

determination showed the alcohol to be identical with that obtained by the action of ozone on 1-isoduryl-1-phenylethylene.

Summary

The direct oxidation of two olefins to the corresponding vinyl alcohols has been achieved. The action of ozone on 1-mesityl-1-phenylethylene

and 1-isoduryl-1-phenylethylene has been found to convert them to 2-mesityl-2-phenylvinyl alcohol and 2-isoduryl-2-phenylvinyl alcohol, respectively. The latter, a new vinyl alcohol, has been prepared also by the dehydration of 1-isoduryl-2-phenylethylene glycol.

URBANA, ILLINOIS

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[CONTRIBUTION OF THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

Synthesis of Polyenes. IV

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The preparations of hexatriene, dimethylhexatriene and an isomer of stilbestrol dimethyl ether by the action of sodamide (or potassium amide) in liquid ammonia on allyl chloride, methylallyl chloride and anethole hydrobromide, respectively, have been described.¹ The over-all reaction involves the elimination of two molecules of halogen acid, as indicated by the equation



It has been shown,^{1b,1c} however, that the reaction probably proceeds in two steps



In the present paper, this method of diene (or polyene) synthesis is applied to a variety of organic halides with the object of ascertaining the scope and mechanism of the reaction.

Discussion

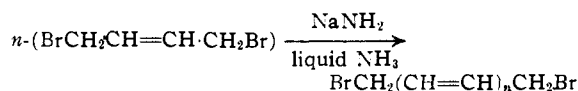
On the basis of the work described in this and previous papers, the following generalization appears to be justified. Alkali amides, in liquid ammonia, react with organic halides of the type RCH_2X to yield substances like the products given in equations (A) and (B) only if the radical R is strongly electronegative. That is, R must be α,β -unsaturated (*e. g.*, vinyl), or aromatic (*e. g.*, phenyl), or an acyl (R_1CO) group, in which R_1 is an aromatic radical. Some of the results obtained are summarized in Table I.

Some comments on the reactions cited are in order. Dibenzoylethylenes can be prepared in the manner indicated only from those phenacyl halides which do not contain substituents (*e. g.*, the nitro group), which react with sodamide in liquid ammonia. When the attempt was made to condense *m*-nitrophenacyl chloride by the use of sodamide, the product was a dark viscous liquid from which no pure compound could be isolated. Furthermore, compounds such as chloroacetone

(1) (a) Kharasch and Sternfeld, *THIS JOURNAL*, **61**, 2318 (1939); (b) Kharasch, Nudenberg and Sternfeld, *ibid.*, **62**, 2035 (1940); (c) Kharasch and Kleiman, *ibid.*, **65**, 11 (1943).

which react rapidly with liquid ammonia are not suitable for the condensation in question.

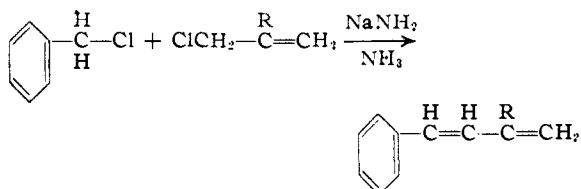
The polymer (m. p. above 350°) formed by the action of sodamide in liquid ammonia on 1,4-dibromobutene-2 has not been identified. However, the condensate is of considerable interest. Its molecular weight (calculated from its bromine content of 11.3%) is 1416. If the reaction proceeds as follows



then the molecule should have 47 conjugated double bonds. Very probably, the highly insoluble product contains a number of distinct polymers. If such is the fact, the calculated number of double bonds refers to an average.

Cinnamyl chloride, when treated with sodamide in liquid ammonia, gave 10% of diphenylhexatriene. No other product was isolated. The nature of the other products formed depended upon the quantity of sodamide used. When the usual 10% excess of sodamide was employed, the product was a chlorinated resin which may be similar to the condensate of hexatriene and allyl chloride.^{1a} When a large excess of sodamide (7 moles per mole of cinnamyl chloride) was used, the product was a hydrocarbon containing three diphenylhexatriene units per molecule.

