

of the theoretical amount. A mass analysis of an aliquot gave the following figures:

Mass	Mass Peak
60	375.97
59	32.53
58	174.41
57	13.36
56	44.4
55	2.85

The isotopic purity is thus 92.3 mole %  $C_4D_6$ .

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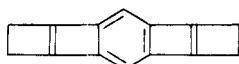
## Identification of Lagidze's Hydrocarbon

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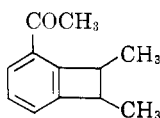
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The hydrocarbon obtained by the reaction of 2-butyne-1,4-diol diacetate and benzene in the presence of aluminum chloride has been identified as 2-phenylnaphthalene. Acetophenone and 2-acetyl-5,6,7,8-tetrahydronaphthalene were also isolated.

The reaction of 2-butyne-1,4-diol diacetate with benzene in the presence of aluminum chloride has been described by Lagidze and Petrov.<sup>1</sup> Two of the products isolated were assigned molecular formulas  $C_{14}H_{10}$  and  $C_{12}H_{14}O$ , on the basis of elemental analysis and molecular weights. These authors suggested that these compounds had structures (I) and (II), respectively.



I



II

Although little degradative evidence was advanced in support of these formulations, the physical and analytical data were difficult to dismiss, particularly for the hydrocarbon. This substance was isomeric with phenanthrene and melted within  $2^\circ$  of that compound. However, a mixture melting point with phenanthrene showed a considerable depression. An x-ray crystallographic examination placed this substance in space group  $P2_1/a$  with two molecules in the unit cell. In the absence of orientational disorder in the crystal, this information is very strong evidence that the molecule has a center of symmetry. While the data did not establish (I) as the structure for the hydrocarbon, other structural possibilities meeting these specifications appear equally improbable. A re-investigation of the products of this reaction seemed indicated.

(1) R. M. Lagidze and A. D. Petrov, *Doklady Akad. Nauk. S.S.S.R.*, **83**, 235 (1952).

A mixture of freshly sublimed aluminum chloride and 2-butyne-1,4-diol diacetate in a molar ratio of approximately 2.5 : 1 was heated at the reflux temperature with excess benzene for six hours. After the lower boiling products had been removed by distillation, a colorless crystalline solid was separated from the viscous residue by sublimation. This solid was established to be Lagidze's hydrocarbon by comparisons of its physical properties with those described.<sup>1</sup> These results are shown in Table I.

TABLE I  
COMPARISON OF CRYSTALLOGRAPHIC DATA

	This Study	Lagidze & Petrov
M.p.	103–104°	103°
<i>a</i>	8.08 ± 0.03 Å	8.10 Å
<i>b</i>	5.85 ± 0.03 Å	5.98
<i>c</i>	35.63 ± 0.12	11.8
$\beta$	94° ± 1°	94°
Space group	$P2_1$ or $P2_1/m$	$P2_1/a$
$d_{obs}$	1.218 g./cm. <sup>3</sup>	1.06–1.16 g./cm. <sup>3</sup>

That this hydrocarbon was actually 2-phenylnaphthalene was established on the basis of the following evidence. Values of the molecular weight determined by freezing point depression and the x-ray data were 196 and 211, respectively, which are in substantial agreement with the value  $188 \pm 10$  reported by Lagidze and Petrov. Elemental analysis corresponded to an empirical formula,  $C_4H_3$ , and hence to a molecular formula,  $C_{16}H_{12}$ . Ozonolysis gave a mixture of benzoic and phthalic acids. Finally, direct comparison of the infrared and ul-

traviolet spectra of the hydrocarbon with those of an authentic sample of 2-phenylnaphthalene<sup>2</sup> and a mixture melting point of the two samples established identity.

The result of the earlier crystallographic study is somewhat disturbing as the x-ray method is generally considered to be absolute as far as determining the presence of a center of symmetry in certain space groups. In the present work, then, white specimens of the hydrocarbon showing excellent optical extinction were examined by precession methods in which  $MoK_{\alpha}$  and  $CuK_{\alpha}$  radiations were employed. The symmetry of the crystals was monoclinic. A summary of the results is given in Table I. The only systematic extinctions that were observed are those for  $OkO$  when  $k$  is odd. However, reflections of the type  $hkl$ , with  $l$  not divisible by three, were very weak or absent and reflections of the type  $hOl$ , with  $h$  odd, were extremely weak. Thus the reflections which require a tripling of the  $c$  axis value given by the previous investigators, and those which violate the space group given by them, are not readily observable unless long exposures are taken and the resulting films are clear.

