[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Cleavage of Phenyl Alkyl Ethers and O-Heterocyclic Compounds by Sodium in Liquid Ammonia[1]

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The extent of cleavage of a number of heterocyclic compounds of the coumaran and chroman types and of phenyl alkyl (aralkyl) ethers by excess sodium in liquid ammonia was determined under relatively uniform conditions. Two paths of cleavage were established: (a) actual reductive cleavage, *e.g.*, benzyl-type ethers and anisole; and (b) β-elimination initiated by traces of sodium amide with subsequent reduction, *e.g.*, phenethyl-type ethers. Sodium amide alone effected cleavage of phenethyl phenyl ether in liquid ammonia yielding some monomeric styrene along with high boiling polymer.

The reductive cleavage of aryl ethers has been studied by numerous investigators using various methods, most of which have involved high temperature conditions. Birch and Freudenberg and their co-workers found that solutions of alkali metals in liquid ammonia were suitable agents for effecting cleavage of certain aryl alkyl ethers. Using sodium in liquid ammonia at atmospheric pressure Birch was able to isolate a 27% yield of phenol from anisole.[3] Lower yields of cresols were obtained from the corresponding tolyl ethers. Freudenberg, Lautsch and Piazolo[4] however, using the more vigorous conditions of potassium in liquid ammonia under pressure at 20°, were able to isolate a theoretical yield of phenol from the cleavage of anisole. Although veratrole was changed under these conditions into guaiacol and some catechol, the ether linkage of dihydroeugenol (4-propylguaiacol) did not undergo reductive cleavage.

Forseeing the application of this reaction to the degradation of lignin, these investigators[4] subjected lignin and several lignans having coumaran, chroman and benzofuran nuclei to the same conditions. The lignans having coumaran and benzofuran rings were cleaved to compounds shown by a titration method to have an additional hydroxyl group which arose presumably from ring-cleavage. A lignin, isolated from spruce wood by extraction with cupric ammonium hydroxide ("cuoxam" process) was treated with potassium in liquid ammonia at 20°. It was recovered to the extent of 80% but not unchanged, for its hydroxyl content was considerably higher, more than could be accounted for by loss of methoxyl groups alone. It was concluded that heterocyclic ether linkages had been broken.

More recently Shorygina, Kefeli and Semechkina[5] subjected cuoxam spruce lignin to nine successive treatments with sodium in liquid ammonia at −33°. Considerable amounts of monomeric products were obtained, in one instance 28%. Two-thirds of this was identified as dihydroeugenol which was also isolated in 80% yield when coniferyl alcohol, a presumed precursor of lignin, was treated in the same manner. Evidence was presented also for the structure of another isolated product, namely, 4-(2-hydroxypropyl)-guaiacol. These workers interpreted these results and the considerable reduction of the molecular weight of the recovered polymeric material as evidence for the presence of many ether linkages between lignin units.

The purpose of this present work was to study the reductive cleavage of a number of model compounds of simple structure to observe their relative behavior under a uniform set of conditions. Several unsubstituted heterocyclic and acyclic ethers were prepared and treated in refluxing liquid ammonia with a 5-molar excess of sodium at −33° for 5 hours.

TABLE I

CLEAVAGE OF ETHERS AND O-HETEROCYCLICS

Ether	Phenolic product (neutral product, yield, %)	Phenol or deriv., A[a]	yield, % B
Anisole	Phenol	63	..
Phenyl propyl ether (−33°)	....	0	..
Phenyl propyl ether (20°)	Phenol	40	..
Phenyl isopropyl ether	....	0	..
Phenyl benzyl ether	Phenol (1,2-diphenylethane, 31; toluene)	85	..
Phenyl phenethyl ether	Phenol (ethylbenzene)	84	..
Phenyl 3-phenylpropyl ether	....	0	..
2-Methylcoumaran	*o*-Propylphenol	54	69
2-Methylbenzofuran	*o*-Propylphenol	55	75
Benzofuran	*o*-Ethylphenol	69	71
Chroman	.... (Dihydrochroman, 57)	0	..
2-Methylchroman	.... (2-Methyldihydrochroman, 45)	0	..
2-Phenylbenzofuran	*o*-Phenethylphenol	..	45
Flavan (2-phenylchroman)	*o*-(3-Phenylpropyl)-phenol	..	71

[a] A = isolated by method A, *i.e.*, the phenol directly; B = isolated by method B, *i.e.*, by direct conversion to the phenoxyacetic acid derivative, yield representing the overall yield of the cleavage and conversion of the phenol to the derivative.

