glycol) or a secondary hydroxyl group (as in cis- and trans-cyclohexene glycols).

This mechanism, involving successive formation of a mono- and cyclic diester of periodic acid would satisfactorily account for the proportionality of the rate of oxidation to the hydrogen-ion concentration in basic media (or the equivalent inverse proportionality to hydroxyl ion concentration) since the more basic the solution, the greater would be the tendency toward saponification of the intermediate monoester before ring closure could occur.

## Summary

The second-order rate constants for the oxidation of ethylene glycol, pinacol, and cis- and trans-cyclohexene glycols by aqueous periodate have been determined over a considerable range in pH. The results have been interpreted on the basis of the suggestion by Criegee that the rate-controlling step of the oxidation is the formation of a cyclic diester of periodic acid.

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# The Action of Sodium on Hexamethylacetone

BY PHILIP G. STEVENS[1] AND JOHN H. MOWAT[2]

In 1934 Favorsky and Nazarov[3] reported that the sodium ketyl of hexamethylacetone formed[4] tetra-t-butylethylene glycol, and that rearrangement of this glycol by means of sulfuric acid yielded tri-t-butylpinacolone. These highly branched chain compounds seemed worth while re-investigating, because this rearrangement of the glycol involves the only known case of a tertiary group migrating in an open chain compound from carbon to carbon,[5] the ketone formed is the only known compound having three tertiary groups attached to a single carbon atom, and because it is not possible to prepare Fisher–Hirschfeld atomic models of either of these complex substances.

It was found that hexamethylacetone readily formed a ketyl with sodium, but the dimolecular ment of phenol ethers [Smith, THIS JOURNAL, **55**, 3718 (1933)], or substituted anilines [Hickinbottom, J. Chem. Soc., 404 (1937)], where again the hindrance to the incoming group is reduced no doubt by the planar configuration of the benzene ring, and the presence of only one hydrogen atom at the place of entry. The only known migrations of a tertiary group from carbon to carbon are found in the Wagner rearrangements of bicyclic terpenes, or their derivatives, such as that of pinene hydrochloride to isobornyl chloride, in which it would appear any hindrance to acceptance of the migrating group is removed by having the place of entry held open by the rigid ring structure. In other cases, the tertiary group may start to shift, but due to its inability to enter a new position, it becomes lost en route as an olefin [Whitmore and Stahly, THIS JOURNAL, **55**, 4153 (1933); Nazarov, C. A., **30**, 4147 (1936)], or, in the case of bicyclic terpenes, may appear in the 4 position as an isopropylidene group, as in the formation of dipentene from pinene. The ease of acceptance of a migrating group by another atom may therefore be as important, in determining the products of a rearrangement, as the actual migration tendencies of the groups themselves.

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(3) Favorsky and Nazarov, Bull. soc. chim., [5] 1, 46 (1934).

(4) After acidification.

(5) Migrations of tertiary groups from carbon to nitrogen are well-known, as in the Hoffman rearrangement of amides [Van Erp, Rec. trav. chim., 14, 1 (1895)], the Beckmann rearrangement of oximes [Wallach and Kempe, Ann., 329, 82 (1903)], and in similar rearrangements in which the nitrogen appears to be stripped bare, at some moment, of all atoms save the adjoining carbon atom, and hence presents no hindrance to the incoming group. Similar migrations from oxygen or nitrogen to carbon are found only in the rearrange-

products of the reaction appeared to be different from those reported by Favorsky and Nazarov. Whereas they obtained a glycol, m. p. 85–86°, b. p. 150° (13 mm.) in 35% yield, our product (5% yield) melted at 117°,[6] boiled at about 200° (13 mm.), and was accompanied by approximately an equal amount of an oil of a much lower boiling point.

The substance, m. p. 117°, presumably the dimolecular reduction product, $C_{18}H_{38}O_2$, reacted as a glycol in that it evolved two equivalents of methane with methylmagnesium iodide and had the correct molecular weight in camphor and in cyclohexane. It was not, however, possible to prove the glycol structure further, although numerous unsuccessful attempts were made to oxidize it back to hexamethylacetone. The stability of the glycol toward lead tetraacetate, and potassium permanganate in pyridine indicated a *trans* configuration, with rotation to the oxidizable *cis* form (possibly the substance of m. p. 85–86° obtained by Favorsky and Nazarov) being completely restricted by the highly branched chain groups.[7]
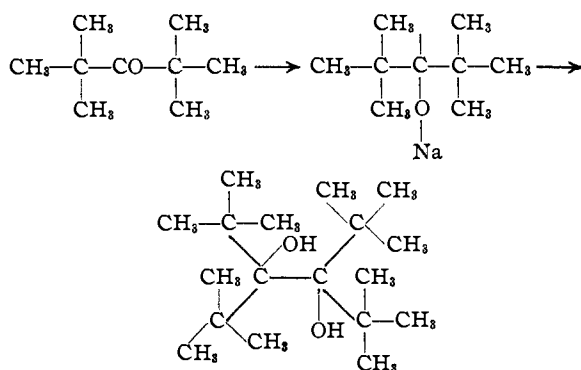
The great reluctance (as evidenced by the low yields)[8] of two di-*t*-butyl substituted carbon atoms to become joined suggested that the glycol might dissociate into free radicals. Although in camphor and in cyclohexane the molecular weight was normal, in benzene at 5° the molecular weight was much below the calculated formula weight, the value becoming, by extrapolation to zero concentration, about one-half the calculated value[9] (Fig. 1). This result indicated extensive

(6) Bartlett, Swain and Woodward, THIS JOURNAL, **63**, 3229 (1941), reported what is obviously the same substance, as melting at 119–121°.

