

liquors. Both crops melted at 173–175° raised to 180–183° dec., after recrystallization from aqueous alcohol.

*Anal.* Calcd. for  $C_{13}H_{21}N_6O_3S \cdot HSO_4$ : C, 35.55; H, 5.28; N, 19.14;  $SO_4$ , 21.87. Found (on material dried 7 hr. at 100° *in vacuo*): C, 35.70; H, 5.31; N, 19.13;  $SO_4$ , 21.55.

**2',3'-Isopropylidene-5'-deoxy-5'-S-(4-thiobutylamine)adenosine.**—This compound was prepared in the usual way by treating dithiobutylamine dihydrochloride (1.25 g.) with sodium in liquid ammonia to a permanent blue color and then condensing the resulting mercaptide with 2',3'-isopropylidene-5'-toluene-*p*-sulfonyl-adenosine (4.6 g.). 2',3'-Isopropylidene-5'-deoxy-5'-S-(4-thiobutylamine)adenosine sesquihydrate (2.45 g.) had m.p. 59° (from hot water).

*Anal.* Calcd. for  $C_{17}H_{26}N_6O_3S \cdot 1.5 H_2O$ : C, 48.43; H, 6.93; N, 19.93. Found: C, 48.80; H, 6.92; N, 19.79.

**5'-Deoxy-5'-S-(4-thiobutylamine)adenosine Sulfate.**—The above isopropylidene nucleoside (1.6 g.) was dissolved in *N* sulfuric acid (20 ml.) and allowed to stand at room temperature for 24 hr. Paper chromatography showed that the product contained only traces of ultraviolet absorbing impurities. However, the oil resulting on addition of ethanol to the acid solution could not be induced to crystallize. This oil was taken up in water and an excess of a saturated aqueous solution of picric acid added. The precipitated picrate was filtered off, washed with a little water, and recrystallized twice from hot water; yield, 1.9 g.; m.p. 174–176° dec.

The purified picrate (1.6 g.) was dissolved in 50% aqueous dimethylformamide (100 ml.) and passed down a column (2 × 15 cm.) of Dowex 1 anion-exchange resin (acetate form, 100–200 mesh). The column was washed with water (100 ml.) and the combined eluate and washings evaporated to dryness *in vacuo*. The residue was taken up in alcohol (*ca.* 10 ml.) and transferred to a centrifuge tube. Sulfuric acid (2 *N*, 1 ml.) was added and the solid precipitate separated by centrifugation and washed with alcohol. The precipitate was redissolved in water, treated with a little decolorizing charcoal, and ethanol was then added to produce a slight opalescence in the solution. 5'-Deoxy-5'-S-(4-thiobutylamine)adenosine sulfate (238 mg.) crystallized slowly over several days, m.p. 166–169° dec., from aqueous ethanol.

*Anal.* Calcd. for  $C_{14}H_{22}N_6O_3S \cdot 0.5 SO_4$ : C, 41.68; H, 5.74; N, 20.83. Found: C, 41.22; H, 5.83; N, 20.34.

**2',3'-Isopropylidene-5'-deoxy-5'-S-(2-thioethylamine)adenosine.**—This compound was prepared by condensing the sodio derivative of 2-thioethylamine (cysteamine) (1.4 g.) in liquid ammonia with 2',3'-isopropylidene-5'-toluene-*p*-sulfonyl-adenosine (9.2 g.).

After working up in the usual way a clear mobile oil (6.0 g.) was obtained which could not be induced to crystallize. It ran as a single compound in water-saturated butanol ( $R_f$  0.64) and

was homogeneous under ultraviolet light and to the ninhydrin and iodoplatinate sprays.

**5'-Deoxy-5'-S-(2-thioethylamine)adenosine Bisulfate.**—The above isopropylidene derivative (1.0 g.) was dissolved in *N* sulfuric acid (25 ml.) and left overnight at room temperature. The product (1.0 g.) was precipitated as its monohydrate by the addition of alcohol and recrystallized from aqueous alcohol; m.p. 188° dec.

*Anal.* Calcd. for  $C_{12}H_{19}N_6O_3S \cdot HSO_4 \cdot H_2O$ : C, 32.57; H, 5.01; N, 19.00; S, 14.49; wt. loss on drying, 4.07. Found: C, 32.75; H, 5.15; N, 19.44; S, 14.20; wt. loss (100° under high vacuum for 3 hr.), 3.75.

