TABLE IV
EFFECT OF TRIETHYLAMINE UPON THE FORMATION OF TAR

	Without Amine		With Amine
Preparation			
Temp.	Room	80	80
Time, hr.	[3.5][a]	3	3
Analyses			
C, %	59.32	52.70	63.46[b]
H, %	5.56	6.13	5.65
O,[c] %	35.12	31.17	30.89
Atoms or groups			
C	3.48	3.43	4.48
H	4.06	5.18	4.85
CO_2H	1	1	1
H[d]/C	1.17	1.51	1.08
$CO_2H/5C$[d]	1.44	1.45	1.12

[a] Time in months. This tar was dissolved in methyl ethyl ketone, treated with decolorizing carbon, precipitated, redissolved and reprecipitated in an attempt to separate a pure compound. [b] A combustion analysis for nitrogen showed none present. [c] Oxygen by difference. [d] For these ratios the hydrogen and carbon attached to the carboxyl group are deducted from the total atoms of hydrogen or carbon, respectively.

hydrocarbon fraction and of the aqueous portion by the above described methods yielded diethyl amine hydrochloride in both fractions.

After the butylmalonic acid was extracted with ether, the acidic aqueous layer was salted and extracted successively with *t*-butyl alcohol, methyl ethyl ketone, and ethyl acetate, which should remove some or all of any aminocarboxylic acid, had any such material formed by one of a variety of methods which might be assumed to have occurred. The tarry residues, obtained by evaporation of the solvent, in each case showed no nitrogen when tested by a sodium fusion–Prussian blue test. In another case the tarry residues were burned in the customary ultimate analysis for nitrogen, but no such gas was collected.

Table IV shows a comparison of the tarry carboxylic acids prepared with and without the amine. The products are essentially the same except for the fact that the action seemed to have been carried further by the amine.

Attempts were also made to repeat the observation recorded in an earlier paper[27] that some nitrogen-containing carboxylic acid was obtained. The conclusion was that traces of triethylamine were difficult to remove and had been codistilled with the acid.

Acknowledgments. The authors are indebted to Dr. Nagy for the combustion analyses and to Professor Nelson for the infrared measurements.

CAMBRIDGE, MASS.

(27) A. A. Morton, M. L. Brown, and E. Magat, *J. Am. Chem. Soc.*, 69, 161 (1947).

[CONTRIBUTION FROM THE SCHOOL OF PHARMACY, DUQUESNE UNIVERSITY]

The Rhodium-Catalyzed Hydrogenation of Ethyl-5,6-benzocoumarin-3-carboxylate[1]

KENNETH J. LISKA AND LEROY SALERNI

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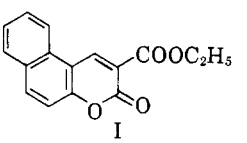
Room temperature, low pressure hydrogenation of ethyl 5,6-benzocoumarin-3-carboxylate (I) employing rhodium (5%) on alumina as the catalyst afforded a decalin derivative, ethyl β-(α-decalyl)isobutyrate (II). The structure of (II) was elucidated by the preparation of the amide and acid derivatives and by an unambiguous synthesis starting with malonic ester.

Since rhodium (5%) on alumina was shown to be effective in the hydrogenation of such aromatic systems as pyridine[2] and arylphosphonic acids,[3] it was thought feasible to use this catalyst in the hydrogenation of ethyl 5,6-benzocoumarin-3-carboxylate (I), in connection with the synthesis of potential oxytocics. It has been shown[4] that the W-1 Raney nickel catalyzed hydrogenation of I yielded a decalin derivative, but only at 2900 pounds per square inch and at 140°; at this temperature, extensive hydrogenolysis of the lactone and ester occurred.



