

[CONTRIBUTION FROM THE LEWIS FLIGHT PROPULSION LABORATORY OF THE NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS]

## Dicyclic Hydrocarbons. I. 2-Akylbiphenyls

BY IRVING A. GOODMAN AND PAUL H. WISE

As part of a program being conducted at this laboratory, involving the investigation of possible components of aviation fuel, a series of five 2-substituted alkylbiphenyls has been synthesized and purified. This series consists of biphenyl compounds substituted in the 2-position by the following radicals: methyl, ethyl, propyl, isopropyl and butyl. The latter three members of the series are being reported for the first time.

The synthesis of 2-methylbiphenyl by several different methods has been reported,<sup>1</sup> but only one of these appeared to give a relatively pure product in appreciable yield. The method of Sherwood, Short and Stansfield,<sup>1c</sup> involving the reaction between *o*-tolylmagnesium bromide and cyclohexanone, followed by dehydration of the carbinol and dehydrogenation of the olefin, gave over-all reported yields of 30–50%. Orchin,<sup>2</sup> using the same method, reported increased yields of carbinol with increase in reflux time of the Grignard reaction mixture.

Orchin<sup>3</sup> reports the synthesis of 2-ethylbiphenyl in 25% over-all yield from ethylmagnesium bromide and 2-phenylcyclohexanone followed by dehydration of the carbinol and dehydrogenation of the resulting olefin. Huber, *et al.*,<sup>4</sup> have prepared it in 77% over-all yield from 2-biphenylmagnesium iodide and acetaldehyde followed by hydrogenolysis of the resulting carbinol.

Because of the ready availability of 2-amino-

biphenyl, from which 2-iodobiphenyl may be synthesized in good yields, and because the latter compound could be conveniently used as a starting material for all of the proposed syntheses with the exception of 2-methylbiphenyl, the method of Huber, *et al.*,<sup>4</sup> with certain modifications, was selected as a general one for the series. A Grignard reaction involving 2-iodobiphenyl invariably yields appreciable quantities of biphenyl, which cannot be adequately separated from 2-methylbiphenyl because of the very close proximity of their boiling points. Consequently the method of Sherwood, Short and Stansfield<sup>1c</sup> was used for the synthesis of 2-methylbiphenyl, with modifications in the dehydration and dehydrogenation steps. The intermediate carbinols were purified in those cases where the compounds were solids at room temperature, but no attempt was made to separate the *cis* and *trans* isomers of the olefins that were obtained as intermediates in this investigation. Direct hydrogenolysis of the carbinols to the corresponding hydrocarbons reported by Huber, *et al.*,<sup>4</sup> could not be duplicated by the present investigators. The alternate procedure of dehydration of the carbinol and hydrogenation of the olefin was used. Because of the thermal instability of 2-vinylbiphenyl, the 2-ethyl derivative was prepared by direct alkylation of the Grignard reagent using diethyl sulfate as the alkylating agent.

It was found that 2-butylbiphenyl could be crystallized in either of two modifications, having melting points about 4° apart. The conditions required for obtaining one or the other modification were not ascertained. The time-temperature melting curve, shown in Fig. 1, was obtained by first determining the curve for the lower-melting sample, then seeding this sample, after melting, with a crystal of the higher-melting modification, thus obtaining two distinct melting plateaus for the same material.

The alkylbiphenyls reported have all been prepared in approximately 500 ml. quantities having a purity of 99–100 mole %, as evidenced by time-temperature melting curves that were determined by methods described by Rossini and co-workers.<sup>5</sup> Final purification of each hydrocarbon consisted generally of fractional distillation through 6 ft. glass columns, packed with 3/16" glass helices, at reduced pressures (15–20 mm.). If this failed to produce the required purity, distillations were conducted in 6-foot Podbielniak columns at reduced pressures.

The physical constants listed in Table I were

(5) Glasgow, Krouskop, Beadle, Axilrod and Rossini, *Anal. Chem.*, **20**, 410 (1948).