The usefulness of the sodamide reaction in the preparation of unsymmetrical phenylated dienes has been demonstrated by the preparation of 1-phenyl-3-methylbutadiene from benzyl chloride and β -methylallyl chloride, as well as by the formation of 1-phenylbutadiene from benzyl chloride and allyl chloride. The other expected products (stilbene and 2,5-dimethylhexatriene in the first instance, and stilbene and hexatriene in the



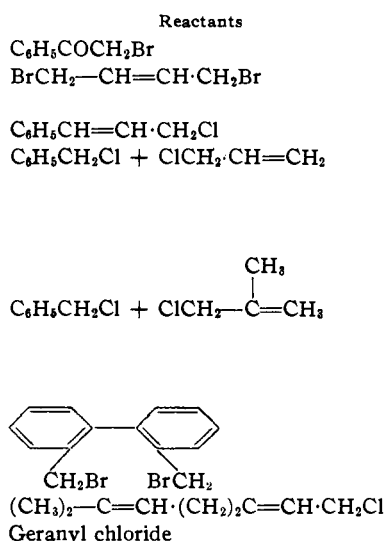
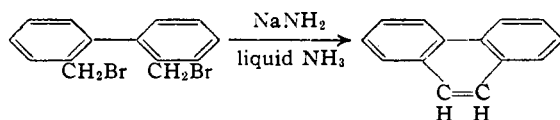


TABLE I

Reactants	Product	Yield, %
$C_6H_5COCH_2Br$ $BrCH_2-CH=CH-CH_2Br$	$C_6H_5COCH=CHCOC_6H_5$ Long chain polymer	42
$C_6H_5CH=CH-CH_2Cl$ $C_6H_5CH_2Cl + ClCH_2-CH=CH_2$	$BrCH_2(CH=CH)_nCH_2Br$ $C_6H_5CH=CH-CH=CH-CH=CHC_6H_5$ $C_6H_5CH=CH-CH=CH_2$	100 10 14
$C_6H_5CH_2Cl + ClCH_2-C(CH_3)=CH_2$	Stilbene Hexatriene Polymers	86
$(CH_3)_2C=CH-(CH_2)_2C=CH-CH_2Cl$	$C_6H_5CH=C(CH_3)-CH=CH_2$ Stilbene 2,5-Dimethylhexatriene Polymerized residue	23 13 35 29
	Phenanthrene	80
	Geranylamine	35

second instance) were also formed. Both of the phenylbutadienes gave adducts with maleic anhydride.

Phenanthrene has been synthesized in a new way. 2,2'-Dibromomethylbiphenyl, when treated with sodamide in liquid ammonia, yielded 80% of phenanthrene. No doubt this reaction



might be extended to the preparation of substituted phenanthrenes which contain no substituents (e. g., the nitro group) that are attacked by sodamide.

The reaction of geranyl chloride, $CH_3C(CH_3)=CHCH_2CH_2C(CH_3)=CHCH_2Cl$ with sodamide in liquid ammonia differs from that of the other substances just described. The major product isolated is a geranylamine, the hydrochloride of which melts at 142–144°. Forster and Cardwell² prepared geranylamine (b. p. 105° (19 mm.)) by treating geranyl chloride with sodium azide, and subjecting the azide thus formed to the action of zinc in glacial acetic acid. They reported that the hydrochloride of their geranylamine melted at 120°. However, it has never been demonstrated that geranyl chloride (as ordinarily prepared) is exclusively the primary chloride the formula of which is given above; it may well be an equilibrium mixture of isomers.³

Mechanism of the Sodamide Condensation.—

A number of condensing agents besides sodamide have been examined; solvents other than liquid ammonia have also been tried. Benzyl chloride was used as the test halide, since its condensa-

tion product, stilbene, is easily isolated. The results obtained are summarized in Table II.

