Ferrichrome A.—The experiment was performed exactly as above except that 5.0 ml. of a solution containing 2.86 μmoles per ml. of iron-free ferrichrome A was used. Electrometric titration revealed 3.1 equivalents titrating with pK_a' of 4.0 and 3.1 equivalents titrating with pK of 9.3. The intact iron complex exhibits only the former buffer zone. After reaction with periodate the titration at pH 9.3 was eliminated and a new titration having the appearance of a dicarboxylic acid appeared with mid-point at pH 4.2.

Isolation of the Acid Moiety of Ferrichrome A.—To 6.5 ml. of a solution containing 148 mg. of iron-free ferrichrome A was added slowly 6.6 ml. of 0.10 N periodic acid. The acidic solution was extracted five times with 5 ml. portions of ether. The combined ether extracts were washed three times with 0.1 N HCl. The ether was evaporated under a stream of warm air and the residue dried overnight over $CaCl_2$. The product (36 mg.) was a white crystalline solid, m.p. 131–134°, very soluble in water, ether and alcohol, insoluble in benzene and petroleum ether Paper chromatography with 1-butanol:formic acid:water::100:15:150 revealed only one spot with R_f 0.87 (spray of 0.04% ethanolic chlor phenol red, pH 7). Electrometric titration gave a neutral equivalent of 72.

Anal. Calcd. for $C_6H_8O_4$: C, 49.99; H, 5.59. Found: C, 49.34; H, 5.34.

Baer test for unsaturation was positive. The ultraviolet absorption spectrum showed a peak at 217 mμ with ϵ_{max} of 10,600. Approximately 10 mg. was dissolved in 2 ml. of water, 0.2 ml. of concd. HCl and 10 mg. of palladium–charcoal catalyst were added, and a slow stream of H_2 then was passed through the solution until the 217 peak had disappeared. The acidic solution was extracted several times with ether. The residue obtained by evaporation of the combined ether extracts was taken up in the minimum volume of ether and crystallized by the addition of benzene. The melting point of the white crystalline solid was 82–84° and showed no depression on admixture with authentic β-methylglutaric acid (m.p. 84–85°, recryst. from benzene) but showed a 20 degree depression with α-methylglutaric acid (m.p. 75.5–77°). The infrared spectrum was identical with that of β-methylglutaric acid (1% KBr pellet).

A sample of pure *trans*-β-methylglutaconic acid, m.p. 130–135°, showed no melting point depression when mixed with our unsaturated acid. The two acids ran as a single spot when chromatographed on paper with a variety of solvents. The authentic acid showed identical ultraviolet and infrared spectra. Further confirmation was obtained by gas phase chromatography. Approximately 1 mg. of the acid was dissolved in 0.05 ml. of ether at 0°. A 5% excess of an ethereal solution of diazomethane, prepared by the method of McKay,[32] was added. After ten minutes, 0.01 ml. of the solution was examined with an Aerograph Model A-110-C Gas Chromatography apparatus at 193° with a helium flow rate of 50 ml./min. on a Craig succinate polyester column. Samples of the pure *cis*- and *trans*-β-methylglutaconic acids were similarly esterified and chromatographed.

Organic acid (di-methyl ester)	Retention volume
cis-β-Methylglutaconic acid	0.205
trans-β-Methylglutaconic acid	.265
Acid from ferrichrome A	.265

The acid content of ferrichrome A was determined quantitatively by the following procedure: 0.50 ml. of a solution containing 2.13 μmoles of iron-free ferrichrome A was treated with periodate as above. One drop of ethylene glycol was added and the solution extracted five times with ether. The ether was evaporated carefully and the crystalline residue quantitatively transferred to a volumetric flask and made up to the mark with 0.01 N HCl. The optical density of this solution at 217 mμ was determined with a Beckman DU spectrophotometer. The amount of acid present was calculated by reference to a standard curve of the authentic acid. Controls showed no iodate carried over during the extraction and the ratio of optical density at 217 mμ to 240 mμ agreed with that of the authentic acid. Duplicate analyses showed 3.1 moles of β-methylglutaconic acid per mole of ferrichrome A.

Acknowledgments.—The authors are indebted to James Cason, J. D. Cawley, Keith Freeman, D. M. Greenberg and R. H. Wiley for gifts of chemicals or advice.

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[32] A. F. McKay, THIS JOURNAL, **70**, 1974 (1948).

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY]

3-Bromo-2,2-dimethylcoumaran and its Reactions

BY CHARLES D. HURD AND ROSTYSLAW DOWBENKO[1]

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The reaction of 2,2-dimethylcoumaran with N-bromosuccinimide yielded a highly reactive 3-bromo-2,2-dimethylcoumaran whose structure was proved by its conversion, *via* the acetate, the alcohol and the ketone, to a bright-red 2,4-dinitrophenylhydrazone, and through its reaction with methylmagnesium iodide which gave the known 2,2,3-trimethylcoumaran. While with zinc in refluxing benzene the bromide gave a polycoumaran, with magnesium or with zinc in ether solution it gave two compounds believed to be stereoisomers of 2,2,2',2'-tetramethyl-3,3'-bicoumaran. With sodium in ether solution 3-bromo-2,2-dimethylcoumaran gave a low yield of 2-isobutenylphenol. Grignard reagents and 3-bromo-2,2-dimethylcoumaran gave mainly 3-alkylated coumarans, which furnishes a convenient method of preparing 2,2,3-trialkylcoumarans from 2,2-dialkylcoumarans.

In continuation of the studies[2] of the cleavage of O-heterocyclic compounds, such as coumarans, chromans and benzofurans, the preparation of a model compound 3-bromo-2,2-dimethylcoumaran and its ring-opening reactions were studied because of intrinsic interest and also in connection with the possibility of application in the degradation of lignin. The results obtained, although hardly suitable to the application in the degradation of coumaran-containing materials, such as lignin, seem worth reporting on their own merit.