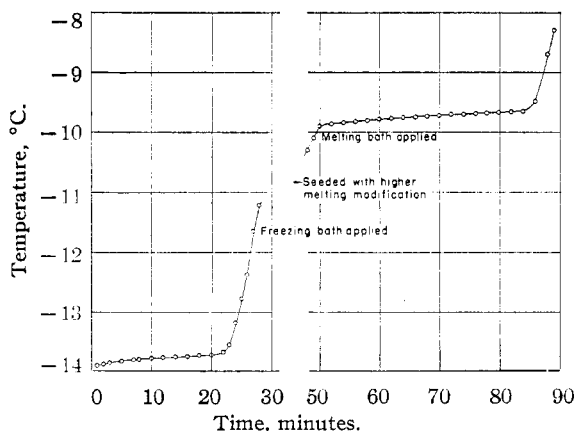


Fig. 1.—Time-temperature melting curves for two crystal-line modifications of 2-butylbiphenyl.

(1) (a) Oddo and Curatolo, *Gazz. chim. ital.*, **251**, 132 (1895); (b) Bamberger, *Ber.*, **30**, 369 (1897); (c) Lehmann and Pasche, *ibid.*, **68**, 1146 (1935); (d) Gomberg and Pernert, *This Journal*, **48**, 1372 (1926); (e) Sherwood, Short and Stansfield, *J. Chem. Soc.*, 1832 (1932).

(2) Orchin, *This Journal*, **67**, 499 (1945).

(3) Orchin, *ibid.*, **68**, 571 (1946).

(4) Huber, Renoll, Rossow and Mowry, *ibid.*, **68**, 1109 (1946).

TABLE I  
 PHYSICAL PROPERTIES OF 2-ALKYLBIPHENYLS

Hydrocarbon	M. p., °C.	B. p. °C. at 760 mm.	$n_D^{20}$	$d_4^{20}$ , g./ml.	$\Delta H_f$ , kcal./ mole	Esti- mated purity, mole %	Heat of comb., <sup>a</sup> kcal./mole	Calcd.	Analyses, % Carbon Found	Hydrogen Calcd.	Found
2-Methylbiphenyl	— 0.20	255.30	1.5914	1.01134	3.13	99.3	1600	92.81	92.82	7.19	7.08
2-Ethylbiphenyl	— 6.13	265.97	1.5805	.99671	3.89	99.9	1740	92.26	92.32	7.74	7.57
2-Propylbiphenyl	— 11.26	277.22	1.5696	.98018	4.86	99.8	1885	91.78	91.63	8.22	8.18
2-Isopropylbiphenyl	24.46	269.77	1.5703	.98227	..	99.9 <sup>b</sup>	1885	91.78	91.73	8.22	8.17
2-Butylbiphenyl	— 9.65 — 13.71	291.20	1.5604	.96763	5.47 <sup>c</sup>	99.1	2030	91.37	91.40	8.63	8.51

<sup>a</sup> ASTM procedure: D240-39. <sup>b</sup> Since only the order of magnitude of  $\Delta H_f$  is significant in this calculation, an average value of 4.0 kcal./mole was used in computing this purity. <sup>c</sup> This value was determined for the lower-melting modification.

determined as follows: The melting points were obtained from the melting curves by use of the graphical method described by Taylor and Rossini.<sup>6</sup> The densities were determined by the method of Forziati, *et al.*,<sup>7</sup> employing a specific gravity balance, and the boiling points were determined by use of a platinum resistance thermometer in an apparatus similar to that described by Quiggle, *et al.*,<sup>8</sup> except that the system was pressurized with dry air from a surge tank and held constant by adjusting a continuous bleed. The refractive indices were determined in a Bausch and Lomb precision oil model refractometer, and the standard ASTM procedure, designated in Table I, was followed in the determination of heats of combustion. The heats of fusion were obtained by use of a method and apparatus similar to that described by Rossini.<sup>9</sup> Since the method is not applicable to hydrocarbons melting near room temperature, no data were obtained for 2-isopropylbiphenyl. The estimated mole % purities, determined according to methods described by Taylor and Rossini,<sup>6</sup> are also included.

