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Monomers Containing Large Alkyl Groups. III. The Synthesis of 2-Alkyl-1,3-butadienes[1,2]

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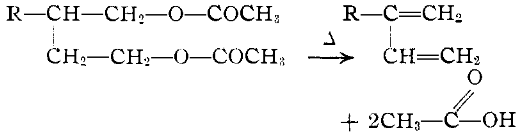
A convenient synthesis of 2-alkyl-1,3-butadienes by the thermal cracking of the diacetates of 2-alkyl-1,4-butanediols under carefully controlled conditions has been developed so that pure products are obtained. This method is particularly suited to compounds having straight chain alkyl groups and the *n*-heptyl and *n*-decyl derivatives have been characterized. By use of the method previously developed for 2-isopropyl-1,3-butadiene from 2-isopropyl-1,4-butanediamine, an improved synthesis of 2-*t*-butyl-1,3-butadiene has been developed. Polymers of these 2-alkyl-1,3-butadienes have been prepared according to the GR-S recipe and their polymerization rates have been studied as a criterion of their purity.

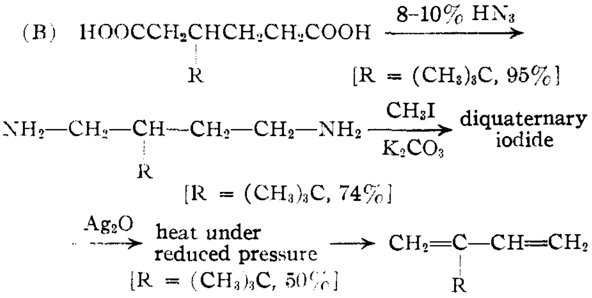
This paper describes the synthesis of 2-*n*-heptyl- and 2-*n*-decyl-1,3-butadienes[5] by cracking the diacetates of the corresponding 1,4-diols[6] and the synthesis of 2-*t*-butyl-1,3-butadiene from the diquaternary hydroxide of the corresponding 1,4-diamine. Previous work[7] has indicated that the cracking of the acetates yields dienes of reasonable purity and repetition of the work of v. Braun and Keller[10] has shown that the decomposition of the diquaternary hydroxide of 2-isopropyl-1,4-butanediamine gives pure isopropyl-1,3-butadiene.

The 2-alkyl-1,3-butadienes which have been reported previously are the following: 2-alkyl group; C_2H_5,[7,8,9,11,12] iso-C_3H_7,[7,8,10] *n*-C_4H_9,[14] iso-C_4H_9,[11] *t*-C_4H_9,[13a,b] *n*-C_5H_{11},[7,8] iso-C_5H_{11}[15] and *n*-C_7H_{15}.[14] With the exception of the 2-ethyl-, 2-isopropyl- and 2-*n*-amyl-1,3-butadienes prepared by Marvel, *et al.*,[7,8] by the thermal cracking of 2-alkyl-3-acetoxy-1-butenes, the 2-isopropylbutadiene prepared by v. Braun and Keller[10] as described in method B below and the 2-*t*-butylbutadiene prepared by Backer and Strating[13a] and Favorskaya,[13b] there is a reasonable doubt that pure 2-alkyl-1,3-butadienes were obtained. The properties of the 2-*t*-butylbutadiene prepared by us agree with the properties of the same product prepared in different ways by the above cited investigators whenever a comparison is possible. The 2-*n*-heptylbutadiene previously prepared by the reaction of *n*-heptylmagnesium bromide with 4-chloro-1,2-butadiene,[14] was impure as indicated by analysis. Melting points of derivatives of this diene, however, were found to be identical with those reported here. The methods described in this paper to synthesize the dienes are indicated below.