TABLE II
REACTIONS OF BENZYL CHLORIDE WITH BASES

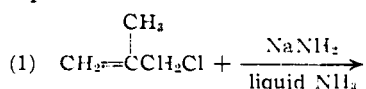
Reagents	Solvent	Product	Yield, %
KOH (powdered)	Liquid ammonia	Benzylamine hydrochloride	5
$NaOC_2H_5$	Liquid ammonia	Benzylamine hydrochloride	5
Na formamide	Liquid ammonia	Benzylamine hydrochloride	5
Na formamide	Formamide	Dibenzyl formamide	55
$NaNH_2$	Ether	Benzylamine hydrochloride	15
$NaNH_2$	Ligroin	Benzyl chloride recovered	
$NaNH_2$	Liquid ammonia	Stilbene	100

These results indicate that, for stilbene formation, sodamide is the only effective condensing agent, and liquid ammonia the only suitable solvent yet found.

The replacement of the chlorine atom in molecules of the type RCH_2Cl by other negative groups may take place either by a unimolecular or by a bimolecular mechanism, or by both. Bearing in mind, however, that sodamide in liquid ammonia condenses RCH_2Cl compounds only when R is an aromatic radical, an aromatic acyl group, or a (substituted or unsubstituted) vinyl group, the most probable mechanism for the reaction under consideration is the following. In solvents of high dielectric constant and in the presence of very strong bases (e. g., sodamide), an atom of hydrogen is probably replaced by an atom of sodium.

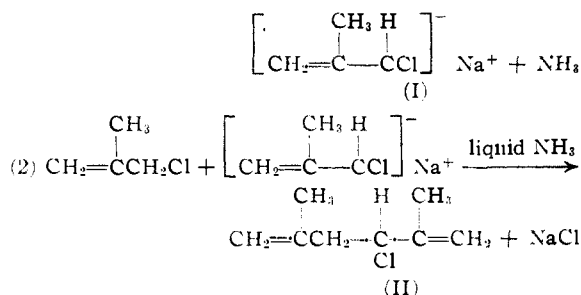


Hence, according to the hypothesis just cited, the reaction of sodamide with methylallyl chloride in liquid ammonia is



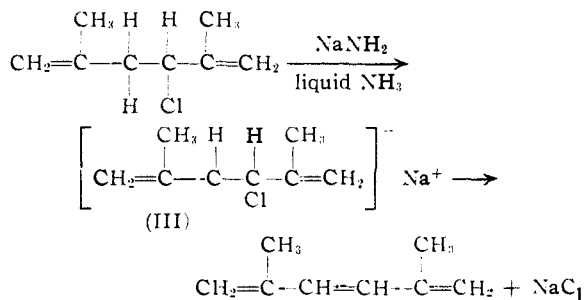
(2) Forster and Cardwell, *J. Chem. Soc.*, **103**, 1343 (1913).

(3) Cf. Kharasch, Kritchevsky and Mayo, *J. Org. Chem.*, **2**, 489 (1937).



This view is supported by the following facts: (1) compound II may be isolated when one mole of sodamide is used for two moles of allyl or methylallyl chloride; (2) whenever sodamide is added to allyl or methylallyl chloride in liquid ammonia, the solution acquires a deep red to purple color which fades as the reaction progresses. Such colors are characteristic of solutions of organo-sodium compounds, *e. g.*, diphenylmethyl sodium or triphenylmethyl sodium.

If (II) is treated with sodamide in liquid ammonia, a deep red color develops momentarily, and the reaction product is 2,5-dimethylhexatriene. Here again the color formation indicates that an organo-sodium intermediate is formed. This intermediate then loses sodium chloride to give 2,5-dimethylhexatriene. Compound III



might also be formed by the interaction of two molecules of (I). Cross condensations of different halides RCH_2X and $\text{R}_1\text{CH}_2\text{X}$ are thus readily explained. The small amounts of very high boiling material formed in the reaction with methylallyl chloride may be due to condensations of (III) with many molecules of (I).