In addition, the earlier estimate of the crystal density appears to be too low. The present value of 1.218 g./cm.<sup>3</sup>, the result of several determinations by the flotation method, leads to a molecular weight of 211 if one assumes six molecules in the unit cell, which is in good agreement with the value of 204 g./mole for 2-phenylnaphthalene. The calculated density of the crystal is 1.212 g./cm.<sup>3</sup>

Finally, our films showed no obvious evidence of disorder in the crystal, such as diffuse reflections or a large temperature factor. These data make it appear highly probable that the compound examined was identical with that previously reported. The present results indicate no restrictions on the molecular symmetry.

Two additional compounds were separated from the lower boiling fraction by distillation. One of these was established as acetophenone by comparison of infrared spectra and 2,4-dinitrophenylhydrazones. A second carbonyl component, b.p. 151–153°/7 mm., was isolated whose physical properties corresponded fairly closely to those reported by Lagidze for the  $C_{12}H_{14}O$  ketone which had been tentatively assigned structure (II).

This ketone was identified as 5,6,7,8-tetrahydro-2-acetonaphthone<sup>3</sup> on the basis of the following evidence. An examination of the infrared spectrum suggested the presence of a conjugated methyl ketone, methylene groups, and a trisubstituted benzenoid ring. An iodoform reaction gave an acid, m.p. 151–152.5°, with a neutral equivalent of 178±2. The elemental analysis of this acid was

consistent with a molecular formula  $C_{11}H_{12}O_2$ .<sup>4</sup> Oxidation of the ketone with potassium permanganate gave a tricarboxylic acid, m.p. 210–219° (dec.), with an equivalent weight of 71.5±2. This acid did not depress the melting point of an authentic sample of benzene-1,2,4-tricarboxylic acid but only slightly depressed that of benzene-1,2,3-tricarboxylic acid. Confirmation of the identity was obtained by conversion to the anhydride, m.p. 165–167° and a mixture melting point with an authentic sample.<sup>5</sup>

These data establish this  $C_{12}H_{14}O$  ketone as 5,6,7,8-tetrahydro-2-acetonaphthone.

#### EXPERIMENTAL

*Reaction of benzene with 2-butyne-1,4-diol diacetate.* To a mixture of 40 g. (0.25 mole) of 2-butyne-1,4-diol diacetate<sup>6</sup> and 420 g. (5.4 moles) of dry benzene was added 78.0 g. (0.59 formula weight) of anhydrous sublimed aluminum chloride over a period of 30 min. After this mixture had been heated at the reflux temperature for 6 hr., it was cooled and then cautiously diluted with 300 ml. of water. The aqueous layer was washed with three 150-ml. portions of benzene. The combined benzene solution was washed with three 100-ml. portions of 1*N* hydrochloric acid and then it was dried over sodium sulfate. After the bulk of the benzene had been removed by distillation, the residue, subjected to a short path distillation, gave 18.7 g. of a liquid fraction, b.p. 43–136°/0.5 mm. and a viscous residue from which 3.0 g. of crystalline hydrocarbon was obtained by sublimation at 150°/0.5 mm. This hydrocarbon, which proved to be 2-phenylnaphthalene, had m.p. 103–104°<sup>2</sup> after resublimation and recrystallization.

*Anal.* Calcd. for  $C_{15}H_{12}$ : C, 94.09; H, 5.92; mol. wt. 204. Found: C, 94.37, 94.39; H, 6.00, 6.18; mol. wt. 196 (Rast), 211 (x-ray).

The yield of liquid products was increased by reaction under dilute conditions. To a vigorously stirred mixture of 157 g. (1.19 moles) of aluminum chloride, 92 g. (1.18 moles) benzene, and 300 ml. of petroleum ether C, 50 g. (0.29 mole) of 2-butyne-1,4-diol diacetate was added over a period of 1 hr. at 60°. The mixture was stirred at the reflux temperature for 24 hr. and then worked up as previously described. The products which distilled at 46–203°/7 mm. weighed 80.3 g. The crude product was distilled through a 20-cm. spiral wire column: 1. 93–140°/24 mm.,  $n_D^{25}$  1.5333, 23 g.; 2. 120–151°/7 mm., 14 g.; 3. 151–153°/7 mm.,  $n_D^{25}$  1.5517, 8.0 g.