(A)



$$R{-}\underset{\displaystyle CH_2{-}CH_2{-}O{-}COCH_3}{CH}{-}CH_2{-}O{-}COCH_3 \xrightarrow{\Delta} R{-}\underset{\displaystyle CH{=}CH_2}{C}{=}CH_2 + 2CH_3{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}OH$$



$$\text{(B)}\quad HOOCCH_2\underset{\displaystyle R}{CH}CH_2CH_2COOH \xrightarrow{8\text{–}10\%\ HN_3} \quad [R = (CH_3)_3C,\ 95\%]$$

$$NH_2{-}CH_2{-}\underset{\displaystyle R}{CH}{-}CH_2{-}CH_2{-}NH_2 \xrightarrow[K_2CO_3]{CH_3I} \text{diquaternary iodide}$$

$$[R = (CH_3)_3C,\ 74\%]$$

$$\xrightarrow{Ag_2O} \text{heat under reduced pressure} \longrightarrow CH_2{=}\underset{\displaystyle R}{C}{-}CH{=}CH_2$$

$$[R = (CH_3)_3C,\ 50\%]$$

Discussion

Route A.—Marvel and Williams[8] have shown that 2-alkylbutadienes prepared by catalytic dehydration of 2-alkyl-3-hydroxy-1-butenes are of doubtful purity due to isomerization of the double bond,[16] whereas the thermal cracking of 2-alkyl-3-acetoxy-1-butene at 400–420° gave the desired pure 2-alkyl diene. Polymerization rate and infrared absorption spectra were used as criteria for determining purity.

On the basis of the above work we were aware that the high temperature cracking procedure (A) might lead to some isomerization. Cracking experiments with the diacetates of 2-isopropyl-, 2-*n*-heptyl- and 2-*n*-decyl-1,4-butanediols at 580–590° (400–410 mm.) gave products whose analyses, physical properties and derivatives indicated strongly that the desired diene was obtained. When these dienes were polymerized, however, it was soon apparent from the slow rates of polymerization that some isomerization of the double bond had taken place giving rise to isomeric impurities which were retarders of the polymerization. We then reduced the temperature of the cracking experiments to the lowest possible point where

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[1] This is the third in a series of papers describing the synthesis of monomers which polymerize to give polymers having alkyl side chains. For the second paper in the series, see C. G. Overberger, E. J. Luhrs and P. K. Chien, THIS JOURNAL, **72**, 1200 (1950).

[2] A portion of this work was supported by a contract from the Office of Naval Research.

[3] A portion of a thesis by Alex Fischman submitted to the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Master of Science. Present address: Warner Institute for Therapeutic Research, New York, N. Y.

[4] A portion of a thesis by Carleton W. Roberts submitted to the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Doctor of Philosophy. Present address: Colgate-Palmolive-Peet, Jersey City, N. J.

[5] For reasons which will be described elsewhere, we are interested in the dienes with large straight-chain alkyl groups.

[6] C. G. Overberger and C. W. Roberts, THIS JOURNAL, **71**, 3618 (1949).

[7] C. S. Marvel, R. L. Myers and J. H. Saunders, *ibid.*, **70**, 1694 (1948).

[8] C. S. Marvel and J. L. R. Williams, *ibid.*, **70**, 3842 (1948).

[9] Pariselle and Simon, *Compt. rend.*, **173**, 86 (1921).

[10] J. v. Braun and W. Keller, *Ber.*, **64**, 2617 (1931).

[11] F. Hofmann, C. Coutelle, K. Meisenburg and K. Delbruck, U. S. Patent 1,082,522, 1913.

[12] W. Ipatieff, *J. prakt. Chem.*, **59**, 517 (1899).

[13] (a) H. J. Backer and J. Strating, *Rec. trav. chim.*, **53**, 525 (1934); (b) I. A. Favorskaya, *J. Gen. Chem.* (*U. S. S. R.*), **18**, 52 (1948); *C. A.*, **42**, 4905 (1948).

[14] W. H. Carothers and G. J. Berchet, THIS JOURNAL, **55**, 2813 (1933).

[15] K. Dimroth, *Angew. Chem.*, **52**, 545 (1939), refers to H. Pallutz, Dissertation, Gottingen, 1935.

[16] For example, from 2-isopropyl-3-hydroxy-1-butene, the isomerized product would be 2,3-dimethyl-1,3-pentadiene.

some diene was still obtained. To do this, we increased the surface of the tube by introducing $^3/_{32}''$ glass helices instead of beads and used only atmospheric pressure to obtain a long contact time.[17] These dienes had essentially the same physical properties as those prepared at the higher temperatures but exhibited a striking difference in polymerization rate clearly demonstrating that less isomerization had occurred. Even the 2-isopropylbutadiene prepared at the lower cracking temperature was not pure (compare the rate of the 2-isopropylbutadiene prepared by route B, which polymerizes at a faster rate (Table IV); see also Marvel, Williams and Baumgarten[18]).