With minor variations due to the physical properties of the ethers to be cleaved and the products formed, essentially the same conditions were used

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(2) University Fellow, 1952–1953; Weyerhaeuser Timber Foundation Fellow, 1953–1954.

(3) A. J. Birch, *J. Chem. Soc.*, 102 (1947).

(4) K. Freudenberg, W. Lautsch and G. Piazolo, *Ber.*, **74**, 1879 (1941).

(5) N. N. Shorygina and T. Ya. Kefeli, *Zhur. Obshchei Khim.*, **17**, 2058 (1947); **18**, 528 (1948); N. N. Shorygina, T. Ya. Kefeli and A. F. Semechkina, *Doklady Akad. Nauk S.S.S.R.*, **64**, 689 (1949); *Zhur. Obshchei Khim.*, **19**, 1558 (1949).

throughout for sake of uniformity in comparing results. The products and yields are presented in Table I. When the ether contained two benzene nuclei it was found necessary to dissolve it in absolute ethyl ether, an inert solvent in this system, in order to disperse it in liquid ammonia. At the end of the reaction period the excess of sodium was decomposed generally with methanol although ethanol was used with the first two compounds in the table.

Although some of the phenolic cleavage products could be isolated directly from the reaction mixture after evaporation of the solvent (method A), others were too weakly acidic to be extracted from an aqueous medium. They were, however, not sufficiently soluble in petroleum solvents to extract by means of potassium hydroxide, methanol and ligroin. Consequently it was necessary to utilize an indirect method in order to obtain an easily isolated product which could be a reasonably accurate measure of the actual yield of the phenol. The procedure (method B) was adapted from that of Synerholm and Zimmerman[6] who prepared a number of aryloxyacetic acids by treating the corresponding phenols with ethanolic ethyl bromoacetate in the presence of sodium ethoxide, the ester being subsequently saponified to the acid. The dried ethereal extract of the neutral and acidic components of the reaction mixture was subjected to this treatment and the solid carboxylic acid extracted and purified. Because in control experiments *o*-propylphenol was converted to the derivative by this method in yields of about 80%, it seems justifiable that the yields given in Table I under method B actually express yields of the corresponding phenols of the order of 25% higher.

From Table I it can be seen that all of the *O*-heterocyclic compounds substantially cleaved except chroman and its 2-methyl homolog. The behavior of the simple ethers, however, gave the best clue to the nature of the reactions taking place. The behavior of anisole was substantially in agreement with the results of Birch or Freudenberg, the reaction conditions being of a severity intermediate between those of the two previous investigations. Both propyl phenyl ether and isopropyl phenyl ether were inert under the normal conditions. Birch has pointed out that the greatest part of the energy required in forming the transition state containing the phenoxide ion and alkyl carbanion is that of formation of the alkyl carbanion,[7] the ease of formation of which decreases with increasing alkyl-substitution of methyl carbanion.

Both 1- and 2-electron cleavage mechanisms for ethers by dissolving metals have been proposed and the merits of these proposals have been summarized by Birch.[7] The initial cleavages of anisole, for example, by these mechanisms are

$$\mathrm{PhOCH_3} \xrightarrow{1e} \mathrm{PhO^-} + \mathrm{CH_3}\cdot;\quad \mathrm{PhOCH_3} \xrightarrow{2e} \mathrm{PhO^-} + \mathrm{CH_3^-}$$

In an electron-rich atmosphere, the methyl carbanion should predominate over the methyl radical. The highly basic methyl carbanion would then undergo immediate exchange with ammonia to form methane and amide ion.

