pair is recovered on treatment with acid. A solution of cyanoanthrone in benzene is thermochromic, showing a dark brown coloration when hot that fades on cooling. Medium–strong infrared bands (in potassium bromide) for 9-cyano-10-anthrone are: 1675, 1595, 1450, 1320, 1270, 930, 810, 760, 720, and 680 cm^{-1}. It shows almost negligible nitrile absorption at 2200 cm^{-1}. From benzene–cyclohexane it has mp 192° with considerable decomposition.

Anal. Calcd for $C_{15}H_9NO$: C, 82.26; H, 4.14; N, 6.40; mol wt, 219. Found: C, 81.79; H, 4.00; N, 6.07, 6.41; mol wt, 219 (mass spectrum).

9-Cyano-10-methoxyanthracene.—This compound was isolated in experiment L by chromatography of the mixture of products precipitated on dilution of the reaction mixture with water. It exhibited an infrared spectrum identical with that of the authentic material.

9-Cyanoanthracene.—This compound was isolated by chromatography of the water-insoluble materials obtained in reactions worked up with excess dry hydrogen chloride. After recrystallization from ethanol, it showed mp 174–176° (lit.[22] mp 174–175°). Strong infrared bands were noted (in potassium bromide) at 2220, 895, 840, 770, and 720 cm^{-1}.

9-Cyano-10-(4′-hydroxy)phenoxyanthracene.—Subsequent to removal of aminonitrile **2b** from water-insoluble material in experiment G, column chromatography yielded the hydroquinone adduct. Recrystallized from carbon tetrachloride, it showed mp 231–232°. Strong–medium bands in the infrared spectrum are (in potassium bromide): 3340, 2220, 1500, 1470, 1440, 1405, 1370, 1285, 1190, 1085, 820, 760, and 730 cm^{-1}.

Anal. Calcd for $C_{21}H_{13}NO_2$: C, 81.10; H, 4.21; N, 4.50; mol wt, 311. Found: C, 80.57; H, 4.35; N, 4.50; mol wt, 311 (mass spectrum).

Nucleophilic Substitution Reactions of 9-Cyano-10-nitroanthracene. Reaction with Sodium Cyanide.—After a 1-hr nitrogen flush of a mixture of sodium cyanide (0.05 g, 10^{-3} mole) in 5 ml of DMF, nitronitrile (0.10 g, 4×10^{-4} mole) was added, and the mixture was stirred under nitrogen at room temperature for 6 hr. Filtration yielded 67 mg of crude 9,10-dicyanoanthracene, contaminated to about 20% with nitronitrile. Column chromatography ultimately yielded pure dinitrile for unequivocal identification. Only traces of other compounds were obtained from this reaction.

Treatment with Potassium Hydroxide.—A mixture of potassium hydroxide (0.11 g, 2×10^{-3} mole) in 5 ml of DMF was flushed for 1 hr with nitrogen, and nitronitrile (0.03 g, 1.0×10^{-4} mole, known to be contaminated with anthraquinone) was added. After stirring for 17 hr under nitrogen, filtration yielded 6.5 mg of a solid identified by infrared analysis as anthraquinone. The filtrate was diluted with 45 ml of water and saturated with ammonium chloride. Extraction with ether and evaporation yielded an orange oil (DMF) from which 13 mg of an orange solid precipitated on dilution with water. Infrared analysis showed that this was a mixture of 9-cyano-10-anthranol and 9-cyano-10-anthrone. Recrystallization from acetic acid yielded material whose infrared spectrum showed it to be rich in enol **2d**.

Paramagnetic Resonance Study.—A 5-ml sample of 2×10^{-2} *M* sodium cyanide in DMF was flushed for 0.5 hr with nitrogen in a side-arm dropping funnel attached at the lower end to a flat epr cell such that the nitrogen exited through the cell. A sample of 9-nitroanthracene (5.6 mg, 2.5×10^{-5} mole) was added, stirred thoroughly by the nitrogen stream, and dropped into the epr cell. An eight-peak spectrum with a 28-gauss line width was observed which did not vary in complexity but diminished in intensity considerably within 3.5 hr.

Registry No.—9-Nitroanthracene, 602-60-8; sodium cyanide, 143-33-9; DMF, 68-12-2; **2a**, 14789-43-6; **2b**, 14789-44-7; diacetamide of **2b**, 14789-50-5; **2c**, 1217-45-4; **2d**, 14789-46-9; **3**, 14789-47-0; 9-bromo-10-nitroanthracene, 14789-48-1; 9-cyano-10-(4′-hydroxy)phenoxyanthracene, 14789-49-2.