**Acknowledgment.**—The authors wish to express their appreciation to Mr. J. F. Thompson for the determination of the physical constants, and to members of the Analytical Chemistry Section for the carbon-hydrogen analyses and the determination of heats of combustion.

### Experimental

**1-(2-Tolyl)-1-cyclohexanol.**—In a 30-gallon glass-lined reactor 6870 g. (40.2 moles) of *o*-bromotoluene reacted with 990 g. (40.7 g. atoms) of magnesium turnings in 38 liters of absolute ether. To the solution of the *o*-tolylmagnesium bromide was gradually added 20 liters of an ether solution of 4000 g. (40.8 moles) of cyclohexanone. The reaction mixture was refluxed overnight with stirring and then hydrolyzed with 40 liters of a saturated aqueous ammonium chloride solution. The ether layer was siphoned from the sludge and washed twice with 40-liter portions of water, then concentrated on the steam-bath. Because of its tendency to dehydrate readily, the carbinol was not fractionated but merely distilled fairly rapidly at low pressure. The bulk of the material boiled at 117–119° at 2 mm. and weighed 4605 g. (54% yield).

(6) Taylor and Rossini, *J. Res. Natl. Bur. Standards*, **32**, 197 (1944).

(7) Forziati, Mair and Rossini, *ibid.*, **35**, 513 (1945).

(8) Quiggle, Tongberg and Penske, *Ind. Eng. Chem., Anal. Ed.*, **6**, 466 (1934).

(9) Rossini, *J. Res. Natl. Bur. Standards*, **11**, 553 (1933).

**1-(2-Tolyl)-1-cyclohexene.**—A solution of 4140 g. (21.8 moles) of 1-(2-tolyl)-cyclohexanol-1 in an equal volume of toluene was passed slowly through an alumina-packed tower at 250–275°. After the aqueous layer (385 g.) was separated from the condensate, the toluene was distilled and the residue vacuum distilled to give 3520 grams (94%) of olefin boiling at 75° at 1 mm. The distillate was fractionated, the bulk of the material boiling at 127.5° at 20 mm.,  $n_D^{20}$  1.5438.

**2-Methylbiphenyl.**—A solution of 1315 g. (7.6 moles) of 1-(2-tolyl)-1-cyclohexene in 2.5 liters of toluene was passed three times through a tower packed with chromia-alumina catalyst and maintained at a temperature of 450–475°. The time for each pass was about two hours. Too rapid a rate of addition resulted in insufficient dehydrogenation, while a slow addition rate caused the formation of large amounts of fluorene, through cyclodehydrogenation. After the toluene was removed, the residue was distilled at reduced pressure to give 1030 g. (80%) of crude hydrocarbon. The refractive index,  $n_D^{20}$ , of the various cuts ranged from 1.585 to 1.591. Several careful fractionations, the final one through a Podbielniak column, were required in order to obtain material of the desired purity, with the physical properties listed in Table I. The yield of this pure material was approximately 32%.

**2-Iodobiphenyl.**—This reagent was prepared essentially according to a procedure described by Gilman, Kirby and Kinney<sup>10</sup> except that the reaction was carried out on a much larger scale. Several 15-mole runs were conducted in a 30-gallon glass-lined reactor, and one 67-mole reaction was carried out in a 100-gallon glass-lined reactor. The crude product was washed with dilute caustic solution, dried, distilled, and fractionated at reduced pressure. Yields of 63–77% were obtained: b. p. 176.5° at 21 mm.,  $n_D^{20}$  1.6615.