TABLE I

PYROLYSIS OF 2-ALKYL-1,4-BUTANEDIOL DIACETATES

2-Alkyl group[a]	Weight of diacetates[e] g. (mole)	Tube temp., °C.[f]	Weight of diene (g.)	Yield,[g] %
iso-C_3H_7[b]	20 (0.208)	435–436	2.33	26
n-C_7H_5[c]	9.87 (0.065)	449–452	2.18	39
n-$C_{10}H_{21}$[d]	19.98 (0.103)	449–454	3.05	24.7

[a] A representative experiment has been chosen. [b] Compare an experiment with 25 g. of diacetate at 596–602° (404–408 mm.), yield 3.28 g. (29%); also 22 g. of diacetate at 595–605° (405 mm.), yield 4 g., 5 g. of diacetate recovered, yield based on recovered diacetate, 54%. [c] Compare an experiment with 22 g. of diacetate at 580–590° (125 mm.), 2 g., 16 g. of diacetate recovered, yield based on recovered diacetate, 65%. [d] Compare an experiment with 14.8 g. of diacetate at 597–603° (406–409 mm.), yield 2.86 g. (31%). [e] Rate of flow, one drop per 8 sec. [f] This temperature is critical within 5 to 10°. A variance of 10 degrees on the low side reduced the yield markedly. [g] Yield not based on recovered diacetate unless otherwise stated.

It should be emphasized that derivatives of the Diels–Alder type do not establish the purity of the desired diene. Likewise, the ultraviolet absorption spectrum does not allow an estimation of purity since the isomerized products are also 1,3-dienes of similar structure.

The polymerization rates[19] for 2-n-heptyl- and 2-n-decylbutadiene prepared by the low temperature cracking procedure indicate that these products are largely the desired 2-alkyl-1,3-butadienes.[20]

The results of the low temperature cracking experiments of the diacetates are summarized in Table I. Since the high temperature cracking experiments do not contribute to the characterization of the dienes, they have been omitted except for several comparisons in Tables I and II. The properties of the dienes are presented in Table III.

Route B.—This procedure is similar to that employed by v. Braun and Keller[10] who prepared 2-isopropylbutadiene by this method. Some anomalies in the physical properties of intermediates described by reference 10 have been clarified and are described in the experimental section along with the experimental modifications employed. 2-t-Butylbutadiene was also prepared by this procedure in good yield (see equations). The polymerization rates of the 2-isopropyl-1,3-butadiene indicate that little or no isomerized product was present. Properties of the dienes and their derivatives are described in Tables II and III, respectively.

TABLE II

2-ALKYL-1,3-BUTADIENES

2-Alkyl group	B.p., °C.	Mm.	n^{25}D	d^{25}_4	Molar refraction Calcd.	Molar refraction Found	Formula	Percentage composition[f] Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	$\lambda_{max.}$, Å.	$\epsilon_{max.}$
Iso-C_3H_7[a]	85–86	Atm.	1.4317	....	...	...	C_7H_{12}	...	...	...	...	2250	18,400
Iso-C_3H_7[b]	85–85.5	Atm.	1.4316	0.7208	32.50	33.80	C_7H_{12}	...	...	...	...	2250	19,500
n-C_7H_{15}[c]	46–47	4.5	1.4499	.7738	52.06	52.87	$C_{11}H_{20}$	86.76	87.10	13.24	13.12	2255	19,700
n-$C_{10}H_{21}$[d]	80–81	2	1.4549	.7908	65.92	66.66	$C_{14}H_{26}$	86.51	86.67	13.48	13.12	2255	20,200
t-C_4H_9[e]	103.5–104	Atm.	1.4265	.7354	38.21	38.42	C_8H_{14}	87.19	87.01	12.81	13.08	2250	23,240

