THE SYNTHESES AND REACTIONS OF ALKYLATED FURANS[1]

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ABSTRACT

The reaction of 2-chloromercurifuran with *t*-butyl bromide does not yield 2-*t*-butylfuran. Instead 2,5-di-*t*-butylfuran, 2,2,7,7-tetramethyloctane-3,6-dione, and 2-*t*-butyl-5-[2,4,4-trimethyl-2-pentyl]furan are produced. Air-oxidation of di-*t*-butylfuran yields *trans*-2,2,7,7-tetramethyl-4-octene-3,6-dione (converted to the *cis* isomer photochemically) which forms a dibromide identical with the dibromo substitution product from tetramethyloctanedione. Cold nitric acid oxidation of di-*t*-butylfuran or tetramethyloctanedione yields 4-hydroxy-5-isonitroso-2,2,7,7-tetramethyloctane-3,6-dione, but hot nitric acid oxidation of the tetramethyloctanedione yields the expected 2-trimethylacetyl-5-*t*-butylisoxazole. The corresponding oxidation product of *t*-butyltrimethylpentylfuran has not been identified, although it yields 2,2,4,4-tetramethylpentanoic acid, indicative of the isoöctyl substituent, upon hydrolysis. The same acid is obtained by permanganate oxidation of Friedel–Crafts-synthesized 2,5-di-[2,4,4-trimethyl-2-pentyl]furan, a compound which yields *trans*-2,2,4,4,9,9,11,-11-octamethyl-6-dodecene-5,8-dione.

Recently alkylfurans have been prepared from furan by Pines and Vesely (13) by use of the boron-trim fluoride-catalyzed reaction with olefins. Earlier Gilman and Wright described the preparation of difurylmethane by reaction of furfuryl chloride with 2-chloromercurifuran (7). At the present time we are reporting the extension of this reaction with chloromercurifuran (I) by use of aliphatic halides.

We have found that *t*-butyl bromide reacts readily with I in chloroform as a medium. The product, however, is not the expected 2-*t*-butylfuran. Instead, 2,5-di-*t*-butylfuran (II), 2,2,7,7-tetramethyloctane-3,6-dione (III), and 2-*t*-butyl-5-[2,4,4-trimethyl-2-pentyl] furan (IV) have been isolated from the reaction mixture in the ratio of about 3 : 1 : 1. The presence of III as a product can be accounted for by the hydrolysis of II while working up the reaction mixture. The yields are low (30% over-all in a typical run). Much resinous material is formed even when the reaction is carried out at reasonably low temperatures (30–40°).

The structures of II and III have been established by the following reactions: When II is treated with bromine water it is converted to 4,5-dibromo-2,2,7,7-tetramethyloctane-3,6-dione (VI). The same product, VI, is formed when III is treated with bromine water. Authentic III was prepared by the method of Wahlberg (19) involving the decarboxylation of 2,2,7,7-tetramethyl-4-carboxy-3,6-octanedione in ether. Kharasch, McBay, and Urry (10) have also described a method for the preparation of III by the action of diacetyl peroxide on pinacolone. Wahlberg (19) has reported a dioxime of III melting at 265°. It is probably an uncorrected value, since in the present investigation the dioxime was found to melt at 277°.

When 2,5-di-*t*-butylfuran (II) is allowed to stand at room temperature over a period of 1 month, it is oxidized, apparently by atmospheric oxygen, to *trans*-2,2,7,7-tetramethyl-4-octene-3,6-dione (V), a pale yellow solid, m.p. 110–111°. The same compound, V, is also formed, along with 4,5-dichloro-2,2,7,7-tetramethyloctane-3,6-dione, when II is treated with acidified hypochlorite solution. Schenck (14, 15, 16, 17, 18) has investigated the autoxidation of furans extensively. In the case of 2,5-dimethylfuran he obtained *trans*-diacetylethylene, a pale yellow solid, m.p. 77–78°.

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Trans-2,2,7,7-tetramethyl-4-octene-3,6-dione (V) is easily converted to the colorless *cis*-modification, m.p. 46°, by exposure to strong sunlight in acetone or hexane solution. Similar observations have been made by Martin, Bett, Romans, and Tidridge (12) in the conversion of *trans*-di-*p*-toluylethylene to the *cis*-isomer by irradiation under mercury vapor light (404.7 mμ). In the case of V, absorption is strong in the region 390–410 mμ, while the *cis*-isomer is relatively transparent over the same range. Of interest, also, is the fact that *trans*-V readily forms a dioxime, m.p. 184°, while *cis*-V fails to react with hydroxylamine. *Trans*-V reacts readily with bromine to form 4,5-dibromo-2,2,7,7-tetramethyloctane-3,6-dione (VI).

The presence of 2-*t*-butyl-5-[2,4,4-trimethyl-2-pentyl]furan (IV) as a product of the reaction between 2-chloromercurifuran (I) and *t*-butyl bromide is surprising but comprehensible. Probably it is formed by an alkylation type of reaction involving two molecules of either *t*-butyl bromide or isobutylene (derived from *t*-butyl bromide) to form diisobutylene (isoöctene), which subsequently alkylates furan.

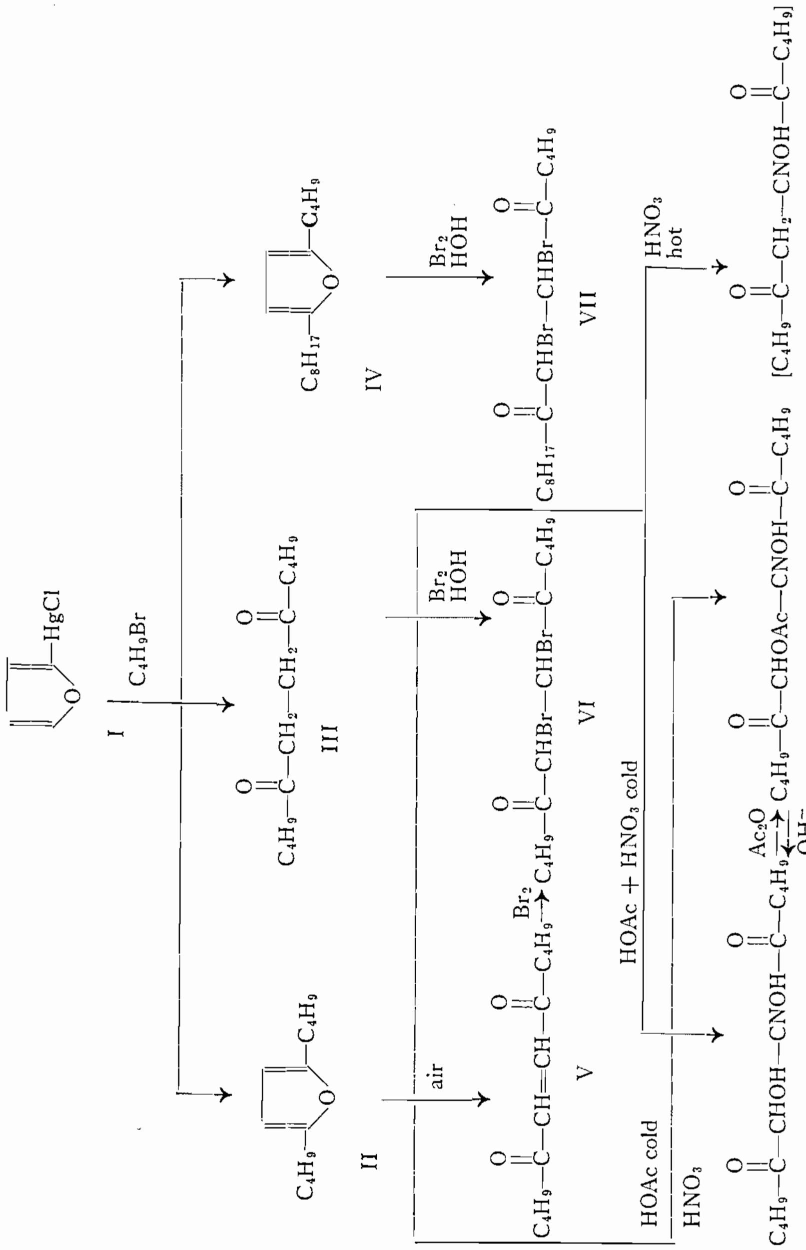
The synthesis of authentic 2-*t*-butyl-5-[2,4,4-trimethyl-2-pentyl]furan (IV) was accomplished by alkylating 2-*t*-butylfuran (prepared by the general method of Pines and Vesely (13)) with diisobutylene. Attempts to prepare IV by the alkylation of 2,4,4-trimethyl-2-pentyl-2-furan with isobutylene failed. When IV is treated with bromine water the product is 4,5-dibromo-2,2,7,7,9,9-hexamethyldecane-3,6-dione (VII).

