OH peak at τ 6.57 and a methyl singlet at τ 8.81. Drying the analytical sample yielded the cyclic dimeric ester **13**.

Anal. Calcd for $C_6H_{14}B_2O_4$: C, 41.94; H, 8.22; B, 12.59; mol wt, 172. Found: C, 42.02; H, 8.27; B, 12.49; mol wt, 169.

Dibutyl 2,2-Dicyanocyclopropaneboronate (**14**).—A solution of 9.9 g of dibutyl 1-bromo-3,3-dicyanopropane-1-boronate in 75 ml of ether was added over a period of 1 hr to 25 ml of anhydrous pyridine stirred at 0° under nitrogen, then allowed to stand 3 hr at room temperature. Treatment with 100 ml of ether and 50 ml of water was followed by washing the organic phase with 1 *M* hydrochloric acid, extracting the washings with butanol, and drying the combined organic phase with magnesium sulfate. Distillation yielded 5.4 g (72%) of dibutyl 2,2-dicyanocyclopropaneboronate (**14**), bp 109–112° (0.02 mm), $n^{31}\text{D}$ 1.4441. The infrared spectrum showed a well-defined cyclopropyl C–H band at 3.22 μ and a strong C≡N band at 4.45 μ; there was no C≡C band in the 6.1-μ region.

Anal. Calcd for $C_{13}H_{21}BN_2O_2$: C, 62.87; H, 8.53; B, 4.36; N, 11.29. Found: C, 62.93; H, 8.57; B, 4.38; N, 11.15.

2,2-Dicyanocyclopropaneboronic Acid.—The butyl ester **14** (3.75 g) was treated with water (20 ml) and the volatile material was distilled under vacuum to yield 87% of 2,2-dicyanocyclopropaneboronic acid, mp 124–126°. The nmr spectrum at 60 Mc in deuterium oxide showed the HDO peak at 274.5 cps downfield from external tetramethylsilane and two groups of peaks attributed to three nonequivalent cyclopropyl hydrogens at 135, 131, 124, 122, 119.5, 112.5, and 108 cps (integrals 0.1, 0.3, 0.3, 0.2, 0.4, 0.4, 0.3; total 2.0) and at 95, 85.5, 83, and 74 cps (integrals 0.5, 0.3, 0.25, 0.15; total 1.2).

Anal. Calcd for $C_5H_5BN_2O_2$: C, 44.20; H, 3.71; B, 7.96; N, 20.62. Found: C, 44.05; H, 3.86; B, 7.77; N, 20.38.

The diethanolamine ester of 2,2-dicyanocyclopropaneboronic acid was prepared from the acid and diethanolamine in acetone and was recrystallized from ethyl acetate, mp 190–192°.

Anal. Calcd for $C_9H_{12}BN_3O_2$: C, 52.72; H, 5.90; B, 5.28; N, 20.49. Found: C, 52.77; H, 6.00; B, 5.07; N, 20.70.

Relative Rates of Displacement of Bromide by Iodide.—A solution of sodium iodide in acetone was added to a solution of the α-bromoalkaneboronic ester and allyl bromide to make the concentration of each of the three reactants 0.25 *M*. The mixture was allowed to stand at 22–24° until no further change of composition was shown by analysis; 1 hr was sufficient. Allyl bromide and allyl iodide were determined by gas chromatography on a 5-ft SE-30 silicone rubber on Chromosorb W column at 0°. Relative rate constants were calculated assuming that reactions were first order in each reactant and that all the sodium iodide had been consumed.

Kinetics of Solvolyses.—Solvents were measured volumetrically and solutions were made approximately 0.05 *M* in the α-bromoalkaneboronic ester. Temperature control was ±0.1°. The pH was determined to ±0.02 unit with a Leeds and Northrup pH meter. The pH value measured at "infinite" time generally differed from the theoretical value by 0.2–0.5 unit. It was assumed that hydrobromic acid concentrations calculated from the pH measurements followed a linear function of the true values.

Rearrangements of *o*-Aminophenyl Esters

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The hydrogenolysis of several N-benzyloxycarbonyl-*o*-aminophenyl esters resulted in isolation of the rearranged N-acyl- or N-alkoxycarbonyl-*o*-aminophenols. The unstable, intermediate *o*-aminophenyl esters could not be isolated. However, hydrogenolysis of some of the original compounds in the presence of acetic anhydride produced N-acetyl-*o*-aminophenyl esters, presumably because acetylation of the amino group formed was more rapid than rearrangement.