Of the three aralkyl phenyl ethers, only the 3-phenylpropyl was unreactive. Benzyl phenyl ether was easily cleaved in agreement with the usual ease of reduction of benzyloxy compounds. The isolation of 1,2-diphenylethane confirmed the original observations of Shorygin and Skoblinskaya.[8] Toluene was also detected but not isolated. The 1,2-diphenylethane probably arises from the displacement of phenoxide ion by the attack of the benzyl carbanion which, although slightly more basic than amide ion, has been shown to have sufficient stability in liquid ammonia to displace bromide from phenethyl bromide.[9] The above mechanism would hold for the benzyl ethers

$$\mathrm{PhOCH_2Ph} \xrightarrow{2e} \mathrm{PhO^-} + \mathrm{PhCH_2^-}$$

after which the benzyl carbanion would change either into toluene or diphenylethane

$$\mathrm{PhOCH_2Ph} + \mathrm{PhCH_2^-} \longrightarrow \mathrm{PhO^-} + \mathrm{PhCH_2CH_2Ph}$$

The non-cleavage of phenyl 3-phenylpropyl ether speaks for insufficient energy to cleave the ether bond to yield a 3-phenylpropyl carbanion.

In the light of this, one may ask why phenyl phenethyl ether underwent cleavage in such high yields. Obviously it could not have been *via* the electrons of the dissolving metal in the manner of anisole or phenyl benzyl ether, otherwise the 3-phenylpropyl ether should have cleaved also. Instead, a β-elimination mechanism is postulated. Amide ion ($\mathrm{NH_2^-}$) is responsible for the effect, and not the dissolving metal. It can be assumed that a trace of this ion was present initially in the system of sodium and ammonia. The amide ion initiates the reaction by extracting a proton at the relatively acidic carbon atom alpha to the benzene ring. Elimination of phenoxide ion, a much weaker base than amide ion, takes place probably by a mechanism analogous to the E2 attack of ethoxide ion on phenethyl bromide

$$\mathrm{PhCH_2CH_2OPh} + \mathrm{NH_2^-} \longrightarrow [\mathrm{Ph}\overset{-}{\mathrm{C}}\mathrm{H}\overset{\curvearrowright}{-}\mathrm{CH_2}\text{-}\overset{\curvearrowright}{\mathrm{O}}\mathrm{Ph}] \longrightarrow \mathrm{PhO^-} + \mathrm{NH_3} + \mathrm{PhCH{=}CH_2}$$

In an experiment in which the ether was treated with a slight excess of sodium amide (no sodium metal) in liquid ammonia, an 84% yield of phenol was isolated along with some styrene and much polymeric material. Styrene has been shown to be polymerized by sodium amide in liquid ammonia[10] and to be both reduced and polymerized by sodium in ammonia,[11] but in the system with excess sodium it was undoubtedly reduced as it was formed by the large excess of free electrons. No polymer formation was observed. The reduction of styrene to ethylbenzene forms more amide ion which ensures continuation of the reaction.

$$2\mathrm{Na} + \mathrm{PhCH{=}CH_2} + 2\mathrm{NH_3} \longrightarrow \mathrm{PhCH_2CH_3} + 2\mathrm{NaNH_2}$$

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[6] M. E. Synerholm and P. W. Zimmerman, *Contrib. Boyce Thompson Inst.*, **14**, 91 (1945).

[7] A. J. Birch, *Quart. Revs.* (*London*), **4**, 69 (1950).

[8] P. P. Shorygin and S. A. Skoblinskaya, *Compt. rend. acad. sci. U. R. S. S.*, **14**, 505 (1937); *C. A.*, **31**, 5777 (1937).

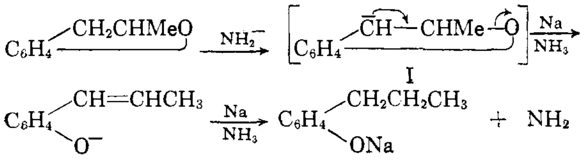
[9] C. B. Wooster and N. W. Mitchell, THIS JOURNAL, **52**, 688 (1930).