The reaction of N-bromosuccinimide[3] with coumarans has been described on several occasions,[4] but the isolation of the resulting bromocoumarans has not been reported. One such compound, 3-bromo-2,2-dimethylcoumaran (II), has been isolated and characterized in the present work.

An attempt to obtain a bromide from 2-methylcoumaran and N-bromosuccinimide in carbon tetrachloride failed because of the almost explosive violence of the reaction and dehydrobromination of the resulting reaction mixture. Although conditions more favorable to the desired course of the reaction and isolation might have been found, this was not

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[1] Weyerhaeuser Timber Foundation Fellow, 1955–1957.

[2] C. D. Hurd and Gene L. Oliver, THIS JOURNAL, **81**, 2795 (1959).

[3] L. Horner and E. H. Winkelmann, *Angew. Chem.*, **71**, 349 (1959).

[4] E. C. Horning and D. B. Reisner, THIS JOURNAL, **72**, 1514 (1950); T. A. Geissman, T. G. Halsall and E. Hinreiner, *ibid.*, **72**, 4326 (1950); M. F. Grundon and N. J. McCorkindale, *J. Chem. Soc.*, 2177 (1957).

attempted, but attention was centered instead on 2,2-dimethylcoumaran (I) which, under usual conditions, gave in a smooth reaction a good yield of a colorless, distillable liquid which subsequently proved to be 3-bromo-2,2-dimethylcoumaran (II). The compound, on standing, rapidly became red to purple and evolved hydrogen bromide. Therefore, no satisfactory analysis could be obtained, but a crystalline phthalimido derivative[5] could be prepared for the purpose of characterization. High temperature and traces of metals seemed to catalyze the decomposition of the bromide.[6]

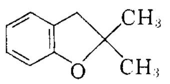
The reaction of 2,2-dimethylcoumaran with two and three moles of the bromosuccinimide proceeded less smoothly than with one mole. The reaction with two moles yielded, in addition to the monobromo compound, a small amount of 3,3-dibromo-2,2-dimethylcoumaran, whose presence was indicated from the fact that the product gave 2,2-dimethyl-3-coumaranone (V) on treatment with potassium acetate in acetic acid and water. The reaction of 2,2-dimethylcoumaran with three moles of N-bromosuccinimide was more complex and gave 3-bromo-2,2-dimethylcoumaran as the only isolable compound.

Structure II is the reasonable one to expect from I by the method of synthesis, and reactions of this compound also furnish supporting evidence for the structure. In the first place, reactivity of the halogen was comparable to that in benzyl bromide. Secondly, the alcohol IV obtained from it by indirect hydrolysis (*via* the acetate III) was oxidizable to a ketone (V); hence, substitution of bromine on the methyl group is ruled out for an alcohol derived from it would have oxidized to an acid. Again, the 2,4-dinitrophenylhydrazone of this ketone was bright red in color, which speaks for the conjugated nature of the ketone. These three items demonstrate that the bromide is of structure II, but the reactions to follow also support this conclusion.

Alcohol IV, mentioned above, seems to be the first recorded example of a simple, stable coumaranol. Ladenburg, *et al.*,[7] have reported 3-hydroxy-2-coumaranone, and Stoermer and König[8] have described a substance, believed to be 3-coumaranol, which was too unstable to be analyzed.

Bromide II gave 2,2-dimethyl-3-coumaranyl ether (VI), although in low yield, when it was heated with aqueous potassium carbonate solution.

Since II is a β-halo cyclic ether it would be expected to react with sodium, if it reacts comparably to 2-(bromomethyl)-tetrahydrofuran, 2-alkyl-3-bromotetrahydropyran and 2,4-dialkyl-3-chlorotetrahydropyran, each of which reacted with sodium to open its heterocyclic ring and form, respectively, 4-penten-1-ol,[9] 5-alkyl-4-penten-1-ol[10] and 2,5-dialkyl-4-penten-1-ol.[11] In the coumaran series Normant[12] obtained a mixture of 2-allylphenol and 2-methylbenzofuran by reaction of sodium or magnesium with 2-(chloromethyl)-coumaran in toluene. Hence II should react analogously with sodium and open its hetero ring. Indeed, in this reaction 2-isobutenylphenol (VII) was formed together with an equal amount of neutral, halogen-free materials which were not characterized. Isobutenylphenol, which was synthesized independently from isopropylmagnesium bromide and salicylaldehyde, was identical to the VII that was prepared from II.



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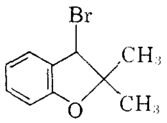

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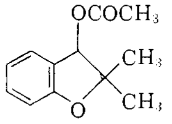

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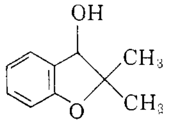
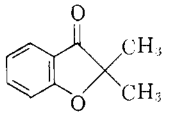
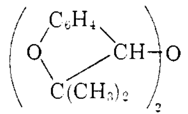


IV



V



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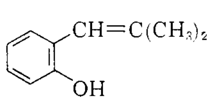
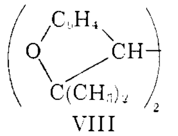


VII



VIII

Treatment of II with magnesium brought about coupling to yield 2,2,2′,2′-tetramethyl-3,3′-bicoumaran (VIII). Carbonation after the reaction with magnesium gave no carboxylic acid. Formation of VIII is analogous to the formation of 1,2-diphenylethane from benzyl bromide[13] or to the coupling of 2-methoxybenzyl bromide[14] with Grignard reagents.

Actually, VIII was a separable mixture of two compounds, one melting at 171° and the other at 98°, one of which should be a *meso* compound and the other a racemic pair. Reasons are given later for eliminating other possible structures.