(7) Criegee, Buchner and Walther, *Ber.*, **73**, 571 (1940).

(8) In the analogous case of dimesityl ketone, Kohler and Baltzly [THIS JOURNAL, **54**, 4015 (1932)] obtained no glycol at all.

(9) Favorsky and Nazarov reported for their glycol a molecular weight in benzene of 261, calculated 286.

dissociation. However no color developed, no absorption of oxygen occurred, and the glycol was recovered unchanged upon evaporation of the benzene. Accordingly it is probable that no dissociation occurred, and that the low values for the molecular weight are due to abnormalities.
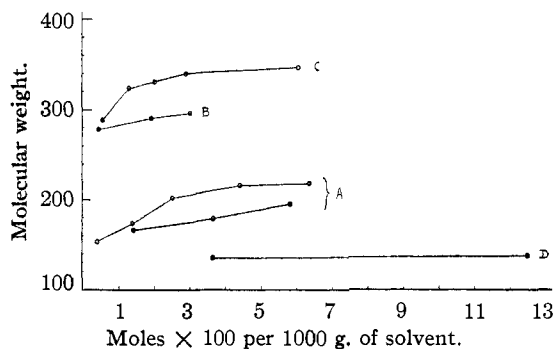


Fig. 1.—A, glycol in benzene; B, glycol in cyclohexane; C, benzpinacol in benzene; D, *p*-nitrotoluene in benzene.

When treated with cold concentrated sulfuric acid, the glycol underwent a reaction, but the products were unlike the expected tri-*t*-butylpinacolone which, according to Favorsky and Nazarov, had $n_D$ 1.4634, and formed an unstable insoluble yellow dibromide, m. p. 74–75°. Our product had $n^{25}_D$ 1.4428, and, while it reacted readily with bromine, it gave no insoluble bromine addition product.

The oil, formed along with the glycol from the ketyl, had, surprisingly, physical properties somewhat similar to those of the substituted pinacolone of Favorsky and Nazarov, and like this, gave an unstable insoluble yellow addition product with bromine, m. p. 75–78.5°, which appeared however to be a tetrabromide. Analysis of the oil gave values (C, 77.2; H, 13.2) corresponding to no satisfactory formula, and further fractionation showed it to be a complex mixture. The comparatively low boiling point, and the molecular weight (218 in benzene) indicated that the material probably had less than 18 carbon atoms, possibly only 14, corresponding to a loss of a *t*-butyl group. Further work with these highly branched chain substances is projected.

## Experimental

**Tetra-*t*-butylethylene Glycol.**—Following the directions of Favorsky and Nazarov, no crystalline products were isolated. Our best results were obtained by avoiding elevated temperatures. In a 500-ml. 3-necked flask fitted with a mercury seal stirrer was placed 0.5 mole (11.5 g.) of powdered sodium. After the air had been displaced by pure dry nitrogen, enough dry ether was added to cover the

<div align="center">MOLECULAR WEIGHT DATA</div>

| Substance | Wt., g. | Solvent | Wt., g. | MPs | MPmix. | ΔT° | Molecular wt. Found | Molecular wt. Calcd. |
|---|---|---|---|---|---|---|---|---|
| Glycol | 0.00881 | Camphor | 0.08486 | 176.5 | 162 | 14.5 | 284 | 286 |
| Glycol | .0192 | Cyclohexane | 15.80 | 1.974 | 2.063 | .089 | 274 | |
| Glycol | .0862 | Cyclohexane | 15.80 | 1.974 | 2.351 | .377 | 291 | |
| Glycol | .1352 | Cyclohexane | 15.80 | 1.974 | 2.555 | .581 | 296 | |
| Glycol | .0501 | Benzene | 12.713 | 4.982 | 4.861 | .121 | 167 | |
| Glycol | .1344 | Benzene | 12.713 | 4.982 | 4.680 | .302 | 179 | |
| Glycol | .2136 | Benzene | 12.713 | 4.982 | 4.542 | .440 | 195 | |
| Glycol | .0211 | Benzene | 17.54 | 1.051 | 1.091 | .040 | 154 | |
| Glycol | .0685 | Benzene | 17.54 | 1.051 | 1.166 | .115 | 174 | |
| Glycol | .1270 | Benzene | 17.54 | 1.051 | 1.235 | .184 | 202 | |
| Glycol | .2230 | Benzene | 17.54 | 1.051 | 1.350 | .299 | 218 | |
| Glycol | .3198 | Benzene | 17.54 | 1.051 | 1.481 | .429 | 219 | |
| Benzpinacol | .0366 | Benzene | 17.54 | 1.072 | 1.110 | .038 | 289 | 366 |
| Benzpinacol | .0839 | Benzene | 17.54 | 1.072 | 1.150 | .078 | 322 | |
| Benzpinacol | .1312 | Benzene | 17.54 | 1.072 | 1.190 | .118 | 330 | |
| Benzpinacol | .1863 | Benzene | 17.54 | 1.072 | 1.235 | .163 | 340 | |
| Benzpinacol | .3880 | Benzene | 17.54 | 1.072 | 1.400 | .228 | 346 | |
| $p$-NO$_2$-toluene | .0896 | Benzene | 17.54 | 1.073 | 1.267 | .194 | 135 | 137 |
| $p$-NO$_2$-toluene | .3007 | Benzene | 17.54 | 1.073 | 1.705 | .632 | 138 | |