[10] J. J. Sanderson and C. R. Hauser, *ibid.*, **71**, 1595 (1949); M. G. Evans, W. C. E. Higginson and N. S. Woodring, *Rec. trav. chim.*, **68**, 1069 (1949).

[11] C. B. Wooster and J. F. Ryan, THIS JOURNAL, **56**, 1133 (1934).

This is the first clear-cut example of ether cleavage by β-elimination brought about by a reagent other than an organometallic compound that has come to our attention. Letsinger and Pollart[12] found that ethyl aryl ethers can be cleaved by propylsodium to give ethylene in yields as high as 74%. Although benzyl ethyl ether has been shown to undergo an apparent β-elimination to yield ethylene by means of either phenyllithium[13] or potassium amide in liquid ammonia,[14] the mechanism has been shown to be an extraction of a proton from the α-carbon of the benzyl followed by an intramolecular *cis* elimination.[12]

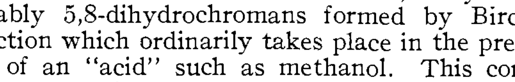
The cleavage of our heterocyclic systems by sodium in liquid ammonia can be explained easily by the mechanisms described for the acyclic systems. The 2-methylcoumaran can be regarded as a β-substituted phenyl phenethyl ether in which the benzene ring is common to both moieties of the ether. Hence the reaction is one of beta elimination starting with the carbanion I.



I

That the benzofurans are reduced to coumarans as the first step was indicated by the rapid initial decolorization of the sodium solution as sodium was added to the solution of the compound in ammonia. Various heterocyclic compounds are known to undergo such reduction under these conditions. Thus, benzofuran and its 2-methyl homolog are analogous to 2-methylcoumaran. 2-Methylcoumaran was shown to be cleaved by a slight excess of sodium amide to *o*-propenylphenol. This reaction has been effected previously by the action of phenyllithium.[15]

Chroman, on the other hand, like the analogous phenyl 3-phenylpropyl ether was not cleaved. The carbanion IIa, analogous to I, could not undergo β-elimination at a C–O bond, hence no opening of the hetero ring. The same argument would hold for the 2-methyl homolog IIb. Chroman and 2-methylchroman, although not cleaved, were changed under conditions of the experiments into neutral substances of the same elementary composition as the expected phenol. Though the exact structure was not determined, they are probably 5,8-dihydrochromans formed by Birch reduction which ordinarily takes place in the presence of an "acid" such as methanol. This condition was fulfilled when methanol was added to decompose the excess of sodium. In an experiment in which the fast-acting acid, ammonium chloride, was used to decompose the sodium, only about a fifth as much reduction of the aromatic ring took place.



IIa, R = H
b, R = CH_3
c, R = C_6H_5

III

2-Phenylbenzofuran, when reduced, and flavan behaved as substituted benzyl phenyl ethers. It is interesting to note that the red color associated with the reduction of stilbene by sodium in liquid ammonia was also characteristic of 2-phenylbenzofuran. Flavan would be expected to be indifferent if carbanion IIc were the functioning position, but the phenyl group brings carbanion III into play. This, obviously, can cleave in the manner of benzyl ethers.

Experimental[16]

Starting Materials.—**2-Methylcoumaran** (b.p. 74.5–76.5° at 10 mm.) was obtained in substantial amount directly as a by-product of the Claisen rearrangement of allyl phenyl ether.

2-Methylbenzofuran (b.p. 89–92° at 17 mm.) was prepared by the bromination of *o*-allylphenyl acetate and subsequent ring closure by sodium ethoxide.

Benzofuran (b.p. 54–56° at 9 mm.) was prepared in three steps from coumarin by decarboxylation of coumarilic acid.