Evidence supporting structure VIII for the 171°-material is: Its infrared and ultraviolet spectra were very similar to those of 2,2-dimethylcoumaran, except that in the former the intensity of the ultraviolet bands was twice that of the bands from 2,2-dimethylcoumaran. The compound was unaffected by boiling solutions of potassium permanganate or dichromate and did not react with bromine in carbon tetrachloride. Its nitration gave a yellow tetranitro derivative.

Attempts at degradation of compound 171° with hydrobromic acid failed, and only oily materials were obtained which could not be purified satisfactorily. On heating the compound with N-bromosuccinimide in carbon tetrachloride, at first bromine was formed and later hydrogen bromide was

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[5] F. Wild, "Characterisation of Organic Compounds," University Press, Cambridge, 1948.

[6] *Cf.* E. Späth, *Monatsh.*, **34**, 1965 (1913), for dehydrohalogenation of *p*-methoxybenzyl halides.

[7] K. Ladenburg, K. Folkers and R. Major, THIS JOURNAL, **58**, 1292 (1936); *cf.* also J. Plöschl, *Ber.*, **14**, 1316 (1881).

[8] R. Stoermer and W. König, *ibid.*, **39**, 492 (1906).

[9] R. Paul, *Bull. soc. chim.*, [5] **2**, 745 (1935).

[10] R. Brandon, J. Derfer and C. Boord, THIS JOURNAL, **72**, 2120 (1950).

[11] W. Parham and H. Holmquist, *ibid.*, **76**, 1173 (1954).

[12] H. Normant, *Bull. soc. chim.*, [5] **12**, 609 (1945).

[13] J. Houben and L. Kesselkaul, *Ber.*, **35**, 2523 (1902).

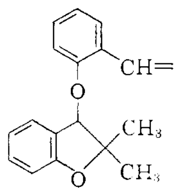
[14] M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall, Inc., New York, N. Y., 1954, Chap. V.

evolved. The yellow dibromo compound which was isolated was inert to a boiling solution of potassium permanganate and remained unchanged on treatment with potassium acetate in refluxing acetic acid, from which it was concluded that nuclear bromination occurred at 5,5′. Nuclear brominations with N-bromosuccinimide were reported by Buu-Hoï[15] who found that anisole and other aromatic ethers are brominated in the benzene ring. Consideration of the extremely pronounced hindrance around the 3,3′-carbon-to-carbon bond in the bicoumaran, as revealed by molecular models, makes it apparent that the approach to carbon 3 by the molecule of bromosuccinimide would be very difficult if at all possible. This steric hindrance probably accounts also for the inertness of VIII toward oxidizing agents.

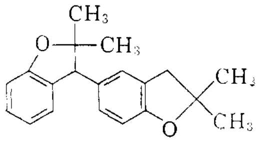
It is known[16] that ethylmagnesium bromide reacts satisfactorily with 4,4′-dimethoxybenzil. Accordingly, a synthesis of VIII was planned starting with 2,2′-dimethoxybenzil[17] and isopropylmagnesium bromide (to be followed by dehydration of the resulting diol and ring closure of the diene) but the 2,2′-isomer was unreactive toward isopropylmagnesium bromide even on prolonged refluxing in benzene.

The lower melting (98°) compound originally was an oil that resisted attempts at crystallization until chromatographic methods were employed. It also was unaffected by boiling potassium permanganate or chromic acid and also failed to discolor bromine in carbon tetrachloride. On nitration it yielded a tetranitro derivative which did not melt below 300°. With N-bromosuccinimide, compound 98° gave a yellow material whose melting point could not be made constant by crystallization or by chromatography.

Although VII seems to be the structure of these two substances, two other isomeric structures (IX, X) may be considered. Compound IX is olefinic and should react with cold permanganate solution, but compounds 171° or 98° failed to react even when heated. Compound X is structurally similar to compound I, and we have shown[18] that I is extensively oxidized by aqueous, alkaline potassium permanganate solution at 65–70°. This strongly suggests that a compound of structure X should be similarly oxidized, certainly by boiling permanganate. Finally, the fact that compounds 98° and 171° have very similar infrared spectra strongly suggests stereoisomerism, not structural isomerism, for the two materials.



IX



X

Zinc powder behaves like magnesium toward II in giving rise to both the 98° and 171° compounds, but it resembled sodium in yielding also the phenolic compound.

Because of possible utility in the preparation of a coumaranylcoumaran (such as X) and because of additional information concerning dehydrobromination of 3-bromo-2,2-dimethylcoumaran, a reaction was studied in which it was attempted to alkylate II with itself. Analogous reactions of benzyl halides are described in the literature. It was shown, for example, by Zincke[19] that benzyl chloride reacts in the presence of metals, as copper, iron, zinc and silver, to form polybenzyls. Even though the condensation of II could not be controlled to produce a dimer, a polymer was obtained when its benzene solution was refluxed with zinc dust. Hydrogen bromide was evolved and an amorphous solid was obtained which did not contain any halogen, was soluble in acetone, benzene and ethyl acetate, but was precipitated by methanol from these solutions. Its molecular weight could not be determined satisfactorily by the cryoscopic approach, since the melting point depression was too small; but this did speak for a substance of a high molecular weight. Its nitration gave a yellow substance, infusible below 300°, which was not analyzed because it exploded in the combustion apparatus. Thus, it must be concluded that the evolution of hydrogen bromide in II is of the same nature as that in benzyl chloride, and is accompanied by self condensation of this compound.

Attempts at preparation of the phenyl ether from II and phenol under various conditions met with failure, hydrolysis and polymerization taking place instead. In one experiment only, when methanol and sodium methoxide[20] were used, was there isolated a $C_{11}H_{14}O_2$ compound, apparently 2,2-dimethyl-3-methoxycoumaran.