[a] Compare high temperature experiments described in footnote b, Table I, b.p. 80–81° (atm.), n^{25}D 1.4324, $\lambda_{max.}$ 2255, $\epsilon_{max.}$ 18,000; b.p. 85–86° (atm.), n^{25}D 1.4312, d^{25}_4 0.7227, $\lambda_{max.}$ 2245, $\epsilon_{max.}$ 15,500. Reference 7 reported a 32% yield on pyrolysis of 2-isopropyl-1,4-butanediol diacetate, b.p. 82–84°, n^{20}D 1.4339; a 23% yield on pyrolysis of 2-isopropyl-3-acetoxy-1-butene, b.p. 85–87°, n^{20}D 1.4345. Reference 8 reported a 54% yield for the same pyrolysis, b.p. 85–87°, n^{20}D 1.4337. [b] Prepared by decomposition of diquaternary hydroxide of 2-isopropyl-1,4-butanediamine, yield 78%. Reference 10 using a similar procedure reported a 70% yield, b.p. 86–87°, n^{22}D 1.4321, $d^{24.5}_4$ 0.7276. [c] Compare high temperature experiment in footnote c, Table I, b.p. 50–52° (3 mm.), n^{25}D 1.4493, d^{25}_4 0.7801, $\lambda_{max.}$ 2255, $\epsilon_{max.}$ 19,100. Reference 14 reported a 21% yield of alleged 2-n-heptylbutadiene, b.p. 52–54° (5 mm.), n^{20}D 1.4511, d^{20}_4 0.7796, but reported an analysis somewhat in error. [d] Compare high temperature experiment in footnote d, Table I, b.p. 75–76° (1 mm.), n^{25}D 1.4549, d^{25}_4 0.7888, $\lambda_{max.}$ 2255, $\epsilon_{max.}$ 20,400. [e] Reference 13a reported a b.p. 104–106° for 2-t-butylbutadiene. Reference 13b reported b.p. 100–101°, d^0_4 0.7510, $d^{17.5}_4$ 0.7367, $n^{17.5}\alpha$ 1.42596. [f] Analyses by Mr. H. S. Clark.

General.—Figure 1 describes the ultraviolet absorption spectra of four pure 1,3-dienes (see Table II, R = n-C_7H_{15}, n-$C_{10}H_{21}$, iso-C_3H_7, t-C_4H_9). All of these dienes have a $\lambda_{max.}$ near 2260 Å. The dienes where R = n-C_7H_{15}, n-$C_{10}H_{21}$ and iso-C_3H_7 all have extinction coefficients, $\epsilon_{max.}$ near 20,000; when R = t-C_4H_9, the extinction coefficient, $\epsilon_{max.}$

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(17) Experiments using these helices but with reduced pressure resulting in a shorter contact time gave little or no yield below 500°.

(18) C. S. Marvel, J. R. L. Williams and H. E. Baumgarten, *J. Polymer Sci.*, **4**, 583 (1949). The rate of polymerization of a 1-alkyl substituted butadiene such as 1-methyl-1,3-butadiene in an emulsion system of the GR-S type is much slower than the rate of polymerization of isoprene; see R. L. Frank, R. D. Emmick and R. S. Johnson, THIS JOURNAL, **69**, 2313 (1947).

(19) It is realized that the rate of polymerization of a 2-alkylbutadiene may be influenced by the size of the 2-alkyl group in an unknown manner. Thus, the long alkyl group in the diene may alter the suggested mechanism of the emulsion polymerization of ordinary water insoluble monomers [W. V. Smith, *ibid.*, **70**, 3695 (1948); W. D. Harkins, *ibid.*, **69**, 1428 (1947)]. The data of reference 18 indicates that no serious abnormalities are present in the polymerization of 2-n-amyl-1,3-butadiene, although it polymerizes at a slower rate than 2-isopropyl-1,3-butadiene.

(20) The temperatures involved in the cracking procedure make any suggestion of a mechanism to explain the isomerization dubious. However, either in radical or cationic catalyzed isomerization, tertiary hydrogens are more susceptible to transfer than secondary hydrogens. This may explain why isomerization occurred in the cracking of the 2-isopropyl diacetate but not in the case of the 2-n-alkyl diacetates. The mechanism of the cracking procedure itself may involve a cyclic intermediate as recently suggested by E. R. Alexander and A. Mudrak, *ibid.*, **72**, 1810 (1950).