(22) W. E. Bachmann and M. C. Kloetzel, *J. Org. Chem.*, **3**, 55 (1938).

The Favorskii Rearrangement of *cis*- and *trans*-Carvone Tribromides. I. Primary Amines[1]

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Received June 7, 1967

The action of primary amines in ether or methanol on *trans*-carvone tribromide II leads to exclusive Favorskii rearrangement and affords iminolactones VII and unsaturated amides VIII. *cis*-Carvone tribromide undergoes a Favorskii rearrangement with amines in methanol to yield the same iminolactones; however, 1,2-elimination of hydrogen bromide occurs in ether to give the bromo unsaturated ketone XIII. Contrary to statements in the literature, it is shown that α-axial halo ketones undergo the Favorskii rearrangement. The importance of solvent polarity in determining the reaction path followed by an α-halo ketone is again emphasized.

Substantial quantities of carvenolide I were required during an investigation of the synthesis of various iridolactones.[3] The preparation of carvenolide I reported by Wallach[4] involved treatment of carvone tribromide II with ammonia to give a basic intermediate, formulated as III or IV, which was converted into carvenolide by steam distillation. It is difficult to visualize a mechanism for the transformation of III or IV into carvenolide I; consequently, we were prompted to reexamine the intermediate "amino ketone." The basic intermediate was isolated in 36% yield from the reaction of carvone tribromide II and ammonia in amyl alcohol using the procedure described by Wallach.[4] Although this compound was too unstable to permit complete characterization, spectral data indicated it possessed the constitution represented by formula V. The nmr spectrum of the basic intermediate was identical with that of carvenolide I except for the presence of a very broad, one-proton signal centered at 6.1 ppm, while the infrared spectrum displayed C=N and N–H stretching vibrations at 6.01 and 3.01 μ, respectively. The extremely facile hydrolysis to carvenolide I is also in accord with the formulation of the intermediate as the iminolactone V (Scheme I).

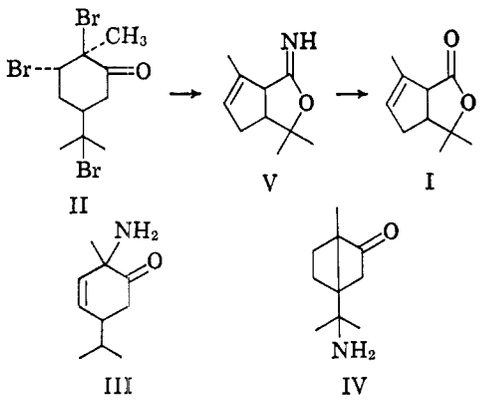
(1) Abstracted from part of the thesis submitted by R. O. H. in partial fulfillment of the requirements for the Ph.D. degree, Purdue University, Jan 1967.

(2) (a) David Ross Research Fellow, Purdue University, 1964–1966; (b) National Institutes of Health, Predoctoral Fellow, 1961–1963.

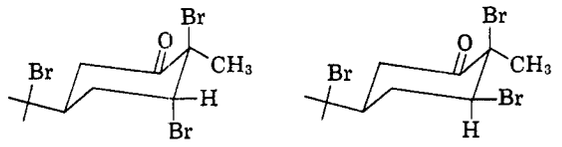
(3) J. Wolinsky, T. Gibson, D. Chan, and H. Wolf, *Tetrahedron*, **21**, 1247 (1965).

(4) O. Wallach and C. Ohlingmacher, *Ann.*, **305**, 245 (1899); O. Wallach, *ibid.*, **414**, 240 (1918).

SCHEME I

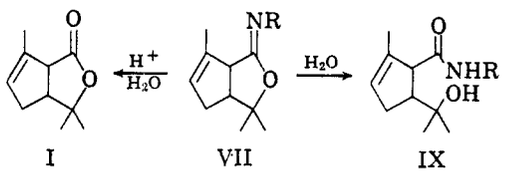


In view of this preliminary result, further studies were directed toward determining the generality and synthetic scope of the reaction of amines with carvone tribromide II and its isomer VI.[5] The presence of the bulky bromoisopropyl group in tribromides IIa and VI renders these compounds conformationally rigid[6] and



allows a test of the role of halogen configuration and solvent polarity in the Favorskii rearrangement.[7]

The reactions of *trans*-carvone tribromide (IIa) with primary amines were conducted at room temperature for about 70 hr. With isopropylamine in diethyl ether, the major product (74% yield) was identified on the basis of spectral and analytical data as the iminolactone VIIa. In addition, a small amount (5.7%) of the unsaturated amide VIIIa was isolated. The iminolactone VIIa was hydrolyzed to carvenolide I upon refluxing with 5% hydrochloric acid and to the hydroxyamide IX when refluxed in 50% aqueous ethanol.