Thus, from the results presented, it may be concluded that whereas II often reacts in the manner of typical β-halo ethers or typical benzylic halides, there are other reactions that differ. The latter point may be illustrated by the following. Whereas substituted benzyl halides undergo with Grignard reagents the so-called coupling reaction[21] in which a 1,2-disubstituted ethane is formed, addition of II to an excess of methylmagnesium iodide, gave, besides a 7% yield of 2-isobutenylphenol (VII) and a 4.2% yield of compound 171°, a 53% yield of 2,2,3-trimethylcoumaran characterized by comparison with an authentic sample[22] and its dinitro derivative.[23] Thus, coupling occurs here to a much lesser extent than with, *e.g.*, 2-methoxybenzyl bromide,[6] in which coupling is the predominant reaction. Incidentally, the formation of 2,2,3-trimethylcoumaran from II additionally supports structure II. Similarly, in the reaction with phenylmagnesium bromide II undergoes phenylation exclusively giving 2,2-dimethyl-3-phenylcoumaran (XII). The latter new compound was synthesized by addition of 3-phenylcoumaranone[24] to an excess of methylmag-

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[15] Ng. Ph. Buu-Hoï, *Ann.*, **556**, 1 (1944).

[16] E. Dodds, L. Goldberg, W. Lawson and R. Robinson, *Proc. Royal Soc.* (*London*), **B127**, 140 (1939).

[17] J. C. Irvine, *J. Chem. Soc.*, **79**, 668 (1901); N. Leonard, R. Rapala, H. Herzog and E. Blout, THIS JOURNAL, **71**, 2997 (1949).

[18] C. D. Hurd and R. Dowbenko, unpublished results.

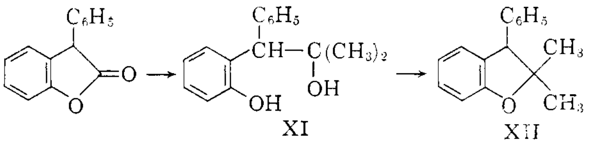
[19] T. Zincke, *Ann.*, **159**, 367 (1871), and subsequent papers.

[20] L. Claisen, *ibid.*, **242**, 210 (1925).

[21] Reference 14.

[22] W. M. Lauer and O. Moe, THIS JOURNAL, **65**, 291 (1943).

[23] C. D. Hurd and R. Dowbenko, *ibid.*, **80**, 4711 (1958).



nesium iodide and cyclization of the resulting *o*-(1-phenyl-2-methyl-2-hydroxypropyl)-phenol (XI)[25] with a refluxing mixture of hydrobromic and acetic acids, and proved to be indistinguishable in all properties from that obtained from II.

It should be noted that the reaction of II with Grignard reagents as illustrated in the present work represents a convenient means of arriving at 2,2,3-trisubstituted coumarans, compounds difficultly accessible by other methods.

Experimental[26]

The starting compounds were prepared as described in ref. 23.

Reaction of 2,2-Dimethylcoumaran with One Mole of N-Bromosuccinimide.—A mixture of 7.4 g. (0.05 mole) of 2,2-dimethylcoumaran, 8.9 g. (0.05 mole) of N-bromosuccinimide, about 0.05 g. of benzoyl peroxide and 150 ml. of dry carbon tetrachloride was refluxed for 2 hr. during which time it became purple. The reaction mixture then was cooled, the solid (4.9 g.) filtered off, the red-colored filtrate washed with saturated sodium chloride solution and dried. Removal of the solvent and distillation of the residue gave, besides a small forefraction and a residue, 7.7 g. (68%) yield of a colorless liquid, b.p. 85–93° at 2 mm. A middle fraction b.p. 90° at 2 mm., $n^{23.5}D$ 1.5666, was analyzed.

Anal. Calcd. for $C_{10}H_{11}BrO$: C, 53.10; H, 4.88. Found: C, 54.41; H, 5.27.

2,2-Dimethyl-3-(N-phthalimido)-coumaran was obtained by refluxing for 16 hr. the bromo compound II and potassium phthalimide in toluene solution. The product appeared as white needles, m.p. 123–127°. The analytical sample, m.p. 128–128.5° (chloroform–hexane), showed a very strong band at 5.84 μ and a weak, sharp band at 5.62 μ in the infrared.

Anal. Calcd. for $C_{18}H_{15}NO_3$: C, 73.70; H, 5.15; N, 4.78. Found: C, 73.59; H, 5.30; N, 5.03.

Reaction of 2,2-Dimethylcoumaran with Two and Three Moles of N-Bromosuccinimide.—Under the same conditions as for one mole of N-bromosuccinimide, there was obtained from 5.20 g. (0.035 mole) of 2,2-dimethylcoumaran and 12.5 g. (0.070 mole) of N-bromosuccinimide in 100 ml. of dry carbon tetrachloride 9.50 g. of an oil, b.p. 87.5–110° (3 mm.). The oil was heated at 100° for 2.5 hr. with 10 g. of anhydrous potassium acetate and 50 ml. of acetic acid and left overnight. The mixture was processed by pouring it into water, extracting with ether and distilling to give fractions from which a compound, m.p. 36–37°, apparently 2,2-dimethyl-3-coumaranone, could be isolated.

A similar reaction of 7.4 g. (0.05 mole) of 2,2-dimethylcoumaran and 26.7 g. (0.15 mole) of N-bromosuccinimide in 100 ml. of dry carbon tetrachloride gave rise to 6.2 g. of a colorless oil, b.p. 85–90° (2.2 mm.), apparently 3-bromo-2,2-dimethylcoumaran, and a large forefraction and tarry residue.

Conversion of 3-Bromo-2,2-dimethylcoumaran into 2,2-Dimethyl-3-coumaranyl Ether (VI).—Thirty-two grams of crude 3-bromo-2,2-dimethylcoumaran was added to a solution of 40 g. of potassium carbonate in 200 ml. of water. The resulting mixture was heated on the steam-bath for 3 hr. The mixture then was cooled, saturated with sodium chloride and extracted with ether. The extract was evaporated to give 24.7 g. of a yellow oil which did not give a Beilstein test for halogen. Although some crystallization could be induced by cooling its solution in a mixture of ether and pentane, this was incomplete and the oil was distilled to give, in addition to a forefraction and a residue, 4.55 g. of a material, b.p. 100–110° (2.2 mm.), which crystallized on standing to give a white solid of m.p. 85–100°. Several recrystallizations from hexane gave an analytical sample of m.p. 104–105°.