2-Phenylbenzofuran (m.p. 119–120°) was prepared in several steps from salicylaldehyde and ethyl phenylbromoacetate essentially by the procedure described by Kawai, Nakamura and Sugiyama.[17]

Flavan (m.p. 43–45°) was prepared by two methods. The method of Hultzsch,[18] *viz.*, heating salicyl alcohol and styrene, was successful only in producing small amounts in low yield. The better though longer plan, adapted from Harries and Busse,[19] involved the hydrogenation of salicylideneacetophenone with palladium-on-charcoal, reduction of the ketone with lithium aluminum hydride, and ring closure of the carbinol with hydrogen chloride in methanol.

2-Methylchroman (b.p. 76° at 3 mm.) was obtained from salicylideneacetone by a procedure similar to that described for flavan. The hydrogenation in methanol, using palladium-on-charcoal, yielded a product (b.p. 98° at 2.5 mm.) having no carbonyl absorption in the infrared. Since the expected ketone was recovered by boiling with 5% sulfuric acid for about 20 min., the intermediate was presumed to be the cyclic acetal, 2-methyl-2-methoxychroman. The final product was obtained by boiling the carbinol for 5 min. in 48% hydrobromic acid.

Chroman (b.p. 68–70° at 3 mm.) was best prepared from coumarin by hydrogenation, reduction to the carbinol, and ring closure by the methods described for 2-methylchroman.

The phenyl alkyl (and aralkyl) ethers, if not commercially available, were prepared by the Williamson synthesis from sodium ethoxide, phenol and the corresponding bromides. The preparation of benzyl phenyl ether differed only in the use of an aqueous medium.

General Procedure.—About 250 ml. of liquid ammonia was distilled from a commercial cylinder into a 500-ml. three-neck round-bottom flask, cooled by Dry Ice and isopropyl alcohol. The flask was fitted with a mechanical stirrer and an open tube condenser cooled by Dry Ice and isopropyl alcohol but protected from moisture by a drying tube containing potassium hydroxide pellets. When all of the ammonia was condensed, the bath was removed and the ammonia allowed to reflux at −33°. The ether, usually 0.03 to 0.1 mole, was then added slowly. Anhydrous ethyl ether (50–100 ml.) was added as a solvent when necessary to dissolve a solid compound or to solubilize it in the ammonia. Small pieces of freshly cut sodium were added cautiously but as quickly as possible to avoid loss of ammonia or introduction of moisture. The stirred mixture was allowed to react for 5 hours at reflux. Excess of sodium was then decomposed by cautious addition of methanol or solid ammonium chloride. The ammonia was allowed to evaporate. The residue was diluted with about 100 ml. of

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(12) R. L. Letsinger and D. F. Pollart, THIS JOURNAL, **78**, 6079 (1956).

(13) G. Wittig and L. Löhman, *Ann.*, **550**, 260 (1942).

(14) C. R. Hauser and S. W. Kantor, THIS JOURNAL, **73**, 1437 (1951).

(15) J. G. Traynham, *J. Sci. Lab. Denison Univ.*, **42**, Art. 4/5, 60 (1951); *C. A.*, **46**, 965 (1952).

(16) All melting points are uncorrected.

(17) S. Kawai, T. Nakamura and N. Sugiyama, *Ber.*, **72**, 1146 (1939).

(18) K. Hultzsch, *J. prakt. Chem.*, **158**, 286 (1942).

(19) C. Harries and G. Busse, *Ber.*, **29**, 378 (1896).

water and acidified with 6 *N* hydrochloric acid. The organic layer was extracted several times by ether (or petroleum pentane if the phenolic material was sufficiently soluble). The organic layer was dried over magnesium sulfate and the product was isolated from it by one of the following methods.

Method A.—If the phenolic cleavage product was sufficiently acidic to be extracted from an ether or pentane solution of the total reaction mixture, it was separated from the neutral components by extracting with 5% sodium hydroxide solution. Subsequent acidification, extraction by ether, and drying yielded the phenol on distillation.