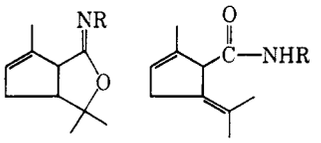
The results of a study of the reactions of *trans*-carvone tribromide (IIa) with a variety of primary amines in ether are summarized in Table I. In each instance a reasonable yield of the corresponding iminolactone was obtained accompanied by lesser amounts of unsaturated amide VIII. Almost identical results were obtained when methanol was used as a solvent. In all cases the assigned structures were in complete accord with spectral and analytical data (see Experimental Section).

(5) J. Wolinsky and R. O. Hutchins, in preparation.

(6) S. Winstein and N. Holness, *J. Am. Chem. Soc.*, **77**, 5562 (1955); E. Eliel, N. Allinger, S. Angyal, and G. Morrison, "Conformational Analysis," John Wiley and Sons, Inc., New York, N. Y., 1965, pp 542–558, and references cited therein.

(7) (a) G. Stork and I. Borowitz, *J. Am. Chem. Soc.*, **82**, 4307 (1960); (b) H. House and H. Thompson, *J. Org. Chem.*, **28**, 164 (1963); (c) H. House and G. Frank, *ibid.*, **30**, 2948 (1965); (d) E. Smissman, T. Lemke, and O. Kristiansen, *J. Am. Chem. Soc.*, **88**, 334 (1966).

TABLE I
REACTION OF *trans*-CARVONE TRIBROMIDE WITH PRIMARY AMINES



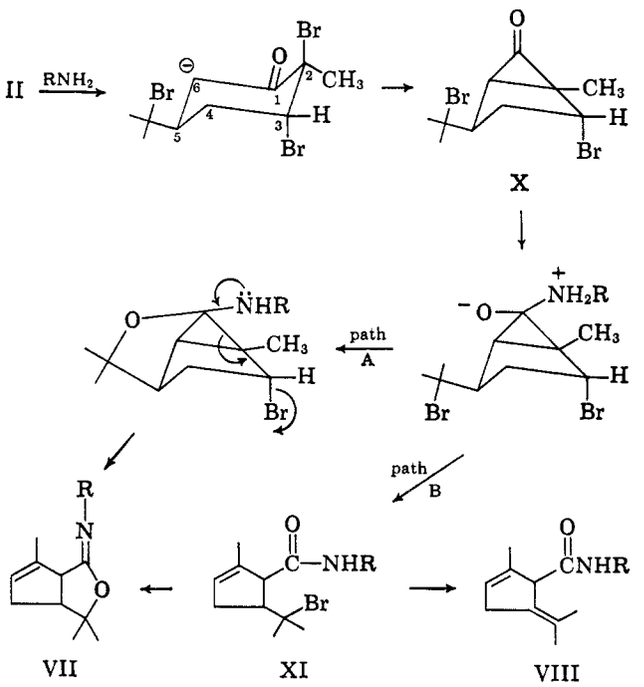
Amine	R	Yield, % VII	Yield, % VIII
Isopropyl	$(CH_3)_2CH$	a, 74.2	a, 5.7
n-Propyl	$CH_3CH_2CH_2$	b, 61.8	b, 11.9
Allyl	CH_2CHCH_2	c, 68.8	c, 17.2
Cyclohexyl	C_6H_{11}	d, 56.8	d, 16.3
Ethyl[a]	CH_3CH_2	e, 70.5	e, 7.5

[a] Benzene used as solvent.

The transformation of tribromide II to the iminolactones VIIa–e undoubtedly involves a Favorskii rearrangement and the conversions appear to be almost free of side reactions. The conformationally rigid carvone tribromide IIa contains an axial α-bromo group and the successful Favorskii rearrangement of this compound supports House's[7c] contention that the conformation of the α-halogen is not a dominant factor in determining whether Favorskii rearrangement will occur.

It is assumed that the conversion of IIa into a cyclopropanone intermediate X[8] occurs with inversion of configuration at C-2 in a nonpolar solvent such as ether.[7a,c] The formation of iminolactones may follow as a consequence of intramolecular cyclization and cleavage of the cyclopropane ring as shown in Scheme II, path A. Alternately, the iminolactones may form by cleavage of X and subsequent base-catalyzed cyclization of the resulting bromoamide XI as shown in path B.

SCHEME II



The unsaturated amides VIII most likely form by dehydrobromination of bromoamides XI. The acid-

(8) See A. Kende, *Org. Reactions*, **11**, 261 (1960), and references cited therein.