I

When a mixture consisting of a one to one- and-one-half ratio of I to rhodium (5%) on alumina was hydrogenated for thirty-nine hours at room temperature and at a hydrogen pressure of 55 pounds per square inch, an oil was obtained. The ultraviolet spectrum of the oily product showed no absorption indicating that aromaticity had been destroyed. An infrared spectrum of the compound revealed a strong band at 1735 cm.$^{-1}$, suggestive

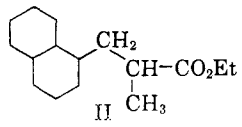
(1) Abstracted from a thesis submitted by O. LeRoy Salerni to the faculty of Duquesne University in partial fulfillment of the requirements for the degree of Master of Science, August 1959.

(2) C. D. Overberger, L. C. Palmer, B. S. Marks, and N. R. Byrd, *J. Am. Chem. Soc.*, 77, 4100 (1955).

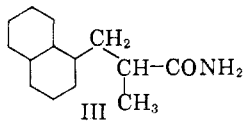
(3) L. D. Freedman, G. O. Doak, and E. L. Petit, *J. Am. Chem. Soc.*, 77, 4262 (1955).

(4) J. E. Gearien and K. J. Liska, *J. Org. Chem.*, 23, 45 (1958).

of an ester and/or lactone grouping. Furthermore, there was no absorption in the alcoholic hydroxyl region, indicating that if hydrogenolysis had occurred, there was subsequent removal of the resulting hydroxyl groups. The compound did not react with acetyl chloride and gave a positive hydroxamic acid test, in support of the findings of the infrared. No decolorization of dilute potassium permanganate solution was observed, indicating that hydrogenation had not stopped at the octalin. On the basis of these findings and elemental analyses, it was possible to propose ethyl β-(α-decalyl)-



II



III

isobutyrate (II) as the hydrogenated product of ethyl 5,6-benzocoumarin-3-carboxylate (I)

Ammonolysis of II, catalyzed by methoxide ion according to the method of Russell,[5] gave a crystalline amide. The nitrogen analysis agreed with that of the expected product, and the compound was identified as β-(α-decalyl)isobutyramide (III).

Alkaline hydrolysis of II and subsequent acidification gave a product which dissolved in 5% sodium bicarbonate solution. The infrared spectrum of the hydrolysis product showed a sharp band at 1707 cm.$^{-1}$ and a weak band centered around 2840 cm.$^{-1}$, characteristic of a carboxyl group, but no absorption attributable to an alcoholic hydroxyl group. The isolation of this hydrolysis product eliminated the possibility of survival of the lactone group during the hydrogenation, for hydrolysis of a lactone would have resulted in recovery of the starting material, or a hydroxy acid which would have given absorption in the alcoholic hydroxyl region of the infrared

To give unequivocal proof of the structure of II, β-(α-decalyl)isobutyramide (III) was synthesized by an unambiguous route. β-(α-Naphthyl)-isobutyric acid, prepared by the scheme of Blicke and Maxwell,[6] was hydrogenated over rhodium (5%) on alumina using a one to one-and-one-half ratio of unsaturated compound to catalyst. The presumed product, β-(α-decalyl)isobutyric acid, obtained as an oil which could not be crystallized, was converted to the amide by treating successively with thionyl chloride and ammonia. The nitrogen analysis supported the desired structure, β-(α-decalyl)isobutyramide (III). The melting point of the compound compared very favorably with the melting point of β-(α-decalyl)isobutyramide obtained from (II) by ammonolysis catalyzed by methoxide ion. There was no depression in mixed melting point.

When a one-to-one weight ratio of catalyst to coumarin ester was employed in low pressure hydrogenations, reduction to the decalin was incomplete as shown by the isolation of the previously reported ethyl 2,3,7,8,9,10-hexahydro-3-keto-1H-naphtho[2,1-b]pyran-2-carboxylate.[4]

It is therefore apparent that the room temperature, low pressure hydrogenation of the coumarin ester (I) to a decalin derivative is possible employing rhodium (5%) on alumina as the catalyst, but that even under these mild conditions hydrogenolysis of the lactone (but not of the ester) is unavoidable.