Method B.—The first method failed when the phenol was too weak to be extracted by aqueous sodium hydroxide and when the reaction mixture was not sufficiently soluble in petroleum solvents. The ether solution of the acidic and neutral components was evaporated and the residual oil taken up in 20–30 ml. of absolute alcohol containing an amount of sodium ethoxide equivalent to a 100% yield of the phenolic component. The resulting solution was refluxed with an equimolar amount of ethyl bromoacetate for 1 to 2 hours. A methanolic solution containing a 10% excess of potassium hydroxide was added, and refluxing was continued for 30 to 60 minutes to saponify the ester. About half of the alcohol was evaporated. The remainder was diluted liberally with cold water and ice. The ice-cold solution was acidified and extracted several times with ether. The carboxylic acid was extracted from the mixture with 10% sodium bicarbonate solution. Acidification of this fraction yielded the solid acid derivative of the phenol or occasionally an oil which gradually solidified. This method was not as satisfactory for the isolation of phenol itself since phenoxyacetic acid seemed to be too soluble in the alcoholic aqueous extracts.

The phenolic products were identified by conversion to the phenoxyacetic acid derivatives and in some cases to the N-phenylcarbamates. Phenol itself was isolated as the crystalline material and not further characterized.

From 20 g. (0.15 mole) of 2-methylcoumaran was obtained by method A 10.8 g. (54%) of *o*-propylphenol distilling at 101–103° at 13 mm. Likewise 7 g. (0.52 mole) of 2-methylbenzofuran yielded 3.9 g. (55%) of the same phenol. The *o*-propylphenoxyacetic acid derivatives, recrystallized from alcohol–water, melted at 102–103° and gave no depression on mixing with each other or with the derivative prepared from the phenol obtained by hydrogenation of *o*-allylphenol.

Anal. Calcd. for $C_{11}H_{14}O_3$: C, 68.02; H, 7.27. Found: C, 67.90; H, 7.52.

The N-phenylcarbamates, recrystallized from hexane (m.p. 107–109°, lit.[20] 111°) also were identical.

From isolation by method B, 5.0 g. of *o*-propylphenoxyacetic acid (69%) was obtained from the cleavage of 2-methylcoumaran. The dried oily product from the cleavage reaction was treated with sodium ethoxide (from 0.86 g. of sodium) and 6.2 g. of ethyl bromoacetate. The resulting ester was saponified with 25 ml. of 10% methanolic potassium hydroxide and the acid isolated as described under the general procedure. In a similar manner 4.0 g. (0.030 mole) of 2-methylbenzofuran yielded 4.4 g. (75%) of the same product, characterized as above.

Benzofuran (15.0 g., 0.127 mole) yielded by method A 10.6 g. (69%) of *o*-ethylphenol, distilling at 91–92° at 13 mm. By method B 4.0 g. (0.034 mole) of benzofuran gave 4.3 g. (71%) of *o*-ethylphenoxyacetic acid which, on recrystallization from methanol–water, melted at 135–137° (lit.[21] 140–141°) and was identical to that prepared directly from the isolated phenol. The melting points of the N-phenylcarbamate (140.5–141.5°) and 3,5-dinitrobenzoate (107–108°) agreed with the literature.[22]

From flavan (3.5 g., 0.083 mole) was obtained by method B 3.2 g. (71%) of *o*-(3-phenylpropyl)-phenoxyacetic acid, m.p. 90–91°. Ether was required to disperse the sparingly soluble flavan in the liquid ammonia. It dissolved during the course of the reaction.

Anal. Calcd. for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71; neut. equiv., 270. Found: C, 75.82; H, 6.40; neut. equiv., 271, 274.

2-Phenylbenzofuran (4.0 g., 0.021 mole), on treatment with sodium, gave a blood-red color before the blue color of the solution containing excess sodium persisted. Ether was required to solubilize the starting material. By method B 2.6 g. (47%) of *o*-phenethylphenoxyacetic acid was isolated. The melting point even on recrystallization three times from hexane was not sharp, but it melted most rapidly in the range 128–130° (lit. 137°).

Anal. Calcd. for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29. Found: C, 75.15; H, 6.54.