The determination of the molecular weight of VII by the Rast method gave values one-half (206) of that required by theory (412). The same is true for 4,5-dibromo-2,2,7,7-tetramethyloctane-3,6-dione (VI). It has been observed that in both instances decomposition of the bromo compound occurs during the heating period of the molecular weight determination. When the chloro derivative of III (4,5-dichloro-2,2,7,7-tetramethyloctane-3,6-dione) was prepared, values comparable with theory have been obtained for this latter compound.

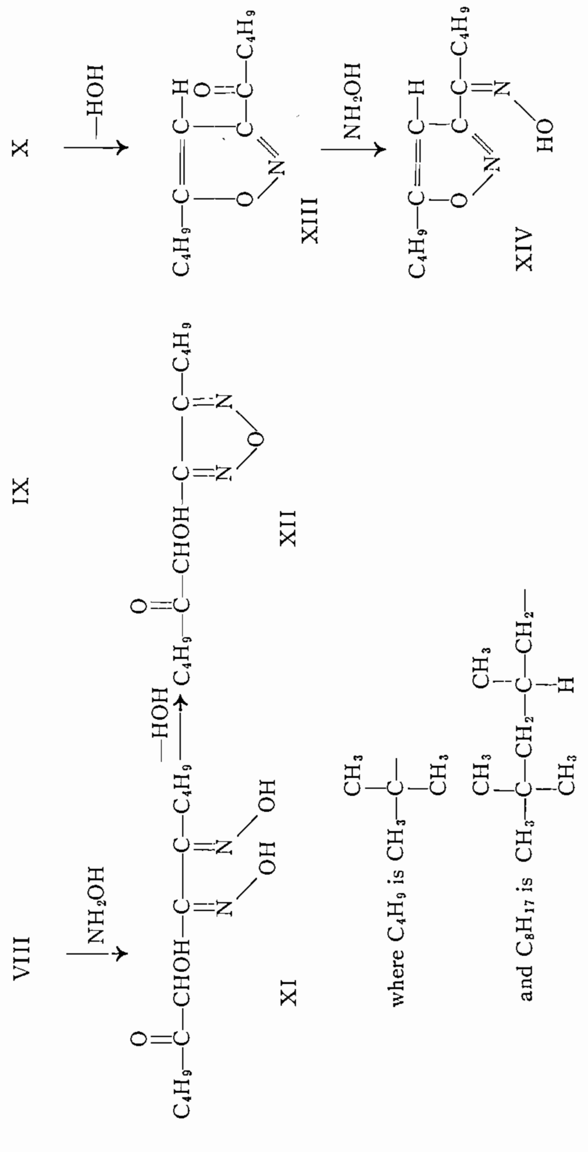
When [2,4,4-trimethyl-2-pentyl]-2-furan is allowed to stand at room temperature, the original water-white liquid slowly turns yellow and, after 6 weeks, crystals appear. These crystals have been shown to be maleic acid by preparation of the di-*p*-nitrobenzyl ester. Oxidation of 2,4,4-trimethyl-2-pentyl-2-furan with neutral permanganate yields the expected 2,2,4,4-tetramethylpentanoic acid. The authentic acid has been prepared by the method of Whitmore, Wheeler, and Surmatis (20).

During the course of the investigation, 2,5-bis[2,4,4-trimethyl-2-pentyl]furan was also prepared. Unlike 2,5-di-*t*-butylfuran (II), it does not undergo autoxidation readily. However, it is easily oxidized to pale yellow *trans*-2,2,4,4,9,9,11,11-octamethyl-6-dodecene-5,8-dione by the action of dilute nitric acid. A similar reaction has been reported by Lutz and Wilder (11) with compounds such as 2,5-diphenylfuran. In this latter case, however, *cis*-1,2-dibenzoylethylene is formed. When *trans*-octamethyldodecenedione, m.p. 78.5–79.5°, is dissolved in hexane and exposed to strong sunlight, through Pyrex for 12 hours, it is converted to the colorless *cis*-modification, m.p. 55.5–56.5°.

Treatment of 2,5-di-*t*-butylfuran (II) with nitric acid under the conditions employed by Lutz and Wilder (11) yields neither the expected *cis*- nor *trans*-2,2,7,7-tetramethyl-4-octene-3,6-dione (V). Instead, there is obtained 4-hydroxy-5-isonitroso-2,2,7,7-tetramethyloctane-3,6-dione (VIII) and 4-acetoxy-5-isonitroso-2,2,7,7-tetramethyloctane-3,6-dione (IX). Treatment of 2,2,7,7-tetramethyloctane-3,6-dione (III) under the same conditions also results in the formation of VIII. When IX is saponified with aqueous sodium hydroxide, VIII is formed. When VIII is treated with acetic anhydride,



HgCl
I
C4H9Br
II
III
IV
C4H9
C8H17
air
Br2
Br2 HOH
V
VI
VII
HOAc cold HNO3
HOAc + HNO3 cold
HNO3 hot
Ac2O
OH−
VIII
IX
X



$$C_4H_9{-}\overset{CH_3}{\underset{CH_3}{C}}{-} \quad C_8H_{17} = CH_3{-}\overset{CH_3}{\underset{CH_3}{C}}{-}CH_2{-}\overset{CH_3}{\underset{H}{C}}{-}CH_2{-}$$

IX is the product. The structure for VIII is supported by the fact that it may also be prepared by the addition of nitrous acid to *cis*-2,2,7,7-tetramethyl-4-octene-3,6-dione (V). A similar addition of nitrosyl chloride to *trans*-dibenzoylethylene has recently been reported by Beelik and Brown (2).