**5'-Deoxy-5'-S-(3-methylthiopropylamine)sulfoniumadenosine ("Decarboxylated S-Adenosylmethionine").**—5'-Deoxy-5'-S-(3-thiopropylamine)adenosine bisulfate (100 mg.) was dissolved in a mixture of equal parts of formic and acetic acids (5 ml.) and to this was added methyl iodide (0.5 ml.). The solution was left in the dark at room temperature for 6 days after which time it was diluted with an equal volume of water and extracted three times with 10-ml. portions of ether. A solution of flavianic acid (2% in *N* HCl, 10 ml.) was then added and the precipitated sulfonium flavianate centrifuged, washed with two 5-ml. portions of cold dilute flavianic acid and then with 5 ml. of cold water. The yield was 127 mg. after drying *in vacuo*. A small portion of the flavianate was rapidly recrystallized from hot water. It melted at 210–214° dec. and gave an analysis consistent with a diflavianate.

*Anal.* Calcd. for  $C_{14}H_{22}N_6O_3S(C_{10}H_8N_2O_8S)_2$ : C, 41.55; H, 3.49. Found: C, 41.55; H, 4.12.

The diflavianate was suspended in 0.4 *N* hydrochloric acid (10 ml.) and extracted with five to six 10-ml. lots of 2-butanone until the aqueous layer was colorless. The aqueous layer was extracted once with ether and then treated with sufficient Dowex 1 in the acetate form to remove chloride ions. The aqueous layer was then lyophilized and the residue taken up in a little water and adjusted to pH 5–6. The yield of sulfonium nucleoside was 146  $\mu$ moles (based on an extinction coefficient of 16,000 at 260  $m\mu$ ). This material migrated towards the cathode at a rate of 3.6 cm./hr. when subjected to paper electrophoresis at pH 5.8 with a voltage gradient of 7 v./cm. It was homogeneous under the ultraviolet lamp (260  $m\mu$ ) and to the ninhydrin, iodoplatinate, and periodate Schiff sprays.

The preparation of the corresponding 5'-deoxy-5'-S-(2-methylthioethylamine)- and (4-methylthiobutylamine)sulfoniumadenosine compounds and the precipitation and decomposition of their flavianates were carried out in a similar manner.

**Acknowledgment.**—The author wishes to thank Mrs. Elizabeth Smallman for her technical assistance. The continued interest of Dr. Herbert Tabor was greatly appreciated.

## Allylic Chlorides. XXVII. The Relative Reactivities of $\gamma$ -Alkylallyl Chlorides

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Received December 10, 1962

Rate and thermodynamic data are presented for the reaction between both potassium iodide in acetone and sodium ethoxide in ethanol and the following allyl chlorides: allyl chloride, *cis*- and *trans*- $\gamma$ -methylallyl chloride, *cis*- and *trans*- $\gamma$ -ethylallyl chloride, *cis*- and *trans*- $\gamma$ -isopropylallyl chloride. All of the  $\gamma$ -alkylallyl chlorides were more reactive than allyl chloride and the *cis* isomer was more reactive than the *trans* isomer, especially with potassium iodide. The reasons for this configurationally related difference in reaction rate is not clear.

During the course of an extended investigation of allylic chlorides their relative reactivities toward potassium iodide in acetone and sodium ethoxide in ethanol were obtained by comparing their rate constants with that of allyl chloride. Thermodynamic data for the reactions of allyl chloride, and of  $\gamma$ -methyl-,  $\gamma$ -ethyl-, and  $\gamma$ -isopropylallyl chlorides have now been obtained. Similar data were reported previously for the 1-chloro-4,4-dimethyl-2-pentenes ( $\gamma$ -*t*-butylallyl chloride).<sup>1</sup>

The  $\gamma$ -alkylallyl chlorides were prepared in a manner similar to that used for the synthesis of the 1-chloro-4,4-dimethyl-2-pentenes.<sup>1</sup> Table I contains the boiling points or boiling ranges, densities, and refractive indices of the chlorides and their alcohol precursors. The isomers were characterized by their physical constants, infrared spectra, g.l.c. analyses, and elemental anal-

(1) L. F. Hatch, H. D. Weiss, and T. P. Li, *J. Org. Chem.*, **26**, 61 (1961).

TABLE I  
 $\gamma$ -ALKYLALLYL ALCOHOLS AND CHLORIDES (R—CH=CHCH<sub>2</sub>Y)

