Anal. Calcd. for $C_{37}H_{42}N_2O_4$: C, 76.78; H, 7.32; N, 4.84. Found: C, 76.51; H, 7.36; N, 4.94.

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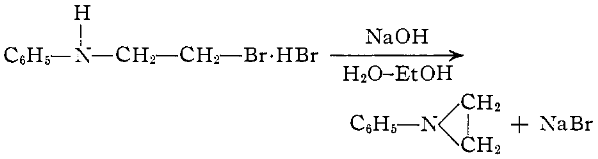
The Synthesis and Polymerization of N-Phenylethylenimine and the Synthesis of N,N'-Diphenylpiperazine

BY HAROLD W. HEINE, BRIJ L. KAPUR AND CLAIR S. MITCH

RECEIVED AUGUST 31, 1953

In the course of studies on the chemistry of ethylenimine we had occasion to synthesize N-phenylethylenimine. This compound was prepared from N-β-bromoethylaniline hydrobromide by a slight modification of the general method of Gabriel,[1] *e.g.*



Although N-phenylethylenimine is formed with considerable readiness and in 68% yield under these conditions the course of the reaction may be so altered that N,N'-diphenylpiperazine is formed as the main reaction product.

The structure of N-phenylethylenimine was established by elementary analysis and by its reaction with hydrobromic acid to form N-β-bromoethylaniline hydrobromide. An infrared analysis showed the absence of any N–H fundamental in the region of 2.9 μ, which is in accord with expectations.

N-Phenylethylenimine rapidly polymerized to a colorless solid when it was emulsified with water or was exposed to air. Polymerization also took place when N-phenylethylenimine was dissolved in methanol or ethanol and exposed to air but at a much slower rate than in water. Nitrogen analysis of the polymer gave a value corresponding to the monomer. Most likely a chain polymer was produced. The polymer was soluble in 90% formic acid and decomposed at 270–275°.

Experimental

N-Phenylethylenimine.—A solution of 115 ml. of 6 *N* sodium hydroxide and 300 ml. of 95% ethanol was placed in a one-liter three-necked flask equipped with a stirrer, condenser and dropping funnel, and the flask immersed in a water-bath held at 50°. To this was added dropwise and with stirring 84.3 g. of N-β-bromoethylaniline hydrobromide[2] dissolved in 120 ml. of water and 80 ml. of 95% ethanol. After the addition was completed the water-bath was raised to 85° for one hour. The condenser was then arranged for downward distillation and 220 ml. of ethanol was removed by distillation. The residue was cooled to room temperature and extracted with six 50-ml. portions of ether. The ethereal solution was dried over sodium sulfate, filtered and distilled until the temperature reached 82°. The residue separated into two layers at this point. The lower layer consisted of water and ethanol. The top layer was removed by means of a suction pipet, dried with sodium sulfate and subjected to vacuum distillation. A fraction of 24.3 g. (68%) boiling at 70–70.5° at 13 mm. or 60.5–61° at 9 mm. was obtained; $n^{25}\text{D}$ 1.5498, $n^{20}\text{D}$ 1.5524.

Anal. Calcd. for C_8H_9N: C, 80.5; H, 7.6; N, 11.8. Found[3]: C, 80.5; H, 7.7; N, 11.8.

The N-phenylethylenimine was converted into N-β-bromoethylaniline hydrobromide by the following procedure: 2.2 g. of N-phenylethylenimine was added quickly to 60 ml. of cold 48% hydrobromic acid. The reaction mixture was refluxed gently for one-half hour and then distilled until 50 ml. of distillate was collected. The residue was cooled in a vacuum desiccator. The crude N-β-bromoethylaniline hydrobromide crystallized on standing. Recrystallization from absolute ethanol gave a 65% yield of pure N-β-bromoethylaniline hydrobromide melting at 138–139°. A mixture of this substance with authentic N-β-bromoethylaniline hydrobromide melted at 137–140°.