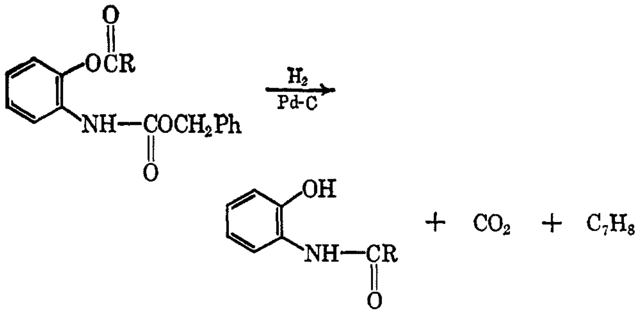
Following the work of Böttcher,[2] there have been several reports on the reduction of *o*-nitrophenyl (or analogous nitronaphthyl) esters by treatment with metal–acid combinations.[2] In all cases the intermediate *o*-aminophenyl esters were not isolated. Presumably these unstable intermediates were first produced and then rapidly rearranged to the N-acyl-*o*-aminophenols, the products actually obtained. Indeed, Ransom[3] and Ransom and Nelson[4] were able to isolate an unrearranged *o*-aminophenyl alkyl carbonate from the reduction of an *o*-nitrophenyl alkyl carbonate at low temperature. These unstable compounds readily rearranged to the N-alkoxycarbonyl-*o*-aminophenols on standing. This type of rearrangement does not occur when the amino and ester groups are *meta* or *para* to each other.[3,5]

Pelczar[6] isolated the unstable intermediate N-methyl-*o*-aminophenyl acetate from the hydrogenolysis of N-methyl-N-benzyloxycarbonyl-*o*-aminophenyl acetate. This compound also readily isomerized to N-methyl-*o*-acetamidophenol.

These facts suggested that *o*-aminophenyl esters might be isolated from the hydrogenolysis of N-benzyloxycarbonyl-*o*-aminophenyl esters. In any event, this reaction appeared to be a convenient way of studying the O to N migration of *o*-aminophenyl esters.

Discussion and Results

Hydrogenolysis of several N-benzyloxycarbonyl-*o*-aminophenylcarboxylate and carbonate esters re-



R = CH_3, C_2H_5, C_6H_5, $i\text{-}C_4H_9O$

sulted in isolation of the rearranged N-acyl- or N-alkoxycarbonyl-*o*-aminophenols. The unstable, intermediate *o*-aminophenyl esters could not be obtained.

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[1] Abstracted in part from the Ph.D. Thesis of C. Ambrosio, The University of Connecticut, 1965.

[2] (a) W. Böttcher, *Ber.*, **16**, 629 (1883); (b) A. Einhorn and B. Pfyl, *Ann.*, **34**, 311 (1900); (c) J. H. Ransom, *Ber.*, **31**, 1055 (1898).

[3] J. H. Ransom, *Am. Chem. J.*, **23**, 1 (1900).

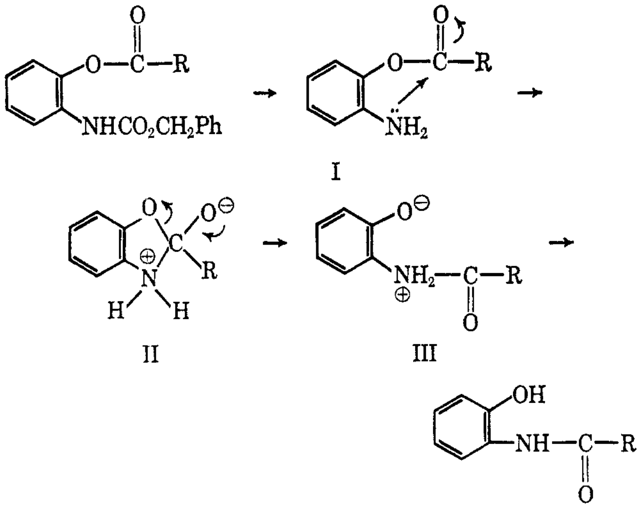
[4] J. H. Ransom and R. E. Nelson, *J. Am. Chem. Soc.*, **36**, 390 (1914).

