mm., $n^{25}\mathrm{D}$ 1.4386, 192 g.; and fraction 3, b.p. 141–151° at 4 mm., $n^{25}\mathrm{D}$ 1.4644, 45 g.

Fraction 1 was shown to be recovered malonic ester (63%). Its infrared spectrum was identical with that of an authentic sample, and was distinctly different from that of an authentic sample of $\gamma$-butyrolactone. Other physical properties are in agreement with the literature values.[3] It should be pointed out that malonic ester and $\gamma$-butyrolactone boil only two degrees apart. The refractive indices, $n^{20}\mathrm{D}$, are 1.4143 and 1.4354, respectively. Raha reports $n^{35}$ 1.3760 for his product, but does not indicate the wave length of light. Fraction 1, with concentrated ammonia, gave malonamide, m.p. 168–169° (lit. value[4] 170°). A mixed melting point with an authentic sample showed no depression.

It should be pointed out that malonic ester ($C_7H_{12}O_4$) and $\gamma$-butyrolactone ($C_4H_6O_2$) have nearly the same percentage composition and saponification equivalent, possibly accounting for Raha's error in interpretation of the elemental analyses. The higher boiling fraction 2, however, should have had a distinctly different analysis, and we cannot account for Raha's claim that all fractions had the same carbon and hydrogen content, and saponification equivalent.

Fraction 2 was shown to be $\beta$-chloroethyl ethyl malonate. Although the elemental analysis is not entirely satisfactory, it is given here to demonstrate that the compound contained chlorine.

*Anal.*[5] Calcd. for $C_7H_{11}O_4Cl$: C, 43.2; H, 5.7; Cl, 18.2. Found: C, 43.8; H, 5.7; Cl, 17.2.

The high carbon and low chlorine can be explained satisfactorily by about 5% of malonic ester as an impurity. Fraction 2, with urea,[6] gave a good yield of barbituric acid, m.p. 256° (lit. value[7] 245°).

*Anal.* Calcd. for $C_4H_4N_2O_3$: C, 37.5; H, 3.11; N, 21.9. Found: C, 37.5; H, 2.82; N, 21.8.

Fraction 2 (10 g.) was shaken for 15 minutes with 60 ml. of concentrated ammonia. After standing for one hour, the crystalline solid was filtered. After recrystallization from hot water there was obtained 4.5 g. (85.6%) of malonamide, m.p. and mixed m.p. 168–169°.[4] A small sample of this malonamide was further identified by bromination,[8] which gave dibromomalonamide, m.p. 201–202° (lit. value[8] 203°).

Raha claimed that the two fractions which he obtained as product, although they boiled as far as 45° apart, gave identical derivatives. It is now obvious why this was so, since both materials differed only in the alcohol portion of the ester.

Fraction 2 accounted for 20% of the original malonic ester.

Fraction 3 was shown to be bis-$\beta$-chloroethyl malonate. With ammonia, using the same procedure described above, malonamide was again obtained. The boiling point was consistent with the literature value.[9] Fraction 3 accounted for 4% of the original malonic ester. Thus, without including intermediate fractions, 87% of the original malonic ester is accounted for as recovered ester, or the two ester-interchange products. If any $\gamma$-butyrolactone was formed at all, it must have been (including intermediate fractions) in less than 6% yield.

Finally, authentic $\beta$-chloroethyl ethyl malonate and bis-$\beta$-chloroethyl malonate were synthesized according to the procedure of Michael and Weiner[10] from malonic ester, ethylene chlorohydrin and hydrogen chloride. The products had identical physical constants and infrared absorption spectra with fractions 2 and 3, respectively.

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[3] See I. Heilbron, "Dictionary of Organic Compounds," Vol. II, Oxford University Press, New York, N. Y., 1953, p. 186.

[4] I. Heilbron, *ibid.*, Vol. III, p. 206.

[5] Analyses were by Clark Microanalytical Laboratory, Urbana, Ill.

[6] The procedure was analogous to that in "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 60.

[7] H. Biltz and H. Wittek, *Ber.*, **54**, 1035 (1921).

[8] J. V. Backes, R. W. West and M. A. Whiteley, *J. Chem. Soc.*, **119**, 364 (1921).

[9] G. M. Bennett, *ibid.*, **127**, 1278 (1925).

[10] A. Michael and N. Weiner, THIS JOURNAL, **58**, 999 (1936).