Alkaline hydrolysis of VIII leads to the formation of ammonia, pivalic acid (trimethylacetic acid), and trimethylpyruvic acid which lends credence to the structure proposed for VIII. Oximation of VIII must occur at the carbonyl function adjacent to the isonitroso function, since the oxime (XI), when steam distilled from alkaline solution, readily loses water and forms the corresponding furazan (XII).

Catalytic hydrogenation of VIII causes the formation of two water-soluble products. In one case, VIII appears to take up 3 moles of hydrogen, while in the other case 1 mole of hydrogen apparently adds. These hydrogenation products have not been investigated further.

When 2,2,7,7-tetramethyloctane-3,6-dione (III) is treated with hot nitric acid, the expected 2-trimethylacetyl-5-*t*-butylisoxazole, XIII, is obtained. Since XIII is a liquid, the oxime, XIV, m.p. 177°, has been prepared, purified, and analyzed. The oxime (XIV) reacts readily with phenylisocyanate and with 2,4-dinitrophenylhydrazine. According to analyses these products seem to be derivatives of XIV rather than of the isomeric 3-*t*-butyl-4-[2-keto-3,3-dimethylbutyl]furazan which might have been expected in consideration of previous work (1, 4).

When 2-*t*-butyl-5-[2,4,4-trimethyl-2-pentyl]furan (IV) is treated with nitric acid (best diluted with acetic acid) a product ($C_{12}H_{21}NO_3$) is produced. This substance, which forms a derivative $(C_8H_{15}NO_2)_n$ upon treatment with hydroxylamine, has not of itself been identified. However it is converted under hydrolytic conditions either with acid or alkali to 2,2,4,4-tetramethylpentanoic acid. The presence of the 2,4,4-trimethyl-2-pentyl substituent in IV is thus established.

We are grateful to DuPont of Canada for generous supplies of furan.

EXPERIMENTAL

All melting points have been corrected against reliable standards. Molecular weights were determined by the Rast method.

2-t-Butylfuran

In a three-necked 250-ml. Grignard-type flask, fitted with a stirrer, reflux condenser, and surrounded by an ice–salt bath at −10°, was placed 68 g. (1.0 mole) of furan (DuPont). To the furan, with stirring, was added 2.5 ml. of boron trifluoride etherate (B&A Code 1471) in 2.5 ml. of anhydrous ether. Into this solution was bubbled 56 g. (2.0 mole) of isobutylene (C. P. Matheson) over a period of 75 minutes. Stirring was continued for another 2 hours at 0°. At the end of this time, the contents of the flask had become dark brown. After 125 ml. of water was added to the flask, the mixture was extracted twice with 100-ml. portions of ether, the ether solution washed with saturated aqueous sodium carbonate solution and then dried over anhydrous calcium chloride. The ether was flashed off leaving a brown liquid as a residue. Fractional distillation through a column as described by Bower and Cook (3) yielded two fractions. The first fraction, a colorless liquid, weighed 3.5 g. (2.8%), b.p. 116–117° at 737 mm.; n_D^{20} 1.4373, n_D^{25} 1.4351, d_4^{20} 0.869.

2,5-Di-t-butylfuran (II)

(a) From 2-Chloromercurifuran (I) and t-Butyl Bromide

A slurry of 121.2 g. (0.4 mole) of 2-chloromercurifuran in 220 ml. of chloroform in a three-necked, round-bottom flask fitted with a stirrer was treated with 5 ml. of 95% ethanol and 137.0 g. (1.0 mole) of *t*-butyl bromide. After it was stirred for 7 minutes, the reaction mixture warmed up to the boiling point of chloroform. The heat reaction subsided after 30 minutes and stirring was continued intermittently for 13 days. It was found that the reaction should be allowed to proceed for a minimum of 4 days. Runs worked up after the initial heat reaction had subsided gave negligible yields. At the end of this time, the dark reddish-brown chloroform solution was filtered from the precipitated mercuric halide, extracted 10 times with 100-ml. portions of water, and then with 100 ml. of 5% aqueous sodium hydroxide solution. The chloroform was flashed off leaving a dark brown oil which was distilled under diminished pressure from a Claisen flask. In this manner, 25.5 g. of faintly yellow oil, b.p. 50–105° (10 mm.), was obtained. Three fractions were obtained from this oil. The first fraction weighed 13.3 g. (18.5%); b.p. 49–53° (5 mm.), 210° (760 mm.); n_D^{20} 1.4376; $d_4^{26.5}$ 0.854; M_D calc., 56.41, found, 56.70. Anal. Calc. for $C_{12}H_{20}O$: C, 79.9; H, 11.1. Found: C, 80.1; H, 11.4.

(b) From 3-Chloromercurifuran and t-Butyl Bromide

When a slurry of 4.9 g. (0.016 mole) of 3-chloromercurifuran, prepared according to the method of Gilman and Wright (7), in 10 ml. of chloroform and 2 ml. of 95% ethanol, was treated with 5.5 g. (0.040 mole) of *t*-butyl bromide the mercurial dissolved and the resulting solution turned reddish-brown over a period of 3 days. After the reaction mixture had been worked up as previously described two oils were obtained by fractional distillation. The first oil weighed 0.56 g. (19%) and boiled at 40–50° at 1–2 mm.

(c) From Furan and t-Butyl Bromide in the Presence of Mercuric Bromide

When a mixture of 34 g. (0.5 mole) of furan, and 36 g. (0.1 mole) of mercuric bromide in 100 ml. of chloroform, was treated with 24 g. (0.18 mole) of *t*-butyl bromide no apparent reaction occurred after stirring for 10 minutes. However, when 15 ml. of 95% ethanol was added to the mixture, heat was evolved immediately and the reaction mixture began to darken. The heat reaction was sustained by the dropwise addition of a further 113 g. (0.82 mole) of *t*-butyl bromide over a period of 30 minutes. After an additional 20 minutes, the reaction mixture was worked up as described in part (*a*), and 3.1 g. (3.5%) of 2,5-di-*t*-butylfuran was obtained.

(d) From Furan and Isobutylene

A second fraction, a colorless liquid, obtained during the preparation of 2-*t*-butylfuran from furan and isobutylene, weighed 3.6 g. (4.0%); b.p. 61–62° at 16–17 mm.; n_D^{20} 1.4369; d_4^{20} 0.837.

All the oils (*a*, *b*, *c*, and *d*) were shown to be identical, since on treatment with bromine they all yielded the same product, 4,5-dibromo-2,2,7,7-tetramethyloctane-3,6-dione (VI).