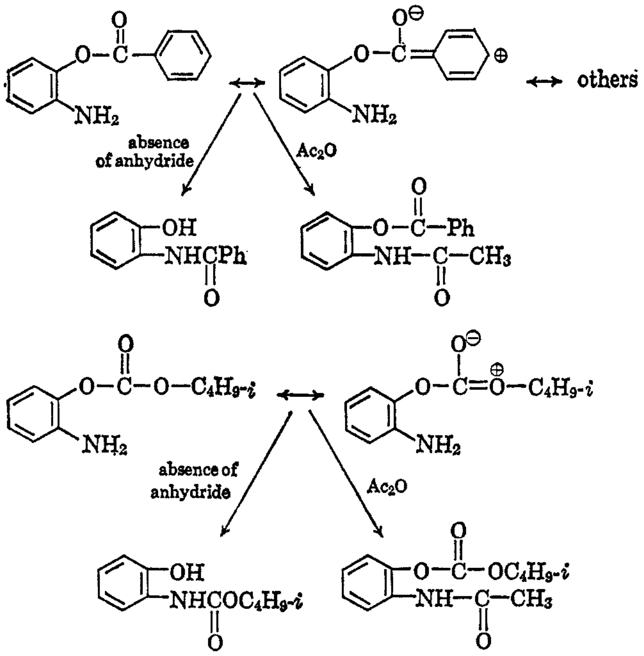
[5] K. Auwers, *Ber.*, **33**, 1923 (1900).

[6] F. A. Pelczar, M.S. Thesis, The University of Connecticut, 1963.

Hydrogenolysis of both N-benzyloxycarbonyl-*o*-aminophenyl benzoate and N-benzyloxycarbonyl-*o*-aminophenyl isobutyl carbonate in the presence of acetic anhydride, however, resulted in the preferential acetylation of the amino group, but hydrogenolysis of the methyl ester in the presence of propionic anhydride and of the ethyl ester in the presence of acetic anhydride resulted in isolation of the rearranged N-acyl-*o*-aminophenol.

In order to speculate on these results it is necessary first to consider the process by which O to N migration undoubtedly occurs. Now, if intermediate I is stabilized, thus inhibiting the formation of II, then it might preferentially undergo a normal acylation reaction of the amino group in the presence of an anhydride. The intermediates, *o*-aminophenyl benzoate and *o*-aminophenyl isobutyl carbonate, can be stabilized by resonance. The intermediates *o*-aminophenyl acetate and *o*-aminophenyl propionate cannot be so stabilized, which may account for the fact that they rearrange even in the presence of an anhydride.





Experimental Section

o-Aminophenol (Eastman, practical grade) required four recrystallizations from 95% ethanol to give shiny white plates, mp 170–171°. All other reagents were of the highest purity available commercially and were used without further purification. Infrared absorption spectra were taken on a Perkin-Elmer Model 137B Infracord. The products were placed in the instrument as potassium bromide disks. A magnetic stirrer was used in all reactions requiring constant stirring.

Benzyl *o*-Hydroxycarbanilate.—*o*-Aminophenol (10.9 g, 0.1 mole) was suspended in 250 ml of practical grade ether. An equivalent of pyridine was added followed by the addition of 20 ml of benzyl chloroformate in 2–3 ml portions with constant stirring over a 1-hr period. The mixture was then shaken several times with water and the water layers were discarded. The ether solution was then shaken four times with 6 *N* potassium hydroxide and the basic solutions were collected and chilled in ice. Acidification with concentrated hydrochloric acid caused the precipitation of 12 g of product (49%), mp 112–115°. Two recrystallizations from dilute ethanol gave white crystals, mp 115–117° (lit.[7] mp 117°).

Isobutyl *o*-Hydroxycarbanilate.—The procedure used was identical with the above description. The molar quantities of reagents were the same as above. The crude product, mp 82–85°, weighed 11.5 g (55%). Two recrystallizations from dilute ethanol gave white crystals, mp 84.5–86° (lit.[8] mp 86°).

***o*-Benzamidophenol.**—The method of Groenvick[9] was applied for the preparation of this compound using *o*-aminophenol and benzoyl chloride. A melting point of 165–167° was observed (lit.[10] mp 167).