Anal. Calcd. for $C_{20}H_{22}O_3$: C, 77.38; H, 7.14. Found: C, 77.61; H, 6.98.

2,2-Dimethyl-3-coumaranyl Acetate (III).—The crude 3-bromo-2,2-dimethylcoumaran (from 0.1 mole of 2,2-dimethylcoumaran) was dissolved in 25 ml. of acetic acid. To the resulting red solution there was added 15 g. (0.15 mole) of freshly fused, finely divided potassium acetate, whereupon the color of the mixture changed to yellow and the temperature rose to 80°. After heating to 120° for 10 min., allowing to stand at room temperature overnight and heating again on the steam-bath for 2.5 hr., the mixture was poured into water. It then was extracted with ether, the resulting extract washed with saturated solutions of sodium bicarbonate and sodium chloride and evaporated to give 20.0 g. of a yellow oil which showed a negative Beilstein test for halogen. After two distillations there was obtained 15.6 g. (75.7% based on 2,2-dimethylcoumaran) of a colorless liquid, b.p. 90–99° (1.5 mm.). A middle fraction, b.p. 98° (1.5 mm.), $n^{25}D$ 1.5076, was analyzed.

Anal Calcd. for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84. Found: C, 70.12; H, 6.71.

2,2-Dimethyl-3-coumaranol.—A solution of 8.0 g. (0.14 mole) of potassium hydroxide in 100 ml. of methanol and 14.5 g. (0.0705 mole) of III was refluxed on the steam-bath for 1 hour and allowed to stand at room temperature overnight. The mixture then was diluted with 200 ml. of water, saturated with sodium chloride and extracted with ether. The extract, after washing, drying and removing the solvent, gave a yellow viscous oil which could not be induced to crystallize. It was distilled to give, in addition to a small forefraction, 9.80 g. (75.8%) of a liquid, b.p. 95–103° (1.5 mm.), which crystallized in the receiver. The analytical sample was prepared by several recrystallizations from a mixture of ether and pentane and it appeared as large, hexagonal plates of m.p. 73.5–74.0°. Its infrared spectrum showed bands at 3.06, 3.37(weak), 3.41, 3.44, 5.16w, 5.26w, 5.60w, 6.21, 6.26, 6.79, 6.86, 7.08, 7.20, 7.29, 7.56, 7.76, 7.90, 8.18, 8.57, 8.70, 8.85, 9.12, 9.60, 9.83, 10.04, 10.52, 10.69, 11.25, 11.56, 11.73, 12.21, 12.55, 13.20, 13.43 μ. The strong hydroxyl band at 3.06, the methyl C–H peaks at 3.4 and the complex bands in the 10–12 μ region are consistent with the structure of 2,2-dimethyl-3-coumaranol.

Anal. Calcd. for $C_{10}H_{12}O_2$: C, 73.14; H, 7.37. Found: C, 73.37; H, 7.31.

Its benzoyl derivative was prepared from the coumaranol and benzoyl chloride in pyridine solution and had a m.p. of 57.5–58.0° (pentane–ether).

Anal. Calcd. for $C_{17}H_{16}O_3$: C, 76.10; H, 6.01. Found: C, 76.46; H, 6.19.

The 1-naphthylcarbamate was prepared from the coumaranol and 1-naphthyl isocyanate in hexane solution and was obtained in the form of white rosettes, m.p. 136–137° (hexane).

Anal. Calcd. for $C_{21}H_{19}NO_3$: C, 75.65; H, 5.74; N, 4.20. Found: C, 75.24; H, 5.67; N, 4.39.

2,2-Dimethyl-3-coumaranone (V).—To a slurry of a complex[27] of chromic oxide (4.5 g.) and dry pyridine (45 ml.) cooled to 20° there was added 2.4 g. (0.015 mole) of 2,2-dimethyl-3-coumaranol, m.p. 72–74°, in 45 ml. of pyridine. The mixture was maintained at a temperature below 30°. Then it was left at 20–25° for 18 hr. after which it was diluted with 200 ml. of water. The resulting mixture was extracted with a mixture of ether and benzene. The extract was washed thoroughly with dilute hydrochloric acid solution and saturated sodium chloride solution. Drying and evaporation of the extract gave 2.3 g. of colorless platelets which, after several recrystallizations from ether–pentane at about −50°, furnished the analytical sample, m.p. 39.0–39.5°, showing a carbonyl band at 5.77 μ in the infrared.

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[24] A. Bistrzycki and J. Flatau, *Ber.*, **30**, 124 (1897).

[25] B. I. Arventi, *Rev. Stiintifica "V. Adamachi,"* **29**, 66 (1943); *C. A.*, **38**, 5217 (1944).

[26] The melting points are uncorrected. The infrared spectra of most of the compounds of interest here are listed in R. Dowbenko, Dissertation, Northwestern University, Evanston, Ill., 1958. Analyses were performed by Miss H. Beck.

[27] G. Poos, G. Arth, R. Beyler and L. Sarett, THIS JOURNAL, **75**, 422 (1953).

Anal. Calcd. for $C_{10}H_{10}O_2$: C, 74.05; H, 6.22. Found: C, 73.50; H, 5.92.

Its 2,4-dinitrophenylhydrazone, prepared in ethanolic sulfuric acid, was obtained as bright-red needles, m.p. 212–213° (95% ethanol).

Anal. Calcd. for $C_{16}H_{14}N_4O_5$: C, 56.14; H, 4.12; N, 16.37. Found: C, 55.69; H, 4.37; N, 16.68.