Phenol was the product of cleavage of all of the acyclic phenyl ethers and was characterized from the phenolic extract of method A by its crystalline state without further attempts at purification. Anisole (10 g., 0.093 mole) yielded 5.5 g. (63%) of phenol. Nothing was obtained from the phenolic extracts from propyl phenyl ether (5.0 g., 0.037 mole), from phenyl 3-phenylpropyl ether (6.0 g., 0.028 mole) nor from isopropyl phenyl ether (8.0 g., 0.059 mole). In the latter example the starting material was recovered by distillation (5.3 g.).

When propyl phenyl ether (5.0 g., 0.037 mole) was treated with sodium in the glass liner of an Ipatieff hydrogenation autoclave and allowed to come to room temperature under 10 atm. pressure, 1.4 g. (40%) of phenol was obtained.

From benzyl phenyl ether (6.0 g.) was obtained 2.6 g. of phenol, 0.9 g. of 1,2-diphenylethane (31%) which on recrystallization from methanol melted at 51–52° (lit.[23] 52°), and some toluene which was not isolated but merely detected by odor. Phenethyl phenyl ether (6.0 g., 0.030 mole) yielded 2.4 g. (84%) of phenol. The neutral extract yielded on distillation 1.2 g. of ethylbenzene (b.p. 132–134°, n^{25}D 1.4930) which agreed with published values (b.p. 136°, n^{25}D [extrapolated from 20°] 1.4937).

Chroman (3.5 g., 0.022 mole) yielded no phenolic extract by method A, even when the dried pentane extract of the acidified reaction mixture was extracted with methanolic potassium hydroxide. The pentane solution yielded 2.0 g. (57%) of the dihydrochroman, b.p. 71–74° at 7 mm., n^{25}D 1.5053. An infrared spectrum showed no significant hydroxyl absorption but did indicate some unchanged chroman (n^{25}D 1.5455). When ammonium chloride instead of methanol was used to decompose the excess sodium the n^{25}D of the product was 1.5378, indicating only about 20% reduction. The ultraviolet spectrum showed peaks at 216 mμ (ϵ_{max} 2600) and at 276 mμ (ϵ_{max} 160).

Anal. Calcd. for $C_9H_{12}O$: C, 79.37; H, 8.88. Found: C, 78.50; H, 8.55.

2-Methylchroman (5.0 g., 0.039 mole) behaved in an analogous manner, yielding 2.3 g. (45%) of a dihydro compound, b.p. 74–77° at 6 mm., n^{25}D 1.4981. Again the infrared spectrum showed evidence of slight contamination with starting material, and the ultraviolet spectrum had peaks similar to chroman at 216 and 276 mμ.

Anal. Calcd. for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 79.09; H, 9.25.

Cleavage with Sodium Amide.—2-Methylcoumaran (5.0 g., 0.037 mole) was treated with an equimolecular amount of sodium amide from 0.86 g. of sodium. The reaction conditions were as described for the reductive cleavage above. The mixture was neutralized with 2 g. of ammonium chloride. *o*-Propenylphenoxyacetic acid was isolated according to method B in 55% yield (4.0 g.), m.p. 115–116°, in agreement with Traynham.[15] The use of two equivalents of sodium amide did not affect the yield.

Under the same conditions 6.0 g. of phenethyl phenyl ether yielded 2.5 g. (84%) of crystalline phenol, isolated by method A. The neutral extract yielded 2.5 g. of a liquid boiling over the 140–155° range and an equal amount of high-boiling material (b.p. 200–270°). The index of refraction of the low boiling distillate (n^{25}D 1.5440) agrees closely with that of styrene (n^{25}D 1.543).

From flavan (3 g.) only the starting material was recovered from the ether extract of the acidified reaction mixture. On recrystallization from methanol, 2.3 g. (77%) was recovered.

Acknowledgment.—Microanalyses were performed by Miss H. Beck.

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[20] L. Claisen, *Ann.*, **418**, 69 (1919).

[21] W. Steinkopf and T. Höpner, *J. prakt. Chem.*, **113**, 140 (1926).

[22] G. Vavon and V. M. Mitchovitch, *Bull. soc. chim.*, [4] **45**, 963 (1929).

[23] R. Kuhn and A. Winterstein, *Helv. Chim. Acta*, **11**, 136 (1928).