Whether a halide of the type RCH_2X (R = aromatic or vinyl group) will condense with itself, therefore, depends upon the ease of replacement of the hydrogen atoms. (The term "acidity" is here intentionally avoided.) If the hydrogen atom is readily replaced, then even potassium hydroxide may function as a condensing agent. Thus, potassium hydroxide reacts with 9-bromofluorene to give difluorenylidene, and other reactions of the same sort are known.

The non-effectiveness of sodamide and potassium amide in solvents other than liquid ammonia may be due to the lower dielectric constants and weak dissolving powers of these media (*e. g.*, benzene, ether).

Experimental

Diphenylhexatriene.—Cinnamyl chloride (15 g. in 100 cc. of dry ether) and sodamide (34 g.) were added in alternate small lots to 400 cc. of liquid ammonia. After the addition, the mixture was stirred for fifteen minutes; the ammonia was then evaporated. The organic residue was taken up in ether. The ether solution was washed with water and dried over anhydrous sodium sulfate; then the ether was evaporated. When the remaining liquid was cooled, 2 g. of diphenylhexatriene separated. This material was collected on a filter; the remaining liquid was distilled. Cinnamyl chloride (1.5 g.) was collected at 85–95° (2 mm.). The temperature then rose rapidly, and 1 g. of diphenylhexatriene distilled at 175–185° (1 mm.). This material solidified in the condenser (m. p. 197–199°). The residue in the flask showed no tendency to distill and turned quite dark during the distillation of the hexatriene. When it cooled, it set to a hard resin from which no crystals could be obtained. This resin still contained chlorine.

Sodamide (18 g.) in liquid ammonia was treated with cinnamyl chloride (15 g.). After working up the reaction mixture in the manner described, 10 g. of a yellow solid was obtained. This substance softened at 150–160° and melted at 165°. Efforts to recrystallize it were unsuccessful.

Anal. Calcd. for $(\text{C}_{18}\text{H}_{16})_2$: mol. wt., 696. Found: Mol. wt. (micro Rast), 697.

The low yields of the diphenylhexatriene of m. p. 199° may be explained by assuming the formation of stereoisomers of this compound; six different forms are possible. Kuhn and Winterstein⁴ prepared diphenylhexatriene from cinnamic aldehyde. Their over-all yield of material melting at 199° was 18%.

Dibenzoyl ethylene.—Phenacyl bromide (10 g. in 40 cc. dry ether) and sodamide (3 g.) were added in alternate small lots to 300 cc. of liquid ammonia. After evaporation of the ammonia, ether and water were added to the reaction mixture. The ether solution was washed with water and dried over anhydrous sodium sulfate; then the ether was evaporated *in vacuo*. Yellow crystals (2.5 g., 42% yield) of dibenzoyl ethylene were obtained. This material, after one crystallization from ethyl alcohol, melted at 111°. The residue was a sirup, containing nitrogen; it was not further investigated.

A method for preparing dibenzoyl ethylene (yield 78–83%) has been described by Lutz.⁵ Bromodiphenacyl,

$\text{C}_6\text{H}_5\text{C}(\text{O})\text{CH}_2\text{CHBrC}(\text{O})\text{C}_6\text{H}_5$, has been obtained by Fritz⁶ from phenacyl bromide by treatment with sodium ethylate in ethyl alcohol. The yield is not given in his paper and the details of the preparation are meager.

Phenanthrene.—2,2'-Dibromomethylbiphenyl (2 g., m. p. 86–87°), in 30 cc. of dry ether was added to a suspension of sodamide made from 1.2 g. of sodium in 100 cc. of liquid ammonia. After the ammonia had evaporated, ether and water were added. The ether solution was washed, dried and evaporated; it left a residue of phenanthrene (0.95 g.; m. p. 97–100°).