2-t-Butyl-5-[2,4,4-trimethyl-2-pentyl]furan (IV)

(a) From 2-Chloromercurifuran (I) and t-Butyl Bromide

The second fraction, obtained during the preparation of 2,5-di-*t*-butylfuran from 2-chloromercurifuran and *t*-butyl bromide (see (*a*) above), weighed 4.2 g. (5.4%); b.p.

98–99° at 10 mm.; n_D^{20} 1.4518; d_4^{20} 0.869. Anal. Calc. for $C_{16}H_{28}O$: C, 81.3; H, 11.9; mol. wt., 236. Found: C, 81.2; H, 11.5; mol. wt., 248.

(*b*) *From 3-Chloromercurifuran and t-Butyl Bromide*

The second oil from the distillation described in (*b*) above weighed 0.40 g. (13%) and boiled at 75–85° at 1–2 mm.

(*c*) *From Furan and t-Butyl Bromide in the Presence of Mercuric Bromide*

From the reaction mixture obtained by treating furan with *t*-butyl bromide in the presence of mercuric bromide, (*c*) above, there was obtained 0.9 g. (1.3%) of 2-*t*-butyl-5-isoöctylfuran.

(*d*) *From 2-t-Butylfuran and Diisobutylene*

In a three-necked 50-ml. Grignard-type flask, fitted with a stirrer, reflux condenser, and cooled externally with tap water (13°), were placed 2.3 g. (0.02 mole) of 2-*t*-butylfuran and 0.5 ml. of boron trifluoride etherate (B&A Code 1471) in 0.5 ml. of anhydrous ether. Diisobutylene, 4.4 g. (0.04 mole), was added dropwise, with stirring, over a period of 20 minutes. After the addition was completed, the reaction mixture was allowed to warm up to room temperature and was stirred for 2 hours. After it had been left for another 16 hours the reaction mixture was poured into 25 ml. of water. Additional ether, 10 ml., was added and the ether phase was washed once with 10 ml. of water, then 10 ml. of saturated aqueous sodium carbonate solution. Finally, the ether solution was dried over anhydrous calcium chloride. After the ether was flashed off, the remaining brown oil was distilled, yielding 3.6 g. (76%) of colorless liquid; b.p. 113–115° at 16–17 mm.; n_D^{20} 1.4522; d_4^{20} 0.839.

All the oils (*a*, *b*, *c*, and *d*) were shown to be identical, since on treatment with bromine they all yielded the same product, VII.

2,2,7,7-Tetramethyloctane-3,6-dione (*III*)

A third fraction from (*a*) above weighed 4.5 g. (4.4%); b.p. 106–107° at 10 mm.; m.p. 16.5–18.0°; n_D^{20} 1.4396. Anal. Calc. for $C_{12}H_{22}O_2$: C, 72.7; H, 11.2. Found: C, 72.0; H, 11.1.

2,2,7,7-Tetramethyloctane-3,6-dione Dioxime

To a solution of 1.0 g. (0.014 mole) of hydroxylamine hydrochloride and 1.0 g. (0.007 mole) of sodium acetate trihydrate in 8 ml. of water was added 0.50 g. (0.0025 mole) of III. This mixture was warmed on the steam bath for 15 minutes, sufficient 95% ethanol being added to dissolve the diketone. A white solid separated. The mixture was cooled, 50 ml. of water added, and the white solid filtered off. The crude product weighed 0.49 g. (99%). It was purified by crystallization from glacial acetic acid yielding 0.10 g. (20%) of white plates; m.p. 277° with decomposition. Anal. Calc. for $C_{12}H_{24}N_2O_2$: N, 12.3. Found: N, 12.2.

2,2,7,7-Tetramethyloctane-3,6-dione Mono-2,4-dinitrophenylhydrazone

To a solution of 0.08 g. (0.0004 mole) of 2,4-dinitrophenylhydrazine in 0.5 ml. of 93% sulphuric acid and 2 ml. of ethanol was added a solution of 0.10 g. (0.0005 mole) of III in 3 ml. of 95% ethanol. After the solution had been left at room temperature for 30 minutes, orange needles began to form. After 6 hours, 0.12 g. (79%) of orange needles was filtered off. Crystallization from ethanol–water gave 0.08 g. (53%) of fine orange needles, m.p. 122–123°. Further purification was achieved by passing a chloroform solution of the product through a chromatographic column containing alumina (Merck

#71707). This procedure gave a material melting at 129–130°. Anal. Calc. for $C_{18}H_{26}N_4O_5$: N, 14.8. Found: N, 14.8.

2,2,7,7-Tetramethyloctane-3,6-dione Bis-2,4-dinitrophenylhydrazone

To a solution of 0.36 g. (0.0018 mole) of 2,4-dinitrophenylhydrazine in 1.5 ml. of 93% sulphuric acid and 20 ml. of 95% ethanol was added a solution of 0.20 g. (0.0010 mole) of III in 5 ml. of 95% ethanol. After the solution had been left at room temperature for 20 minutes, yellowish-orange needles began to form. After 1 hour, 0.24 g. (40%) of crude product was filtered off, m.p. 150–165°. Crystallization from 95% ethanol gave 0.10 g. (17%) of orange needles, m.p. 228°. Anal. Calc. for $C_{24}H_{30}N_8O_8$: N, 20.1. Found: N, 19.4.

trans-*2,2,7,7-Tetramethyl-4-octene-3,6-dione* (*V*)

A 7-g. sample of 2,5-di-*t*-butylfuran which had been left for 45 days was observed to have formed a crystalline precipitate. The light yellow solid was filtered off. It weighed 0.08 g. and melted at 105–107°. Crystallization from methanol–water gave 0.05 g. of faintly yellow plates, m.p. 110–111°. Anal. Calc. for $C_{12}H_{20}O_2$: C, 73.4; H, 10.3. Found: C, 73.7; H, 10.2.

trans-*2,2,7,7-Tetramethyl-4-octene-3,6-dione Dioxime*

A solution of 0.10 g. (0.0005 mole) of the unsaturated diketone, V, 0.10 g. (0.0014 mole) of hydroxylamine hydrochloride, and 0.10 ml. of pyridine in 1.5 ml. of 95% ethanol was refluxed for 1.5 hours on the steam bath. At the end of this time, the ethanol was removed in a current of air. A white solid precipitated. After 5 ml. of water had been added to the mixture, the solid material was filtered off and washed free from pyridine on the filter. The crude material weighed 0.10 g. and melted at 156–164° with decomposition. Crystallization from ethanol–water gave 0.04 g. (35%) of purified product melting at 184°. Anal. Calc. for $C_{12}H_{22}N_2O_2$: C, 63.7; H, 9.80; N, 12.4. Found: C, 63.7; H, 10.1; N, 12.3.

cis-*2,2,7,7-Tetramethyl-4-octene-3,6-dione* (*V*)

A pale yellow solution of 0.06 g. (0.0003 mole) of *trans*-V in 10 ml. of hexane was placed in a Pyrex flask in bright sunlight for 3 hours. At the end of this time, the solution was colorless. After the hexane was removed in a current of air at room temperature, there remained 0.06 g. (100%) of colorless flat needles, m.p. 44.5–45.0°. Anal. Calc. for $C_{12}H_{20}O_2$: C, 73.4; H, 10.3. Found: C, 74.1; H, 10.3.