R	Y	Isomer	-B.p., °C. (mm.)		$d_4^{25}$		$n_D^{25}$	
			This work	Literature	This work	Literature	This work	Literature
CH <sub>3</sub>	OH	<i>cis</i>	119.8–120.5 (747)	120.5 (752) <sup>a</sup>	0.8685 (20)	0.8662 (20) <sup>a</sup>	1.4311 (25)	1.4321 (25) <sup>b</sup>
		<i>trans</i>	83.5–84.0 (748)	83.8 (747) <sup>b</sup>	0.9395 (20)	0.9426 (20) <sup>a</sup>	1.4350 (25)	1.4360 (25) <sup>b</sup>
	Cl	<i>trans</i>	84.0–84.7 (742)	84.0 (747) <sup>b</sup>	0.9247 (20)	0.9295 (20) <sup>a</sup>	1.4347 (20)	1.4341 (20) <sup>b</sup>
CH <sub>3</sub> CH <sub>2</sub>	OH	<i>cis</i>	56.0–56.8 (20)	41.2–41.7 (7) <sup>c,d</sup>	0.8566 (20)	0.8529 (20) <sup>c,d</sup>	1.4343 (20)	1.43407 (20) <sup>c,d</sup>
		<i>trans</i>	57.0–57.5 (20)	42.0–42.2 (7) <sup>c</sup>	0.8470 (20)	0.8471 (20) <sup>c</sup>	1.4350 (20)	1.43407 (20) <sup>c</sup>
	Cl	<i>cis</i>	49.5–50.5 (100)	106–108 <sup>c,e</sup>	0.9177 (20)	0.9159 (20) <sup>c,e</sup>	1.4399 (20)	1.43902 (20) <sup>c,e</sup>
		<i>trans</i>	51–52 (100)	60.8–62.0 (149) <sup>c</sup>	0.9090 (20)	0.92176 (20) <sup>c</sup>	1.4380 (20)	1.43992 (20) <sup>c</sup>
(CH <sub>3</sub> ) <sub>2</sub> CH	OH	<i>cis</i>	63.4 (20)		0.8355 (25)		1.4320 (25)	
		<i>trans</i>	64.2–65.0 (20)		0.8327 (25)		1.4337 (25)	
	Cl	<i>cis</i>	45–46 (50)		0.8863 (25)		1.4345 (25)	
		<i>trans</i>	47.5–49.0 (50)		0.8865 (25)		1.4365 (25)	

<sup>a</sup> L. F. Hatch and S. S. Nesbitt, *J. Am. Chem. Soc.*, **72**, 727 (1950). B.p. 124.1° (748 mm.) also reported by W. G. Young, S. H. Sharman, and S. Winstein *ibid.*, **82**, 1367 (1960), and 121° by W. G. Young and L. J. Andrews, *ibid.*, **66**, 421 (1944). <sup>b</sup> W. G. Young, S. H. Sharman and S. Winstein, *ibid.*, **82**, 1376 (1960). <sup>c</sup> G. Smets, *Trav. lab. chim. gen., Univ. Lowain*, **67** (1942–1947); *Acad. Roy. Belg. Classe Sci., Mem.*, Collection in 8°, **21**, 3–74 (1947); *Chem. Abstr.*, **44**, 8315 (1950). <sup>d</sup> Contained 15% *trans* isomer. <sup>e</sup> Contained 30% *trans* isomer.

yses (for compounds not previously reported in the literature). The purity of the *cis* and *trans* isomers of the same compound also was confirmed by the melting points of their 3,5-dinitrobenzoates. No depression in melting point was observed when the 3,5-dinitrobenzoates prepared from the alcohols were mixed with those prepared from the corresponding chlorides.

The isomeric  $\gamma$ -isopropylallyl alcohols and chlorides have not been reported in the literature. The acetylenic alcohol, 4-methyl-2-pentyn-1-ol, required for their preparation was obtained by the reaction between the Grignard reagent of 3-methyl-1-butyne and formaldehyde.<sup>2,3</sup> This acetylenic alcohol was reduced to *cis*-4-methyl-2-penten-1-ol over a palladium-calcium carbonate catalyst,<sup>4,5,6</sup> and to *trans*-4-methyl-2-penten-1-ol by sodium in liquid ammonia.<sup>5,6,7</sup> Phosphorus trichloride was used in the conversion of the alcohols to the chlorides.

The kinetic studies with allyl chloride were made at 20°, 30°, and 40° for the reaction with potassium iodide and at 30°, 35°, and 40° with sodium ethoxide and these data are in Table II. The rate constant with potassium iodide at 20° is less than that reported by both Tamele and co-workers and Hatch, Gordon, and Russ.<sup>8</sup> A plot of  $\log k$  vs.  $1/T$  of the rate data obtained for the reaction with sodium ethoxide gave a rate constant of  $3.45 \times 10^{-4}$  l. mole<sup>-1</sup> sec.<sup>-1</sup> at 50°. This value is slightly higher than the one reported previously ( $3.11 \times 10^{-4}$  l. mole<sup>-1</sup> sec.<sup>-1</sup>).<sup>9</sup>