TABLE III

DERIVATIVES OF 2-ALKYL-1,3-BUTADIENES

2-Alkyl group	Maleic anhydride adduct, m.p., °C.	Naphthoquinone adduct, m.p., °C.	Anthraquinones, m.p., °C.
iso-C_3H_7	85.5–86[b]	68–68.5[e]	45–45.5[i,j]
iso-C_3H_7[a]	85.5–86[c]	68–68.5[e]	45–45.5[i,j]
t-C_4H_9[a]	123.5–124[d]	90–90.5[f]	104–104.5[k]
n-C_7H_{15}	....	78.2–78.7[g]	87.8–88.5[l]
n-$C_{10}H_{21}$	....	77.1–78[h]	102.2–103[m]

[a] Prepared by decomposition of diquaternary hydroxides. [b] Reference 7 reported a m.p. of 86–86.5°. [c] Mixed melting point with adduct from pyrolysis showed no depression. Mixed melting point of both samples with a sample of 2-isopropyl-1,3-butadiene maleic anhydride adduct obtained from Professor Marvel gave no depression. [d] Reference 13 gave a m.p. 123.5–124° from benzene. [e] *Anal.* Calcd. for $C_{17}H_{18}O_2$: C, 80.28; H, 7.14. Found: C, 80.44; H, 6.67. Mixed melting point of adduct from both syntheses gave no depression. [f] Reference 13 reported a m.p. 89.5–90°. [g] Reference 14 reported a m.p. 80.5–81°. [h] *Anal.* Calcd. for $C_{24}H_{32}O_2$: C, 81.77; H, 9.15. Found: C, 81.55; H, 8.98. A mixed melting point with the adduct from high temperature pyrolysis showed no depression. [i] Mixed melting point of both samples showed no depression, m.p. 45–46°. [j] A. T. Peters and F. M. Rowe, *J. Chem. Soc.*, 181 (1945), reported m.p. 45°, prepared from 2-(4′-isopropylbenzoyl)-benzoic acid. [k] Reference 13 reported m.p. 104–104.5°; reference *k* reported m.p. 104° from 2-(4′-*t*-butylbenzoyl)-benzoic acid. [l] Reference 14 reported m.p. 87° recrystallized from alcohol but their analysis is poor. R. H. Harris, G. J. Mariott and J. C. Smith, *J. Chem. Soc.*, 1838 (1936), reported m.p. 76°. Our *Anal.* Calcd. for $C_{21}H_{22}O_2$: C, 82.34; H, 7.17. Found: C, 82.26; H, 7.39. [m] *Anal.* Calcd. for $C_{24}H_{20}O_2$: C, 82.72; H, 8.10. Found: C, 83.01; H, 7.99. A mixed melting point with the adduct from the high temperature pyrolysis showed no depression.

is somewhat greater, ϵ = 23,000.[21] These data strongly support a 1,3-diene structure.

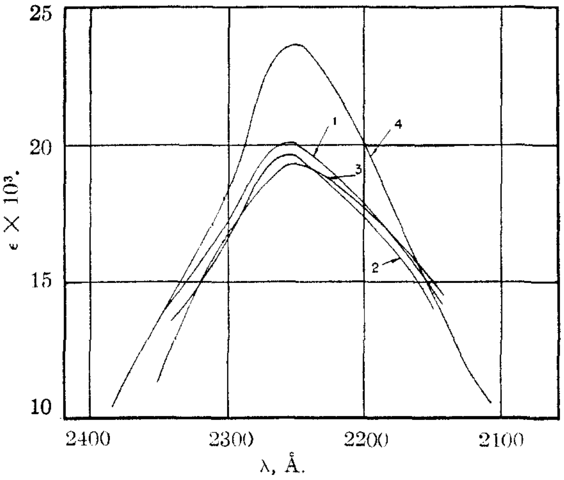

Fig. 1.—Ultraviolet absorption spectrum of: (1) 2-*n*-decyl-1,3-butadiene; (2) 2-*n*-heptyl-1,3-butadiene; (3) 2-isopropyl-1,3-butadiene; (4) 2-*t*-butyl-1,3-butadiene.

The physical properties (solubility, intrinsic viscosity and second-order transition temperatures) of polymers prepared from these dienes will be described elsewhere. Polymerizations were carried out using the standard GR-S recipe[22] (Table IV).