sodium, and hexamethylacetone (0.5 mole, 71 g.) was added with stirring at such a rate that the flask never became more than slightly warm. A dark red color developed. After several days, 50 ml. of dry ether was added and the stirring continued until all the sodium had dissolved. At the end of the reaction (one to two weeks), the red color had disappeared, and a colorless precipitate had formed. The products were poured slowly into a well-stirred mixture of crushed ice and dilute acetic acid, and the neutral organic products were extracted with ether, the ether solution washed with sodium carbonate solution, and water, and then dried over anhydrous sodium sulfate. After removal of the ether by distillation, the ketone and di-$t$-butylcarbinol mixture distilled at 65–75° (23 mm., 74 g.), leaving a viscous residue, which upon dilution with 10 ml. of absolute methanol, and cooling, deposited about 7 g. of the glycol. On recrystallization from methanol, it melted at 116–117°, 5 g. *Anal.* Calcd. for $C_{18}H_{38}O_2$: C, 75.4; H, 13.4. Found: C, 75.5, 75.2; H, 13.4, 13.8. Zerewitinoff data: 0.1381 g. gave 23.6 ml. of methane (25°, 755.1 mm.): 1.99 active hydrogen; 0.1165 g. gave 16.55 ml. of methane (25°, 754 mm.): 1.81 active hydrogen.

Attempts to oxidize the glycol with lead tetraacetate in benzene solution at 25 and 100° failed. Most of the glycol was recovered. Small amounts of volatile products were obtained, but these could not be identified. No oxidation with potassium permanganate in boiling pyridine occurred, even after 6.5 hours, 0.414 g. of glycol being recovered from 0.430 g.

**Dehydration of the Glycol.**—The glycol, 4.0 g., was added in small portions over one and one-half hours to 15 ml. of concentrated sulfuric acid, cooled to −20° The glycol dissolved slowly, forming a light yellow solution. This was then warmed, and allowed to stand at 25° for one hour, whereupon an oil separated. The mixture was poured into 50 ml. of chipped ice, the precipitated oil separated, washed with water and potassium carbonate solution, and then steam distilled. About 1.75 ml. of a liquid came over readily, which was separated, dried over sodium sulfate and filtered, $n^{25}$D 1.4428. This material

reduced potassium permanganate in acetone slowly, and absorbed bromine in carbon tetrachloride at once, but no insoluble bromide was formed, corresponding to the behavior of the ketone of Favorsky and Nazarov. On distillation, the oil boiled over a wide range, 41–120° (25 mm.) and was obviously a complex mixture of unsaturated substances. That portion of the oily dehydration product which did not readily steam distil, could be steam distilled only with great difficulty. About 0.25 ml. was thus distilled, $n^{25}$D 1.4673. While it absorbed bromine in carbon tetrachloride rapidly, it likewise formed no insoluble yellow bromide.

The non-crystalline by-product of the dimolecular reduction of hexamethylacetone, remaining after the precipitation of the glycol, was collected from several runs, and distilled, boiling mainly at 125–126° (14 mm.) $n^{25}$D 1.4626. On redistillation, the main fraction boiled at 68° (0.8 mm.), $n^{25}$D 1.4659, $d^{25}_4$ 0.9047. *Anal.* Found: C, 77.2; H, 13.6. When treated with bromine in Skelly Solve A solution, it formed an unstable insoluble yellow precipitate, which could not be recrystallized, m. p. 75–78.5°. *Anal.* Calcd. (mol. wt. 212) for a tetrabromide: Br, 60.2. Found: Br, 60.2. More careful refractionation of the liquid revealed that it was a mixture, and further work with it was abandoned.

### Summary

1. The action of sodium on hexamethylacetone leads to the formation of a tetra-$t$-butylethylene glycol different from that reported by Favorsky and Nazarov.

2. Molecular weight determinations of the glycol are normal in camphor and cyclohexane, but abnormal in benzene.

3. Dehydration of the glycol yields products which appear to be quite different from those obtained by Favorsky and Nazarov from their glycol.

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