The kinetic and thermodynamic data (Table II) follow the same general patterns as those reported for the  $\gamma$ -*t*-butylallyl chlorides<sup>1</sup> with the exception of the relative rates for the *cis* and *trans* isomers with sodium ethoxide. With this reagent the *cis* isomer is slightly less reactive than the *trans* isomer when the  $\gamma$ -alkyl group is *t*-butyl, but slightly more reactive when the group is methyl, ethyl or isopropyl. Geometrical

configuration is an appreciably greater factor in determining reaction rate with potassium iodide than with sodium ethoxide. As yet there has been no inclusive theory proposed to explain these facts. Bunnett and Reinheimer<sup>10</sup> have noted that "these observations are remarkable because steric hindrance should, if anything, make the *cis* isomer less reactive than the *trans*." They also point out that kinetic effects previously reported<sup>1</sup> approximate the expectations from London theory. The enhanced reactivity of the *cis* isomer may be the result of London interactions causing a reduction of transition state free energy by action between the attacking nucleophile and the nearby *cis*- $\gamma$ -alkyl groups.

Our study of the relative reactivities of allylic chlorides is concluded with this paper. It is hoped that the data will be of assistance to others in evaluating the role of geometrical configuration in determining the reactivity of compounds of this type.

### Experimental<sup>11</sup>

**Allyl Chloride.**—The allyl chloride was purchased<sup>12</sup> and distilled before use.<sup>13</sup>

**$\gamma$ -Alkylallyl Chlorides.**—The  $\gamma$ -alkylallyl chlorides used in this investigation were synthesized from acetylenic hydrocarbons by methods previously described.<sup>1</sup> The boiling point or range, density, and refractive index of the allyl chlorides and their allyl alcohol precursors are in Table I. Their infrared spectra are in agreement with the assigned structures and photostatic copies of the spectra are available. The *trans*-crotyl alcohol used to prepare *trans*-crotyl chloride was purchased.<sup>12</sup> The purity of the compounds was determined by gas-liquid chromatography.

The following analyses were obtained<sup>14</sup> for the compounds not reported previously in the literature.

*Anal.* Calcd. for C<sub>6</sub>H<sub>12</sub>O (*cis*-4-methyl-2-penten-1-ol): C, 71.95; H, 12.08. Found: C, 70.98; H, 11.52.

*Anal.* Calcd. for C<sub>6</sub>H<sub>12</sub>O (*trans*-4-methyl-2-penten-1-ol): C, 71.95; H, 12.08. Found: C, 71.82; H, 12.03.

*Anal.* Calcd. for C<sub>8</sub>H<sub>11</sub>Cl (*cis*-1-chloro-4-methyl-2-pentene): C, 60.76; H, 9.35; Cl, 29.89. Found: C, 60.45; H, 9.11; Cl, 29.57.

*Anal.* Calcd. for C<sub>8</sub>H<sub>11</sub>Cl (*trans*-1-chloro-4-methyl-2-pentene): C, 60.76; H, 9.35; Cl, 28.89. Found: C, 61.16; H, 9.58; Cl, 29.59.

**4-Methyl-2-pentyn-1-ol.**—This acetylenic alcohol, a precursor of the 4-methyl-2-penten-1-ols, has not been reported previously

(2) H. H. Guest, *J. Am. Chem. Soc.*, **47**, 860 (1925).  
 (3) H. Gilman and W. E. Catlin, "Organic Syntheses," Coll. Vol. I, A. H. Blatt, Ed., John Wiley and Sons, Inc., New York, 1944, p. 188.  
 (4) I. M. Heilbron, E. R. H. Jones, J. T. McComble, and B. C. L. Weeden, *J. Chem. Soc.*, **84** (1945).  
 (5) F. Sondheimer, *ibid.*, **877** (1950).  
 (6) L. Crombia and S. H. Harper, *ibid.*, **1712** (1950).  
 (7) K. N. Campbell and L. T. Eby, *J. Am. Chem. Soc.*, **63**, 216 (1941).  
 (8) (a) M. Tamele, C. J. Ott, K. E. Marple, and G. Hearne, *Ind. Eng. Chem.*, **33**, 115 (1941); (b) L. F. Hatch, L. B. Gordon, and J. J. Russ, *J. Am. Chem. Soc.*, **70**, 1093 (1948).  
 (9) L. F. Hatch and H. E. Alexander, *ibid.*, **71**, 1037 (1949).

(10) J. F. Bunnett and J. D. Reinheimer, *ibid.*, **84**, 3284 (1962).  
 (11) All melting point temperatures are corrected.  
 (12) Distillation Products Industries, Eastman Organic Chemicals.  
 (13) Data for allyl chloride were obtained by Michio Makita.  
 (14) Clark Microanalytical Laboratory, Urbana, Ill.