TABLE IV

POLYMERIZATION OF 2-ALKYL-1,4-BUTADIENES

2-Alkyl group	Time[d] (hr.)	Conversion, %
iso-C_3H_7[a]	24	*ca.* 20
iso-C_3H_7[a]	120	85.6
iso-C_3H_7[b]	24	*ca.* 20
iso-C_3H_7[c]	18.3	64.3
n-C_7H_{15}	47.5	83.4
n-$C_{10}H_{21}$[a]	48.0	21.6
n-$C_{10}H_{21}$[b]	45.5	61.0
t-C_4H_9	21	35.8

[a] Prepared by high temperature cracking. [b] Prepared by low temperature cracking. [c] Prepared by decomposition of diquaternary hydroxide. [d] All polymerizations are of the GR-S type. Control experiments with isoprene were made on all runs. Compare with data of reference 18, 2-isopropyl-1,3-butadiene, 67.5% in 24 hours; 2-ethyl-1,3-butadiene, 87.5% in 25 hours; 2-*n*-amyl-1,3-butadiene, 64% in 40 hours.

Experimental[23]

Procedure A. Pyrolysis of 2-Alkyl-1,4-butanediol Diacetates.—The 2-alkyl-1,4-butanediol diacetate was added dropwise to a thick-walled Pyrex glass tube (21 mm. o.d., 15 mm. i.d.) in a vertical position packed with 3/32 in. glass helices for 13 in., of which 12 in. were heated. The glass well for the thermocouple extended to within four in. of the bottom of the helix-packing. A receiver cooled by a Dry Ice mixture was placed at the bottom of the tube from which a side arm led to two Dry Ice traps. The diacetate was added at a rate of 1 drop/8 sec. under a very small pressure head of nitrogen. After the diacetate had been added, the tube was removed from the furnace as soon as possible and allowed to cool. Usually ether was used to wash down the tube and traps although cyclohexane and octane were used for the 2-*n*-decyl compound. All washings and pyrolysates were washed with small portions of water, 10% sodium carbonate solution and dried over anhydrous magnesium sulfate. The dienes were purified by careful fractionation from a modified center-tube column useful for fractionation of from 1 to 5 g. of material. All the yields reported are of purified product. The data are reported in Tables I and II.

The high temperature pyrolysis experiments were carried out in a similar manner except that the tube was packed with Pyrex glass beads for 12 in., the upper 6 in. of which were heated. These experiments were carried out under reduced pressure and the diacetate was added at a rate of 1 drop/sec.

2-Alkyl-1,3-butadiene Maleic Anhydride Adducts.—The procedure of Marvel, Myers and Saunders[7] was employed. The solid products were recrystallized twice from a benzene-petroleum ether (b.p. 60–68°) mixture and dried under vacuum at room temperature for 12 hours (Table III).

2-Alkyl-1,3-butadiene Naphthoquinone Adducts.—This procedure was similar to that described by reference 14 and "Organic Syntheses."[24] After the reaction, the solution was chilled and if no solid precipitated on scratching, 20 ml. of water was added. The resulting solid was removed by filtration and recrystallized twice with "Norite" from 40% ethyl alcohol–water solution. The pure product (Table III) was dried under vacuum for 24 to 36 hours.

2-Alkyl-9,10-anthraquinone.—This procedure was similar to that described by reference 14 and "Organic Syntheses"[24] except that oxygen was used instead of air. After the reaction, the suspended material usually appeared light tan in color. The solid products were collected, washed with water and recrystallized from a water–alcohol mixture (Table III).

Procedure B. Preparation of β-Alkyl Adipic Acids.—β-Isopropyladipic acid was prepared by the procedure of v. Braun[25] with the following modifications. From 35.59 g. (0.25 mole) of 4-isopropylcyclohexanol,[26] 106.5 g. of potas-

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(21) Compare $\lambda_{max.}$ 2170 Å., $\epsilon_{max.}$ 21,000 for butadiene in hexane; $\lambda_{max.}$, 2200 Å., $\epsilon_{max.}$, 24,000 for isoprene in hexane [Dimroth, *Angew. Chem.*, **52**, 545 (1949)].

(22) C. S. Marvel, G. E. Inskeep, R. Deanin, A. E. Juve, C. H. Schneider and M. M. Goff, *Ind. Eng. Chem.*, **39**, 1486 (1947).

(23) All melting points are corrected unless otherwise noted.