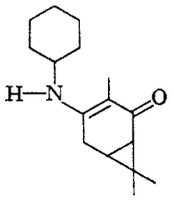
catalyzed ring opening of the iminolactones VII during the reaction work-up was also considered, but this possibility was eliminated because the unsaturated amides VIII were also isolated when water or acid was omitted from the work-up procedure.

The absence of side products in the reaction of *trans*-carvone tribromide (II) with primary amines in ether is noteworthy in view of results obtained by other investigators with related compounds. For example, Stevens[9] reported that the reaction of 2-bromo-2-methylcyclohexanone (XII) with methylamine in benzene gave 2-N-methylamino-2-methylcyclohexanone and no mention was made of products arising from a Favorskii rearrangement. When benzene was used as a solvent for the reaction of carvone tribromide II and ethylamine, only VIIe and VIIIe, products of Favorskii rearrangement, were obtained. The striking difference between the path followed by compounds with similar configuration at the α-halo position illustrates the difficulty in attempting to predict the reaction of an unstudied α-halo ketone and suggests that relatively minor structural differences exert a large influence on the path ultimately followed.

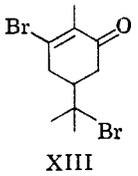
The marked influence of structural difference and solvent polarity on the behavior of α-halo ketones is further illustrated by the action of primary amines in ether on *cis*-carvone tribromide (VI) which produced 3-bromo-5-(2-bromoisopropyl)-2-methyl-2-cyclohexenone (XIII) in 87.5% yield and the iminolactone VIIa in only 3.5% yield. In this instance *trans*-1,2-elimination of hydrogen bromide completely overshadows the Favorskii rearrangement.

The structure of the unsaturated bromo ketone XIII was deduced on the basis of analytical and spectral data (see Experimental Section). Compound XIII is very sensitive to heat and undergoes further dehydrobromination on distillation to give 3-bromocarvacrol (XIV). In fact, 3-bromocarvacrol (XIV) can be isolated in 74% yield if the reaction mixture from cyclohexylamine and carvone tribromide VI in ether is distilled rather than worked up by crystallization.

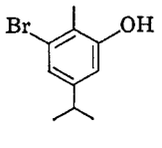
The yield of unsaturated ketone XIII was reduced to 52% by allowing the reaction mixture of tribromide VI and cyclohexylamine in ether to proceed for 7, rather than for 2 days. A new, acid-soluble, bromine-free solid was isolated in 27% yield. This solid showed an ultraviolet maximum at 314 mμ (ϵ 34,600) and strong infrared absorption at *ca.* 6.5 μ which is characteristic of a β-aminovinyl ketone and, accordingly, the solid is assigned structure XV. The nmr spectrum is in agreement with this formulation. Compound XV can be pictured as arising from XIII by replacement of the β-bromine with cyclohexylamine[10]



XV



XIII



XIV

(9) C. Stevens, I. Kundt, M. Munk, and M. Pillai, *J. Org. Chem.*, **30**, 2967 (1965).

(10) W. Benson and A. Pohland, *Chem. Rev.*, **66**, 161 (1966).

and base-induced intramolecular cyclization to generate the cyclopropane ring.[11]

In contrast to the elimination observed when ether was used as a solvent, *cis*-tribromide VI gave only Favorskii products, VIIa (63.8%) and VIIIa (1%), when treated with isopropylamine in methanol.

The difference in behavior of the isomeric dibromides II and VI when acted upon by amines in ether can be attributed to the *trans*-diaxial orientation of the β-hydrogen and α-bromine in *cis* VI. This structural feature permits dehydrobromination to compete with and overshadow the Favorskii rearrangement in a nonpolar solvent such as ether. The rate of E2 elimination brought about by amines is not strongly dependent on solvent polarity.[12] The Favorskii rearrangement, on the other hand, requires a polar transition state for the removal of an α-hydrogen and the formation of an enolate ion. The rate of enolate ion formation should be greatly accelerated by an increase in solvent polarity. Although quantitative data are not available, Cram[13] has cited an increase in rate of 10^6 in the formation of a carbanion on passing from tetrahydrofuran to methanol. A rate increase of much smaller magnitude could turn the tide in favor of a Favorskii rearrangement when methanol is employed as solvent.

Evidence that proton removal and enolate formation is rate determining,[14] or at least comparable in rate with subsequent steps in the Favorskii rearrangement, was provided by the recovery of starting materials and products which were free of deuterium as indicated by mass spectral analysis, after tribromides II and VI were kept for a short time with N,N-dideuterioisopropylamine in ether.