Poly-N-phenylethylenimine.—Two grams of N-phenylethylenimine was shaken with 25 ml. of water. The emulsion rapidly became milky-white and a precipitate formed within an hour. This material was filtered and dried; yield 1.94 g. The polymer turned brown at 230° and gradually shriveled and melted completely at 270–275°.

Anal. Calcd. for $(C_8H_9N)_n$: N, 11.8. Found: N, 11.6.

N,N'-Diphenylpiperazine.—To 17.6 g. of N-β-bromoethylaniline hydrobromide was added a solution containing 6 g. of NaOH in 10 ml. of water. Two layers formed. Twenty ml. of water was added and the mixture heated in a water-bath at 85° for two hours. The oily layer solidified, was filtered and dried. The product was recrystallized from methanol yielding 5.0 g. (67%) of white crystals melting at 163–164°. The literature value for N,N'-diphenylpiperazine is 164°.[4]

Acknowledgment.—We wish to thank Dr. Nelson R. Trenner of the Merck Laboratories, Rahway, N. J., for the infrared analysis.

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(1) S. Gabriel, *Ber.*, **21**, 1049 (1888); S. Gabriel and R. Stelzner, *ibid.*, **28**, 2929 (1895).

(2) W. J. Pearlman, THIS JOURNAL, **70**, 871 (1948).

(3) Analyses performed by Clark Microanalytical Laboratory, Urbana, Ill.

(4) D. S. Pratt and C. O. Young, THIS JOURNAL, **40**, 1428 (1918).

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Cyclic Vinyl Ethers as Reagents for the Introduction of Isoprene Units into Organic Compounds

BY WILLIAM E. PARHAM AND HOWARD E. HOLMQUIST[1]

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An extension of the previously described olefin synthesis[2,3] to 3-methyl-2,3-dihydrofuran (V) should offer a convenient method for the stepwise introduction of isoprene units into organic compounds which form Grignard reagents. Likewise, extension of the reaction to 4-methyl-3,4-dihydro-2H-pyran (I) should result in the formation of compounds structurally related to certain natural products (phytol, etc.). The availability[4] of the cyclic vinyl ethers I and V has permitted evaluation of these methods, and this report describes the synthesis of two new alkenols containing isoprene units.

The reaction of isobutylmagnesium bromide with the crude dichloride obtained from I and chlorine resulted in the formation of 2-isobutyl-3-chloro-4-methyltetrahydropyran (III) (35% yield), boiling at 60–75° (4 mm.). The boiling range and varia-

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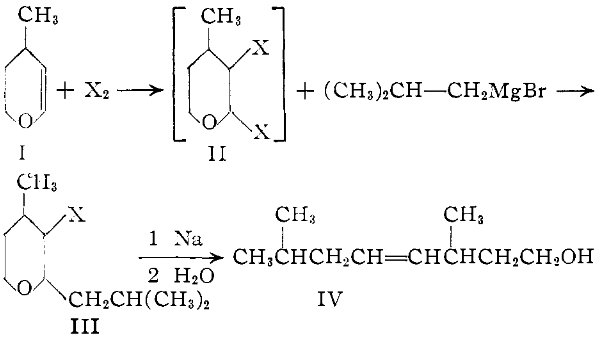
(1) From the Ph.D. thesis of Howard Holmquist, University of Minnesota, 1951.

(2) *Cf.* (a) M. Jacobson, THIS JOURNAL, **72**, 1489 (1950); (b) R. Paul and O. Riobe, *Compt. rend.*, **224**, 474 (1947).

(3) (a) R. C. Brandon, J. M. Derfer and C. E. Boord, THIS JOURNAL, **72**, 2120 (1950); (b) L. Crombie and S. H. Harper, *J. Chem. Soc.*, 1707 (1950).

(4) W. E. Parham and H. E. Holmquist, THIS JOURNAL, **73**, 913 (1951).

tion in refractive index of the product were expected, since III has three asymmetric centers and would therefore exist as a mixture of racemates.