4,5-Dibromo-2,2,7,7-Tetramethyloctane-3,6-dione (*VI*)

(*a*) *From 2,5-Di-t-butylfuran* (*II*)

To 50 ml. of saturated bromine water was added 0.5 g. (0.0028 mole) of 2,5-di-*t*-butylfuran. After 2 minutes, a white solid began to form, mixed with the oil. The mixture was allowed to stand for 10 hours, at the end of which time 0.41 g. of crude product was obtained. Crystallization from absolute methanol yielded 0.25 g. (25%) of colorless needles (m.p. 117.5°) with a characteristic sweet odor. Anal. Calc. for $C_{12}H_{20}Br_2O_2$: C, 40.5; H, 5.66; Br, 44.9. Found: C, 40.6; H, 5.63; Br, 45.6.

(*b*) *From 2,2,7,7-Tetramethyloctane-3,6-dione* (*III*)

In this instance the mixture of bromine water and diketone had to be warmed on the steam bath to promote the reaction. The yield of purified product, m.p. 117.5°, was 4.5%.

(*c*) *From* trans-*2,2,7,7-Tetramethyl-4-octene-3,6-dione* (*V*)

A solution of 0.04 g. (0.0002 mole) of the diketone, V, in 10 ml. of 10% methanol solution of bromine was warmed on the steam bath for 30 minutes, and then allowed to stand overnight at room temperature. Water was then added and a white solid separated. The crude product was purified by crystallization from methanol–water. It weighed 0.04 g. (56%) and melted at 117.5°.

All three products were shown to be identical by mixture melting point.

4,5-Dichloro-2,2,7,7-Tetramethyloctane-3,6-dione

When 3.6 g. (0.02 mole) of 2,5-di-*t*-butylfuran was treated with sodium hypochlorite solution (Javelle water, 7% available chlorine) in excess and the resulting mixture was acidified with hydrochloric acid a pale yellow solid formed in about 3 minutes. Crystallization from methanol gave 0.90 g. (25%) of pale yellow plates, m.p. 110–111°. This compound was shown to be *trans*-III by mixture melting point with an authentic sample.

Further treatment with acidified hypochlorite solution yielded a second solid which, when crystallized from methanol (11.3 ml./g.), gave 1.43 g. (27%) of coarse white needles, m.p. 125–126°. Anal. Calc. for $C_{12}H_{20}Cl_2O_2$: Cl, 26.6; mol. wt., 267. Found: Cl, 26.9; mol. wt., 282.

6,7-Dibromo-2,2,4,4,9,9-hexamethyldecane-5,8-dione (*VII*)

When 0.5 g. (0.002 mole) of 2-*t*-butyl-5-[2,4,4-trimethyl-2-pentyl]furan, IV, was treated with excess bromine water over a period of 6 days, 0.02 g. (23%) of white needles formed. Crystallization from isopropyl alcohol–water gave 0.010 g. (12%) of white needles, m.p. 80–81°. Anal. Calc. for $C_{16}H_{28}Br_2O_2$: C, 46.6; H, 6.84; Br, 38.8. Found: C, 47.0; H, 6.86, Br,39.0.

2-Chloromercuri-5-t-butylfuran

A solution of 0.50 g. (0.0040 mole) of 2-*t*-butylfuran in 5 ml. of 95% ethanol was added to 24 ml. of mercurating solution as described by Gilman and Wright (7). After the mixture had been left at room temperature with occasional shaking for 48 hours, the resulting light brown solid, 0.52 g., was removed by filtration. Crystallization from ethanol–water gave 0.33 g. (23%) of white stubby needles, m.p. 164–165°. A mixture melting point of the substance with 2-chloromercuri-5-*t*-butylfuran, m.p. 164–165°, prepared according to the method of Gilman and Wright (7) and Gilman and Calloway (6) showed no depression. Gilman and Burtner (5) report the melting point as 174–175°. Although these mercurials were adequate for derivative identification, it seems evident that one of these two reactions must give an abnormal product. Anal. Calc. for $C_8H_{11}ClHgO$: C, 26.7; H, 3.09. Found: C, 26.4; H, 3.10.

[2,4,4-Trimethyl-2-pentyl]-2-furan

In a 500-ml. three-necked round-bottom flask, fitted with a stirrer, reflux condenser, and cooled externally with tap water (12°), was placed 136 g. (2.00 mole) of furan (DuPont). Addition of 5 ml. of boron trifluoride etherate (B&A Code 1471) in 5 ml. of anhydrous ether over a period of 15 minutes caused the formation of a small amount of brown insoluble substance. To this mixture was added 112 g. (1.00 mole) of diisobutylene (Shell Oil Co.) over a period of 25 minutes. Stirring was continued for another 2 hours at 12° and then for an additional 17 hours at 25°. The dark brown mixture was washed three times with 75-ml. portions of water and twice with 50-ml. portions of saturated aqueous sodium carbonate solution, followed by a further two washings with 75-ml. portions of water. After filtering, a brown liquid, which fluoresced green, was obtained. It was dried over anhydrous calcium chloride. Fractional distillation yielded two products. The first fraction, a colorless liquid, weighed 32 g. (18%) and had b.p. 72–73° at 12–13 mm.; n_D^{20} 1.4567; d_4^{20} 0.877. Anal. Calc. for $C_{12}H_{20}O$: C, 79.9; H, 11.1. Found: C, 80.2; H, 11.2.

2,5-Di-[2,4,4-trimethyl-2-pentyl]furan

A second fraction, a very pale yellow oil, from the preceding distillation, weighed 21 g. (14%). It had b.p. 113–144° at 1–2 mm.; n_D^{20} 1.4651; d_4^{20} 0.866. Anal. Calc. for $C_{20}H_{36}O$: C, 82.1; H, 12.4. Found: C, 82.1; H, 12.2.

Oxidation of [2,4,4-Trimethyl-2-pentyl]-2-furan

(*a*) *Autoxidation to Yield Maleic Acid*

When pure trimethylpentylfuran was allowed to stand at room temperature, the original colorless liquid took on a yellow color over a period of 6 weeks and colorless crystals (needles) began to deposit. These crystals, after being washed with hexane, had m.p. 141–142°. They were identified as maleic acid both by mixture melting point with authentic maleic acid, prepared by the method of Hurd, Roe, and Williams (9), and also by mixture melting point of the di-*p*-nitrobenzyl ester with authentic di-*p*-nitrobenzyl ester of maleic acid. No success attended our efforts to isolate a second moiety as the result of the autoxidation of the trimethylpentylfuran.