(24) C. F. H. Allen and A. Bell, "Organic Syntheses," Vol. 22, John Wiley and Sons, Inc., New York, N. Y., 1942, p. 37.

(25) J. v. Braun and G. Werner, *Ber.*, **62**, 1050 (1929).

(26) We are indebted to the Dow Chemical Corporation, Midland, Michigan, for generous samples of 4-iso-propyl and 4-*t*-butyl cyclohexanols.

sium permanganate and 17.8 g. of potassium hydroxide in 3.5 l. of water, there was obtained 40 g. (85%) of β-isopropyl adipic acid. The manganese dioxide was removed by filtration and washed with 50 ml. of methanol. The filtrate and washings were concentrated under reduced pressure to 200 ml. From the concentrate, 5.0 g. of 4-isopropylcyclohexanol was recovered. To the concentrate was added 100 ml. of concentrated hydrochloric acid with stirring, and the precipitated β-isopropyladipic acid was removed by filtration. Recrystallization from an ether–petroleum ether (b.p. 30–60°) mixture gave 37.0 g. (91.5%, based on recovered cyclohexanol) of white product, m.p. 80–81.5°. An analytical sample prepared by recrystallizations from toluene melted at 81.7–82.3° (75°, 50%)[24] (85°, no yield).[27]

Anal.[28] Calcd. for $C_9H_{16}O_4$: C, 57.43; H, 8.57; neut. equiv., 94. Found: C, 57.49; H, 8.53; neut. equiv., 94.

If the β-isopropyladipic acid does not readily crystallize on addition of concentrated hydrochloric acid, the oil can be extracted with ether and the product distilled, to give starting material and product, b.p. 142–146° (1 mm.). This distillate crystallizes on standing and can be recrystallized as described above.

In a similar way, 78 g. (0.385 mole) of 4-*t*-butylcyclohexanol gave in one oxidation 85 g. (84.2%) of β-*t*-butyladipic acid, m.p. 115–115.5° (117°, 87%, prepare by oxidation with nitric acid and ammonium vanadate).[29]

Both β-isopropyl- and β-*t*-butyladipic acids were also prepared using the procedure described by Ellis[30] for the preparation of adipic acid from cyclohexanol.

From a solution of 1 g. of ammonium vanadate in 1900 ml. of 50% nitric acid at 65°, there was added dropwise with stirring at such a rate to maintain the temperature of 60–65° (3.18 moles) of 4-substituted cyclohexanol (6 hours). After an additional eight hours of stirring and cooling in an ice-bath, the precipitate was collected by filtration and washed with a minimum volume of ice-water and recrystallized twice from boiling water (2 ml./1 g. of wet acid). Reworking of mother liquors gave a total yield of 85% in the case of β-isopropyladipic acid, m.p. 82.5–83°. The preparation of β-*t*-butyladipic acid was accomplished in 75% yield, m.p. 115–116°.

Preparation of 2-Alkyl-1,4-butanediamines.—The procedure was similar to that employed by reference 10 who omitted many experimental details. Hydrazoic acid was used in benzene solution prepared from 167.9 g. (2.33 moles) of 90% sodium azide and 66 ml. of concentrated sulfuric acid giving an 8% benzene solution. The procedure in "Organic Reactions"[31] was modified by using benzene as a solvent and a reaction temperature in the preparation of the hydrazoic acid solution of from 15–17°. If the specified temperature of <10° is used, a lower yield of hydrazoic acid is obtained. From 16.5 g. (0.088 mole) of β-isopropyladipic acid in 50 ml. of concentrated sulfuric acid, there was obtained on dropwise addition of 9.64 g. (0.224 mole) of hydrazoic acid solution at such a rate to maintain the temperature at 43–47° (3 hours), 10.6 g. (92%) of 2-isopropyl-1,4-butanediamine. The reaction mixture was stirred until the temperature had reached 30° and cooled in an ice-bath. The sulfuric acid layer was separated, added to 150 g. of cracked ice and made strongly alkaline with 50% aqueous sodium hydroxide. The oil layer was separated and taken up in ether; two layers formed in addition to the original aqueous phase, one an ether–amine layer and the other a water–amine layer. These layers were dried over sodium hydroxide pellets and the ether layer then removed. Continuous extraction with ether is a more successful but time consuming operation. The residue from the ether solution was distilled over sodium through a 10-plate fractionating column under dry nitrogen, b.p. 85.5° (11 mm.), 82–82.5° (9 mm.), n^{25}_D 1.4804, d^{25}_4 1.0293 (88–90° (16 mm.), 80%).[10]

The dihydrochloride of 2-isopropyl-1,4-butanediamine was prepared in benzene–ethanol solution with dry hydrogen chloride and recrystallized from an ethanol–ethyl acetate mixture to give a white solid, m.p. 199–200° uncor.