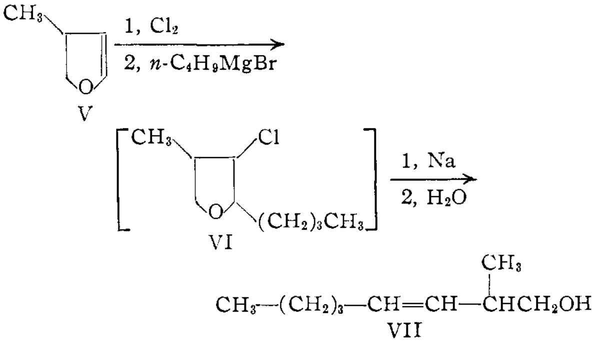


I II III IV

Because of the instability of III no attempt was made to further characterize the product, or to separate it into pure stereoisomers. Conversion of I into 2-isobutyl-3-bromo-4-methyltetrahydropyran by reaction of its dibromide with isobutylmagnesium bromide was accomplished in only 19% yield.[5]

Reaction of the β-chloro and β-bromo ethers III with finely divided sodium gave 3,7-dimethyl-4-octene-1-ol (IV) in 75 and 81% yields, respectively. The new alkenol boiled over a narrow range, which was expected since differences in physical properties of *cis* and *trans* isomers in this series have previously been shown[3b] to be slight. The structure of the new alkenol was established by its conversion to perhydrogeraniol by catalytic reduction. The reduced alcohol had physical properties corresponding to those of perhydrogeraniol, and its allophanate was shown, by mixed melting studies, to be identical to the allophanate obtained from an authentic sample of perhydrogeraniol. IV was further characterized by a study of its reaction with chlorine in chloroform; a 50% yield of the corresponding dichloride and a 26% yield of cyclic halogen-containing ether[6] was obtained.

The method employed for the synthesis of 2-methyl-3-octene-1-ol (VII) from 3-methyl-2,3-dihydrofuran (V) is summarized in the equations



V VI VII

The higher over-all yield (48.5%) observed for this reaction sequence is in keeping with the previous observation concerning the alkylations of α-haloethers with normal and branched Grignard reagents.[2a,3b] Though no proof of structure of the new alcohol was obtained, its composition, as well as that of its allophanate, were consistent with the calculated values for VI.

Experimental

2-Isobutyl-3-chloro-4-methyltetrahydropyran (III).—A solution of II (93.8 g., 0.96 mole) in dry ether (100 ml.) was chilled in a chloroform–Dry Ice bath and chlorine gas was introduced until the solution developed a yellow color. The cold solution was then added to a well-stirred Grignard solution prepared from isobutyl bromide (260 g., 1.9 mole), magnesium (47 g., 1.9 mole) and dry ether (325 ml.). The addition was made at a rate sufficient to cause vigorous refluxing of the ether (over an hour). Ether (50 ml.) was added and the mixture was stirred and warmed at the reflux temperature for an additional hour. Saturated ammonium chloride solution was added to decompose the Grignard complexes and the ether layer and extracts were collected and dried over potassium carbonate and magnesium sulfate. The product (64.3 g., 35% yield) was collected at 60–75° (2 mm.); $n^{22}\text{D}$ 1.450–1.456.

2-Isobutyl-3-bromo-4-methyltetrahydropyran (b.p. 52–88° (2 mm.); $n^{25}\text{D}$ 1.4627–1.4698, 19% yield) was obtained by a procedure similar to that described for III.

3,7-Dimethyl-4-octen-1-ol (IV).—A solution of III (64.3 g., 0.34 mole) in dry ether (100 ml.) was slowly added to a stirred suspension of 18 g. of sodium sand in 100 ml. of ether. The heat of reaction was sufficient to cause the ether to reflux. Stirring was continued for three hours after the addition was complete. The excess sodium was then removed by the addition of water (dropwise) while the solution was being chilled and stirred. The ether layer and extracts were dried over anhydrous magnesium sulfate and distilled to give as main fraction, 39.6 g. (75%) of IV, boiling at 57–60° (0.5 mm.). A sample boiling at 68° (2 mm.); $n^{25}\text{D}$ 1.4438, had the following composition.