Reaction of 3-Bromo-2,2-dimethylcoumaran with Sodium.—To the sodium powder (from 1.8 g., 0.078 g. atom, of sodium) suspended in 100 ml. of ether there was added dropwise a solution of 7.30 g. (0.032 mole) of 3-bromo-2,2-dimethylcoumaran in 100 ml. of ether. A white solid precipitated, but heat was not evolved. After all the bromide was added and the mixture was warmed for a short time, a reaction started as evidenced by refluxing of the solvent. After stirring and refluxing for 3 hr. the brown color changed to greenish, and the mixture was stirred and refluxed for an additional 3.5 hr. The excess of sodium was destroyed with methanol and water and then the mixture was acidified and extracted with ether. The ether extract was separated into a fraction soluble in sodium hydroxide and a neutral fraction. The latter gave on distillation at 1.7 mm. two fractions: b.p. 55–72°, 0.30 g., and b.p. 72–168°, 0.40 g. The orange-colored residue (2.90 g.) decomposed on further heating. These materials were not investigated. The alkali-soluble fraction gave on distillation 0.60 g. (13%) of 2-isobutenylphenol (VII), b.p. 76.5° (2.2 mm.), whose reaction with ferric chloride and whose infrared spectrum were identical with those of authentic 2-isobutenylphenol. Its 1-naphthylcarbamate melted at 122.5–123.5° and did not show any depression in the melting point on admixture of the authentic 2-isobutenylphenyl 1-naphthylcarbamate.

Preparation of 2-Isobutenylphenol (VII).—The preparation of this compound was based on the method of Pauly and Buttlar[28] who treated ethylmagnesium halide with salicylaldehyde. Thus, from 111 g. (0.9 mole) of isopropyl bromide, 21.9 g. (0.9 g. atom) of magnesium and 36.6 g. (0.30 mole) of salicylaldehyde there was obtained after processing 26 g. of a liquid, b.p. 106–108° (14–20 mm.), and a large amount of yellow residue. After washing the liquid with sodium bisulfite, bicarbonate and chloride solutions it was dried and distilled to obtain 19.3 g. (43.5%) of 2-isobutenylphenol, b.p. 98–104.5° at 13 mm. A middle fraction, b.p. 104.5° at 13 mm., $n^{25}D$ 1.5539, gave with ferric chloride a greenish color which rapidly changed to brown; ultraviolet spectrum (in methanol): λ_{max} 285 mμ (ϵ_{max} 2980), λ_{max} 242 mμ (ϵ_{max} 7300); reported[29] constants for 2-isobutenylphenol: b.p. 81° at 6 mm., $n^{20}D$ 1.5590.

Anal. Calcd. for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 80.48; H, 7.61.

2-Isobutenylphenyl 1-naphthylcarbamate was prepared in the usual manner and melted at 122.5–123.5° (ligroin).

Anal. Calcd. for $C_{21}H_{19}NO_2$: C, 79.47; H, 6.03; N, 4.41. Found: C, 79.50; H, 5.89; N, 5.15.

2-Isobutenylphenyl 3,3-dinitrobenzoate was prepared by heating the phenol and the acid chloride in pyridine solution and was obtained as lemon-yellow crystals, m.p. 69–70°.

Anal. Calcd. for $C_{17}H_{14}N_2O_6$: C, 59.65; H, 4.12; N, 8.18. Found: C, 59.23; H, 3.98; N, 8.70.

Reaction of 3-Bromo-2,2-dimethylcoumaran with Magnesium.—To 1.74 g. (0.0715 g. atom) of magnesium turnings covered with 10 ml. of dry ether there was added 16.2 g. (0.0715 mole) of the bromide dissolved in 60 ml. of ether. After addition of a small portion of the bromide solution the reaction started immediately and an additional 150 ml. of dry ether was added to the reaction mixture which assumed initially a blue color which then changed to deep-purple. After all the bromide solution was added the mixture was refluxed for 0.5 hr. whereupon the color changed to dark-red, but became purple again on cooling. The mixture then was poured onto a mixture of ether and powdered Dry Ice and was allowed to stand 1 hr. The mixture was acidified with 40 ml. of iced hydrochloric acid. The layers were separated and the aqueous layer was extracted exhaustively with ether. The combined extract was separated into acidic, phenolic and neutral fractions. No residue was obtained on evaporation of the acidic fraction, and only a negligible amount of phenolic material from the corresponding phenolic fraction which was not investigated further. The neutral fraction, 10.8 g., consisted of a red oil mixed with a solid. The solid was filtered off and washed with cold pentane to give 1.7 g. of slightly pink crystals, m.p. 169.5–170.5°. The analytical sample, prepared by several recrystallizations from absolute ethanol, melted at 170–171°. The compound did not react with boiling aqueous potassium permanganate or potassium dichromate solutions and did not decolorize bromine in carbon tetrachloride, ultraviolet spectrum (in methanol): shoulder at 287 mμ (ε 6900), λ_{max} 281 mμ (ϵ_{max} 7650).

Anal. Calcd. for $C_{20}H_{22}O_2$: C, 81.60; H, 7.53; mol. wt., 294. Found: C, 82.05; H, 7.24; mol. wt. (in camphor), 295, 302.

Nitration[23] of the above compound 171° gave a **tetranitro derivative** (apparently 2,2,2′,2′-tetramethyl-5,5′,7,7′-tetranitro-3,3′-bicoumaran), yellow prisms (from acetone–methanol), m.p. 283–285° (m.p. block).

Anal. Calcd. for $C_{20}H_{18}N_4O_{10}$: C, 50.63; H, 3.87; N, 11.85. Found: C, 50.44; H, 3.63; N, 11.62.