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## A New Synthesis of Neopentyl Alcohol[1]

BY JOSEPH HOFFMAN[2] AND CECIL E. BOORD

RECEIVED NOVEMBER 24, 1954

In the course of an investigation on the preparation of 2,4,4-trimethyl-2-pentyl (isoöctyl) hydroperoxide by mixing diisobutylene[3] with an aqueous solution consisting of sulfuric acid and hydrogen peroxide,[1] it was found that the hydroperoxide could be prepared if the acid concentration of the aqueous phase was less than 45%. When the percentage of acid in the aqueous phase was increased to 65–70, no hydroperoxide was found at the end of a run (as evidenced by lack of active oxygen) even though most of the diisobutylene had disappeared during the course of mixing. When the aqueous acid layer was poured onto cracked ice, a viscous oil separated. This suggested that the hydroperoxide although formed was being degraded almost as rapidly.

The acid-catalyzed degradation of hydroperoxides has been observed previously.[4–8] It has been postulated to proceed through the initial scission of the oxygen–oxygen bond followed by rearrangement.[6–8] It is reasonable to assume that the extent of rearrangement as well as the nature of the group or groups participating in it will vary with the structure of the molecule. One might predict that the decomposition of isoöctyl hydroperoxide (involving only the migration of a neopentyl group) would result in the formation of neopentyl alcohol.

$$(CH_3)_3CCH_2C(CH_3)_2OOH \xrightarrow{H^+} (CH_3)_3CCH_2OH + CH_3COCH_3$$

It was suspected, therefore, that the unidentified oil was crude neopentyl alcohol, and subsequently this was confirmed.

It was thought that perhaps a new synthetic method for the preparation of this alcohol might be developed by further study of the reaction. A series of experiments was performed in which hydrogen peroxide and diisobutylene (DIB) were allowed to react in varying ratios in sulfuric acid solution. As the $H_2O_2$/DIB ratio was increased, a point of diminishing returns was reached at about 2/1. In each experiment an organic product was recovered by dilution of the aqueous acid phase; this was identified as being mainly neopentyl alcohol. The acetone produced by the degradation of the hydroperoxide reacted with hydrogen peroxide to form acetone peroxide. A small amount of methyl neopentyl ketone was identified in the unreacted DIB phase; this ketone can be accounted for by the

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[1] This work was presented before the Division of Organic Chemistry at the 121st Meeting of the American Chemical Society, at Milwaukee, Wis., April 2, 1952. It was taken in part from the dissertation submitted by Joseph Hoffman to the Graduate School of The Ohio State University, in 1951, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] Firestone Tire and Rubber Co. Fellow, 1949–1951.

[3] Commercial diisobutylene comprises approximately 85% 2,4,4-trimethyl-1-pentene and 15% 2,4,4-trimethyl-2-pentene.

[4] H. Hock and S. Lang, *Ber.*, **77**, 257 (1944).

[5] R. Criegee and H. Dietrich, *Ann.*, **560**, 135 (1948).

[6] R. Criegee, *ibid.*, **560**, 127 (1948).

[7] M. S. Kharasch, A. Fono and W. Nudenberg, *J. Org. Chem.*, **15**, 748 (1950).

[8] M. S. Kharasch and J. G. Burt, *ibid.*, **16**, 150 (1951).

migration of a methyl rather than the neopentyl group in the rearrangement step.

In the distillation of the crude neopentyl alcohol evidence was seen for two by-products (b.p. 81 and 106°) which were not identified. The absence of *t*-amyl alcohol (b.p. 101.8°) was established, however, indicating that the degradation of the hydroperoxide did not occur *via* a neopentylcarbonium ion mechanism, which would undoubtedly result in the formation of some of this alcohol.[9] Yields of distilled neopentyl alcohol were about 40%, based on DIB.

If it is assumed that most of the DIB used up in the process must have been converted initially to hydroperoxide, then it is obvious that only about one-half of the hydroperoxide decomposes according to the mechanism which produces neopentyl alcohol.

**Experimental Procedure.**—Hydrogen peroxide (30%) (160 g.) was treated with 350 g. of cold sulfuric acid (95%) with vigorous stirring, the temperature being maintained below 25° by an ice-bath. After addition was complete and the temperature of the acid solution had fallen to 5°, DIB (112.2 g. 1 mole) was added over a one-hour period (only one-fourth was added during the first half-hour); the temperature was maintained at 6–8°. After one hour of further stirring, the temperature rose to 10° and after another 20 minutes to 20°. The temperature remained at 20° for 10 minutes and then rapidly returned to 10°. (Caution: The temperature should not be allowed to rise above 25° as there is danger of the reaction becoming uncontrollable; at about 40° the contents may be sprayed or blown from the flask. Vigorous stirring and good cooling are essential.) At this point, the reaction was considered complete, and a drop of the reaction mixture when added to a potassium iodide–glacial acetic acid solution liberated little if any iodine. The product was filtered, cold, on a sintered glass funnel with suction to remove the crystalline acetone peroxide. The lower acid layer of the filtrate was then run into cracked ice (100 g.) and water (350 g.). The neopentyl alcohol concentrate which formed (70.0 g.) was removed. To the diluted acid layer was added an equal volume of a saturated ammonium sulfate solution, and the resulting solution then was extracted with ether. The ether extracts were combined with the alcohol concentrate, the ethereal solution washed with sodium carbonate solution, dried over anhydrous sodium sulfate, and concentrated.