Anal. Calcd. for $C_{10}H_{20}O$: C, 76.84; H, 12.90. Found: C, 77.00; H, 12.76.

Proof of Structure of IV.—A solution of IV (5.8 g., 0.037 mole) in ethanol was reduced with hydrogen (37 p.s.i.) using 0.1 g. of platinum oxide as catalyst. The yield of perhydrogeraniol, b.p. 85–95° (7 mm.), was 5.1 g. (88%). Most of this product boiled at 64–65° (2 mm.), $n^{25}\text{D}$ 1.4435. The allophanate, prepared in the usual manner from the reduced alcohol, melted at 119° (recrystallized from dilute ethyl alcohol). The melting point of perhydrogeraniol allophanate has been reported[7] to be 117–118°. Another sample of the allophanate was prepared from an authentic sample of perhydrogeraniol. A mixture of the two samples showed no depression in melting point. A sample of the allophanate derived from reduced IV had the following composition.

Anal. Calcd. for $C_{12}H_{24}O_3N_2$: C, 58.99; H, 9.90. Found: C, 59.17; H, 10.04.

Reaction of IV with Chlorine.—A solution of IV (11.3 g., 0.072 mole) in chloroform was treated with excess chlorine in chloroform. Decolorization of chlorine was rapid and heat and hydrogen chloride were evolved. The reaction mixture was distilled and two fractions were collected: (A) 3.8 g. (26%), b.p. 60–66° (3.5 mm.), $n^{23}\text{D}$ 1.4514; and (B) 8.2 g. (50%), boiling at 108–114° (3.5 mm.).

The low boiling product (b.p. 57–58° (1 mm.), $n^{23}\text{D}$ 1.4518) gave negative tests for alcohol and was formulated as cyclic haloether.

Anal. Calcd. for $C_{10}H_{19}OCl$: C, 62.97; H, 10.04. Found: C, 62.72; H, 10.00.

The high boiling fraction (b.p. 108–111° (3 mm.), $n^{24}\text{D}$ 1.4760) had the composition calculated for the chlorine addition product of IV.

Anal. Calcd. for $C_{10}H_{20}OCl_2$: C, 52.86; H, 8.87. Found: C, 53.00; H, 8.50.

2-Methyl-3-octen-1-ol (VII).—The addition of 15.2 g. (0.21 mole) of chlorine to a solution of 17.9 g. (0.21 mole) of

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(5) The use of bromides instead of chlorides for such reactions is known to give inferior results. *Cf.* ref. 3a.

(6) The intermediate halonium ion reacts not only with the halide ion to give the dihalide, but also with the oxygen atom of the hydroxyl group to give the cyclic halogen-containing ether. It is of interest to note that the reaction of IV with bromine in carbon tetrachloride, under analogous conditions, gave only a 10% yield of product corresponding to dibromide (b.p. 110–118° (2 mm.), $n^{24}\text{D}$ 1.5080), and a 47% yield of product corresponding to cyclic bromoether (b.p. 55–60° (2.5 mm.), $n^{24}\text{D}$ 1.4718). The bromine-containing derivatives were unstable and consequently were not further investigated.

(7) W. Kimel and A. C. Cope, THIS JOURNAL, **65**, 1992 (1943).

V in 100 ml. of dry ether, chilled in a chloroform–Dry Ice bath, gave a pale yellow solution, which was added to a Grignard solution prepared from 10.2 g. (0.42 atom) of magnesium, 60 g. of *n*-butyl bromide and 125 ml. of dry ether. The procedure from this point was the same as that described for the preparation of IV. The amount of sodium used for the ring cleavage step was 8.6 g. The product was boiled at 84–88° (9 mm.) and weighed 14.7 g. (48,5% based on V). The properties of a sample purified by refractionation were: b.p. 62° (2 mm.), $n^{25}\mathrm{D}$ 1.4440.