(*b*) *Permanganate Oxidation to Yield 2,2,4,4-Tetramethylpentanoic Acid*

When 9.0 g. (0.05 mole) of [2,4,4-trimethyl-2-pentyl]-2-furan and 200 ml. of water were placed in a 1-liter, three-necked flask equipped with stirrer and reflux condenser and finely ground potassium permanganate was added over a period of 2 days, 23.8 g. (0.15 mole) of the latter was consumed. During the addition period the flask was heated on a steam bath. After the manganese dioxide had been filtered off, the clear colorless filtrate was acidified with hydrochloric acid whereupon an oil separated. The oil failed to crystallize after chilling to 5° and seeding with authentic 2,2,4,4-tetramethylpentanoic acid prepared by the method of Whitmore, Wheeler, and Surmatis (20). The mixture was extracted with ether (3 times with 75 ml. portions) and the ether solution dried over anhydrous sodium sulphate. After the ether was flashed off there remained 3.5 g. (43%) of a colorless oil. Distillation gave 2.3 g. (29%) of colorless oil, b.p. 82° at 2–3 mm. Preparation of the amide by a conventional method gave thin plates, m.p. 68.0–69.5°. A mixture melting point of the amide with authentic amide of tetramethylpentanoic acid showed no depression.

trans-*2,2,4,4,9,9,11,11-Octamethyl-6-dodecene-5,8-dione*

When 2.9 g. (0.01 mole) of 2,5-di-[2,4,4-trimethyl-2-pentyl]furan was treated with 20 ml. of 35% nitric acid solution at room temperature a yellow solid formed over a period of 8 days. The crude material weighed 1.7 g. When it was crystallized from 90% methanol (13 ml./g.) 1.3 g. (42%) of pale yellow needles, m.p. 78.5–79.5°, was obtained. Anal. Calc. for $C_{20}H_{36}O_2$: C, 77.8; H, 11.8. Found: C, 77.8; H, 11.9.

cis-*2,2,4,4,9,9,11,11-Octamethyl-6-dodecene-5,8-dione*

A pale yellow solution of 0.20 g. (0.0006 mole) of the *trans*-isomer in 2 ml. of hexane was irradiated with sunlight through Pyrex for 12 hours over a period of 2 days. When the hexane was removed under diminished pressure there remained 0.20 g. (100%) of white solid, m.p. 53–54°. Crystallization from methanol gave 0.16 g. (80%) of white crystals, m.p. 55.5–56.5°. Anal. Calc. for $C_{20}H_{36}O_2$: C, 77.8; H, 11.8. Found: C, 77.8; H, 11.9.

4-Hydroxy-5-isonitroso-2,2,7,7-tetramethyloctane-3,6-dione (VIII)

(a) From 2,2,7,7-Tetramethyloctane-3,6 dione (III) and Nitric Acid

When 0.25 g. (0.0013 mole) of III was treated with 6 ml. of 35% nitric acid a precipitate formed within 15 minutes. After the solution had been left for 2 days, 0.38 g. of crude white solid was filtered off. Crystallization from hexane gave 0.14 g. (46%) of white needles, m.p. 162°. Anal. Calc. for $C_{12}H_{21}NO_4$: C, 59.2; H, 8.70; N, 5.75. Found: C, 59.4; H, 8.55; N, 5.35.

(b) From 2,5-Di-t-butylfuran (II) and Nitrous Acid

To an aqueous solution of nitrous acid, prepared by dissolving 0.5 g. of sodium nitrite in 4 ml. of water and adding excess hydrochloric acid, was added 0.25 g. (0.0014 mole) of 2,5-di-*t*-butylfuran. After the solution was left for 30 minutes a crystalline substance formed. It weighed 0.13 g. Crystallization from petroleum ether (60–70°) gave 0.03 g. (90%) of white needles melting at 162°. The product was identical with that obtained by the action of nitric acid on III.

(c) From cis-*2,2,7,7-Tetramethyl-4-octene-3,6-dione (V) and Nitrous Acid*

A solution of 0.010 g. (0.00005 mole) of *cis*-V in 1 ml. of dioxane and 1 ml. of water was treated with 0.2 g. (0.003 mole) of sodium nitrite and 0.5 ml. of glacial acetic acid. The mixture was allowed to stand for 12 hours. At the end of this time, 4 ml. of water was added. A white solid separated. Crystallization from hexane gave 0.005 g. (41%) of white needles, m.p. 162°.

(d) From 4-Acetoxy-5-isonitroso-2,2,7,7-tetramethyloctane-3,6-dione (IX)

A solution of 0.10 g. (0.00035 mole), of IX in 1 ml. of 5% aqueous sodium hydroxide was prepared by adding the sodium hydroxide solution dropwise to the solid material. In 4 minutes, solution was complete. The solution was slightly yellow in color. After 5 minutes a precipitate appeared. On the addition of 3 ml. of water the precipitate did not dissolve. The solution had a pH of 11 (Hydrion Paper). The precipitate was filtered off, washed with water, and dried by suction. It weighed 0.05 g. (59%) and melted at 160–161°. A mixture melting point with authentic VIII was not depressed.

(e) From 2,5-Di-t-butylfuran (II) and Nitric Acid

A solution of 5.0 g. (0.028 mole) of 2,5-di-*t*-butylfuran in 30 ml. of glacial acetic acid was added slowly to a rapidly stirred solution of 5 ml. of 70% nitric acid in 10 ml. of glacial acetic acid. Heat was evolved and a temperature of 25–30° was maintained throughout the reaction time by means of a water bath. Oxides of nitrogen were evolved during the addition. After 45 minutes a heavy white crystalline precipitate formed and the liquid became lime-green in color. The white solid was filtered off, washed with glacial acetic acid, and dried by suction on the filter. The washings were added to the filtrate, which was set aside to check for further precipitation. The product weighed 1.05 g. (15%) and melted at 162°. Crystallization from ethanol–water, methanol–water, and petroleum ether did not raise the melting point. No further precipitation occurred in the filtrate. After the addition of 150 ml. of water a gummy precipitate, weighing 4.0 g., was obtained. The filtrate from this operation was shown to contain trimethylpyruvic acid. The phenylhydrazone of this acid was prepared according to the procedure of Glucksmann (8), who reported the melting point as 157–158°. We found the melting point to be 166.5°. Anal. Calc. for $C_{12}H_{16}N_2O_2$: N, 12.7. Found: N, 12.6.

Fractional crystallization of the 4.0 g. of crude gummy solid from petroleum ether (60–64°) yielded 0.6 g. (9%) of white needles, m.p. 162°, which were shown to be VIII for an over-all yield of 24%.

4-Acetoxy-5-isonitroso-2,2,7,7-tetramethyloctane-3,6-dione (IX)

(*a*) *From 2,5-Di-t-butylfuran (II), Nitric Acid, and Glacial Acetic Acid*

From the preceding fractional crystallization, there was also isolated 0.5 g. (6%) of coarse white crystals, m.p. 104–105°. Anal. Calc. for $C_{14}H_{23}NO_5$: C, 58.9; H, 8.18; N, 4.91. Found: C, 59.0; H, 8.12; N, 4.92.