**2-Ethylbiphenyl.**—In a typical Grignard reaction 11,200 g. (40 moles) of 2-iodobiphenyl reacted with 973 g. (40 g. atoms) of magnesium turnings in 38 liters of dry ether in a 30-gallon glass-lined reactor. To this solution of 2-biphenylmagnesium iodide there was added 20 liters of an ether solution containing 12,340 g. (80 moles) of diethyl sulfate. The reaction mixture was refluxed three hours with stirring after the addition was completed and then hydrolyzed with 20 liters of a 10% hydrochloric acid solution. The ether solution was washed once with 20 liters of dilute sodium bicarbonate solution and twice with equal volumes of water, and the ether was stripped off. The residue was transferred to a stainless steel reactor and refluxed five hours with 20 liters of 10% sodium hydroxide in 50% ethanol to destroy the excess diethyl sulfate. The product was separated by diluting the mixture with water and then washed twice and stripped under reduced pressure. By chilling the distillate, biphenyl was crystallized out and 1360 g. was removed by filtering the chilled mixture. The filtrate was fractionated in a high-efficiency vacuum column, and an additional 1150 g. of biphenyl was separated in the initial fractions. This represents a 40% yield of biphenyl. By continuing the distillation 3056 g. (42%) of pure 2-ethylbiphenyl was isolated.

(10) Gilman, Kirby and Kinney, *Tex. Journal*, **51**, 2860 (1929).

**Ethyl-(2-biphenyl)-carbinol.**—The Grignard reagent, 2-biphenylmagnesium iodide, was prepared by adding 5040 g. (18 moles) of 2-iodobiphenyl in absolute ether to 440 g. (18 g. atoms) of magnesium in a 10-gallon glass-lined reactor. The total volume of ether used was 7 liters. To this solution there was added 1160 g. (20 moles) of propionaldehyde in 7 liters of absolute ether. The complex was hydrolyzed with 10 liters of dilute hydrochloric acid (1.5 liters concentrated hydrochloric acid), and the aqueous layer was drawn from the reactor. The ether layer was washed with 10 liters of dilute sodium bicarbonate and then with an equal volume of water, and the ether was evaporated on a steam-bath. The carbinol crystallized out and was recrystallized from neohexane to give 2000 g. (52%) of nearly colorless crystals. Concentration of the mother liquors and distillation of the residue gave 250 g. of biphenyl and 700 g. of a higher-boiling liquid which was presumed to be a mixture of carbinol and olefin. A sample of the carbinol recrystallized for analysis melted at 65.1–65.3°.

*Anal.* Calcd. for  $C_{15}H_{16}O$ : C, 84.86; H, 7.60. Found: C, 84.87; H, 7.62.

**1-(2-Biphenyl)-1-propene.**—A solution of 2000 g. (9.4 moles) of ethyl-(2-biphenyl)-carbinol in 4 liters of toluene was passed slowly through an alumina-packed tower at 275–325°. After removing the aqueous layer from the condensate, the toluene was distilled, and the residue was vacuum distilled to give 1520 g. (83%) of olefin, b. p. 166° at 23 mm. [No attempt was made to separate the geometrical isomers, but the olefin was fractionated, and one refractive index plateau,  $n_D^{20}$  1.6148, b. p. 158° at 15 mm. was observed at the end of the distillation.]

**Ozonization of 1-(2-Biphenyl)-1-propene.**—A sample of the olefin was dissolved in absolute alcohol and converted to the ozonide in an ozonizer of the Henne-Perilstein<sup>11</sup> type. The ozonide solution was hydrogenated as described in the same reference to give the carbonyl compounds. After reduction was completed, the products were fractionated. The lower-boiling portion gave a 2,4-dinitrophenylhydrazone melting at 164–165° after one recrystallization. A sample mixed with an authentic sample of the 2,4-dinitrophenylhydrazone of acetaldehyde melted at 164–166°. The higher-boiling fragment formed an oxime, m. p. 116–117°. *Anal.* Calcd. for  $C_{15}H_{11}NO$ : N, 7.10. Found: N, 7.04, 7.18. The melting point of the oxime of 2-phenylbenzaldehyde is reported<sup>12</sup> to be 115°. This aldehyde also gave a semicarbazone, m. p. 210–212°. *Anal.* Calcd. for  $C_{14}H_{13}N_3O$ : N, 17.56. Found: N, 17.54, 17.50. This establishes the position of the double bond, and the compound is proved to be 1-(2-biphenyl)-1-propene.