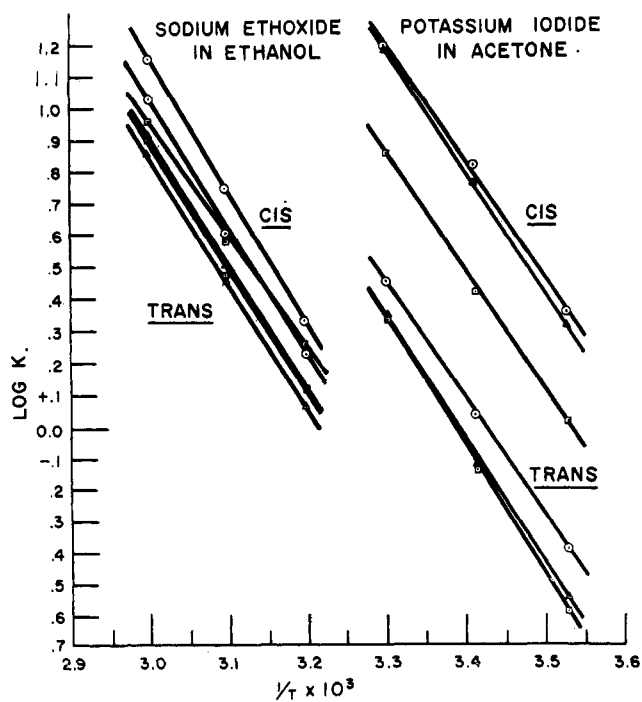


Fig. 1.—Plot of  $\log k$  vs.  $1/T$  for the reaction between  $\gamma$ -alkyl-allyl chlorides and sodium ethoxide in ethanol, and potassium iodide in acetone: crotyl chloride = O; 1-chloro-2-pentene = □; 1-chloro-4-methyl-2-pentene = Δ.

in the literature; b.p. 68.5–69.0° (20 mm.);  $d_{25}^{25}$ , 0.8799;  $n_D^{20}$ , 1.4431.

*Anal.* Calcd. for  $C_6H_{10}O$ : C, 73.43; H, 10.27. Found: C, 73.67; H, 10.52.

**3,5-Dinitrobenzoates.**—The 3,5-dinitrobenzoates of the alcohols were prepared by the standard procedure. The 3,5-dinitrobenzoates of the chlorides were prepared by the reaction of the chlorides with the silver salt of 3,5-dinitrobenzoic acid.

**4-Methyl-2-pentyn-1-ol.**—M.p. 71–72°. *Anal.* Calcd. for  $C_{13}H_{14}N_2O_6$ : C, 53.42; H, 4.14; N, 9.59. Found: C, 53.82; H, 4.10; N, 9.48.

**cis-4-Methyl-2-penten-1-ol.**—M.p. 64.5–65°. *Anal.* Calcd. for  $C_{13}H_{14}N_2O_6$ : C, 53.06; H, 4.80; N, 9.52. Found: C, 53.05; H, 4.59; N, 9.66.

**trans-4-Methyl-2-penten-1-ol.**—M.p. 63.5°. *Anal.* Calcd. for  $C_{13}H_{14}N_2O_6$ : C, 53.06; H, 4.80; N, 9.52. Found: C, 53.44; H, 4.62; N, 9.63.

**cis-1-Chloro-4-methyl-2-pentene.**—M.p. 64.0°. *Anal.* Calcd. for  $C_{13}H_{14}N_2O_6$ : C, 53.06; H, 4.80; N, 9.52. Found: C, 53.24; H, 4.54; N, 9.47.

**trans-1-Chloro-4-methyl-2-pentene.**—M.p. 63.0°. *Anal.* Calcd. for  $C_{13}H_{14}N_2O_6$ : C, 53.06; H, 4.80; N, 9.52. Found: C, 52.85; H, 5.05; N, 9.78.

**Kinetic Studies.**—The procedures used were the same as those previously described.<sup>1</sup> The rate constants were obtained from the standard second-order rate equation by plotting  $\log b(a-x)/a(b-x)$  vs. time. The energies of activation were obtained by plotting  $\log k$  against reciprocal of the absolute temperature (Fig. 1) and the entropies of activation were calculated from the Eyring equation. Both rate data and thermodynamic data are in Table II. Temperatures were maintained at  $\pm 0.05^\circ$ .

