penyl unsaturation determined from infrared spectra, for several typical laboratory prepared products as well as some commercial samples. Here it is apparent that the amount of propenyl unsaturation increases with the preparation temperature, catalyst concentration and with certain surface conditions exemplified here by added steel wool. With regard to the catalytic effect of surfaces in the promotion of propenyl unsaturation it is seen that silicone oils apparently act as surface deactivators. The low propenyl unsaturation content of commercial samples is indication of mild preparatory conditions or acid hydrolysis during catalyst removal.

TABLE III

PROPENYL UNSATURATION IN POLYPROPYLENE GLYCOLS

Preparatory conditions			Propenyl unsaturation
Temp., °C.	Final mol. wt. number avg.	Final cat. concn., % wt.	By infrared absorp., meq. C=C/g.
Laboratory products before catalyst removal			
120	2500	0.1	0.013
140	2400	.07	.042
160	2000	.18	.105
140	2000	.2	.023
140	2000	.3	.046
140	2000	.5	.130
160	1400	.5	
With added steel wool surface			.18
160	1600	0.5	
With added silicone oil			.028
Commercial samples containing no catalyst			
..	2000	..	
	Sample A		0.008
	Sample B		.010
	Sample C		.06
	Sample D		0

The reaction mechanism whereby the unsaturation arises is not known with any degree of certainty. Certain facts are suggestive, however. Work in this Laboratory on the thermal stability of polypropylene glycol in the presence of known dehydration catalysts, such as activated alumina, and under neutral and alkaline conditions, gave no indication that unsaturation develops by thermal degradation. The recent work of Price and his co-workers[16] on the stereospecific polymerization of ethylene oxide using mainly Lewis acid catalyst systems where a solid surface is present, showed the product to have one end completely unsaturated. It might be possible, therefore, that the solid surfaces present in the reactors in the synthesis of polypropylene glycol, even in alkaline medium, contribute to the generation of propenyl unsaturation. In any event, it is believed the unsaturation in polypropylene glycol arises from an alternate reaction path, competing with the polymerization step, whose velocity depends on the above-cited reaction variables, and not from thermal degradation of the product. The mechanism presented by St. Pierre and Price might well be operative, although it does not suggest why only the *cis*-propenyl isomer should be obtained.

Removal of propenyl unsaturation from polypropylene glycol is relatively easy by treatment with either a mineral acid or a strong acid ion exchanger. However, its occurrence is troublesome in that the loss of functionality limits the polymer molecular weight during synthesis and the formation of propylene glycol initiator engendered in its production starts new polymer chains throughout the course of the reaction. This latter phenomenon leads to a broad molecular weight distribution. Allyl unsaturation, although of a somewhat more permanent nature, can be corrected by hydroxylation[3] or severe acid hydrolysis.

Acknowledgments.—The authors wish to thank Dr. J. N. Cosby and Dr. A. V. Tobolsky for valuable advice and discussion.

MORRISTOWN, N. J.

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[16] C. C. Price, "Polyoxides," talk presented as part of North Jersey A.C.S. Lecture Series, Feb. 11, 1958.

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF TENNESSEE EASTMAN CO., DIVISION OF EASTMAN KODAK CO.]

Preparation of Substituted 4-Pentenals

BY KENT C. BRANNOCK

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Methods have been developed for the preparation of substituted 4-pentenals by the rearrangement of allyl alkenyl ethers, produced by the acid-catalyzed elimination of allyl alcohol from aldehyde diallyl acetals. Usually, the allyl alkenyl ethers are produced as transitory intermediates which are not isolated. Some of the reactions and derivatives of the substituted 4-pentenals are discussed.

The rearrangement of allyl vinyl ether to 4-pentenal at 252–255° was first reported in 1938 by Hurd and Pollack.[1] The kinetics of the rearrangement were studied later by Schuler and Murphy,[2] who found the reaction in the vapor phase to be homogeneous and first order, in accordance with a mechanism proposed by Hurd and Pollack.[3] Paul, *et al.*,[4] found that allyl vinyl ether rearranged to 4-pentenal to the extent of 20% after 96 hr. at 80° and 36% after 72 hr. at 100°. The rearrangement of a mixture of 2-pentenyl vinyl ether and 1-pentenyl vinyl ether at 220° was also reported by Hurd and Pollack.[3]

A method of producing 2-alkenylcrotonaldehydes by heating diallyl acetals of crotonaldehyde

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[1] C. D. Hurd and M. A. Pollack, THIS JOURNAL, **60**, 1905 (1938).

