[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF TEMPLE UNIVERSITY]

The Decarboxylation of 1-Phenylcycloparaffin-1-carboxylic Acids

BY FRANCIS H. CASE

The syntheses of the first four members of the homologous series of phenylcycloparaffins, with the exception of phenylcyclobutane, have been effected by various unrelated methods,[1] and in some cases there is a considerable discrepancy between the physical constants for the same hydrocarbon as recorded by various authors. The object of this investigation was to test the feasibility of obtaining these hydrocarbons by a general method involving the decarboxylation of the corresponding 1-phenylcycloparaffin-1-carboxylic acids.

A review of the literature indicates that most decarboxylation reactions involving the decomposition of salts of cycloparaffin carboxylic acids have proceeded in an anomalous manner. Thus, Colman and Perkin,[2] on distilling the calcium salt of cyclobutane carboxylic acid, obtained ethylene, hydrogen, methane, carbon dioxide, and various ketones, but no cyclobutane. From the distillation of barium hexahydrobenzoate with sodium methylate, Zelinsky[3] obtained a mixture of di- and tetrahydrobenzene, and by similarly treating the barium salt of hexahydroterephthalic acid, the same author[4] obtained benzene, but no cyclohexane. The distillation of the calcium salt of 2-phenylcyclopropane-1-carboxylic acid with sodium hydroxide by Buchner[5] yielded styrene and allylbenzene, but no phenylcyclopropane.

By heating the barium salt of the appropriate 1-phenylcycloparaffin-1-carboxylic acid with an excess of dry sodium methylate in a vacuum[6] it was found possible to obtain all four of the phenylcycloparaffins mentioned above in yields which increased with increasing molecular weight. The high-boiling material which accompanied the hydrocarbons of lower molecular weight was ketonic in nature. The hydrocarbon fraction from 1-phenylcyclopropane-1-carboxylic acid was impure and was treated with dilute potassium permanganate solution at 0° to remove unsaturated hydrocarbons.[1b] Since the oxidation product of the reaction was benzoic acid, and no other acids could be isolated, the impurity was in all probability propenylbenzene. The purity of the final product was attested by the fact that the density remained unchanged after successive treatments with permanganate, and its identity with phenylcyclopropane was indicated by the agreement of its physical constants with those described in the literature. The structure of the other hydrocarbons synthesized was established by the agreement of their physical constants with some of those already reported, and by the fact that dilute permanganate solution was not reduced by them at ordinary temperatures.

Of the acids required for decarboxylation, 1-phenylcyclopropane-[7] and -butane[8]-1-carboxylic acids have been described elsewhere. The cyclopentane and -hexane acids were prepared by the action of tetramethylene and pentamethylene bromide, respectively, on the sodium derivative of phenylacetonitrile. In the cases of the second and fourth acids the yields were cut down considerably by extensive resin formation, and when hexamethylene bromide was used, nothing but resin could be obtained. From *o*-xylylene bromide, by the same reaction, a small yield was obtained of 2 - phenylhydrindene - 2 - carboxylic acid, but again resin formation predominated.

It was found that the nitriles containing the cyclopentane and -hexane rings were rather resistant to hydrolysis by alcoholic potash, and considerable amounts of their amides were isolated as intermediate products.

Experimental

Synthesis of the 1-Phenylcycloparaffin-1-carboxylic Acids.—To the sodium derivative prepared by treating two moles of sodium amide suspended in absolute ether with one mole of phenylacetonitrile, was added one mole of the requisite alkylene dibromide, and the mixture refluxed for ten hours. It was then poured on ice and extracted with ether. Under these conditions the higher

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[1] Phenylcyclopropane: (a) Kishner, *J. Russ. Phys.-Chem. Soc.*, **45**, 950 (1913); (b) Lespieau, *Compt. rend.*, **190**, 1129 (1930). Phenylcyclopentane: (c) Borsche and Menz, *Ber.*, **41**, 190 (1908); (d) Zelinsky, *Ber.*, **58**, 2755 (1925); (e) von Braun, *ibid.*, **60**, 2557 (1927). Phenylcyclohexane: (f) Kursanoff, *Ann.*, **318**, 309 (1901); (g) Bodroux, *Ann. chim.*, [10] **11**, 511 (1929); (h) Neunhoeffer, *J. prakt. Chem.*, **133**, 95 (1932), give the most important methods of preparation.

[2] Colman and Perkin, *J. Chem. Soc.*, **51**, 228 (1887).

[3] Zelinsky, *Ber.*, **41**, 205 (1908).

[4] Zelinsky, *ibid.*, **34**, 3800 (1901).

[5] Buchner, *ibid.*, **36**, 3785 (1903).

[6] Mai, *ibid.*, **22**, 2133 (1889).

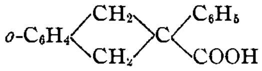
[7] Knowles and Cloke, THIS JOURNAL, **54**, 2028 (1932).