**Reaction with Potassium Iodide in Acetone.**—The plot of  $\log b(a-x)/a(b-x)$  vs. time for allyl chloride gave a straight line between 28 and 70% changed at 20°, between 33 and 78% at 30°, and between 51 and 68% at 40°. *cis*-Crotyl chloride gave a straight line between 20 and 74% changed at 10°, between 27 and 75% at 20°, and between 45 and 62% at 30°. Similar data for the *trans* isomer are 33 and 62% changed at 10°, 34 and 65% at 20°, and 34 and 67% at 30°. *cis*-1-Chloro-2-pentene gave a straight line between 26 and 50% changed at 10°, 33 and 63% at 20°, and 31 and 50% at 30°. Similar data for the *trans* isomer are 22 and 57% changed at 10°, 35 and 64% at 20°, and 48 and 68% at 30°. *cis*-1-Chloro-4-methyl-2-pentene gave a straight line between 46 and 76% changed at 10°, 40 and 75% at 20°, and 47 and 71% at 30°. Similar data for the

TABLE II  
REACTION RATES, RELATIVE REACTIVITIES, AND ENERGIES AND ENTROPIES OF ACTIVATION FOR  $\gamma$ -ALKYLALLYL CHLORIDES ( $R-CH=CHCH_2Cl$ )

R	Isomer	Potassium iodide in acetone $k \times 10^4$ , mole <sup>-1</sup> sec. <sup>-1</sup> , °K			Sodium ethoxide in ethanol			Relative reactivity		$E_a$ , Kcal. mole <sup>-1</sup>		$\Delta S^\ddagger$ , cal. deg. <sup>-1</sup> mole <sup>-1</sup>	
		283	303	313	323	333	KI <sup>a</sup>	NaOC <sub>2</sub> H <sub>5</sub> <sup>b</sup>	KI	NaOC <sub>2</sub> H <sub>5</sub>	KI	NaOC <sub>2</sub> H <sub>5</sub>	
H <sup>c</sup>	<i>cis</i>	1.01 ± 0.04 <sup>d</sup>	3.00 ± 0.11	1.12 ± 0.01	3.45 <sup>e</sup>	38.6 ± 1.9	1.00	1.00	19.5	23.1	-10.4	-2.92	
CH <sub>3</sub>	<i>trans</i>	18.1 ± 0.42 <sup>f</sup>	42.5 ± 1.9	5.92 ± 0.14	15.3 ± 0.4	29.4 ± 1.4	17.9	4.44	15.8	19.2	-17.1	-12.2	
CH <sub>3</sub> CH <sub>2</sub>	<i>cis</i>	7.20 ± 0.08 <sup>g</sup>	7.55 ± 0.22	4.60 ± 0.11	11.1 ± 0.4	25.5 ± 0.3	3.03	3.22	16.1	19.4	-19.7	-12.1	
	<i>trans</i>	1.94 ± 0.04	5.80 ± 0.14	3.64 ± 0.19	10.1 ± 0.5	21.4 ± 0.7	7.13	2.92	16.9	17.1	-15.1	-19.2	
(CH <sub>3</sub> ) <sub>2</sub> CH	<i>cis</i>	1.94 ± 0.04	5.80 ± 0.14	3.64 ± 0.19	8.05 ± 0.22	21.4 ± 0.7	1.92	2.33	18.2	18.4	-14.4	-15.6	
	<i>trans</i>	15.3 ± 0.4	41.4 ± 1.4	3.50 ± 0.08	8.78 ± 0.20	22.5 ± 0.2	15.1	2.54	17.1	19.2	-13.0	-13.2	
(CH <sub>3</sub> ) <sub>3</sub> C <sup>h</sup>	<i>trans</i>	2.08 ± 0.04	6.05 ± 0.30	3.14 ± 0.14	7.65 ± 0.28	19.8 ± 0.4	2.06	2.22	17.9	19.3	-14.7	-13.3	
	<i>cis</i>	8.25 ± 0.08	23.4 ± 0.4	2.00 ± 0.01	5.08 ± 0.05	12.3 ± 0.4	8.15	1.47	17.1	18.4	-14.0	-12.2	
	<i>trans</i>	1.92 ± 0.02	5.56 ± 0.05	2.86 ± 0.03	7.65 ± 0.08	19.7 ± 0.1	1.90	2.22	18.1	19.9	-13.8	-11.6	