[2] F. W. Schuler and G. W. Murphy, *ibid.*, **72**, 3155 (1950).

[3] C. D. Hurd and M. A. Pollack, *J. Org. Chem.*, **3**, 550 (1939).

[4] R. Paul, G. Roy, M. Fluchaire and G. Collardeau, *Bull. soc. chim France*, 121 (1950).

at 150 to 300° has been described[5]; thus, the methallyl acetal of crotonaldehyde, when pyrolyzed at 210–260°, gives 2-methallylcrotonaldehyde in 74% yield.

No other use has been made of this type of rearrangement for the preparation of aliphatic aldehydes, probably because of the difficulty in obtaining the requisite substituted allyl vinyl ethers. Hurd and Pollack[1] obtained allyl vinyl ether in 12–19% yields from acetaldehyde diallyl acetal and phosphorus pentoxide in quinoline, in 51% yield from allyl 2-bromoethyl ether (obtained in poor yield from a two-step reaction sequence) and potassium hydroxide, and in very poor yield by refluxing acetaldehyde diallyl acetal with *p*-toluenesulfonic acid. Paul, *et al.*,[4] modified and improved somewhat the procedure of Hurd and Pollack for the dehydrobromination of allyl 2-bromoethyl ether and also obtained allyl vinyl ether in 71% yield from acetylene and allyl alcohol. Watanabe and Conlon[6] recently described the preparation of allyl vinyl ether in 75% yield by the mercuric acetate-catalyzed transetherification of butyl vinyl ether with allyl alcohol.

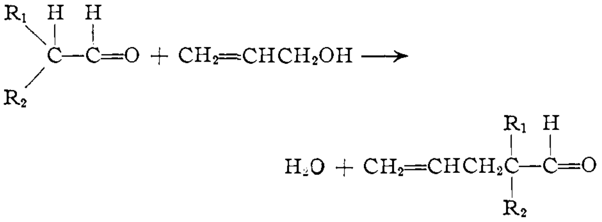
Duhamel[7] described the preparation of butyl vinyl ether by the acid-catalyzed elimination of butyl alcohol from acetaldehyde dibutyl acetal. In this Laboratory a number of alkyl ethers of enols had been prepared from the acetals of higher aldehydes using the procedure of Duhamel. In the work described in this paper, the reaction was extended to some allyl acetals. Distillation of acetaldehyde diallyl acetal from a small amount of phosphoric acid gave allyl vinyl ether in 48% conversion. When isobutyraldehyde diallyl acetal was subjected to the same treatment at virtually the same temperature, no allyl isobutenyl ether was obtained; instead, a 77% yield of its rearrangement product, 2,2-dimethyl-4-pentenal, was obtained (procedure A).

A number of 2,2-dialkyl-4-pentenals were prepared in good yield by the procedure outlined above, and in no case was any of the intermediate allyl ether of enols isolated.

Distillation of the allyl acetal of butyraldehyde (a monoalkyl-substituted acetaldehyde) from an acidic catalyst gave both the rearrangement product and the allyl ether of the enol form of the aldehyde. Similar treatment of the methallyl acetals of both monoalkyl-substituted and dialkyl-substituted acetaldehydes gave only the rearrangement products, substituted 4-methyl-4-pentenals; however, some of the intermediate methallyl ethers of the enols may have been present in the methallyl alcohol recovered from the reaction mixtures, since treatment of the recovered alcohol with 2,4-dinitrophenylhydrazine gave the derivative of the original aldehydes.

The recovery of the lower 2,2-dialkyl-4-pentenals was complicated by the fact that most of them form azeotropes with allyl alcohol. This complication was overcome easily by washing the mixture with water to remove the allyl alcohol.