**2-Propylbiphenyl.**—A solution made of 685 g. (3.52 moles) of 1-(2-biphenyl)-1-propene in one liter of absolute alcohol was mixed with 85 g. of UOP nickel catalyst and hydrogenated at 75° and an initial pressure of 1500 p. s. i. After removal of the catalyst and solvent, the hydrocarbon was distilled to give an essentially quantitative yield of crude material which was then fractionated carefully in a high efficiency column at 20 mm. to yield 592 g. (86%) of pure hydrocarbon.

**Dimethyl-(2-biphenyl)-carbinol.**—This carbinol was prepared essentially according to a procedure previously described by Bradsher and Amore<sup>13</sup> and Mowry, *et al.*,<sup>14</sup> except that the reaction was carried out on an 18-mole scale in a 10-gallon glass-lined reactor. The crude carbinol was recrystallized from neohexane. A yield of 57% of pure carbinol was obtained. A sample of the carbinol, recrystallized three times for analysis, melted at 72.0–72.5°.

*Anal.* Calcd. for  $C_{15}H_{16}O$ : C, 84.86; H, 7.60. Found: C, 84.66; H, 7.64.

**2-(2-Biphenyl)-1-propene.**—A solution of 1500 g. (7.1 moles) of dimethyl-(2-biphenyl)-carbinol in 2 liters of toluene was dehydrated as described above for the 1-(2-biphenyl)-1-propene and essentially as reported by Mowry, *et al.*<sup>12</sup> The crude product was fractionated at reduced pressure to give 1180 g. (86%) of olefin, b. p. 149° at 20 mm.,  $n_D^{20}$  1.5942. None of the fractions could be induced to crystallize.

**2-Isopropylbiphenyl.**—A solution of 800 g. (4.1 moles) of 2-(2-biphenyl)-1-propene in one liter of absolute alcohol was mixed with 80 g. of UOP nickel catalyst and hydrogenated at 100° and an initial pressure of 1500 p. s. i. After the catalyst was filtered and the solvent distilled, the hydrocarbon was distilled to give essentially quantitative yields of crude product, which was fractionated at reduced pressure. Three fractionations, the final one in a 6-foot Podbielniak column, were required to obtain the desired purity in approximately 43% yield.

**1-(2-Biphenyl)-1-butene.**—The Grignard reagent, 2-biphenylmagnesium iodide was prepared, as described above, from 5040 g. (18 moles) of 2-iodobiphenyl; 440 g. (18 gram atoms) of magnesium and a total of 7 liters of absolute ether, in a 10-gallon glass-lined reactor. To this solution was gradually added a solution of 1440 g. (20 moles) of *n*-butyraldehyde (tech. grade, fractionated and dried) in 7 liters of absolute ether. The reaction mixture was refluxed and stirred overnight, then hydrolyzed with 4 liters of saturated aqueous ammonium chloride solution. The clear ether solution was siphoned off, the remaining sludge was extracted with an additional 4 liters of ether, and the combined ether extracts were concentrated on the steam-bath. No crystallization occurred even after standing for several days. The residue was therefore distilled at reduced pressure. Partial dehydration occurred, and a total of 2650 g. of crude olefin-carbinol mixture was collected as a yellow viscous liquid. A solution of this mixture in 4 liters of toluene was passed slowly through an alumina-packed tower at 300°. After the aqueous layer was separated, the toluene was distilled and the residue distilled at reduced pressure, giving 2520 g. (46% over-all) of olefin,  $n_D^{20}$  1.6008, b. p. 148–150° at 10 mm. This was fractionated and showed two b. p. plateaus at 167 and 172° at 18 mm., but the separation was not sharp. All of the fractions showed a positive Beilstein test for halogen.

**Ozonization of 1-(2-Biphenyl)-1-butene.**—A sample of the olefin was ozonized as described above for 1-(2-biphenyl)-1-propene. The low-boiling portion of the products gave a 2,4-dinitrophenylhydrazone melting at 151.5–153.5° after two crystallizations. A sample mixed with an authentic sample prepared from propionaldehyde melted at 151–154°. The higher-boiling fragment formed an oxime melting at 116.5–118° after one recrystallization and showed no depression when mixed with a corresponding sample obtained from the ozonization of 1-(2-biphenyl)-1-propene. This establishes the position of the double bond, and the compound is proved to be 1-(2-biphenyl)-1-butene.