EXPERIMENTAL[7]

Ethyl 5,6-benzocoumarin-3-carboxylate was prepared from 2-hydroxy-1-naphthaldehyde by the method of Smith and Horner.[8] The 2-hydroxy-1-naphthaldehyde was prepared from 2-naphthol by the method of Russell and Lockhart.[9]

Ethyl β-(α-decalyl)isobutyrate (II). A solution of ethyl 5,6-benzocoumarin-3-carboxylate (4.0 g., 0.015 mol.) in 175 ml. of absolute ethanol was hydrogenated at a pressure of 55 p.s.i. and at room temperature, using 6 g. of rhodium (5%) on alumina as the catalyst. After 39 hr., absorption of hydrogen ceased and the catalyst and solvent were removed. The crude yield was 3.30 g. (89%). Fractional distillation in a Todd Fractionating Apparatus yielded 1.55 g. (42%) of colorless mobile oil, b.p. 134–136° at 2 mm., n_D^{25} 1.4803. There was no absorption in the ultraviolet.

Anal. Calcd. for $C_{15}H_{28}O_2$: C, 75.90; H, 10.82. Found: C, 75.95; H, 10.81.

β-(α-decalyl)isobutyramide (III). A. Ethyl β-(α-decalyl)-isobutyrate (1.0 g., 0.004 mol.) was added to 3 ml. of a 6% ammonia in methanol solution plus 6 ml. of sodium methoxide solution (0.1 g. sodium in 100 ml. of absolute ethanol). The mixture was allowed to stand in a stoppered flask at room temperature for 48 hr. Reducing the volume of the solution to 2 ml. and chilling deposited 0.75 g. of white crystals, m.p. 110–115°. After three recrystallizations from dilute ethanol, 0.25 g. (30%) of product, m.p. 129–131°, was obtained.

Anal. Calcd. for $C_{14}H_{25}ON$: N, 6.27. Found: N, 6.35.

β-(α-decalyl)isobutyric acid. A solution of β-(α-naphthyl)-isobutyric acid (3.0 g., 0.013 mol.) in 150 ml. of absolute ethanol was hydrogenated at room temperature using 4.5 g. of rhodium (5%) on alumina catalyst at a hydrogen pressure of 55 p.s.i. Hydrogenation was allowed to proceed until the theoretical amount of hydrogen was absorbed (15 hr.). Distillation of the product at reduced pressure gave 2.05 g. (67%) of colorless thick oil, b.p. 172–176° at 1.0–1.2 mm. There was no absorption in the ultraviolet.

β-(α-decalyl)isobutyramide (III). B. For proof of structure, III was also synthesized by the following route: A mixture of 1.0 g. (0.004 mol.) of β-(α-decalyl)isobutyric acid and 0.8 g. of thionyl chloride was heated in an all-glass apparatus equipped with drying tube on the steam

(5) P. R. Russell, *J. Am. Chem. Soc.*, **72**, 1853 (1950).

(6) F. F. Blicke and C. E. Maxwell, *J. Am. Chem. Soc.*, **61**, 1780 (1939).

(7) Melting and boiling points are uncorrected. Analyses by Galbraith Labs, Knoxville, Tenn.

(8) L. I. Smith and J. W. Horner, *J. Am. Chem. Soc.*, **60**, 678 (1938).

(9) A. Russell and L. Lockhart, *Org. Syntheses*, **22**, 63 (1942).

bath for 3 hr. The solution was then chilled and poured into 4 ml. of cold 28% ammonia water and stirred. The precipitated amide was purified by three recrystallizations from dilute ethanol and amounted to 0.75 g. (84%) of white crystals, m.p. 129.5–132°, mixture m.p. with amide derived from the benzocoumarin (II).

Anal. Calcd. for $C_{14}H_{25}ON$: N, 6.27. Found: N, 6.15.