A procedure which obviated the necessity of recovering the allyl alcohol from these aqueous wash solutions was developed. Thus, one mole of allyl alcohol is refluxed, with slightly more than one mole of the aldehyde in the presence of an acidic catalyst such as *p*-toluenesulfonic acid, and an inert, high-boiling solvent such as *p*-cymene (procedure B). The excess aldehyde serves to remove azeotropically the water formed in the reaction, and the high-boiling solvent serves to raise the temperature of the mixture. With this procedure, one-half mole of water per mole of allyl alcohol (corresponding to acetal formation) is evolved fairly rapidly; a second half-mole of water (corresponding to the elimination of allyl alcohol from the acetal and formation of more acetal by the allyl alcohol as it is eliminated) is obtained more slowly. Eventually, one mole of allyl alcohol reacts with one mole of a dialkyl-substituted acetaldehyde to produce one mole of water and one mole of a 2,2-dialkyl-4-pentenal.



$$R_1R_2CH{-}CH{=}O + CH_2{=}CHCH_2OH \longrightarrow H_2O + CH_2{=}CHCH_2C(R_1)(R_2){-}CH{=}O$$

In the only experiment with an aldehyde having two α-hydrogen atoms, butyraldehyde was converted in fair yield to 2-allyl-2-ethyl-4-pentenal by the one-step process described above, using two moles of allyl alcohol to one of butyraldehyde.

The one-step process was not satisfactory when applied to methallyl alcohol, because of the ease with which this substance undergoes acid-catalyzed isomerization to isobutyraldehyde.

The one-step process is simpler when applied to higher boiling aldehydes containing one α-hydrogen, such as cyclohexanecarboxaldehyde. In this case, no high-boiling solvent is required, and a small amount of an azeotropic agent, such as benzene, is employed to remove the water (procedure C).

In the only experiment involving a secondary allyl alcohol, 1-penten-3-ol reacted with isobutyraldehyde, according to procedure C, to give an excellent yield of *trans*-2,2-dimethyl-4-heptenal.[8] The *trans* configuration was shown by infrared spectral data. The homogeneity of the product was indicated by gas–liquid partition chromatography, by the sharpness of its boiling point, and by the fact that the melting point of its crude derivative was virtually unchanged by recrystallization.

The properties of the aldehydes prepared by procedures A, B and C are given in Table I.

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(5) R. H. Saunders, U. S. Patent 2,501,144 (1950).

(6) W. H. Watanabe and L. E. Conlon, THIS JOURNAL, **79**, 2828 (1957).

(7) A. Duhamel, *Bull. soc. chim. France*, 156 (1956).

(8) The specificity of this rearrangement is similar to that shown in the reaction of formaldehyde with 1-heptene, leading to *trans*-3-octen-1-ol [A. T. Blomquist, M. Passer, C. S. Schollenberger and J. Wolinsky, THIS JOURNAL, **79**, 4972 (1957)]. The fact that *trans* products are obtained in these cases may possibly be better explained by a non-planar transition state rather than by the planar one postulated by Blomquist. Whatever the conformation of the transition state may be, the two hydrogen atoms borne by the carbon atoms between which the new double bond is developed must be opposed and out of the plane of the three carbon atoms of the allylic system.