(*b*) *From 4-Hydroxy-5-isonitroso-2,2,7,7-tetramethyloctane-3,6-dione (VIII)*

When 0.12 g. (0.0005 mole) of VIII was warmed on the steam bath with 5 ml. of acetic anhydride for 5.5 hours, a pale yellow solution resulted. Addition of 50 ml. of water to this solution caused the separation of a colorless oil which crystallized on standing for 15 hours at room temperature. It weighed 0.05 g. (35%) and melted at 96–103°. Crystallization from hexane gave coarse white needles, m.p. 105°. A mixture melting point with the product obtained in (*a*) above showed no depression.

4-Hydroxy-5-isonitroso-2,2,7,7-tetramethyloctane-3,6-dione Monoxime (XI)

To a solution of 1.0 g. (0.014 mole) of hydroxylamine hydrochloride and 1.0 ml. (0.013 mole) of pyridine in 10 ml. of 95% ethanol was added 0.58 g. (0.0024 mole) of VIII. The resulting solution was refluxed for 2 hours, then the ethanol removed in a current of air and 15 ml. of water added. The resulting white solid was filtered off and dried by suction. The crude product weighed 0.67 g. and melted at 172°. Crystallization from benzene gave 0.40 g. (65%) of white plates melting at 193–194° with decomposition. Anal. Calc. for $C_{12}H_{22}O_4N_2$: C, 55.8; H, 8.59; N, 10.8. Found: C, 55.9; H, 8.36; N, 10.6.

4-Hydroxy-5-isonitroso-2,2,7,7-tetramethyloctane-3,6-dione Mono-2,4-dinitrophenylhydrazone

To a solution of 0.16 g. (0.0008 mole) of 2,4-dinitrophenylhydrazine in 1 ml. of 93% sulphuric acid and 3 ml. of 95% ethanol was added a solution of 0.243 g. (0.001 mole) of VIII in 7 ml. of 95% ethanol. The resulting solution was allowed to stand at room temperature for 18 hours. At the end of this time, 75 ml. of water was added to the reaction mixture causing the precipitation of 0.34 g. (100%) of a yellowish-orange solid, m.p. 180–185°. Crystallization from ethanol–water gave 0.22 g. (65%) of coarse orange needles, m.p. 210–211°. Anal. Calc. for $C_{18}H_{25}N_5O_7$: N, 16.6. Found: N, 16.3.

3-t-Butyl-4-[2-keto-1-hydroxy-3,3-dimethylbutyl]furazan (XII)

To 5 ml. of 5% aqueous sodium hydroxide solution was added 0.24 g. (0.0009 mole) of XI. The solid dissolved readily and in 2 minutes the solution began to turn yellow. The solution was immediately steam distilled and a colorless oil obtained as a distillate. This oil, on standing, crystallized to a white solid which weighed 0.03 g. (14%) and melted at 62°. Crystallization from methanol–water did not raise the melting point. Anal. Calc. for $C_{12}H_{20}N_2O_3$: C, 60.0; H, 8.39; N, 11.7. Found: C, 60.0; H, 8.43; N, 11.3.

The alkaline residue from the steam distillation above yielded a phenylhydrazone which was identified as the phenylhydrazone of trimethylpyruvic acid by mixture melting point with an authentic sample, m.p. 166.5°. This melting point (water–ethanol crystallization) is higher than that (157–158°) previously reported (8).

2,4-Dinitrophenylhydrazone of 3-t-Butyl-4-[2-keto-1-hydroxy-3,3-dimethylbutyl]furazan

To a solution of 0.034 g. (0.00017 mole) of 2,4-dinitrophenylhydrazine, in 0.25 ml. of 93% sulphuric acid and 1 ml. of 95% ethanol, was added a solution of 0.05 g. (0.0002 mole) of XII in 2 ml. of 95% ethanol. After the solution was left at room temperature for 6 hours, an orange-colored crystalline solid began to separate. Seven days later 0.07 g. (98%) of orange prisms, m.p. 264–266°, was filtered off. Crystallization from glacial acetic acid gave 0.03 g. (42%) of pure product, m.p. 270–271°, with decomposition. Anal. Calc. for $C_{18}H_{24}N_6O_6$: N, 20.0. Found: N, 20.1.

2,4-Dinitrophenylhydrazone of Trimethylpyruvic Acid

Trimethylpyruvic acid was prepared according to the method of Glucksmann (8). Treatment of an aqueous solution of the acid with an excess of a saturated solution of 2,4-dinitrophenylhydrazine in 2% hydrochloric acid solution readily gave the 2,4-dinitrophenylhydrazone in the form of long canary-yellow needles. When purified by crystallization from ethanol–water it melts at 176.0–176.5°. Anal. Calc. for $C_{12}H_{14}N_4O_6$: N, 18.1. Found: N, 17.5.

Alkaline Hydrolysis of 4-Hydroxy-5-isonitroso-2,2,7,7-tetramethyloctane-3,6-dione (VIII) to Yield Pivalic Acid (Trimethylacetic Acid) and Trimethylpyruvic Acid

A solution of 1.0 g. (0.004 mole) of VIII in 20 ml. of 5% aqueous sodium hydroxide turned yellow when warmed and ammonia was given off. The solution was acidified with sulphuric acid and steam distilled. A colorless oil was obtained as a product, mixed with water. The mixture was extracted with ether and the ether extract dried over Drierite. After the ether was evaporated, 0.49 g. of faintly yellow liquid remained. A 0.1 g. portion of this liquid was dissolved in 2 ml. of ether and treated with excess ammonia solution. When the solution was evaporated to dryness a white crystalline substance melting at 132° was obtained. Sublimation under diminished pressure (15 mm. Hg) gave a pure product melting at 138°. A mixture melting point with ammonium pivalate (ammonium trimethylacetate) showed no depression.

In another experiment 0.13 g. (0.005 mole) of VIII was dissolved in 5 ml. of 5% aqueous sodium hydroxide and warmed on the steam bath for 1 hour. At the end of this time, the solution was acidified with hydrochloric acid and treated with an excess of a saturated solution of 2,4-dinitrophenylhydrazine in 2% hydrochloric acid solution. A canary-yellow precipitate formed. On crystallization from ethanol–water this substance gave canary-yellow needles melting at 176.0–176.5°. A mixture melting point with the 2,4-dinitrophenylhydrazone of trimethylpyruvic acid showed no depression.

3-Trimethylacetyl-5-t-butylisoxazole (XIII)

When 2.7 g. (0.013 mole) of 2,2,7,7-tetramethyloctane-3,6-dione (III) in 40 ml. of glacial acetic acid was treated with 5 ml. of nitric acid (70%; sp. gr. 1.42) and warmed on the steam bath for 2 hours, oxides of nitrogen were evolved. After the darkening solution had been concentrated to a volume of 20 ml. it was made alkaline by the addition of 10% sodium carbonate solution. A red oil separated which was taken up in ether and dried over anhydrous sodium sulphate. After the ether was flashed off there remained 2.7 g. (99%) of a reddish-brown oil. Distillation gave 1.5 g. (55%) of orange-colored oil, b.p. 90–100° at 2 mm. The compound was converted to its oxime for analysis.