Anal. Calcd. for $C_9H_{18}O$: C, 76.02; H, 12.75. Found: C, 76.40; H, 12.76.

The allophanate of VII, crystallized out of dilute ethanol, melted at 141–142°.

Anal. Calcd. for $C_{11}H_{20}O_3N_2$: C, 57.86; H, 8.83. Found: C, 57.97; H, 8.83.

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The Chlorination of 2,3-Dimethylbutadiene: Configuration of the Solid Dichloride

BY HENRY M. HELLMAN, J. WALTER HELLMAN AND KURT MISLOW

RECEIVED AUGUST 31, 1953

Interest in the stereochemistry of 1,4-addition[1] prompted us to investigate the nature of the 1,4-adduct of chlorine and 2,3-dimethylbutadiene. The diene, whose principal conformation has variously been reported as s-*cis*[2] and as s-*trans*[3] affords a mixture of *cis*- and *trans*-1,4-dibromo-2,3-dimethyl-2-butenes on bromination.[4]

We have prepared *trans*-1,4-dichloro-2,3-dimethyl-2-butene by the reaction of the *trans*-1,4-diol and phosphorus trichloride, and we have demonstrated that the same solid is one of the products formed from the direct chlorination of 2,3-dimethylbutadiene. Unfortunately we have been unable to prepare the *cis* isomer, and the question of the formation of this substance by direct 1,4-addition must therefore be left open for the present.

Experimental[5]

***trans*-2,3-Dimethyl-2-butene-1,4-diol.**—This compound was prepared by hydrolysis in 31% yield of the diacetate, m.p. 37–38°, according to the procedure of Sweeting and Johnson.[4] There was obtained a white crystalline solid, m.p. 81–82° from ether or ethanol (lit.[4] m.p. 57–58°). The bisphenylurethan melted at 156–157° (lit.[4] m.p. 157.0–157.5°). It is conceivable that the diol reported by Sweeting and Johnson is a crystalline modification of that obtained in this work.

Anal. Calcd. for $C_6H_{12}O_2$: C, 62.10; H, 10.41. Found: C, 62.09; H, 10.42.

***trans*-1,4-Dichloro-2,3-dimethyl-2-butene.**—(A) A solution of 11.0 g. (0.095 mole) of the *trans*-1,4-diol and 7.6 g. of anhydrous pyridine was added slowly to 8.8 g. (0.064 mole) of phosphorus trichloride while the temperature of the reaction mixture was kept below 10°. Water was added to the reaction mixture after completion of the addition. The product was extracted with ether, and the ether layer washed with sodium bicarbonate and dried over drierite. Distillation gave 5.0 g. (33%) of the desired compound, b.p. 65° (6.8 mm.), crystals from hexane, m.p. 30°.

Anal. Calcd. for $C_6H_{10}Cl_2$: C, 47.10; H, 6.58; Cl, 46.32. Found: C, 47.26; H, 6.78; Cl, 46.20.

The infrared spectrum[6] of a 5% solution of the compound in carbon tetrachloride exhibited pronounced absorption maxima at the following wave lengths (μ): 3.40, 6.88, 7.25, 7.95, 8.25, 8.59, 9.24, 10.73, 11.44, 14.20. It should be noted that the 7.95 maximum has been associated[7] with compounds of the type $RR'C{=}CR''CH_2Cl$.

(B) A saturated solution of chlorine in carbon tetrachloride (250 ml., 0.61 mole) was added to a solution of 50.0 g. (0.61 mole) of 2,3-dimethylbutadiene[8] in 200 ml. of purified[9] carbon tetrachloride. Throughout the addition, which took 3.5 hours, vigorous stirring was maintained, and the temperature of the reaction mixture was kept near −20°. The reaction mixture was distilled, but no clean-cut fractions could be obtained; at the same time some dehydrochlorination was evidently taking place. Five cuts were collected at fairly arbitrary intervals: 35–44° (42 mm.), 46–49° (31 mm.), 39–43° (20 mm.), 55–65° (5 to 6 mm.), 65–72° (5.3 mm.). The last two fractions were combined and chilled to 0°. The crystals which formed were separated from the supernatant liquid and after recrystallization from ligroin afforded 12.0 g. (13%), m.p. 32–34° (lit.[10] m.p. 35°, b.p. 80–84° (18 mm.)). The infrared spectrum was identical with that of the sample prepared by procedure (A), and the substance gave *trans*-1,4-acetoxy-2,3-dimethyl-2-butene, m.p. 37–38°, upon acetolysis according to the method described for the 1,4-dibromide.[4]