TABLE I

ALDEHYDES PREPARED

Aldehyde	Procedure	Yield, %	B.p. °C.	B.p. Press., mm.	$n^{20}\mathrm{D}$	2,4-DNPH,[b] M.p., °C.	Analyses, % Calcd. C	Calcd. H	Found C	Found H
2-Ethyl-4-pentenal[a]	A	37	137–138	Atm.	1.4262	110–111	74.95	10.78	75.04	10.65
2,2-Dimethyl-4-pentenal	A	77	124–125	Atm.	1.4203	117–118	74.95	10.78	74.91	10.72
	B	89	124–126	Atm.	1.4200	.....	...	...	...	...
2-Ethyl-2-methyl-4-pentenal	A	82	149–151	Atm.	1.4313	114–115	76.06	11.18	75.98	11.35
	B	78	150	Atm.	1.4312	.....	...	...	...	...
2-Ethyl-2-butyl-4-pentenal	A	73	209–212	Atm.	1.4447	136–136.5	78.51	11.98	78.24	12.22
2-Ethyl-4-methyl-4 pentenal	A	63	158.5–159	Atm.	1.4340	91.5–92.5	76.06	11.18	76.40	11.53
2-Allyl-2-ethyl-4-pentenal	B	36	49.2–53.2	4.7–5.0	1.4563	153–154	78.89	10.60	78.26	10.65
2,2,4-Trimethyl-4-pentenal	A	73	147.5–148	Atm.	1.4321	131–132	76.06	11.18	76.16	11.30
2,4-Dimethyl-2-ethyl-4-pentenal	A	87	172–173	Atm.	1.4415	94–95	77.09	11.50	77.26	11.65
1-Allylcyclohexanecarboxaldehyde	C	84	105–107	32	1.4701	156–157	78.89	10.59	78.72	10.92
2-Allyl-2-norcamphanecarboxaldehyde	C	91	120	26	1.4894	146–148	80.43	9.72	80.04	9.87
1-Allylcyclopentanecarboxaldehyde	B	72	137–140	Atm.	1.4622	124.5–125	78.14	10.21	77.87	10.29
trans-2,2-Dimethyl-4-heptenal	B	89	168	Atm.	1.4326	121–122	77.08	11.50	77.25	11.78

[a] Accompanied by 21% of allyl 1-butenyl ether, b.p. 115–120°, $n^{20}\mathrm{D}$ 1.4281. *Anal.* Calcd. for $C_7H_{12}O$: C, 74.95; H, 10.78. Found: C, 74.67; H, 10.75. [b] 2,4-Dinitrophenylhydrazones; all gave satisfactory analyses.

TABLE II

NEOALKYL ALCOHOLS PREPARED

Alcohol	Yield, %	B.p. °C.	B.p. Press, mm.	$n^{20}\mathrm{D}$	Analyses, % Calcd. C	Calcd. H	Found C	Found H
2,2-Dimethyl-1-pentanol	94	152.5–153	Atm.	1.4251	72.4	13.8	72.27	13.98
2-Ethyl-2-methyl-1-pentanol[a]	92	174–175	Atm.	1.4358	73.9	13.85	73.77	14.01
2,2,4-Trimethyl-1-pentanol[b]	88	166–166.5	Atm.	1.4300	...	...	...	...
2,4-Dimethyl-2-ethyl-1-pentanol	86	186–188	Atm.	1.4396	74.9	14.0	74.84	14.02
1-Propylcyclohexanemethanol	88	64–66	*ca.* 1	1.4732	76.9	12.8	76.83	12.91
1 Propylcyclopentanemethanol	90	80	7	1.4632	75.93	12.76	75.67	12.85
2-Propyl-2-norcamphanemethanol	91	88–92	2.5	1.4909	78.53	11.98	78.34	12.02
2,2-Dimethyl-1-heptanol[c]	93	191.5–192	Atm.	1.4336	74.93	13.97	75.06	13.93

[a] Reported by F. C. Whitmore and D. E. Badertscher, THIS JOURNAL, **55**, 1559 (1933), to have b.p. 75.5–76° (15 mm.), $n^{20}\mathrm{D}$ 1.4353. [b] Reported by M. A. Terentieff, *Bull. soc. chim. France,* [4] **37,** 1555 (1925), to have b.p. 164–167°, $n^{20}\mathrm{D}$ 1.4236. [c] Reported by F. C. Whitmore and D. E. Badertscher, THIS JOURNAL, **55,** 1559 (1933), to have b.p. 88–89° (15 mm.), $n^{20}\mathrm{D}$ 1.4339.