<sup>a</sup> Allyl chloride as 1.00 with  $k = 1.01 \times 10^{-4}$  at 293°K. <sup>b</sup> Allyl chloride as 1.00 with  $k = 3.45 \times 10^{-4}$  at 323°K. <sup>c</sup>  $k = 8.50 \pm 0.30 \times 10^{-4}$  at 313°K. for KI,  $k = 0.334 \pm 0.008 \times 10^{-4}$  at 303°K., and  $k = 0.583 \pm 0.011 \times 10^{-4}$  at 308°K. for NaOC<sub>2</sub>H<sub>5</sub>. <sup>d</sup> Lit.  $k = 1.40 \times 10^{-4}$  [L. F. Hatch, L. B. Gordon, and J. J. Russ, *J. Am. Chem. Soc.*, **70**, 1093 (1948)]. <sup>e</sup> This value was obtained by extrapolation. <sup>f</sup> Lit.  $k = 3.11 \times 10^{-4}$  [L. F. Hatch and H. E. Alexander, *ibid.*, **71**, 1037 (1949)]. <sup>g</sup> Lit.  $k = 11.6 \times 10^{-4}$  [L. F. Hatch and S. S. Nesbitt, *ibid.*, **73**, 358 (1951)]. <sup>h</sup> Literature  $k = 2.18 \times 10^{-4}$  (see ref. f). <sup>i</sup> L. F. Hatch, H. D. Weiss, and T. P. Li, *J. Org. Chem.*, **26**, 61 (1961).

*trans* isomer are 43 and 64% changed at 10°, 40 and 70% at 20°, and 48 and 69% at 30°. The number of points used to characterize the straight lines was between six and nine.

The following molar concentrations ( $a = \text{KI}$ ,  $b = \text{chloride}$ ) were used. Allyl chloride:  $a = 0.2871$  (20°), 0.1968 (30°), 0.09543 (40°);  $b = 0.03904$  (20°), 0.03933 (30°), 0.01999 (40°). *cis*-Crotyl chloride:  $a = 0.1962$  (10°, 20°), 0.07730 (30°);  $b = 0.03923$  (10°, 20°), 0.02000 (30°). *trans*-Crotyl chloride:  $a = 0.3849$  (10°), 0.1962 (20°), 0.1496 (30°);  $b = 0.03849$  (10°), 0.03923 (20°), 0.02000 (30°). *cis*-1-Chloro-2-pentene:  $a = 0.1961$  (10°), 0.1955 (20°), 0.1010 (30°);  $b = 0.04000$  (10°), 0.03989 (20°), 0.02040 (30°). *trans*-1-Chloro-2-pentene:  $a = 0.3824$  (10°), 0.1961 (20°), 0.1996 (30°);  $b = 0.03900$  (10°), 0.04000 (20°), 0.02040 (30°). *cis*-1-Chloro-4-methyl-2-pentene:  $a = 0.2000$  (10°, 20°), 0.1020 (30°);  $b = 0.04000$  (10°, 20°), 0.02000 (30°). *trans*-1-Chloro-4-methyl-2-pentene:  $a = 0.4000$  (10°), 0.2000 (20°), 0.2120 (30°);  $b = 0.04000$  (10°, 20°), 0.02000 (30°).

**Reaction with Sodium Ethoxide in Ethanol.**—A plot of  $\log b(a-x)/a(b-x)$  vs. time for allyl chloride gave a straight line between 19 and 57% changed at 30°, 28 and 56% at 35° and 13 and 52% at 40°. *cis*-Crotyl chloride gave a straight line between 42 and 68% changed at 40°, 31 and 61% at 50°, and 37 and 68% at 60°. Similar data for the *trans* isomer are 47 and 66% changed at 40°, 36 and 60% at 50°, and 37 and 58% at 60°. *cis*-1-Chloro-2-pentene gave a straight line between 48

and 66% changed at 40°, 38 and 56% at 50°, and 44 and 59% at 60°. Similar data for the *trans* isomer are 41 and 58% changed at 40°, 37 and 49% at 50°, and 35 and 55% at 60°. *cis*-1-Chloro-4-methyl-2-pentene gave a straight line between 45 and 68% changed at 40°, 25 and 60% at 50°, and 40 and 64% at 60°. Similar data for the *trans* isomer are 45 and 68% changed at 40°, 42 and 62% at 50°, and 50 and 64% at 60°. The number of points used to characterize the straight lines was between six and nine.

The following molar concentrations ( $a = \text{chloride}$ ,  $b = \text{CH}_3\text{CH}_2\text{ONa}$ ) were used. *cis*-Crotyl chloride:  $a = 0.1020$  (40°), 0.05183 (50°), 0.05174 (60°);  $b = 0.04833$  (40°, 50°, 60°). *trans*-Crotyl chloride:  $a = 0.1016$  (40°), 0.05147 (50°), 0.05180 (60°);  $b = 0.04833$  (40°, 50°, 60°). *cis*-1-Chloro-2-pentene:  $a = 0.1032$  (40°), 0.05182 (50°), 0.05281 (60°);  $b = 0.04926$  (40°, 50°, 60°). *trans*-1-Chloro-2-pentene:  $a = 0.1042$  (40°), 0.05009 (50°), 0.05283 (60°);  $b = 0.04926$  (40°, 50°, 60°). *cis*-1-Chloro-4-methyl-2-pentene:  $a = 0.1063$  (40°), 0.05279 (50°), 0.05335 (60°);  $b = 0.05076$  (40°, 50°, 60°). *trans*-1-Chloro-4-methyl-2-pentene:  $a = 0.1103$  (40°), 0.05480 (50°), 0.05278 (60°);  $b = 0.05076$  (40°, 50°, 60°).