The crude neopentyl alcohol was distilled on a small (1.2 × 30 cm.) helices-packed column at atmospheric pressure. Hot water was circulated through the take-off condenser during distillation to prevent crystallization of the neopentyl alcohol (b.p. 110–111°; lit. 110–111°,[10,11] 111° (730 mm.)[12]); 37.0 g., or a yield of 42% based on the DIB, was obtained. The neopentyl alcohol was redistilled and a heart-cut of the distillate was twice sublimed at 0.5 mm. and room temperature to obtain a prime sample (m.p. 54.5–55.5°, lit.[11] 55–56°).

The organic layer (10.5 g.) remaining from the original reaction mixture and containing mostly DIB was now washed with aqueous sodium carbonate and dried over anhydrous sodium sulfate. After removal of the unreacted DIB by distillation, a 2,4-dinitrophenylhydrazone derivative was prepared from the residue. This was shown to be identical with the same derivative prepared from an authentic sample of methyl neopentyl ketone by its melting point (100.5 to 101.5°, lit.[13] 101–102°); a mixed melting of the two derivatives showed no depression.

The crystalline acetone peroxide (27.2 g.) isolated from the reaction mixture by filtration, was washed thoroughly with water, then with a small amount of alcohol and finally with benzene. Upon sublimation *in vacuo* at room temperature, a crystalline material having a melting point of 132–133° was obtained (lit. for acetone peroxide, m.p. 132–133°,[5] 132°[14]).

**Acknowledgment.**—Thanks go to Dr. Kenneth W. Greenlee for his continual interest and ready coöperation in extending the facilities of the American Petroleum Institute Research Project 45.

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(11) A. Scattergood, W. H. Miller and J. Gammon, Jr., *ibid.*, **67**, 2150 (1945).

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## The Preparation of Tetra-*t*-butoxysilane and Tri-*t*-butoxyfluorosilane

BY J. FRANKLIN HYDE AND JAMES W. CURRY

RECEIVED JANUARY 15, 1955

Previously reported attempts to synthesize tetra-*t*-butoxysilane have not been successful, or at least have not been fully documented.[1] Ridge and Todd[2] treated silicon tetrachloride with the various isomeric butyl alcohols and found that the yield of tetralkoxysilane is nil when *t*-butyl alcohol is used. They showed that *t*-butyl chloride and silica are the products of this reaction. This behavior appears to be characteristic of tertiary alcohols,[3] the result being that *t*-alkoxysilanes cannot be prepared by the normal, unmodified procedure involving alcoholysis of chlorosilanes.[4]

Miner and co-workers treated silicon tetrachloride with *t*-butyl alcohol in the presence of pyridine and isolated di-*t*-butoxydichlorosilane as the product of the reaction.[5,6] They then subjected this compound to the action of additional *t*-butyl alcohol, again in the presence of pyridine, and obtained tri-*t*-butoxychlorosilane. Under these conditions they were unable to cause replacement of the fourth chlorine atom by the *t*-butoxy group.

Backer and Klasens[7] obtained tri-*t*-butoxychlorosilane from sodium *t*-butoxide and silicon tetrachloride in refluxing petroleum ether. When they treated the tri-*t*-butoxy compound with an excess of sodium *t*-butoxide in a sealed tube for 15 hours at 170°, they found the reaction products to be sodium tri-*t*-butoxysilanolate and hexa-*t*-butoxydisiloxane. They were unable to isolate any tetra-*t*-butoxysilane. The only product which could be identified by Hyde and Kookootsedes[8] when they

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(1) H. Breederveld and H. I. Waterman, *Rec. trav. chim.*, **72**, 166 (1953). In this paper there is a very brief mention of the successful synthesis of tetra-*t*-butoxysilane from tri-*t*-butoxybromosilane and sodium *t*-butoxide. However, physical data and a complete description of the synthesis were not reported. NOTE ADDED IN PROOF.—After this manuscript had been submitted for publication, it was learned that Breederveld and Waterman had published recently their synthesis of tetra-*t*-butoxysilane (H. Breederveld and H. I. Waterman, *Rec. trav. chim.*, **73**, 871 (1954)).

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(5) G. W. Pedlow, Jr., and C. S. Miner, Jr. (to Minnesota Mining and Manufacturing Co.), U. S. Patents 2,566,364 and 2,566,365, September 4, 1951.

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(8) J. F. Hyde and G. J. Kookootsedes, unpublished data.