[8] Case, *ibid.*, **55**, 2927 (1933).

alkylene bromides yielded large amounts of ether-insoluble resins, which could not be made to crystallize. The ether-soluble material was isolated and distilled *in vacuo* over a rather wide range. Hydrolysis with alcoholic potash yielded the desired acids, but in the reaction of tetramethylene and pentamethylene bromides the corresponding amides were also obtained in amounts depending on the time of hydrolysis. Their conversion to the acids was brought about by refluxing with concd. hydrochloric acid and sodium nitrite.

TABLE I

DATA ON 1-PHENYLCYCLOPARAFFIN-1-CARBOXYLIC ACIDS

Bromide	Acid	M. p., °C.	Yield,[a] %	Analyses, % Calcd. H	Calcd. C	Found H	Found C
$Br(CH_2)_2Br$	$(CH_2)_2C(C_6H_5)COOH$	86–7	37.8	6.22	74.04	6.35	74.07
$Br(CH_2)_3Br$	$(CH_2)_3C(C_6H_5)COOH$	106–7	14.5				
$Br(CH_2)_4Br$	$(CH_2)_4C(C_6H_5)COOH$	158–9	45.8	7.42	75.75	7.51	75.43
$Br(CH_2)_5Br$	$(CH_2)_5C(C_6H_5)COOH$	121	22.2	7.90	76.42	8.36	76.68
$Br(CH_2)_6Br$	$(CH_2)_6C(C_6H_5)COOH$		0				
o-$C_6H_4(CH_2Br)_2$		194–5	8.3	5.93	80.63	6.21	80.63

[a] Based on bromide.

Amide of 1-Phenylcyclopentane-1-carboxylic Acid.—This compound crystallizes from benzene, m. p. 157–158°.

Anal. Calcd. for $C_{12}H_{15}ON$: C, 76.24; H, 7.94. Found: C, 76.16; H, 8.11.

Amide of 1-Phenylcyclohexane-1-carboxylic Acid.—Crystallizes from a mixture of benzene and petroleum ether, m. p. 95–96°.

Anal. Calcd. for $C_{13}H_{17}ON$: C, 76.80; H, 8.44. Found: C, 76.94; H, 8.44.

TABLE II

PHYSICAL PROPERTIES OF THE PHENYLCYCLOPARAFFINS

	Obtained by	B. p., °C. In vacuo		Normal		Density	Refr. index	Yield, %	Analyses, % Calcd. H	Calcd. C	Found H	Found C
C_9H_{10}	Decarboxylation	79–80	(37)	171	(771)	d_4^{20} 0.9317	n_D^{20} 1.5285	5.5	8.54	91.46	8.76	91.23
	Lespieau[1b]			170.5	(760)	d^{20} .9397	n_D^{20} 1.5291					
	Kishner[1a]			173.6	(758)	d_0^{20} .9401	n_D^{16} 1.5342					
$C_{10}H_{12}$	Decarboxylation	101–102	(41)	190–191	(755)	d_4^{20} .9378	n_D^{20} 1.5277	28.1	9.16	90.84	9.33	91.00
$C_{11}H_{14}$	Decarboxylation	116–117	(37)	216	(755)	d_4^{20} .9499	n_D^{20} 1.5309	57.1	9.66	90.34	10.07	90.32
	Von Braun[1e]			215		d_4^{23} .9553	n_D^{23} 1.5330					
	Zelinsky[1d]			215–217		d_4^{19} .9503	n_D^{19} 1.5305					
$C_{12}H_{16}$	Decarboxylation	127–128	(30)	238	(759)	d_4^{20} .9502	n_D^{20} 1.5329	64.0	10.07	89.93	9.97	90.27
	Kursanoff[1f]			239	(745)	d_0^{20} .9441						
	Neunhoeffer[1h]					d_4^{26} .9375	n_{He}^{26} 1.5249					
	Bodroux[1g]			238–240	(743)	d^{16} .947	n_D^{16} 1.528					

Decarboxylation of the 1-Phenylcycloparaffin-1-carboxylic Acids.—An intimate mixture of one mole of the barium salt of the acid and three moles of dry sodium methylate was distilled under a pressure of 40 mm. until no more liquid was obtained. The time required was generally two to three hours. The external temperature required increased with increasing molecular weight (350° for C_9H_{10} to 450° for $C_{12}H_{16}$). The resulting oil was subjected to several fractional distillations *in vacuo*. The hydrocarbons of lower molecular weight were accompanied by considerable amounts of high-boiling ketonic material, but this was almost absent in the case of phenylcyclohexane.

The phenylcyclopropane fraction first obtained was contaminated by unsaturated material which was removed by oxidation with 1% permanganate solution at 0°. This process also undoubtedly destroyed some of the phenylcyclopropane, thus further decreasing the yield. The purity of the product was shown by the fact that its density was unchanged by two successive oxidations. Since the only oxidation product obtained was benzoic acid, the impurity indicated is propenylbenzene, $C_6H_5CH{=}CHCH_3$. Like Lespieau's hydrocarbon, the final product did not readily absorb bromine, but fumed strongly in its presence.