**2-Butylbiphenyl.**—A solution of 1650 g. (7.9 moles) of 1-(2-biphenyl)-1-butene in a small quantity of absolute alcohol was mixed with 300 g. of UOP nickel catalyst. The relatively large amount of catalyst was required because of the halogen impurity present. The olefin was hydrogenated in a 3-liter bomb at 90° and an initial hydrogen pressure of 1650 p. s. i. over a period of 20 hours. After removal of catalyst and solvent, the hydrocarbon was distilled at reduced pressure, yielding 1540 g. (92%) of crude hydrocarbon. This was carefully fractionated in a high efficiency column at 20 mm.

## Summary

1. The physical constants of five pure 2-substituted alkylbiphenyls, together with a description of the preparative method for each, have been presented. The synthesis, purification, and

(11) Henne and Perilstein, *THIS JOURNAL*, **65**, 2183 (1943).

(12) Fanto, *Monatsh.*, **19**, 588 (1898).

(13) Bradsher and Amore, *THIS JOURNAL*, **65**, 2017 (1943).

(14) Mowry, *et al.*, *ibid.*, **70**, 1917 (1948).

physical constants of all but the 2-methyl and 2-ethyl derivatives have been described for the first time.

2. 2-Butylbiphenyl has been shown to exist in two distinct crystalline modifications.

CLEVELAND, OHIO

RECEIVED DECEMBER 3, 1949

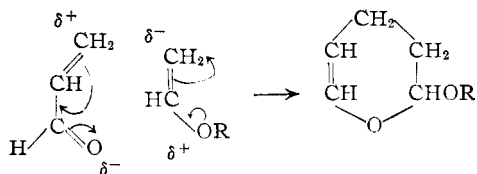
[CONTRIBUTION FROM THE CENTRAL RESEARCH DEPARTMENT, MONSANTO CHEMICAL CO.]

## The 1,4-Addition of Vinyl Ethers to $\alpha,\beta$ -Unsaturated Carbonyl Compounds

BY RAYMOND I. LONGLEY, JR., AND WILLIAM S. EMERSON

The dimerization of  $\alpha,\beta$ -unsaturated carbonyl compounds such as acrolein, crotonaldehyde, methyl vinyl ketone and phenyl vinyl ketone is well known.<sup>1</sup> Acrolein adds acrylonitrile and methyl acrylate to the 1,4-conjugated system to give 2-cyano-3,4-dihydro-1,2-pyran and 2-carbomethoxy-3,4-dihydro-1,2-pyran, respectively.<sup>2</sup>

We have found that  $\alpha,\beta$ -unsaturated carbonyl compounds add vinyl ethers even more readily than they dimerize.<sup>3</sup> This is not surprising in view of the polarization of the molecules.



Acrolein, crotonaldehyde, methacrolein, cinnamaldehyde,  $\beta$ -furylacrolein, methyl vinyl ketone, benzalacetone and benzalacetophenone have been found to undergo this addition. Methyl vinyl ether, ethyl vinyl ether, *n*-butyl vinyl ether, ethyl isopropenyl ether and *n*-butyl cyclohexenyl ether served as dienophiles. Fourteen 2-alkoxy-3,4-dihydro-1,2-pyrans have been synthesized in this manner in yields of 25–87% as shown in Table I.

In these additions ethyl vinyl ether gave higher yields than methyl vinyl ether. Crotonaldehyde was appreciably less reactive than acrolein, since it required a 50° higher temperature for comparable yields. Methacrolein gave lower yields than most of the other  $\alpha,\beta$ -unsaturated carbonyl compounds, since it dimerized far more readily.