In summary, carvone tribromides II and VI undergo a Favorskii rearrangement with primary amines in methanol. While tribromide II shows similar behavior in ether, tribromide VI undergoes almost exclusive 1,2-elimination in this solvent. It is concluded that axial α-halo ketones undergo the Favorskii rearrangement and that changes in solvent polarity have a profound effect on the rate of competing reactions.

Experimental Section[15]

The Reaction of Ammonia with Carvone Tribromide.—Carvone tribromide, prepared from 30 g of carvone by the procedure described by Wallach,[4] was dissolved in 140 ml of dry amyl alcohol and ammonia was bubbled into the solution for 1 hr. After standing for 2 hr the mixture was poured into dilute sulfuric acid. The acidic solution was extracted with ether and then neutralized at 0° with potassium hydroxide solution. The resulting mixture was extracted with ether. The ether solution was dried and the ether removed to afford 12.3 g of a light brown oil. A sample, purified by evaporative distillation, λ_{max} 3.01 and 6.01 μ, showed a nmr spectrum

(11) A. Baeyer, *Ber.*, **27**, 1919 (1894); G. Wagner, *ibid.*, **27**, 1652, 2270 (1894).

(12) R. G. Pearson and D. C. Vogelsong, *J. Am. Chem. Soc.*, **80**, 1048 (1958).

(13) D. J. Cram and L. Gosser, *ibid.*, **85**, 3890 (1963).

(14) R. Deghenghi, G. Schilling, and G. Papineau-Couture, *Can. J. Chem.*, **44**, 789 (1966).

(15) All boiling and melting points are uncorrected. Nuclear magnetic resonance spectra were measured at 60 Mc with a Varian Associates A-60 spectrometer. Chemical shifts are given as δ values in parts per million with reference to tetramethylsilane as an internal standard. Infrared spectra were recorded on Perkin-Elmer Models 221, 421, or Infracord spectrophotometers. Microanalyses were performed by Dr. C. S. Yeh and associates.

superposable on the nmr spectrum of carvenolide except for a broad signal at 6.08 ppm. Heating the oil in aqueous acetone gave carvenolide which was recrystallized from pentane and showed mp 41–42°.

Reactions of *trans*-Carvone Tribromide (II). Isopropylamine in Ether.—To a stirred solution of 30.0 g (0.0768 mole) of *d-trans*-carvone tribromide II[4] in 300 ml of anhydrous ether was added dropwise over a 15-min period 50 g (0.84 mole) of isopropylamine. The mixture was stirred at room temperature for 67 hr and was then filtered to remove 30.3 g (94%) of isopropylamine hydrobromide. The filtrate was extracted three times with 10% aqueous sulfuric acid and dried over magnesium sulfate. Removal of the ether left a white solid which after trituration with pentane weighed 0.90 g (5.7%). Recrystallization from ethanol–water gave long, silky, white needles of the unsaturated amide VIIIa: mp 126–132° (slight dec); infrared maxima at 2.94, 6.07, and 6.61 μ characteristic of –C(=O)NH–. The nmr spectrum displayed a doublet centered at 1.08 (J = 6.5 cps, $(CH_3)_2CHN$), broad signals at 1.67 and 1.75 ($CH_3C{=}C$), multiplets between 3.6 and 4.2, and a multiplet at 5.50 ppm (C=CH–).

Anal. Calcd for $C_{13}H_{21}NO$: C, 75.37; H, 10.21; N, 6.76. Found: C, 75.65; H, 10.43; N, 6.82.

The aqueous sulfuric acid extracts obtained above were neutralized and extracted with ether. The ether solution was dried and distilled *in vacuo* to give 11.7 g of a colorless liquid, bp 67–68° (1 mm), which showed strong absorption at 5.92 μ and nmr signals at 0.92, 0.96, 1.03, and 1.07 ($(CH_3)_2CHN$), 1.24 and 1.32 ($(CH_3)_2C$–O–), 1.83 ($CH_3C{=}C$), 2.40 (–CH_2–), 2.78, 3.63, and 5.21 ppm (CH=C).

Anal. Calcd for $C_{13}H_{21}NO$: C, 75.31; H, 10.21; N, 6.76. Found: C, 75.03; H, 9.87; N, 7.04.