***o*-Acetamidophenol.**—The method of Raiford and Greider[11] was followed. We observed a melting point of 203–205° (lit.[11] 200°).

***o*-Propionamidophenol.**—The method of Groenvick[9] was applied for the preparation of this compound. A melting point of 74–75° was observed (lit.[12] mp 78°).

Benzyl *o*-Benzoyloxycarbanilate (N-Benzyloxycarbonyl-*o*-aminophenyl Benzoate).—*o*-Aminophenol (10.9 g, 0.1 mole) was dissolved in 200 ml of anhydrous tetrahydrofuran (THF) and placed in a 500-ml round-bottom flask, equipped with a drying tube. An equivalent quantity of pyridine was added followed by the addition of an equivalent quantity of benzyl chloroformate. The mixture was stirred for 1 hr. The pyridine hydrochloride was filtered off and the solution was transferred to a 500-ml, two-neck, round-bottom flask, equipped with a drying tube and a dropping funnel. Two drops of sulfuric acid was added and then a solution of 23 g (0.1 mole) of benzoic anhydride in 50 ml of THF was added dropwise, with stirring over a 1-hr period. The THF was evaporated and the resulting dark brown solid was washed with dilute sodium hydroxide, filtered, washed with water, and recrystallized from dilute ethanol, giving white crystals, 15 g (43%), mp 106–109°. An infrared spectrum showed the presence of two carbonyl functions: a sharp peak at 1725 cm^{-1} (urethan, identical with that observed for benzyl *o*-hydroxycarbanilate) and a shoulder at 1740 cm^{-1} (ester). Three recrystallizations from hexane and two from pentane gave an analytical sample, mp 108.2–109.2°.

Anal. Calcd for $C_{21}H_{17}NO_4$: C, 72.60; H, 4.94. Found: C, 72.46, 72.68; H, 5.31, 5.44.

This compound was also prepared from the reaction of benzoyl chloride with benzyl *o*-hydroxycarbanilate by a Schotten-Bauman method, the reaction of benzoyl chloride and pyridine with benzyl *o*-hydroxycarbanilate, and the reaction of benzoic anhydride and sulfuric acid catalyst with benzyl *o*-hydroxycarbanilate. Yields of 58, 70, and 70%, respectively, were obtained.

Benzyl *o*-Acetoxycarbanilate (N-Benzyloxycarbonyl-*o*-aminophenyl Acetate).—Benzyl *o*-hydroxycarbanilate (2.43 g, 0.01 mole) was placed in a 150 ml, two-neck, round-bottom flask, equipped with a drying tube and a dropping funnel. Fifty milliliters of THF and 1 ml of pyridine were added followed by the dropwise addition of 1 ml of acetyl chloride in 20 ml of THF,

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(7) P. Chabrier, H. Najer, and R. Giudicelli, *Bull. Soc. Chim. France*, 1353 (1955).

(8) R. E. Nelson and W. C. Aitkenhead, *J. Am. Chem. Soc.*, **48**, 1680 (1926).

(9) E. Groenvick, *Bull. Soc. Chim. France*, [2] **25**, 173 (1876).

(10) H. Hübner, *Ann.*, **210**, 387 (1882).

(11) L. C. Raiford, and C. E. Greider, *J. Am. Chem. Soc.*, **46**, 430 (1924).

(12) H. E. Fierz-David and W. Kuster, *Helv. Chim. Acta*, **22**, 92 (1939).

with constant stirring for 1 hr. The pyridine hydrochloride was filtered and the THF was evaporated, leaving about 10 ml of solution which was cooled overnight. A light pink solid precipitated, mp 94–96°, 2.3 g (75%). An infrared spectrum showed the presence of two carbonyl groups: a sharp peak at 1725 cm^{-1} (urethan) and a shoulder at 1735 cm^{-1} (ester). For analysis, a sample was recrystallized three times from hexane and twice from pentane, giving hard white crystals, mp 96.0–96.2°.

Anal. Calcd for $C_{16}H_{15}NO_4$: C, 67.36; H, 5.30. Found: C, 67.20, 67.21; H, 5.50, 5.58.