The remaining filtrate from which the compound 171° was separated was freed from the solvent and a 3.65-g. sample was chromatographed on 200 g. of alumina (Merck, chromatography grade) and eluted with hexane containing successively higher amounts of ether. The fractions eluted with 5% ether in hexane contained 1.50 g. of an oily solid of varying melting points. The fractions eluted with 10% ether in hexane contained 1.60 g. of a brown oil which failed to crystallize. The oily solid was recrystallized from methanol to give 1.35 g. (37.2%) of a compound, m.p. 86–90°. The analytical sample, prepared by several recrystallizations from methanol, melted at 98°. Like the higher melting compound, it was inert to potassium permanganate, potassium dichromate and bromine; ultraviolet spectrum (in methanol): λ_{max} 292 mμ (ϵ_{max} 8100), λ_{max} 284 mμ (ϵ_{max} 8200). For comparison, the ultraviolet spectrum of 2,2-dimethylcoumaran was measured (in methanol): shoulder at 288 mμ (ε 3460), λ_{max} 281 mμ (ϵ_{max} 4120), λ_{max} 225 mμ (ϵ_{max} 7200).

Anal. Calcd. for $C_{20}H_{22}O_2$: C, 81.60; H, 7.53; mol. wt., 294. Found: C, 81.55; H, 6.99; mol. wt. (in camphor), 304, 244.

Nitration of the above compound 98° gave a **tetranitro derivative** as pinkish microscopic needles not melting below 300° (acetone–methanol).

Anal. Calcd. for $C_{20}H_{18}N_4O_{10}$: C, 50.63; H, 3.87; N, 11.85. Found: C, 51.07; H, 3.79; N, 12.39.

Reaction of 3-Bromo-2,2-dimethylcoumaran with Zinc.—A small portion of a solution of 8.6 g. (0.038 mole) of 3-bromo-2,2-dimethylcoumaran in 50 ml. of ether was added to a stirred suspension of 6.5 g. (0.10 g. atom) of zinc dust in 150 ml. of ether. The mixture was warmed for a short period of time until a yellow color which developed changed to an intense green as the reaction proceeded. The rest of the solution was added dropwise with stirring, and the green mixture refluxed for 6 hr., then stirred at room temperature overnight. After a customary separation, there was obtained 0.30 g. of a green-colored phenolic fraction and a neutral yellow sirup which showed a green fluorescence. On dilution with ether–hexane the latter deposited 0.80 g. (14%) of the impure compound 171°, m.p. 167–169°. The residual oil amounted to 4.5 g. A 1.5-g. sample of the oil was chromatographed on alumina and eluted with 2% ether-in-hexane to obtain 0.55 g. (30%) of greenish needles of impure compound 98°, m.p. 89–94°.

Reaction of 3-Bromo-2,2-dimethylcoumaran with Zinc in Benzene Solution.—To a mixture of 10 g. of zinc dust and 200 ml. of dry benzene there was added 14.4 g. of 3-bromo-2,2-dimethylcoumaran and the resulting reddish mixture was heated while the color changed to deep-purple, then to light-brown. The mixture was refluxed for 6 hr. during which time hydrogen bromide came off vigorously. The mixture was left overnight, then was filtered and the resulting filtrate evaporated to give a brown oil. Dissolving the oil in acetone and adding methanol gave 10.6 g. of a slightly yellow powder melting at 213–220° and giving only a faint Beilstein test for halogen. It was soluble in acetone, ethyl acetate and benzene, but was precipitated from these solutions by methanol. It was further purified by reprecip-

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[28] H. Pauly and R. V. Buttlar, *Ann.*, **383**, 230 (1911).

[29] Q. R. Bartz, R. F. Miller and R. Adams, THIS JOURNAL, **57**, 371 (1935).

itations from acetone, then from boiling butanol, to obtain a yellowish amorphous powder melting with decomposition at 245–280° and no longer giving a positive Beilstein test. Molecular weight determination on an approximately 10% solution in camphor gave a 1.2° depression of the m.p. of camphor.

Anal. Calcd. for $C_{10}H_{10}O$ (polycoumaran): C, 82.14; H, 6.91. Found: C, 80.57; H, 6.40.

Nitration of this polycoumaran gave a yellow solid, m.p. 145–150° dec., which, upon purification by reprecipitation with methanol from an acetone solution, did not melt below 300° and exploded in the combustion apparatus on attempted analysis.

Reaction of Compound 171° with Two Moles of N-Bromosuccinimide.—A mixture of 1.039 g. (3.54 mmoles) of the above compound 171°, 1.260 g. (7.08 mmoles) of N-bromosuccinimide, 50 ml. of carbon tetrachloride and about 5 mg. of benzoyl peroxide was refluxed on the steam-bath whereupon the mixture assumed a brown color. After 2.5 hr. the mixture became lemon-yellow and evolved hydrogen bromide. At this point heating was discontinued, the mixture was cooled and washed with water and sodium bicarbonate solution. Drying and evaporating the solution gave 1.5 g. of a yellow solid, m.p. 115–160°, which was recrystallized from hexane to give 0.950 g. of yellow hard crystals of m.p. 170–174°. The compound was not attacked by boiling potassium permanganate and was recovered unchanged after refluxing for 5 hr. its solution in acetic acid with potassium acetate

Anal. Calcd. for $C_{20}H_{20}Br_2O_2$: C, 53.12; H, 4.46. Found: C, 53.15; H, 4.42.

An analogous reaction of compound 98° with two moles of N-bromosuccinimide gave lemon-yellow crystals m.p. 168–170°. On repeated recrystallizations from hexane the melting point could not be obtained constant. Similarly, chromatography on alumina did not give good results since the melting point could not be made constant. Recrystallization from hexane of the chromatographic fractions gave a material with a melting point of 197–215°.