Hydroxyamide IX.—A solution of 1.0 g of iminolactone VIIa in aqueous ethanol was heated for 2 days. The solvent was removed to leave a white solid which was recrystallized from aqueous ethanol and showed mp 170–171°; 3.1, 6.2, and 6.5 μ; and nmr signals at 1.08, 1.11, 1.18, and 1.22 (isopropyl-N), 1.18 and 1.30 ($(CH_3)_2C$–O–), 1.70 ($CH_3C{=}C$), 2.50, 2.65, 3.10, a wide multiplet centered at 4.1 ($CH(CH_3)_2$), 4.70 (CH=C), and 6.1 ppm (–NH).

Anal. Calcd for $C_{13}H_{23}NO_2$: C, 68.98; H, 10.69. Found: C, 69.42; H, 10.40.

When 10 g of iminolactone VIIa was heated for 3 days with 5% hydrochloric acid, there was obtained, after extraction, distillation, and crystallization, 3.9 g of carvenolide.

Cyclohexylamine in Diethyl Ether.—A mixture of 25.0 g (0.064 mole) of *trans*-carvone tribromide (II) and 50.7 g (0.512 mole) of cyclohexylamine in 300 ml of anhydrous ether was stirred for 72 hr. The mixture was worked up as described above to give 31.0 g (89.6%) of cyclohexylamine hydrobromide and 6.3 g of a neutral fraction. The neutral fraction was dissolved in ethanol, treated with Norit, and water added. On cooling, 2.6 g (16.3%) of fluffy white needles, mp 141–147°, were obtained. Repeated recrystallization from aqueous ethanol raised the melting point to 143–147°. The unsaturated amide VIIId showed maxima at 2.90, 5.95–6.10, and 6.55 μ and nmr signals at 1.69 ($CH_3C{=}C$–), superimposed upon broad absorption between 1.0 and 2.5, broad multiplets centered at 3.04 and 3.72, and a broad multiplet at 5.52 ppm (CH=C–).

Anal. Calcd for $C_{16}H_{25}NO$: C, 77.67; H, 10.19; N, 5.66. Found: C, 76.96; H, 10.31; N, 6.04.

Work-up of the aqueous sulfuric acid extracts gave 9.10 g (56.8%) of a colorless liquid, bp 98–101° (0.25 mm), which solidified at *ca.* 0°. The iminolactone VIId showed infrared peaks at 3.43, 5.95, 7.94, 8.95, 10.19, and 12.42 μ and the nmr spectrum displayed singlets at 1.26 and 1.35 ($(CH_3)_2$–C–O), superimposed on a broad methylene signal, a broad signal at 1.83 ($CH_3C{=}C$–), a series of multiplets between 2.2 and 3.7, and a broad signal centered at 5.25 ppm (–C=CH–).

Anal. Calcd for $C_{16}H_{25}NO$: C, 77.67; H, 10.19; N, 5.66. Found: C, 76.99; H, 9.83; N, 5.76.

***n*-Propylamine in Diethyl Ether.**—A mixture of 20.0 g (0.0512 mole) of *trans*-carvone tribromide (II) and 24.2 g (0.41 mole) of *n*-propylamine in 250 ml of ether was stirred for 70 hr. Filtration gave 19.8 g (86%) of *n*-propylamine hydrobromide. The solvent was removed from the filtrate and 1.25 g (11.9%) of crystalline neutral material, mp 111–116°, deposited from the resulting oil. Recrystallization of this neutral product from hexane and then from ethanol–water gave long silky needles, mp 115–118°, which displayed peaks at 2.93, 6.00, 6.59, and 8.1 μ. The nmr spectrum of amide VIIIb exhibited a triplet centered at 0.88 (J = 7 cps, CH_3CH_2), a multiplet at 1.44 ($CH_3CH_2CH_2$–), a broad vinyl methyl resonance centered at 1.72, multiplets at 2.4, 3.15, and 3.85, and a broad signal at 5.60 ppm (–C=CH–).

Anal. Calcd for $C_{13}H_{21}NO$: C, 75.31; H, 10.21; N, 6.76. Found: C, 75.03; H, 10.13; N, 6.73.

The liquid which remained after removal of amide VIIIb was distilled *in vacuo* to give 6.50 g of iminolactone VIIb, bp 72–75° (0.5 mm), $n^{20}D$ 1.4815, whose infrared resembled that of the iminolactones described earlier. The nmr spectrum was consistent with the formulation of the liquid as the iminolactone VIIb.

Anal. Calcd for $C_{13}H_{21}NO$: C, 75.31; H, 10.21; N, 6.76. Found: C, 75.32; H, 10.44; N, 6.81.