"Polymer" from 1,4-Dibromobutene-2.—1,4-Dibromobutene-2 (24 g., m. p. 53°) in 75 cc. of benzene was added to 14.5 g. of sodamide in 500 cc. liquid ammonia. The mixture was stirred for three hours; then the ammonia was evaporated, and a solution of 11 g. ammonium bromide in 200 cc. water was added. The flocculent precipitate was collected on a filter, washed thoroughly with water and dried; yield, 6 g. of fine brown powder which did not melt at 350°.

Anal. Calcd. for $\text{C}_{96}\text{H}_{96}\text{Br}_2$: C, 81.4; H, 7.0; Br, 11.6. Found: C, 82.17; H, 6.43; Br, 11.10.

Geranyl Chloride.—Geranyl chloride (64 g. or 0.37 mole) (b. p. 78–81° at 3–4 mm.) in 300 cc. of ether, and sodamide (22 g. or 0.55 mole) were added in alternate

(4) Kuhn and Winterstein, *Helv. Chim. Acta*, **11**, 87 (1928).

(5) Lutz, "Organic Syntheses," **20**, 29 (1940).

(6) Fritz, *Ber.*, **28**, 3032 (1895).

small lots to 1500 cc. of liquid ammonia. The reaction mixture was then stirred for four hours. The material was worked up in the usual manner, with ether as the solvent. The ether was removed from the dried ether solution and the residue was distilled *in vacuo*. The following fractions were collected: (I) 27–62° (1 mm.), a small forerunner; (II) 62–65° (1 mm.), 20 g., 35% yield; (III) higher boiling residue containing halogen. Fraction III deposited crystals after it had cooled. Fraction I contained a mixture of hydrocarbons and geranylamine. Fraction II was geranylamine. Fraction III was a mixture of geranylamine and geranyl chloride which, when heated, gave geranylamine hydrochloride and a hydrocarbon. When a portion of the geranylamine was treated in ligroin with hydrogen chloride, a white precipitate of geranylamine hydrochloride was obtained, m. p. 142–144°.

Anal. Calcd. for $C_{10}H_{20}NCl$: N, 7.38. Found: N, 7.54.

Phenylmethylbutadiene.—Sodamide (43 g., 1.1 mole) and a mixture of benzyl chloride (63 g., 0.5 mole) with β -methylallyl chloride (45 g., 0.544 mole) were added in alternate small lots over a period of about forty-five minutes to 1500 cc. of liquid ammonia. The reaction mixture was then stirred for three hours. The liquid ammonia was evaporated, and the residue taken up in a mixture of low boiling ligroin and ether. The ether–ligroin solution was washed four times with water, and dried over anhydrous sodium sulfate. The ether and ligroin were removed by distillation on a water-bath. After removal of the solvents, stilbene separated from the residue. It was collected on a Büchner funnel and washed with low boiling ligroin. All operations were carried out as rapidly as possible. Six grams (18%) of stilbene was thus obtained. After the ligroin had been removed from the filtrate, the residue was distilled *in vacuo* into a receiver cooled with a carbon dioxide–acetone mixture. The following fractions were obtained: (I) 25–67° (2 mm.), 11.3 g. of liquid containing a small amount of solvent, some 2,5-dimethylhexatriene and some phenylmethylbutadiene; (II) 67–70° (2 mm.) or 105–108° (12 mm.), 16.8 g., 23.3% of 1-phenyl-3-methylbutadiene which crystallized in the receiver; (III) above 70° (1 mm.), 30 g. of material which crystallized on cooling. Fraction III was a mixture of stilbene, phenyl-3-methylbutadiene and polymerized dimethylhexatriene. In the literature, the following data are given for 1-phenyl-3-methylbutadiene: m. p. 27°, b. p. 115° (18 mm.)⁷; b. p. 124° (32 mm.)⁸; m. p. 37°, b. p. 105° (12 mm.)⁹; m. p. 28°, b. p. 117° (16 mm.)¹⁰.