TABLE III

ACETALS USED

Acetal	Yield, %[b]	B.p. °C.	B.p. Press., mm.	$n^{20}\mathrm{D}$	Analyses, % Calcd. C	Calcd. H	Found C	Found H
Butyraldehyde diallyl	66	129	150	1.4300	70.6	10.6	70.69	10.40
Isobutyraldehyde diallyl[a]	72	174–176	730	1.4278	..	..	...	...
2-Methylbutyraldehyde diallyl	56	138–139	155	1.4328	71.7	10.9	71.51	10.64
2-Ethylhexanal diallyl	45	88–90	5	1.4413	74.3	11.6	74.36	11.93
Butyraldehyde dimethallyl	39	97	16	1.4371	72.7	11.1	72.71	11.19
Isobutyraldehyde dimethallyl	42	93	18	1.4360	72.7	11.1	72.68	11.20
2-Methylbutyraldehyde dimethallyl	43	58	1.5	1.4400	73.6	11.3	73.94	11.48

[a] Reported by R. Panradl, *Reichstoffe und Aromen,* **6,** 33 (1956), to have b.p. 51.5–52° (6 mm.), $n^{20}\mathrm{D}$ 1.4263. [b] In some cases based on only one experiment and, therefore, not necessarily optimum.

These readily accessible aldehydes provide a source of many new aliphatic compounds, such as alcohols of the neoalkyl type and their derivatives.

It is appropriate to describe here a few of the reactions of some of the 2,2-dialkyl-4-pentenals and their derivatives. The carbon–carbon double bonds of these compounds are readily reduced over palladium-on-alumina; the carbonyl groups are not reduced under moderate conditions. Indeed, fairly drastic conditions are required for the reduction to the saturated alcohols over Raney nickel. The properties of several alcohols of the neoalkyl type prepared by reduction of 2,2-dialkyl-4-pentenals are given in Table II.

As has been reported for pivalaldehyde,[9] 2,2-dimethyl-4-pentenal undergoes the Cannizzaro reaction to give fair yields of 2,2-dimethyl-4-penten-1-ol and 2,2-dimethyl-4-pentenoic acid.

Treatment of 2,2-dimethylvaleraldehyde (as its dimethyl acetal) with cold concentrated sulfuric

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(9) J. B. Conant, C. N. Webb and W. C. Mendum, THIS JOURNAL, **51**, 1246 (1929).

acid gave both rearrangement products,[10] 3-methyl-2-hexanone and 2-methyl-3-hexanone, resulting from migration of the methyl and propyl groups, respectively.

When 1-propylcyclohexanecarboxaldehyde was treated with cold concentrated sulfuric acid, the exclusive rearrangement product was 1-cyclohexyl-1-butanone. None of the ring-enlargement product, 2-propylcycloheptanone, was isolated.

Experimental[11]

Materials.—The acetals used were prepared by the usual method using calcium chloride. Their properties are listed in Table III.

Procedure A.—The following examples are representative. The temperatures, of course, may vary considerably when different acetals are used.

(a) **Allyl Vinyl Ether from Acetaldehyde Diallyl Acetal.**—Acetaldehyde diallyl acetal (168.5 g., 1.19 moles), was combined with 0.2 ml. of 85% phosphoric acid and distilled through a 1-ft. packed column into a receiver containing 2 g. of anhydrous potassium carbonate. Over a 1.5-hr. period 131 g. of distillate was collected at 66–95° while the temperature of the reaction mixture was 140–144°. The still residue weighed 34.5 g. The distillate was then redistilled from the potassium carbonate to give, after a small forerun, 53 g. of the allyl vinyl ether–allyl alcohol azeotrope,[6] b.p. 64–66°, n^{20}D 1.4115 (containing about 48 g. (48%) of allyl vinyl ether); 39 g. of allyl alcohol, b.p. 95–98°; and a residue of 34 g., which was largely acetaldehyde diallyl acetal.

(b) **2,2-Dimethyl-4-pentenal.**—Isobutyraldehyde diallyl acetal (389 g., 2.29 moles), was combined with 0.2 ml. of 85% phosphoric acid and distilled through a 1-ft. Vigreux column at a rate such as to maintain the head temperature in the range of 95–117°. Over a 2.5-hr. period 370 g. of distillate was collected while the temperature of the reaction mixture was in the 130–140° range. The distillate was washed three times with 500-ml. portions of water to remove the allyl alcohol, and the remaining organic phase was distilled to give, after a small forerun, 198 g. of 2,2-dimethyl-4-pentenal.