**Acknowledgment.**—The authors are indebted to The Robert B. Welch Foundation for the financial support of this research.

## The Synthesis of 1,8-Diphenylnaphthalene

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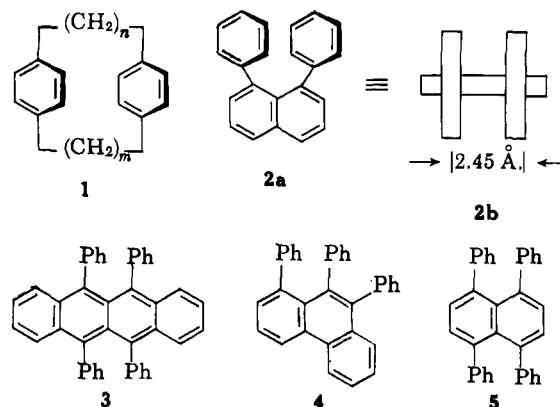
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Received April 8, 1963

1,8-Diphenylnaphthalene (2) has been prepared by reaction of 8-phenyl- $\Delta^8,10$ -octal-1-one (6) with phenylmagnesium bromide followed by dehydration and dehydrogenation. 1,7-Diphenylnaphthalene (8) has been similarly obtained by reaction of 7-phenyl-1-tetralone (9) with phenylmagnesium bromide followed by dehydration and dehydrogenation. The physical properties of 1,8-diphenylnaphthalene (2) are consistent with the hypothesis that this molecule exists in a ground state conformation in which the two benzene rings are parallel to one another and perpendicular to the plane of the naphthalene ring.

A number of interesting properties of the paracyclophanes **1**<sup>2</sup> have been ascribed to existence of these molecules in conformations in which the two benzene rings lie parallel to one another. The possibility of a transannular electron delocalization (or at least a polarization) between the two benzene rings has been suggested<sup>2</sup> to explain the ability of substituents in one ring of these materials to influence the reactivity of the second benzene ring. From a consideration of the geometry of naphthalene (C-1 and C-8 bonds parallel and separated by 2.45 Å),<sup>3</sup> it appeared probable that the same face-to-face arrangement of two benzene rings could be achieved in 1,8-diphenylnaphthalene (2) as illustrated in the top view **2b**. Presumably the phenyl rings in this molecule **2** would be incapable of free rotation<sup>4</sup> and would be constrained to conformations in which both benzene rings are perpendicular to the plane of the naphthalene ring with the consequence that conventional  $\pi$ -orbital overlap (*i.e.*, resonance interaction) between each benzene ring and the naphthalene system would be prevented. Since it appeared

that the preparation of 1,8-diphenylnaphthalenes with a variety of substituents on the phenyl rings might offer synthetic advantages over the preparation of the corresponding paracyclophanes and since it was clear from the preparation of compounds such as **3**,<sup>5</sup> **4**,<sup>6</sup> and **5**<sup>7</sup> that 1,8-diphenylnaphthalene (2) was capable of existence, we have explored possible synthetic paths to this hydrocarbon and report here its synthesis.



(1) (a) Union Carbide Corporation Predoctoral Fellow in Chemistry, 1962-1963; (b) Allied Chemical Corporation Fellow, 1960-1962.

(2) (a) For a review of earlier work see D. J. Cram, *Rec. Chem. Progr.*, **20**, 71 (1959); (b) for more recent studies see D. J. Cram and D. I. Wilkinson, *J. Am. Chem. Soc.*, **82**, 5721 (1960).

(3) "Tables of Interatomic Distances and Configurations in Molecules and Ions," *Chem. Soc. (London), Spec. Publ.*, No. **11**, (1958).

(4) For example, an optically active form of the much less hindered 1-(2-carboxyphenyl)naphthalene has been obtained by D. M. Hall, S. Ridgwell, and E. F. Turner, *J. Chem. Soc.*, 2498 (1954).

(5) (a) C. Moureu, C. Dufraisse, and P. M. Dean, *Compt. rend.*, **182**, 1440 (1926); (b) C. F. H. Allen and L. Gilman, *J. Am. Chem. Soc.*, **58**, 937 (1936); (c) I. Gillet, *Bull. soc. chim. France*, 1135, 1141 (1950).

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