Attempted Preparation of *cis*-1,4-Dichloro-2,3-dimethyl-2-butene.—A solution of 14.0 g. (0.120 mole) of *cis*-2,3-dimethyl-2-butene-1,4-diol,[4] bisphenylurethan m.p. 147–148° (lit.[4] m.p. 147–148°), in 9.6 g. of anhydrous pyridine was added slowly to 17.1 g. (0.125 mole) of phosphorus trichloride while the temperature of the reaction mixture was kept below 10°. The product, worked up as described for the *trans* isomer, gave on distillation 3.1 g. of a material, b.p. 83–84° (13.5 mm.), $n^{25}\mathrm{D}$ 1.4620, $d^{25}{}_4$ 0.974.

Anal. Calcd. for $C_6H_{10}Cl_2$: C, 47.10; H, 6.58; Cl, 46.32. Found: C, 57.65; H, 9.13; Cl, 23.24.

Possibly, an explanation of the failure of the reaction to give the expected product may be found in a consideration of side reactions involving cyclization, which would be less likely to occur with the *trans* isomer. The analysis is suggestive of a mixture of products.

The *p*-bromobenzenesulfonate of the diol, prepared in the usual way, formed well defined tabular crystals from ether which rapidly turned brown and black on exposure to air. The instability of this derivative was deemed sufficient reason for discontinuing an alternate approach to the synthesis of the *cis*-dichloride, based on a displacement reaction by chloride on the brosylate.

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(1) K. Mislow and H. M. Hellman, THIS JOURNAL, **73**, 244 (1951); K. Mislow, *ibid.*, **75**, 2512 (1953).

(2) N. Hannay and C. Smyth, *ibid.*, **65**, 1931 (1943).

(3) G. J. Szasz and N. Sheppard, *Trans. Faraday Soc.*, **49**, 358 (1953).

(4) O. J. Sweeting and J. R. Johnson, THIS JOURNAL, **68**, 1057 (1946).

(5) Microanalyses are by W. Manser, Zurich.

(6) A Baird model B instrument with 0.1-mm. cells was employed. In this connection, the assistance afforded by correspondence with Dr. Ralph Nusbaum and his staff, Spectroscopy Section, Atomic Energy Project, U. C. L. A., Los Angeles, Calif., is gratefully acknowledged.

(7) L. F. Hatch and G. E. Journeay, THIS JOURNAL, **75**, 3712 (1953).

(8) L. W. Newton and E. R. Coburn, *Org. Syntheses*, **22**, 40 (1942).

(9) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., New York, N. Y., 1941, p. 365.

(10) R. Ya. Levina, *et al.*, *J. Gen. Chem.* (*U.S.S.R.*), **23**, 725 (1953).

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The Direction of Free Radical Addition to $CF_2{=}CFCl$

BY ALBERT L. HENNE AND DOROTHY W. KRAUS

RECEIVED AUGUST 28, 1953

In our preceding paper,[1] we have interpreted the free radical condensation of CF_3I with $CF_2{=}CFCl$ as directed to $CF_3{-}CFCl{-}CF_2I$, and that of CCl_3Br with $CF_2{=}CFCl$ as directed to $CCl_3{-}CFCl{-}CF_2Br$; this has been criticized by Miller,[2] with

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(1) A. L. Henne and D. W. Kraus, THIS JOURNAL, **73**, 5303 (1951)

(2) W. T. Miller and J. Howald, 122d A.C.S. Meeting, 12K, Sept., 1952.