Allylamine in Ether.—A mixture of 20.0 g (0.0512 mole) of II and 29.2 g (0.512 mole) of allylamine in 300 ml of ether was stirred at room temperature under a nitrogen atmosphere for 70 hr. The liquid layer of allylamine hydrobromide was removed and the ether was distilled to leave an orange oil, which partly solidified. The residue was triturated with pentane and filtered to afford 1.23 g of fluffy needles. Recrystallization from hexane and then ethanol–water gave long, fibrous needles, mp 111–114°, whose infrared spectrum was similar to the amides described earlier. The nmr spectrum showed a vinyl methyl resonance at 1.71, broad multiplets at 3.06, 3.88, and 5.00, and a complicated multiplet between 5.21 and 5.64 ppm (–C=CH–, –C=CH_2).

Anal. Calcd for $C_{13}H_{19}NO$: C, 76.07; H, 9.32; N, 6.82. Found: C, 75.95; H, 9.40; N, 6.96.

The filtrate obtained after removal of the amide VIIIc was distilled to give two fractions: (a) 7.20 g of iminolactone VIIc, bp 79–83° (0.75 mm), and (b) 0.60 g of amide VIIIc, bp 120–126° (0.65 mm). A redistilled sample of iminolactone VIIc showed bp 57° (0.18 mm), $n^{20}D$ 1.4947. The nmr spectrum exhibited three methyl signals at 1.26, 1.33, and 1.87, a multiplet centered at 2.37 (–CH–CH_2CH=C–), multiplets at 2.79, 3.5, and 3.76, and complex signals between 4.91 and 6.1 ppm (–C=CH, –CH=CH_2).

Anal. Calcd for $C_{13}H_{19}NO$: C, 76.07; H, 9.32; N, 6.82. Found: C, 75.79; H, 9.28; N, 6.83.

Ethylamine in Benzene.—A mixture of 7.82 g (0.020 mole) of tribromide II, 4.50 g (0.200 mole) of anhydrous ethylamine, and 100 ml of dry benzene was kept in a stoppered flask at room temperature for 70 hr. The ethylamine hydrobromide (7.30 g, 96.5%) and benzene were removed affording a tan oil from which white fluffy crystals separated on standing. The residue was triturated with pentane and the solid collected by filtration. Recrystallization from ethanol–water gave silky, white needles, mp 130–133°, showing infrared peaks at 2.83 and 6.28 μ. The nmr spectrum exhibited a triplet methyl resonance centered at 1.08 (J = 7 cps), a vinyl methyl at 1.70, multiplets between 2.8 and 3.5, a broad signal at 3.82 (–C=C–CH–C=O), and a multiplet centered at 5.55 ppm (C=CH–).

Anal. Calcd for $C_{12}H_{19}NO$: C, 74.56; H, 9.93; N, 7.24. Found: C, 74.43; H, 9.87; N, 7.16.

The filtrate remaining after the separation of amide VIIIe was distilled and gave 2.72 g (70.5%) of colorless iminolactone VIIe: bp 60° (0.35 mm); $n^{20}D$ 1.4809; infrared, 5.90 μ. The nmr spectrum of this product was consistent with its assignment as iminolactone VIIe.

Anal. Calcd for $C_{12}H_{19}NO$: C, 74.56; H, 9.93; N, 7.24. Found: C, 74.27; H, 9.82; N, 7.22.

From the residue after distillation of VII was obtained an additional 90 mg of amide VIIIe.

Reactions of *cis*-Carvone Tribromide (VI). A. Isopropylamine in Ether.—A mixture of 30 g (0.076 mole) of *dl-cis*-carvone tribromide (VI), 35.3 g (0.597 mole) of isopropylamine, and 450 ml of dry ether was stirred at room temperature under a nitrogen atmosphere for 70 hr. The isopropylamine hydrobromide (*ca.* 21 g) was removed and the solution was extracted three times with 5% aqueous sulfuric acid, three times with 5% aqueous sodium hydroxide solution, once with water, and then dried over anhydrous magnesium sulfate. The solvent was carefully removed under reduced pressure to give 20.6 g of an oily residue which solidified on standing. Repeated recrystallization from hexane followed by sublimation afforded colorless prisms, mp 44.5–46°, which showed infrared peaks at 5.95, 6.17, 7.17, 8.97, 9.1, and 10.32 μ and λ_{max} 250 mμ (ϵ 12,870). The nmr spectrum of the unsaturated ketone XIII

displayed a broad singlet at 1.87 ($(CH_3)_2$-C-Br), a triplet centered at 1.87 (J(homoallylic) = *ca.* 1.5 cps, CH_3-C=C-CH_2), and a series of multiplets between 2.0 and 3.1 ppm.

Anal. Calcd for $C_{10}H_{14}Br_2O$: C, 38.74; H, 4.55; Br, 51.55. Found: C, 38.47; H, 4.81; Br, 51.53.