Reaction of 3-Bromo-2,2-dimethylcoumaran with Phenol in Methanol Solution: 2,2-Dimethyl-3-coumaranyl Methyl Ether.—To a solution of 5.6 g. (0.06 mole) of phenol and 3.2 g. (0.06 mole) of sodium methoxide in 50 ml. of methanol there was added 12.7 g. (0.056 mole) of 3-bromo-2,2-dimethylcoumaran dissolved in 10 ml. of methanol whereupon heat was evolved. The mixture was refluxed for 2 hr., after which most methanol distilled off and the residue was poured into water and the resulting mixture was extracted with ether. The extract was washed with sodium hydroxide solution and water, then was dried and evaporated to give 10 g. of a light-yellow oil. This was distilled to give, in addition to a forefraction and a residue, 5.60 g. of a colorless liquid, b.p. 62–62.5° (0.3 mm.). Redistillation gave an analytical sample, b.p. 71–72° (0.3 mm.), $n^{25}D$ 1.5167.

Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.13; H, 7.91. Found: C, 74.41; H, 7.61.

Reaction of 3-Bromo-2,2-dimethylcoumaran with Methylmagnesium Iodide.—To a stirred solution of the Grignard reagent (prepared from 6.75 g., 0.28 g. atom, of magnesium and 40 g., 0.28 mole, of methyl iodide in a total of 100 ml. of ether) there was added dropwise over a period of 1.5 hr. a solution of 16.8 g. (0.074 mole) of 3-bromo-2,2-dimethylcoumaran in 100 ml. of ether, while the reaction mixture was allowed to reflux gently. After completion of addition the mixture was refluxed for 8 hr., then was allowed to stand at room temperature for 8 hr. and finally was poured into a mixture of 100 ml. of hydrochloric acid and 200 g. of ice. Customary separation gave a phenolic and a neutral fraction. The phenolic fraction, 0.75 g. (7%), showed an infrared spectrum identical with that of 2-isobutenylphenol except for a weak band at 5.97 μ, absent in the spectrum of authentic 2-isobutenylphenol. The neutral fraction, 11.6 g., was composed of a brown oil and white crystals. The crystals gave after purification 0.45 g. (4.2%) of compound 171°. The remaining oil was distilled to give, in addition to about 2 g. of a green-brown residue, 7.10 g. (52.7%) of a liquid, b.p. 67.5–71° at 3 mm., which was shown to be 2,2,3-trimethylcoumaran by analysis, comparison of its infrared spectrum[23] with that of the authentic compound, as well as by comparison of the dinitro derivatives[23] of the two compounds. The fraction, b.p. 70° at 3 mm., $n^{25}D$ 1.5165, was analyzed.

Anal. Calcd. for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.31; H, 8.49.

Reaction of 3-Bromo-2,2-dimethylcoumaran with Phenylmagnesium Bromide.—To a solution of the Grignard reagent (prepared from 5.83 g., 0.24 g. atom, of magnesium and 37.6 g , 0.24 mole, of bromobenzene in a total of 350 ml. of ether) there was added with stirring over a period of 25 min. a solution of 15.4 g. (0.0677 mole) of 3-bromo-2,2-dimethylcoumaran in 150 ml. of ether. After 15 hr. of reflux the mixture was allowed to stand at room temperature for 24 hr., then was poured onto iced hydrochloric acid and worked up in the usual manner to obtain an ether extract which was washed with sodium hydroxide solution and then evaporated. Two distillations of the residue gave 9.9 g. (65%) of a colorless liquid, b.p. 123.5–128° at 1.7 mm., m.p. about 7°. Its infrared spectrum was indistinguishable from that of an authentic sample of 2,2-dimethyl-3-phenylcoumaran prepared below. An analytical sample was obtained by redistillation, b.p. 87° at 0.12 mm., $n^{25}D$ 1.5735.

Anal. Calcd. for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C, 85.65; H, 6.91.

Reaction of 3-Phenyl-2-coumaranone with Methylmagnesium Iodide.—To a solution of methylmagnesium iodide prepared from 0.15 mole of the reagents in 250 ml. of ether there was added with stirring over a period of 15 min. 10.5 g. (0.050 mole) of 3-phenyl-2-coumaranone,[24] m.p. 109–111°, in 130 ml. of benzene. The resulting solution was refluxed for 2.5 hr. and then allowed to stand at room temperature overnight. When this was poured into dilute hydrochloric acid it gave a solution whose evaporation gave 11.65 g. of a slightly colored solid, m.p. 87–114°. Recrystallization from a mixture of acetone and hexane gave 9.50 g. (78.5%) of *o*-(1-phenyl-2-methyl-2-hydroxypropyl)-phenol, m.p. 125–128°. The analytical sample was obtained by recrystallization from carbon tetrachloride, m.p. 132.0–132.5°.

Anal. Calcd. for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 80.17; H, 7.39.

The **monobenzoate** was obtained by the Schotten–Baumann procedure, m.p. 108–109° (hexane). It showed a hydroxyl band at 2.78 μ and a carbonyl band at 5.83 μ in the infrared.

Anal. Calcd. for $C_{23}H_{22}O_3$: C, 79.74; H, 6.40. Found: C, 80.02; H, 6.11.

2,2-Dimethyl-3-phenylcoumaran.—A mixture of 10.5 g. of the crude *o*-(1-phenyl-2-methyl-2-hydroxypropyl)-phenol, m.p. 100–110°, and 150 ml. of 1:1 acetic–48% hydrobromic acid was refluxed for 4 hr. After allowing it to stand at room temperature overnight the mixture was diluted with water and extracted with hexane–ether. The extract was washed thoroughly with a sodium hydroxide solution, water and a saturated sodium chloride solution, and then was dried and evaporated. The residue was distilled to give 4.3 g. (44%) of 2,2-dimethyl-3-phenylcoumaran, b.p. 111–120° at 0.6 mm. A middle fraction, b.p. 114–116° at 0.6 mm., $n^{25}D$ 1.5731, was analyzed.

Anal. Calcd. for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C, 86.10; H, 7.03.

EVANSTON, ILL.