(c) **2-Ethyl-4-methyl-4-pentenal.**—Butyraldehyde dimethallyl acetal (386.8 g., 1.95 moles), was combined with 0.2 ml. of 85% phosphoric acid and distilled through a 1-ft. Vigreux column. Over a 3-hr. period 368 g. of distillate was collected at 113–160° while the temperature of the reaction mixture was 160–175°. Fractional distillation gave 144 g. of impure methallyl alcohol (theoretical, 141 g.), b.p. 112.5–114.5°, and 154.4 g. of 2-ethyl-4-methyl-4-pentenal. Treatment of a 10-ml. portion of the recovered methallyl alcohol with 2,4-dinitrophenylhydrazine reagent gave a small amount of the butyraldehyde derivative, m.p. 123°, indicating the possible presence of 1-butenyl methallyl ether.

Procedure B.—The following examples are representative.

(a) **2,2-Dimethyl-4-pentenal.**—A mixture of isobutyraldehyde (108 g., 1.5 moles), allyl alcohol (58 g., 1 mole), *p*-cymene (200 g.) and *p*-toluenesulfonic acid (0.25 g.) was heated under a 2-ft., packed, distillation column topped by a Dean–Stark trap for a period of 32 hr. During this time the temperature of the reaction mixture rose slowly from 83 to 140°, and 20.5 ml. of water layer (containing some allyl alcohol) was separated. Fractional distillation of the reaction mixture gave 22.1 g. of isobutyraldehyde, b.p. 62–64°; a 1.9-g. intermediate fraction; and 101 g. of 2,2-dimethyl-4-pentenal.

(b) **2-Allyl-2-ethyl-4-pentenal.**—A mixture of butyraldehyde (72 g., 1 mole), allyl alcohol (116 g., 2 moles), benzene (25 ml.) and *p*-toluenesulfonic acid (0.25 g.) was heated under a distillation column topped by a Dean–Stark trap for 24 hr. At the end of this time 19.5 ml. of water had separated. Diphenyl ether (200 g.) was added to the reaction mixture and heating was continued for 6 days, during which time the temperature of the reaction mixture rose from 132 to 156° and an additional 17.9 ml. of water layer separated. Distillation of the reaction mixture gave, after removal of benzene, a crude fraction, 73.7 g., b.p. 50–90° (4–5 mm.), which on redistillation gave 55 g. of 2-allyl-2-ethyl-4-pentenal.

Procedure C. 1-Allylcyclohexanecarboxaldehyde.—A mixture of cyclohexanecarboxaldehyde (448 g., 4 moles), allyl alcohol (242 g., 4.17 moles), benzene (60 ml.), and *p*-toluenesulfonic acid (0.5 g.) was heated under a 2-ft. packed, distillation column topped by a Dean–Stark trap for 22 hr. During this period the temperature in the flask rose from 114 to 158°, and 82 ml. of water layer separated. Distillation of the reaction mixture gave, after removal of benzene and a small forerun, 512 g. of 1-allylcyclohexanecarboxaldehyde and 56 g. of residue.

Hydrogenation of the Terminal Double Bond. (a) **1-Propylcyclohexanecarboxaldehyde.**—Hydrogenation of 1-allylcyclohexanecarboxaldehyde (152 g., 1 mole), was carried out in 100 ml. of benzene over 5 g. of 5% palladium-on-alumina at room temperature and 3 atm. An absorption of 0.99 mole was obtained in 18 hr. Most of the hydrogenation occurred in the first 3–4 hr. The catalyst was removed by filtration, and the filtrate was distilled to give, after removal of benzene, 132.5 g. (86%) of 1-propylcyclohexanecarboxaldehyde, b.p. 94–95.5° (20 mm.), n^{20}D 1.4559. The infrared spectrum showed no $>C{=}C<$ absorption.

Anal. Calcd. for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.64; H, 12.01.

The 2,4-dinitrophenylhydrazone melted at 182–182.5°.

Anal. Calcd. for $C_{16}H_{22}N_4O_4$: C, 57.47; H, 6.63. Found: C, 57.32; H, 6.76.