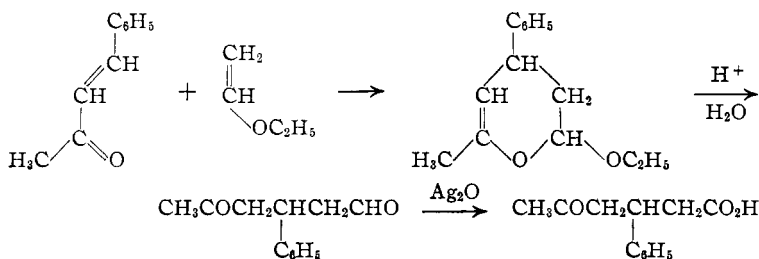
In order to ascertain the structures of these products, 2-ethoxy-3,4-dihydro-1,2-pyran was hydrolyzed with dilute hydrochloric acid to glutaraldehyde, which was identified as its *p*-nitrophenylhydrazone. 2-Methoxy-4-methyl-3,4-dihydro-1,2-pyran and 2-methoxy-5-methyl-3,4-

dihydro-1,2-pyran were hydrolyzed similarly and the resulting substituted glutaraldehydes were oxidized without isolation to the known 3-methyl- and 2-methylglutaric acids, respectively. 2-Ethoxy-6-methyl-4-phenyl-3,4-dihydro-1,2-pyran was hydrolyzed to 5-oxo-3-phenylhexanal. Oxidation yielded the known 5-oxo-3-phenylcaproic acid.

The authors are grateful to Dr. George F. Deebel and Mr. Richard Anderson for the preparation of the ethyl isopropenyl ether.

### Experimental

**Starting Materials.**—Acrolein and methacrolein were obtained from the Shell Chemical Co. Crotonaldehyde, benzalacetone, benzalacetophenone and cinnamaldehyde were Eastman Kodak Co. "pure" products, whereas furylacrolein and methyl vinyl ketone were the "practical" grade redistilled. Methyl vinyl ether was obtained from both the Matheson Co. and Carbide and Carbon Chemicals Corp. Ethyl vinyl ether and *n*-butyl vinyl ether came from the General Aniline and Film Co. Ethyl isopropenyl ether was prepared as described in the literature.<sup>4</sup> *n*-Butyl cyclohexenyl ether was prepared by boiling under reflux a benzene solution of cyclohexanone and excess butanol in the presence of *p*-toluenesulfonic acid, while



the evolved water was collected in a Dean and Stark trap. The pure ether boiled at 90–91° (17 mm.), (80–81° (10 mm.)),  $n_D^{25}$  1.4577.

**Condensations.**—All of the condensations were effected by heating the  $\alpha,\beta$ -unsaturated carbonyl compound and the vinyl ether in a bomb in the presence of 0.10–1.00% of hydroquinone. The conditions and yields obtained are summarized in Table I. The properties of the various 2-alkoxy-3,4-dihydro-1,2-pyrans are summarized in Table II.

**Glutaraldehyde** was prepared essentially by the method of Woods and Sanders.<sup>5</sup> A mixture of 300 cc. of water, 25 cc. of concentrated hydrochloric acid and 120 g. of 2-ethoxy-3,4-dihydro-1,2-pyran was stirred for twenty-two minutes, during which time the temperature rose to 38° and the mixture became clear. After standing one and one-

(4) Dolliver, Gresham, Kistiakowsky, Smith and Vaughan, *THIS JOURNAL*, **60**, 440 (1938).

(5) Johannissian and Akumian, *Bull. Univ. Etat. R. S. S. Arménie*, No. 5, 245 (1930); *Chem. Zentr.*, **101**, II, 552 (1930).

(6) Woods and Sanders, *THIS JOURNAL*, **68**, 2111 (1946).

(1) See particularly Alder, Offermanns and Rüden, *Ber.*, **74**, 905, 926 (1941), and Alder and Rüden, *ibid.*, **74**, 920 (1941).

(2) Anzilotti, Fiat Final Report No. 1157, PB 85174, U. S. Department of Commerce, January 21, 1948.

(3) Since this paper was submitted, a paper on the same subject by Smith, Norton and Ballard was presented at the Philadelphia Meeting of the American Chemical Society, Division of Organic Chemistry, April 9, 1950.