*Identification of the hydrocarbon as 2-phenylnaphthalene.* A sample (501 mg.) of the hydrocarbon (m.p. 103–104°) in 50 ml. of ethyl acetate was treated for 16 min. at 0° with a stream of ozone at a rate of 15.1 mg. of ozone per minute. At the completion of the addition, 30 ml. of glacial acetic acid and 10 ml. of 35% hydrogen peroxide were added and the solution was heated at the reflux temperature for 20 hr. After the solvent had been removed by distillation under reduced pressure, the solid residue was dissolved in 25 ml. of 10% aqueous sodium bicarbonate. The solution was extracted with ether and then acidified with dilute hydrochloric acid. The solution was extracted with two 100-ml. portions of ether, the ether solution was dried over sodium sulfate, and then the solvent was removed by distillation. Sublimation of the residue at 85°/0.1 mm. gave 212 mg. of a

(4) J. W. Williams and J. M. Osborn, *J. Am. Chem. Soc.*, **61**, 3438 (1939).

(5) The authors wish to thank Dr. L. I. Smith for samples of benzene-1,2,3-tricarboxylic acid and benzene-1,2,4-tricarboxylic acid.

(6) A. W. Johnson, *J. Chem. Soc.*, 1009 (1946).

(2) F. D. Chattaway and W. H. Lewis, *J. Chem. Soc.*, 869 (1894).

(3) G. Baddely, E. Wrench, and R. Williams, *J. Chem. Soc.*, 2110 (1953).

solid mixture. Resublimation of this material gave benzoic acid m.p. 115–120° which, after recrystallization from water, melted at 120–122° alone or when mixed with an authentic sample, and phthalic anhydride, m.p. 125–132°, the identity of which was also established by a mixture melting point and by comparison of infrared spectra.

Final confirmation of the structure of the hydrocarbon<sup>7</sup> was obtained by comparison of it with 2-phenylnaphthalene.

*Identification of fraction 3 as 5,6,7,8-tetrahydro-2-acetonaphthone.* Small portions of a solution containing iodine (10 g.) and potassium iodide (20 g.) in water (100 ml.) were added to a mixture of 1.0 g. of fraction 3, (b.p. 151–153°,  $n_D^{25}$  1.5517), described above, 5 ml. of 10% sodium hydroxide, and 20 ml. of dioxane, until a permanent color appeared. The mixture was diluted with water to 150 ml. The iodoform was separated by filtration and the filtrate was treated with two 20-ml. portions of ether. The aqueous solution was acidified to pH 2 with concentrated hydrochloric acid. After the excess free iodine had been reduced by the addition of sodium bisulfite, the product was separated from the solution by extraction with three 50-ml. portions of ether. The residue, after removal of the ether by distillation, was dissolved in 50 ml. of 10% aqueous sodium bicarbonate. The crude acid was collected after acidification of the basic solution with hydrochloric acid. Purification of the acid proved to be difficult. However, it was found that after the acid had been sublimed at 125°/0.5 mm., it could be recrystallized from petroleum ether B to give colorless

(7) A similar conclusion regarding the structure of this hydrocarbon was obtained by G. Maier, *Ber.*, **90**, 2949 (1957).

crystals melting at 151–152.5°. 5,6,7,8-Tetrahydro-2-naphthoic acid has been reported to melt at 153°.<sup>4</sup>

*Anal.* Calcd. for  $C_{11}H_{12}O_2$ : C, 74.98; H, 6.87; neut. equiv. 176. Found: C, 75.30; H, 6.87; neut. equiv. 178.0, 178.7.