(b) **2,2-Dimethylvaleraldehyde.**—Hydrogenation of 2,2-dimethyl-4-pentenal (112 g., 1 mole), was carried out over 2.5 g. of 5% palladium-on-alumina at room temperature and 2 atm. An absorption of 1.0 mole of hydrogen was obtained after 12 hr. Distillation gave 101 g. (88.5%) of 2,2-dimethylvaleraldehyde, b.p. 126–127°, n^{20}D 1.4060. The infrared spectrum confirmed the absence of $>C{=}C<$.

Anal. Calcd. for $C_7H_{14}O$: C, 73.63; H, 12.36. Found: C, 73.51; H, 12.47.

The 2,4-dinitrophenylhydrazone melted at 117–117.5°. A mixture of this compound with the 2,2-dimethyl-4-pentenal derivative melted at 113–114°.

Anal. Calcd. for $C_{13}H_{18}N_4O_4$: C, 53.0; H, 6.13. Found: C, 53.12; H, 6.32.

Hydrogenation to Saturated Alcohols. 2,2-Dimethyl-1-pentanol.—2,2-Dimethyl-4-pentenal (181 g., 1.6 moles), in 150 ml. of methanol, was hydrogenated over 15 g. of Raney nickel at 125° and 100 atm. for 5 hr. The catalyst was removed by filtration, and the filtrate was distilled to give, after removal of methanol, 175 g. (94%) of 2,2-dimethyl-1-pentanol, b.p. 152.5–153°, n^{20}D 1.4251.

The alcohols described in Table II were all prepared from the aldehydes by hydrogenation over Raney nickel in methanol at 125 to 150° and 100 to 170 atm.

Canizzaro Reaction of 2,2-Dimethyl-4-pentanal.—The reaction was carried out as described for pivalaldehyde.[9] 2,2-Dimethyl-4-penten-1-ol, b.p. 151–152°, n^{20}D 1.4380, was obtained in 60% yield.

Anal. Calcd. for $C_7H_{14}O$: C, 73.6; H, 12.3. Found: C, 73.51; H, 12.45.

2,2-Dimethyl-4-pentenoic acid, b.p. 92–93° (8.5 mm.), n^{20}D 1.4338, was obtained in 41% yield.

Anal. Calcd. for $C_7H_{12}O_2$: C, 65.5; H, 9.44; neut. equiv., 128. Found: C, 65.72; H, 9.36; neut. equiv., 128.

Preparation and Rearrangement[10] of 2,2-Dimethylvaleraldehyde Dimethyl Acetal.—The dimethyl acetal of 2,2-dimethyl-4-pentenal, b.p. 162–163.5°, n^{20}D 1.4259, was prepared in 58% yield in the usual manner from the aldehyde, methanol and calcium chloride.

Anal. Calcd. for $C_9H_{18}O_2$: C, 68.3; H, 11.4. Found: C, 68.45; H, 11.51.

Hydrogenation of 2,2-dimethyl-4-pentenal dimethyl acetal (248 g., 1.57 moles), over 15 g. of Raney nickel at 75° and 70 atm. gave 230 g. (92%) of 2,2-dimethylvaleraldehyde dimethyl acetal, b.p. 163.5–164.5°, n^{20}D 1.4165.

Anal. Calcd. for $C_9H_{20}O_2$: C, 67.5; H, 12.5. Found: C, 67.23; H, 12.54.

To a stirred mixture of 300 ml. of benzene and 300 ml. of concentrated sulfuric acid at 5° was added 80 g. (0.5 mole) of 2,2-dimethylvaleraldehyde dimethyl acetal over a 10-min.

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[10] S. Danilov and E. Venus-Danilova, *Ber.*, **59**, 377 (1926).