The other phenylcycloparaffins obtained were inert toward 1% permanganate solution at room temperature. The identity of the phenylcyclohexane with that reported in the literature was further confirmed by the preparation of its *p*-nitro derivative, m. p. 56–57° (Neunhoeffer gives 57).

Summary

1. The first four members of the homologous series of phenylcycloparaffins have been synthesized by a general method involving the de-

carboxylation of the corresponding 1-phenylcycloparaffin - 1 - carboxylic acids. Of these, phenylcyclobutane has not previously been reported.

2. The preparation of 1-phenylcyclopentane and -cyclohexane-1-carboxylic acids and of 2-phenylhydrindene-2-carboxylic acid is described.

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Studies in the Rearrangements of Phenyl Ethers. The Course of the Reaction in the Presence of Foreign Aromatic Bodies

BY RICHARD A. SMITH

The mechanism of the rearrangement of phenyl ethers to substituted phenols is still an open question despite some twenty years of study of the reaction. Discussions of possible mechanisms are to be found in publications of Claisen and Tietze,[1] Kursanoff,[2] Niederl and Storch,[3] and Sowa, Hinton and Nieuwland.[4]

In the present communication it will be shown that these rearrangements in the presence of anhydrous aluminum chloride appear to be intermolecular instead of intramolecular. The isomerizations of isopropyl phenyl and *p*-cresyl ethers, and isobutyl phenyl ether have been studied. Isopropyl phenyl ether isomerizes to mono- and di-isopropyl substituted phenol; when this ether was treated with aluminum chloride in the presence of a foreign aromatic compound, diphenyl ether, the yield of isopropylphenols was halved. The other products were *p*-isopropyl diphenyl ether and its isomer, the *o*-substituted ether. Similarly, isopropyl *p*-cresyl ether isomerizes to *o*-isopropyl-*p*-cresol; in the presence of diphenyl ether less of this product was obtained, and the substituted diphenyl ethers were again obtained. In the presence of benzene very little of the substituted phenol was obtained; instead a fair yield of cumene was observed. Isobutyl phenyl ether isomerizes to *p*-butylphenol; in the presence of benzene, however, the primary product was *t*-butylbenzene.

Experimental

Preparation of the Ethers.—The alkyl phenyl ethers were prepared by the same general method. An equivalent of sodium was added to excess ethyl alcohol (95%); an equivalent of the phenol was added to the resulting solution. A 10% excess of the appropriate alkyl bromide was then added and the whole refluxed for six hours. Excess of alkyl halide and alcohol were then removed by distillation on a steam-bath. The sodium bromide was washed out with water, and the phenolic compounds with 15% sodium hydroxide. The remaining material was water washed, dried with anhydrous sodium sulfate and purified by distillation. The yields varied from 80–90%. The ethers have been prepared by previous workers and the agreement in physical properties is satisfactory. The physical properties and references to earlier preparations are listed in the table.

Rearrangement of the Ethers.—Each phenyl ether was rearranged to the corresponding substituted phenol with anhydrous aluminum chloride. To one mole of the ether in a round-bottomed flask surrounded by a cooling bath was added in small portions one mole of aluminum chloride. The heat generated was absorbed by the external cooling bath of cold water. The whole was then allowed to stand for twenty-four hours at room temperature. Hydrolysis was accomplished by pouring the resulting viscous mass on chopped ice; hydrochloric acid was used to complete the hydrolysis and to keep the aluminum in solution. The organic products were separated, water washed, and extracted with 15% sodium hydroxide. The quantity of unrearranged ether was always small. The alkaline solution was neutralized with hydrochloric acid and the organic liquid which separated removed, washed with water, dried with anhydrous sodium sulfate, and purified by distillation. In each case the resulting phenol, or phenols, has been prepared previously and the agreement in physical properties is satisfactory. The physical properties and references to former preparations appear in the table.

Rearrangements in the presence of a foreign aromatic body were performed in a similar manner. The aluminum chloride was added to a solution of the alkyl phenyl ether in benzene or diphenyl ether. The subsequent working up of products was the same except that the alkali insoluble liquid was also worked up. This was water washed, dried with anhydrous sodium sulfate and separated into its components by fractional distillation. In one case two solid products were obtained; di-*t*-butylbenzene, which was distilled and recrystallized from alcohol; and tri-*t*-butylbenzene, which remained as a residue upon distillation and was recrystallized from alcohol. All products obtained, except two, have been previously obtained and the agreement in physical properties is satis-

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(1) Claisen and Tietze, *Ber.*, **58**, 275 (1925).

(2) Kursanoff, *J. Russ. Phys.-Chem. Soc.*, **46**, 815 (1914); *C. A.*, **9**, 1753 (1915).

(3) Niederl and Storch, THIS JOURNAL, **55**, 284 (1933).

(4) Sowa, Hinton and Nieuwland, *ibid.*, **55**, 3402 (1933).