A procedure identical with that described for benzyl *o*-benzoylcarbanilate was also used. In the second step of the reaction 12 ml of acetic anhydride in 20 ml of THF was added as described above. A dark red-brown solid was obtained which, after drying in a vacuum desiccator over sulfuric acid, turned light orange, mp 90–96°, 12 g (40%). Several recrystallizations from hexane gave white crystals, mp 95–96°.

Benzyl *o*-Propionyloxycarbanilate (N-Benzyloxycarbonyl-*o*-aminophenyl Propionate).—A procedure identical with that described for benzyl *o*-benzoyloxycarbanilate was used. In the second step 14 ml of propionic anhydride in 20 ml of THF was added as described above. A dark red solid was obtained which, after drying in a vacuum desiccator over sulfuric acid, turned light pink, mp 80–82°, 14 g (44%). An infrared spectrum was essentially identical with the methyl ester, benzyl *o*-acetoxycarbanilate, described above. After five recrystallizations from hexane, an analytical sample was obtained as long, fluffy, white needles, mp 82.0–82.5°.

Anal. Calcd for $C_{17}H_{17}NO_4$: C, 68.22; H, 5.72. Found: C, 68.45, 68.67; H, 5.76, 5.96.

N-Benzyloxycarbonyl-*o*-aminophenyl Isobutyl Carbonate.—Benzyl *o*-hydroxycarbanilate (2.43 g, 0.01 mole) was placed in a 250-ml, two-neck, round-bottom flask, equipped with a drying tube and a dropping funnel. Anhydrous ether (100 ml) and 1.5 ml of pyridine were added followed by the addition of 2.8 ml of isobutyl chloroformate in 20 ml of ether, dropwise, with stirring over a 0.5-hr period. After the pyridine hydrochloride was filtered and the ether was evaporated, a pale yellow oil was obtained. A small portion of the oil was taken up in boiling hexane and cooled overnight. White silky needles precipitated, mp 77.5–79.0°. The infrared spectrum showed two strong, sharp, carbonyl peaks at 1725 (urethan) and 1750 cm^{-1} (carbonate). The remainder of the oil was dissolved in ethanol and poured over crushed ice. A yellow white solid, mp 76–78°, was obtained. The product weighed 3.2 g (93%). After four recrystallizations from pentane, an analytical sample was obtained as long, white, fluffy needles, mp 78.5–79.0°.

Anal. Calcd for $C_{19}H_{21}NO_5$: C, 66.44; H, 6.12. Found: C, 66.01, 65.86; H, 6.35, 6.49.

Hydrogenolysis of N-Benzyloxycarbonyl-*o*-aminophenyl Esters.—The following procedure was used for all hydrogenolysis reactions. To a weighed sample of ester dissolved in 50–75 ml of an anhydrous solvent there was added 20 wt % of palladium-on-charcoal catalyst (Matheson Co., 10%, Lot No. 301200), and the mixture was shaken in a Parr low-pressure hydrogenation apparatus at 35–60 psi. The catalyst was filtered off, the solvent was evaporated, and the resultant product was then characterized.

A. **Benzyl *o*-Benzoyloxycarbanilate.**—(1) One gram (0.003 mole) of ester in absolute ethanol with 0.2 g of catalyst was shaken for 20 hr at 60 psi. A light brown solid, mp 164–165°, 0.5 g (83%), was obtained. An infrared spectrum and a mixture melting point showed the compound to be rearranged *o*-benzamidophenol. (2) One gram of ester in THF with 0.2 g of catalyst was shaken for 20 hr at 50 psi. The results were essentially the same as above. (3) One gram of ester in THF with 0.2 g of catalyst was shaken for 5 hr. A small sample of the solution was added at once to a saturated solution of trichloroacetic acid in THF in the hope of precipitating any unrearranged *o*-aminophenyl benzoate. This did not occur. The work-up of the remainder of the solution gave the same results as above. (4) An attempt was then made to conduct the hydrogenolysis under acidic conditions so that the amino ester formed might be stabilized as a salt and thus be prevented from rearranging. One gram of ester, 0.5 g (0.003 mole) of trichloroacetic acid in ether with 0.2 g. of catalyst was shaken for 5 hr. A dark brown solid was obtained which was recrystallized from heptane, mp 108–109°, mmp 108–109° with starting ester. Thus, in the presence of the strong acid, hydrogenolysis of the ester did not occur.