[11] Boiling points and melting points are uncorrected. The latter were determined using a Fisher–Johns melting-point apparatus.

period. Stirring was continued for 30 min. at 5°, and the reaction mixture was poured onto 1 l. of crushed ice. The mixture was extracted with ether, and the combined extracts were dried over potassium carbonate. Distillation gave, after removal of ether and benzene and a small forerun, 36.3 g. (64%) of a mixture of two ketones, b.p. 136–137°, $n^{20}\text{D}$ 1.4060. The two components were shown by gas chromatography to be present in about a 3:2 ratio. The two expected rearrangement products are 3-methyl-2-hexanone and 2-methyl-3-hexanone, and the former should predominate.

Anal. Calcd. for $C_7H_{14}O$: C, 73.8; H, 12.3. Found: C, 73.78; H, 12.33.

Rearrangement of 1-Propylcyclohexanecarboxaldehyde.—1-Propylcyclohexanecarboxaldehyde (102 g., 0.66 mole), was added over a 10-min. period to a stirred mixture of 300 ml. of benzene and 300 ml. of concentrated sulfuric acid at 5–10°. Stirring was continued for 30 min. at 5–6°, and the mixture was poured onto cracked ice and treated as in the preceding example. The sole ketonic product was 58.5 g (57%) of 1-cyclohexyl-1-butanone, b.p. 92.5–93.5° (13.5 mm.), $n^{20}\text{D}$ 1.4532, which was shown by gas chromatography to be homogeneous. The product gave a 2,4-dinitrophenylhydrazone, m.p. 114.5–115.5°, and a semicarbazone, m.p. 154–155°. Reported[12] values are: for 1-cyclohexyl-1-butanone, b.p. 79° (6 mm.), $n^{20}\text{D}$ 1.4531; 2,4-dinitrophenylhydrazone, m.p. 114°; semicarbazone, m.p. 155°.

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Methylene, CH_2. Stereospecific Reaction with *cis*- and *trans*-2-Butene

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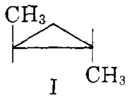
Methylene from the photolysis of diazomethane exhibits stereospecific addition to the 2-butenes both in the formation of the 1,2-dimethylcyclopropanes and the 2-pentenes. Not only do these facts help confirm the existence of methylene as an intermediate species, but they also show that photolytically-produced methylene exists in a singlet, rather than a triplet, state both in the gas phase and in solution.

Introduction

Much work appearing in recent literature attests to the existence of intermediate reactive species, called carbenes or methylenes, consisting of carbon atoms with two singly covalently-bonded substituents and two non-bonded electrons.[2] The electrophilic, non-free radical character of some carbenes has been established by relative rate[3–5] and stereospecificity[2c,6–9] studies of their additions to various olefins. These additions appear to be of the three-center, rather than free-radical, type.[4] As a consequence of these findings and the fact that reactions involving a change in multiplicity are slow,[10] the two non-bonded electrons of a carbene must be in a singlet state at the time of the addition to the two paired π-electrons of the olefin. The quantum state of the carbene molecule at the point of its creation remained open to question, however. If the carbene was in a triplet state when created, the inhomogeneous magnetic field provided by high-atomic weight covalently-bonded substituents, such as halogens, could have catalyzed the interconversion of the triplet to a singlet state.[11,12]

Therefore, we have studied the addition of methylene itself to the 2-butenes, feeling that the presence of two hydrogen atoms, rather than larger substituents, would minimize the possibilities of interconversion. Our major criterion is the stereospecificity of addition or its lack, the former indicating a three-center addition and thereby a singlet state for the carbene.[2c,9] The stereospecific addition of methylene would thus yield *trans*-1,2-dimethylcyclopropane (I) from *trans*-2-butene, and *cis*-1,2-dimethylcyclopropane (II) from *cis*-2-butene. This type of system provides then a unique contradiction to the generally acceptable principle that knowledge of the structure of reaction products is a poor guide for distinguishing between structures which differ in electron arrangement.



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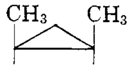

II

A preliminary report concerning this work[2c] has been criticized by Kistiakowsky and Sauer on the basis that we had not considered the efficiency of this reaction.[13] A low relative efficiency would make interconversion of a triplet to a singlet state

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[1] National Science Foundation pre-doctoral fellow. This manuscript is taken from a portion of Robert C. Woodworth's thesis for the Ph.D. degree, August, 1956.

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