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[CONTRIBUTION FROM THE MIDWEST RESEARCH INSTITUTE]

Aryl and Alkylchlorodialkoxysilanes[1]

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Good yields of chlorodiethoxymethylsilane, suitable for use in alkylation and arylation reactions, are obtained by the ethanolysis of methyltrichlorosilane. The synthesis of chlorodiethoxyphenylsilane, chloro-*p*-chlorophenyldiethoxysilane, and *p*-anisylchlorodiethoxysilane in high yields, and the preparation of their intermediates is described.

In the synthesis of silane monomers for use in high temperature resin systems, it was necessary to prepare certain methyl- and arylalkoxychlorosilanes as intermediates. The alkylation and arylation of these compounds with various organometallic reagents will be described in a subsequent publication.

Although the alcoholysis of silicon tetrachloride has been discussed by numerous investigators, and the stability of the various chlorosilicates against redistribution has been studied, considerably less information is available in the literature regarding the methyl- and arylalkoxychlorosilanes. The reported experimental details are seldom complete, but it appears that, as in the case of the alcoholysis of silicon tetrachloride, mixtures of all possible alkoxychlorosilanes are obtained regardless of the stoichiometry of the reactants, and that yields of individual alkoxychlorosilanes are not high. Treating 6.0 mol. of methyltrichlorosilane with 7.2 mol. of ethanol, Andrianov[2] obtained only 35.9 per cent chlorodiethoxymethylsilane and 21.3 per cent dichloroethoxymethylsilane. Servais[3] reports chlorodiethoxymethylsilane and chlorodiethoxyphenylsilane, but omits properties and yields. Rosnati prepared chlorodimethoxyphenylsilane.[4] Redistribution reactions have been studied both with regard to the preparation and stability of alkoxyalkylchlorosilanes.[2,5,6] It appears that alkoxychloromethylsilanes are more stable than the chlorosilicates against redistribution, and may be distilled at atmospheric pressure without significant changes in their composition.

In our laboratory, the ethanolysis of methyltrichlorosilane resulted in a complex mixture which contained all possible products. However, with a suitable proportion of reactants, chlorodiethoxymethylsilane was obtained in about a 72% conversion. Although the components of the crude alcoholysis mixture were difficult to separate by distillation, the use of an efficient fractionating column gave a 63% yield in fractions suitable for use in alkylation and arylation reactions.

Ethanolysis of aryltrichlorosilanes, however, gave the arylchlorodialkoxysilanes in yields between 88 and 95% even when simpler distillation procedures were used.

The alkoxychlorosilanes were prepared by the action of anhydrous ethanol on the chlorosilane in the absence of any solvent, and the products were collected by fractional distillation. Approximations of the purity of the distillation fractions were carried out by vapor phase chromatography. A sample from each distillation fraction was chromatographed and the identity of each peak was assigned on the basis of the stoichiometry of the starting materials, the known tendency of these systems to form all possible alkoxychlorosilanes, and a comparison of the elution times for the various peaks on the different chromatograms.

With the assumption that peak area is proportional to weight per cent of the component in each fraction on the chromatogram, the weight per cent of each alkoxychlorosilane in all the distillation fractions was calculated. The data are shown in Table I.

In distilling a typical reaction product with a 30-plate Oldershaw column no sharp breaks in the

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(1) This research was supported in whole or in part by the United States Air Force under Contract AF 33(616)-3675, monitored by the Materials Laboratory, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio.

(2) K. A. Andrianov, S. A. Golubtsov, and N. P. Lobusevich, *J. Gen. Chem. U.S.S.R.*, **26**, 207 (1956).

(3) R. C. Servais (to Dow Chemical Co.), U. S. Patent **2,485,928**, Oct. 25, 1949.

(4) L. Rosnati, *Gazz. chim. ital.*, **78**, 516 (1948); *Chem. Abstr.*, **43**, 1006 (1949).

(5) Dow Corning Corp., Brit. Patent **653,238**, May 9, 1951; *Chem. Abstr.*, **46**, 1025 (1952).

(6) M. Kumada, *J. Inst. Polytech. Osaka City Univ.*, Ser. C., 2, 139 (1952).