By heating equivalent amounts of 1-phenyl-2-methylbutadiene and maleic anhydride in dry benzene in a sealed tube at 100° for six hours, 4-methyl-6-phenyl-1,2,3,6-tetrahydrophthalic anhydride was obtained. The white product, after two crystallizations from ligroin (b. p. 107–118°) melted at 90–91°.

Anal. Calcd. for $C_{15}H_{14}O_3$: C, 74.36; H, 5.82. Found: C, 74.56; H, 6.14.

(7) V. Grignard, *Ann. Chim.*, [7] **24**, 486 (1901).

(8) A. Klages, *Ber.*, **35**, 2651 (1902).

(9) Kohler and Heritage, *Am. Chem. J.*, **43**, 486 (1910).

(10) Auwers and Eisenlohr, *J. prakt. Chem.*, [2] **84**, 46 (1911).

4-Methyl-6-phenyl-1,2,3,6-tetrahydrophthalic acid (m. p. 194°, with dec.) was obtained by heating a small portion of the corresponding anhydride in boiling water for one-half hour.

Anal. Calcd. for $C_{15}H_{16}O_4$: C, 69.21; H, 6.20. Found: C, 69.42; H, 6.73.

The 1-phenyl-3-methylbutadiene was hydrogenated in methyl alcohol solution in the presence of platinum oxide. The product was isoamylbenzene (b. p. 193° (740 mm.); n_D^{20} 1.4831). Ipatieff and Schmerling¹¹ report for isoamylbenzene b. p. 197–199° (760 mm.) (cor.); n_D^{20} 1.4835.

Phenylbutadiene.—The procedure used to prepare this compound was the same as that for preparing phenylmethylbutadiene from benzyl chloride and methylallyl chloride. Benzyl chloride (63 g., 0.5 mole), allyl chloride (40 g., 0.52 mole) and sodamide (44 g., 1.1 mole) were used in 1500 cc. of liquid ammonia. The ether and ligroin were removed from the reaction mixture by distillation at reduced pressure. The receiver was cooled with carbon dioxide–acetone mixture. Crystals, probably hexatriene, separated from the cooled ether–ligroin distillate. After all the solvent was removed, 9 g. of material was collected at 63–65° (2–3 mm.). This fraction was phenylbutadiene (14% yield) which when redistilled boiled at 75–77° (6 mm.). When the heating was continued, the residue suddenly polymerized with the evolution of much heat and with a marked darkening of the material. The material remaining in the distilling flask solidified when it cooled; it was probably a mixture of stilbene with polymerized material.

By heating equivalent amounts of 1-phenylbutadiene and maleic anhydride, 6-phenyl-1,2,3,6-tetrahydrophthalic anhydride was obtained. The product, after three crystallizations from ligroin (b. p. 107–118°), melted at 119–120°. Diels and Alder¹² report 120° as the melting point of this compound.

When 6-phenyl-1,2,3,6-tetrahydrophthalic anhydride was heated with boiling water for thirty minutes, the corresponding acid was obtained, m. p. (on rapid heating) 200–203° (dec.).

Anal. Calcd. for $C_{14}H_{14}O_4$: C, 68.26; H, 5.73. Found: C, 68.33; H, 6.02.

Summary

1. The condensing action of sodamide on cinnamyl chloride, phenacyl bromide, 2,2'-dibromomethylbiphenyl, 1,4-dibromobutene-2 and geranyl chloride is described. The same reagent also condenses benzyl chloride with allyl and methylallyl chlorides.

2. A mechanism for the reaction is suggested.

CHICAGO, ILLINOIS

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(11) Ipatieff and Schmerling, *This Journal*, **60**, 1476–1479 (1938).

(12) Diels and Alder, *Ber.*, **62**, 2085 (1939).