Anal. Calcd. for $C_7H_{20}N_2Cl_2$: C, 41.35; H, 9.92. Found: C, 41.28; H, 9.60.

In an identical manner there was obtained from 21.63 g. (0.107 mole) of β-*t*-butyladipic acid in 75 ml. of concentrated sulfuric acid and 20 g. (0.165 mole) of hydrazoic acid, 14.7 g. (95.4%) of 2-*t*-butyl-1,4-butanediamine, b.p. 87–88.5° (9 mm.), $n^{22.5}_D$ 1.4790.

Anal. Calcd. for $C_8H_{20}N_2$: C, 66.60; H, 13.98; N, 19.42. Found: C, 66.59; H, 13.75; N, 19.44.

The dihydrochloride of 2-*t*-butyl-1,4-butanediamine was prepared in a 50% ether-alcohol medium with dry hydrogen chloride and recrystallized from an ethanol–ethyl acetate mixture to give a white powdery solid, m.p. 233.5–235° dec.

Anal. Calcd. for $C_8H_{22}N_2Cl_2$: C, 44.24; H, 10.21; N, 12.90; Cl, 32.65. Found: C, 44.41; H, 10.28; N, 13.20; Cl, 32.31.

Preparation of the Diquaternary Salts of the 2-Alkyl-1,4-butanediamines.—The diquaternary methiodides of 2-isopropyl- and 2-*t*-butyl-1,4-butanediamine were prepared using a modified procedure of Gardiner and Stevens[32] for quaternization of primary aromatic monoamines.

From 52 g. (0.4 mole) of 2-isopropyl-1,4-butanediamine, 110.5 g. (1.6 moles) of anhydrous potassium carbonate in 900 ml. of anhydrous ethanol (commercial) and 340 g. (2.4 moles) of methyl iodide at gentle reflux there was obtained 165 g. (87.8%) of salt, m.p. 235–240° dec., uncor., after recrystallization from anhydrous ethanol. Reference 10 used dimethyl sulfate and potassium iodide and obtained a compound, m.p. 240°, which they noted decomposed on recrystallization to give a lower melting compound.

Anal. Calcd. for $C_{13}H_{32}N_2I_2$: C, 33.20; H, 6.86; I, 53.85. Found: C, 32.98; H, 6.58; I, 53.85.

In an analogous manner with the exception that sodium hydroxide also was added there was obtained from 45 g. (0.313 mole) of 2-*t*-butyl-1,4-butanediamine, 355 g. (2.5 moles) of methyl iodide, 49.9 g. (1.25 moles) of sodium hydroxide and 500 ml. of anhydrous methanol, 113 g. (74.6%) of diquaternary iodide, m.p. 236–240° dec.

Anal. Calcd. for $C_{14}H_{34}N_2I_2$: C, 34.72; H, 7.08; I, 52.41. Found: C, 34.63; H, 6.86; I, 52.42.

2-Alkyl-1,3-butadienes.—The diquaternary methiodides were converted to the corresponding substituted ammonium hydroxides in a manner identical with that reported by reference 10 and Cope and Overberger.[33]

The residual "ammonium" hydroxides were decomposed at a temperature of 110–120° at 25–80 mm. The distillates were collected in Dry Ice traps and extracted with ethyl ether. The ether solutions were washed with water and dried over anhydrous potassium carbonate. Fractionating through a 30-cm. helices-packed column of the ether solution and redistillation of fractions gave the dienes (Table II).

Ultraviolet Absorption Spectra.—Ultraviolet absorption spectra were determined with a Beckman quartz ultraviolet spectrophotometer in purified cyclohexane[34] as a solvent. The cell length used in all experiments was 1 cm.

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