3-Trimethylacetyl-5-t-butylisoxazole Oxime (XIV)

A solution of 1.0 g. (0.0048 mole) of 3-trimethylacetyl-5-*t*-butylisoxazole (XIII) in 10 ml. of absolute ethanol was treated with 1.39 g. (0.02 mole) of hydroxylamine hydrochloride and 1.58 g. (0.02 mole) of pyridine. The mixture was refluxed for 2 hours at the end of which time the alcohol was removed in a current of air. After the addition of water to the mixture, a yellow gummy mass formed. The material was taken into solution in hot hexane and on cooling 0.10 g. of white needles, m.p. 168–170°, with decomposition, was obtained. A second crop weighed 0.22 g., m.p. 146–155. The total yield of crude product was 31%. Subsequent crystallization from hexane and ethanol–water gave 0.10 g. (9.3%) of white needles, m.p. 177° (decomposition with gas formation). Anal. Calc. for $C_{12}H_{20}N_2O_2$: C, 64.2; H, 8.99; N, 12.5; mol. wt., 224. Found: C, 64.1; H, 9.08; N, 12.2; mol. wt., 213.

When 3-trimethylacetyl-5-*t*-butylisoxazole oxime (XIV) was treated with 2,4-dinitrophenylhydrazine, a yellow product, which melted at 184°, was obtained. According to analysis this may be 3-trimethylacetyl-5-*t*-butylisoxazole dinitrophenylhydrazone. Anal. Calc. for $C_{18}H_{23}N_5O_5$: C, 55.5; H, 5.95; N, 18.0. Found: C, 55.5; H, 6.03; N, 18.4.

When 0.10 g. (0.00045 mole) of the isoxazole oxime, XIV, in 2.5 ml. of absolute ether was treated with 0.07 g. (0.0006 mole) of phenylisocyanate for 12 days some N,N′-diphenylurea had precipitated. Decantation of the etherous supernatant layer followed by evaporation left 0.16 g. of white solid which was crystallized from hexane, 0.11 g. (71%), m.p. 121.5–122.5°. This product may be N-[5-*t*-butylisoxazol-3-methanoyl]-N-*t*-butyl-N′-phenylurea. Further crystallization of this substance from ethanol–water gave 0.075 g. (49%), m.p. 123.0–123.8°. Anal. Calc. for $C_{19}H_{25}N_3O_3$: C, 66.4; H, 7.34. Found: C, 67.0; H, 7.38.

Catalytic Hydrogenation of 4-Hydroxy-5-isonitroso-2,2,7,7-tetramethyloctane-3,6-dione (VIII)

When 1.0 g. (0.004 mole) of VIII in 50 ml. of absolute ethanol was hydrogenated for 44 hours at 50 p.s.i.g., using a total of 0.3 g. of platinum oxide catalyst in 0.1 g. portions, 13 lb. (pressure) of hydrogen was absorbed. (A Parr low-pressure hydrogenation apparatus was used.) The drop in pressure corresponded to 0.013 mole of hydrogen or 3 moles of hydrogen per mole of 4-hydroxy-5-isonitroso-2,2,7,7-tetramethyloctane-3,6-dione (*VIII*). When the ethanol was removed under diminished pressure there remained 0.94 g. of a thick yellow oil which slowly changed to a gummy solid. Fractional crystallization from water yielded two products.

The first product, clusters of flat rectangles, weighed 0.17 g. (17%), m.p. 136°. Anal. Calc. for $C_{12}H_{27}NO_4$: C, 57.8; H, 10.9; N, 5.62. Found: C, 57.9; H, 10.9; N, 5.66.

The second product, which crystallized in the form of fine white needles, weighed 0.02 g. (1.9%) and melted at 150°. Anal. Calc. for $C_{12}H_{23}NO_4$: C, 58.8; H, 9.45; N, 5.71. Found: C, 58.7; H, 9.58; N, 6.34.

Action of Nitric Acid on 2-t-Butyl-5-[2,4,4-trimethyl-2-pentyl]furan (IV) to Form $C_{12}H_{21}NO_3$

A solution of 2.3 g. (0.010 mole) of IV in 25 ml. of glacial acetic acid was added dropwise to a stirred solution of 5 ml. of nitric acid (70%; sp. gr. 1.42) in 15 ml. of glacial acetic acid at 23–24°. After 35 minutes, a crystalline precipitate began to form. Stirring was continued for 2 hours. The precipitate was filtered off, washed with glacial acetic acid, and dried by suction. It weighed 0.69 g. (30%) and melted at 175–176°. The filtrate was allowed to stand for 1 hour. No further precipitation occurred. Crystallization of the crude material from ethanol–water gave 0.55 g. (24%) of colorless needles, m.p. 177.5°. Anal. Calc. for $C_{12}H_{21}NO_3$: C, 63.4; H, 9.31; N, 6.16; mol. wt., 227. Found: C, 63.5; H, 9.24; N, 6.24; mol. wt., 236.

The same product resulted when IV was treated with an aqueous solution of nitrous or nitric acid, but the yields were much lower.

When a solution of 0.25 g. (0.0011 mole) of $C_{12}H_{21}NO_3$ in 5 ml. of 95% ethanol was treated with 0.38 g. (0.0055 mole) of hydroxylamine hydrochloride and 0.45 g. (0.0055 mole) of anhydrous sodium acetate a reaction occurred during 36 hours of reflux. Subsequently when water was added 0.03 g. (12%) of original $C_{12}H_{21}NO_3$ was recovered. Further aqueous dilution precipitated 0.16 g. (64 wt. %) which, crystallized from methanol–water, left 0.10 g. (40 wt. %), m.p. 143–144° with gassing. Anal. Calc. for $C_8H_{15}NO_2$: C, 61.1; H, 9.40; N, 8.91; mol. wt., 157. Found: C, 61.5; H, 9.33; N, 8.92; mol. wt., 258.

2,2,4,4-Tetramethylpentanoic Acid from $C_{12}H_{21}NO_3$

(*a*) *Alkaline Hydrolysis*

When 0.05 g. (0.00022 mole) of $C_{12}H_{21}NO_3$ was treated with 2 ml. of hot 5% aqueous sodium hydroxide solution the solid slowly dissolved during 20 minutes and ammonia was evolved. The system, cooled and acidified by hydrochloric acid, yielded 0.01 g. (29%), m.p. 40–44°. Crystallization from methanol–water raised this melting point to 44.0–44.5°. A mixture melting point with authentic 2,2,4,4-tetramethylpentanoic acid (20) was not depressed.

(*b*) *Acid Hydrolysis*

During 12 hours a system comprising 0.56 g. (0.0025 mole) of $C_{12}H_{21}NO_3$ in 20% hydrochloric acid was boiled under reflux. The resulting yellow oil (0.41 g.) dissolved almost entirely in 5% aqueous sodium hydroxide. The solution, after ether extraction, was acidified to give 0.23 g. (58%) of tetramethylpentanoic acid, m.p. 43.5–44.5°. A mixture melting point was not lowered.

The acidic filtrate, treated with dinitrophenylhydrazine in methanolic hydrochloric acid, yielded a dinitrophenylhydrazone, m.p. 170–172°.

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