B. **Benzyl *o*-Acetoxycarbanilate.**—One gram (0.003 mole) of ester in ether with 0.2 g of catalyst was shaken for 1.5 hr at 40 psi. A white solid, mp 190–200°, 0.300 g (60%), was obtained. One recrystallization from 30% acetic acid raised the melting point to 204–205°. An infrared spectrum was identical with that of *o*-acetamidophenol, which when mixed with the product gave no depression of the melting point.

C. **Benzyl *o*-Propionyloxycarbanilate.**—One gram (0.003 mole) of ester in ether with 0.2 g of catalyst was shaken for 1 hr at 38 psi. A light yellow oil was obtained which was taken up in hexane and cooled overnight. Yellow-white crystals precipitated, mp 73–75°, 0.320 g (64%). An infrared spectrum of the sample was identical with that of *o*-propionamidophenol, which when mixed with the product gave no depression of the melting point.

D. **N-Benzyloxycarbonyl-*o*-aminophenyl Isobutyl Carbonate.**—The ester (0.500 g, 0.0015 mole) in ether with 0.1 g of catalyst was shaken for 1 hr at 35 psi. A pale yellow oil resulted which was taken up in pentane and cooled overnight. White crystals precipitated, mp 89–90°, 0.65 g (55%). An infrared spectrum was identical with that of isobutyl *o*-hydroxycarbanilate, which when mixed with the product gave no depression of the melting point.

E. **Benzyl *o*-Benzoyloxycarbanilate with Acetic Anhydride.**—The ester (1.74 g, 0.005 mole) and 1 ml of acetic anhydride in ether with 0.2 g of catalyst was shaken for 2 hr at 40 psi. An oily liquid resulted which was taken up in pentane and cooled overnight. White crystals precipitated, mp 125–130°, 0.750 g. An infrared spectrum showed the presence of two carbonyl groups: 1730–1735 (phenyl benzoate) and 1690–1695 cm^{-1}. (-NH-CO-CH_3). This agrees with the spectrum of the N-acetyl-O-benzoyl derivative of *o*-aminophenol previously reported[13] and is significantly different from the N-benzoyl-O-acetyl isomer also reported.[13] One recrystallization from pentane gave white crystals, mp 139–140°. This agrees with previous reported melting points.[13,14]

F. **Benzyl *o*-Acetoxycarbanilate with Propionic Anhydride.**—The ester (1.35 g, 0.005 mole) and 1 ml of propionic anhydride in ether with 0.2 g of catalyst were shaken for 1.5 hr at 35 psi. A white solid, mp 200–203, 0.650 g (86%), was obtained. The infrared spectrum was identical with that of *o*-acetamidophenol, which when mixed with the product gave no depression of the melting point.

G. **Benzyl *o*-Propionyloxycarbanilate with Acetic Anhydride.**—The ester (1.4 g, 0.005 mole) and 1 ml of acetic anhydride in ether with 0.2 g of catalyst were shaken for 2 hr at 38 psi. The resulting pale yellow oil was taken up in pentane and cooled for several weeks. Yellow-white crystals precipitated, mp 73–75°, 0.825 g (48%). An infrared spectrum was identical with that of *o*-propionamidophenol, which when mixed with the product gave no depression of the melting point.

H. **N-Benzyloxycarbonyl-*o*-aminophenyl Isobutyl Carbonate with Acetic Anhydride.**—The ester (0.343 g, 0.002 mole) and 0.15 ml of acetic anhydride in ether with 0.050 g of catalyst was shaken for 1.5 hr at 40 psi. The resulting pale yellow oil was taken up in pentane and cooled overnight. White crystals precipitated, mp 60–63°, 0.116 g. An infrared spectrum showed the presence of two carbonyl groups: 1750 (carbonate) and 1650 cm^{-1} (amide). Thus, acetylation of the amino group occurred, producing N-acetyl-*o*-aminophenyl isobutyl carbonate. Two recrystallizations from pentane gave an analytical sample in the form of white needles, mp 63.2–64.2°.

Anal. Calcd for $C_{13}H_{17}NO_4$: C, 62.14; H, 6.82. Found: C, 61.79, 61.77; H, 6.85, 6.98.

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