A mixture of 1.0 g. of this ketone, 5 ml. of 10% aqueous sodium hydroxide, 5.0 g. of potassium permanganate, and 75 ml. of water, was heated at the reflux temperature and stirred vigorously for 30 min. An additional 5.0 g. of permanganate was added during the next hour. After an additional 3 hr. of heating and stirring, the solution was acidified and sufficient sodium sulfite was added to reduce the manganese dioxide. The product was extracted with several portions of ether. After the ether had been removed by distillation, the product was recrystallized from a carbon tetrachloride-petroleum ether B mixture to give a colorless acid, m.p. 195–202° (dec.), neut. equiv. 71.7, which did not depress the melting point of benzene-1,2,4-tricarboxylic acid<sup>5</sup> but only depressed the melting point of benzene-1,2,3-tricarboxylic acid by 1°. Positive identification of this acid was attained by conversion to the anhydride by sublimation at 210°/1 mm. The product obtained did not depress the melting point of benzene-1,2,4-tricarboxylic acid anhydride, m.p. 165–167°.

*Acetophenone.* A sample of fraction 1, on treatment with 2,4-dinitrophenylhydrazine reagent, gave a 2,4-dinitrophenylhydrazone, m.p. 240–245° which did not depress the melting point of an authentic sample of benzophenone-2,4-dinitrophenylhydrazone, m.p. 243–246°.

Treatment of 0.5 g. of fraction 1 with sodium hypiodite yielded 0.2 g. of an acid, m.p. 120–122°. A mixture of this acid and benzoic acid melted at 120–122°.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MARYLAND]

## Pyrolysis of Esters. XIII. Pyrolysis of Amides<sup>1,2</sup>

WILLIAM J. BAILEY AND CHARLES N. BIRD<sup>3</sup>

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Amides have been shown to pyrolyze in a manner very similar to that of esters but at a higher temperature. Pyrolysis of *N*-(2-acetoxyethyl)-*N*-ethylacetamide produced cleavage at both the ester and the amide linkages to form *N*-ethylacetamide and vinyl acetate as well as acetic acid and *N*-vinyl-*N*-ethylacetamide. Cleavage of *N*-(1,3-dimethylbutyl)acetamide occurred at 590° to produce acetamide plus impure 4-methyl-1-pentene. Cleavage of the corresponding *N*-methyl dialkylated derivative occurred at 570° to produce *N*-methylacetamide plus a mixture of 4-methyl-1-pentene and 4-methyl-2-pentene. Similarly, cleavage of *N*-(1,3-dimethylbutyl)acetanilide occurred at 510° to produce a 91% yield of acetanilide and a 72% yield of a mixture of the two possible olefins. Pyrolysis of the *tert*-alkylamide, *N*-(1,1,3,3-tetramethylbutyl)acetamide also occurred at 510° to produce acetamide and a mixture of two olefins.

It was shown in this laboratory that the pyrolysis of esters was an excellent method for the synthesis of strained dienes, such as 1,2-dimethylene-4-cyclohexene,<sup>4</sup> provided that charring was eliminated. Since the pyrolysis usually follows the Hofmann rule in direction of elimination, many interesting monomers and olefins can be prepared by this procedure.<sup>5</sup> Although the pyrolysis of esters

has been widely used, very little information is available concerning the pyrolysis of the nitrogen analogs, the amides. Primary amides are known to dehydrate when they are heated to produce good yields of the corresponding nitriles and, under slightly more vigorous conditions, to produce the corresponding imide plus ammonia and the carboxylic acid.<sup>6</sup> None of these reactions is, however,

(1) Previous paper in this series, *J. Org. Chem.*, **22**, 1189 (1957).

(2) Presented before the Division of Organic Chemistry at the 132nd National Meeting of the American Chemical Society, New York, N. Y., September 1957.

(3) Office of Naval Research Fellow, 1951–55.

(4) W. J. Bailey and J. Rosenberg, *J. Am. Chem. Soc.*, **77**, 73 (1955).

(5) (a) W. J. Bailey and C. King, *J. Am. Chem. Soc.*, **77**, 75 (1955); (b) W. J. Bailey, J. J. Hewitt, and C. King, *J. Am. Chem. Soc.*, **77**, 357 (1955); (c) W. J. Bailey, J. J. Hewitt, and F. A. Naylor, *J. Org. Chem.*, **22**, 1076 (1957).

(6) (a) R. S. Boehner and C. E. Andrews, *J. Am. Chem. Soc.*, **38**, 2503 (1916); (b) R. S. Boehner and A. L. Ward, *J. Am. Chem. Soc.*, **38**, 2505 (1916); (c) D. Davidson and M. Karten, *J. Am. Chem. Soc.*, **78**, 1066 (1956).