The 2,4-dinitrophenylhydrazone of unsaturated bromo ketone XIII crystallized from ethyl acetate–ethanol as shimmering orange needles, mp 153–155.5°.

Anal. Calcd for $C_{16}H_{18}Br_2N_4O_4$: C, 39.22; H, 3.70; N, 11.43; Br, 32.61. Found: C, 39.19; H, 3.67; N, 11.19; Br, 32.35.

The aqueous sulfuric acid extract obtained above was made basic with aqueous sodium hydroxide solution and extracted with ether. The ether solution was dried over anhydrous magnesium sulfate and distilled to give 0.55 g (3.5%) of iminolactone VIIa. Approximately 1 g of nondistillable red resin remained as a pot residue.

Cyclohexylamine in Ether, Short Reaction Time, Distillative Work-up.—A mixture of 20.0 g of *cis*-carvone tribromide (VI), 75 g of cyclohexylamine, and 250 ml of ether was stirred at room temperature for 24 hr. The mixture was worked up as described above except that the neutral fraction was distilled and gave 11.7 g (74%) of 3-bromocarvacrol, bp 114–115° (1.2 mm), which was identified on the basis of its infrared and nmr spectra. Work-up of the acidic extract afforded a 12–15% yield of iminolactone VIId.

Cyclohexylamine in Ether, Long Reaction Time.—The reaction of *cis*-carvone tribromide (VI) with cyclohexylamine was carried out as described in the case of the reaction with isopropylamine except that the mixture was allowed to stir at room temperature for 7 days. Distillation of the neutral fraction afforded 4.9 g (52%) of 3-bromocarvacrol. The aqueous sulfuric acid extracts were neutralized with aqueous sodium hydroxide solution and extracted with methylene chloride. The methylene chloride solution was dried over anhydrous magnesium sulfate and all volatile material was removed *in vacuo* to give 2.74 g (27%) of crystalline residue. Repeated recrystallizations from hexane gave straw yellow prisms, mp 143.5–144°, which displayed strong infrared absorption at 6.5 μ and λ_{max} 314 mμ (ϵ 34,600). The nmr spectrum exhibited singlets at 0.90, 1.23 (2 CH_3–), and 1.68 (CH_3-C=C–) superimposed on a very broad signal attributed to methylene and methine protons, multiplets between 2.3 and 2.7, and two broad signals centered at *ca.* 3.50 and 4.68 ppm (–NH– and –CH–N–).

Anal. Calcd for $C_{16}H_{25}NO$: C, 77.68; H, 10.19; N, 5.66. Found: C, 77.97; H, 10.35; N, 5.81.

The same compound was isolated when the unsaturated bromo ketone XIII was allowed to stir with cyclohexylamine in ether for 70 hr.

Isopropylamine in Methanol.—A solution of 10.0 g (0.0255 mole) of *dl-cis*-carvone tribromide (VI), 15.1 g (0.255 mole) of isopropylamine, and 100 ml of absolute methanol was stirred at room temperature under a nitrogen atmosphere for 45 hr. The solvent was removed under diminished pressure and ether was added. The resulting precipitate of isopropylamine hydrobromide was removed by filtration and the filtrate was washed with 10% aqueous sulfuric acid. The ether solution was dried over anhydrous magnesium sulfate and the ether was removed to leave 1.02 g of a pale yellow oil. Recrystallization from *n*-hexane afforded 32 mg (1%) of the isopropyl amide VIIIa. No other neutral product could be isolated in pure form.

The sulfuric acid extract was made basic with aqueous sodium hydroxide and extracted with ether. Distillation of the ether extracts gave 3.35 g (63.5%) of iminolactone VIIa, bp 50–53° (0.3 mm).

When a similar reaction was conducted with 5 g of tribromide VI in 100 ml of dry ether containing 2 ml of methanol, there was obtained 3.08 g (77.8%) of unsaturated bromo ketone XIII and 0.437 g (16.6%) of basic iminolactone VIIa.

Registry No.—IIa, 15095-60-0; VI, 15093-23-9; VIIa, 15093-24-0; VIIb, 15093-25-1; VIIc, 15093-26-2; VIId, 15093-27-3; VIIe, 15093-28-4; VIIIa, 15093-29-5; VIIIb, 15093-30-8; VIIIc, 15153-12-5; VIIId, 15093-31-9; VIIIe, 15093-32-0; IX, 15093-33-1; XIII, 15093-18-2; XIII (2,4-dinitrophenylhydrazone), 15093-19-3; XIII, 15093-20-6; XV, 15093-21-7; I, 5587-65-5.