TABLE II

PROPERTIES OF THE CONDENSATION PRODUCTS

Compd.	Formula	B.p., °C.	Mm.	$n^{20}D$	Analyses, % Calcd. C	Calcd. H	Calcd. Cl	Found C	Found H	Found Cl
I	$PhCMe_2CH_2CH_2Cl$	76–78	3	1.5197	72.30	8.28	19.24	72.63	8.50	19.24
II	$PhCMe_2CHPHMe$	129–131	2	1.5619	91.01	8.99		90.72	9.00	
III	p-$C_6H_4(CMe_2CH_2CH_2Cl)_2$	171–173	2.5	[a]	66.88	8.42	24.70	66.63	8.39	24.98
IV	PhC_5H_8Me[b]	67–69	3	1.5183						
V	$PhCH_2CHMe_2$	37–38	7	1.4870						
VI	$PhCH_2C(Me)_2Ph$[c]	114–115[d]	5	1.5589						
VII	$PhC_6H_{10}Me$	90–92	6	1.5125	89.59	10.41		90.10	10.21	
VIII	p-$Me_2CHCH_2C_6H_4C_6H_{10}Me$[e]	133–134	7	1.5070	88.62	11.38		89.11	11.30	

[a] Crystalline; m.p. 67–68°. [b] L. Schmerling, J. P. Luvisi and R. W. Welch, THIS JOURNAL, **77**, 1774 (1955). [c] F. Bodroux, *Compt. rend.*, **132**, 1333 (1901). [d] Deposits about 2.5% of crystalline *meso*-2,3-diphenylbutane, m.p. 121–123°. [e] Oxidation with chromium trioxide dissolved in dilute sulfuric acid and acetic acid yielded terephthalic acid.

Procedures.—Three general procedures were used, resulting in the data summarized in Table I.

Method A.—A solution of the dichloride in about one-third of the total amount of benzene used was added gradually to a stirred mixture of the catalyst and the remainder of the benzene. Stirring was continued for about 0.5–1.0 hour after all the solution had been added, the product was permitted to stand for about 10 minutes, and the upper layer was separated from the catalyst layer, washed with dilute alkali and with water, dried over anhydrous potassium carbonate and distilled.

Method E.—The mixture of reactants and catalyst in an erlenmeyer flask was permitted to stand for 18 hours.

Method S.—The mixture of reactants and catalyst was stirred at ice-bath temperature for 8 hours. The product was then allowed to stand at room temperature overnight before being treated in the above described method. Most, if not all, of the hydrogen chloride produced was evolved at the lower temperature.

The reaction products were identified by means of their infrared spectra as well as their physical and chemical properties.

1-Chloro-3-phenyl-3-methylbutane (I).—Hydrolysis of the Grignard reagent prepared from 20 g. of I yielded 13 g. (18%) of pentylbenzene, b.p. 59.5° at 6 mm., $n^{20}D$ 1.4929. Infrared analysis indicated that the product was pure *t*-pentylbenzene.

Reaction of β-Chloro-*t*-butylbenzene (IX) with Methylcyclohexane.—Thirty-four grams (0.2 mole) of IX[11] was added during 45 min. to a stirred mixture of 100 g. (1.0 mole) of methylcyclohexane and 5 g. of aluminum chloride. Stirring was continued for an additional hour. About 3 g. (0.08 mole) of hydrogen chloride was absorbed in a soda lime tower in the exit line. Distillation of the washed upper layer liquid product yielded 6 g. (22%) of isobutylbenzene (V), 8 g. (25%) of the (methylcyclohexyl)-isobutylbenzene (VIII), and 10 g. of higher boiling product.

Reaction of 1,2-Diphenyl-2-methylpropane (VI) with Methylcyclohexane.—A solution of 1 g. of isopropyl chloride in 21 g. (0.1 mole) of VI was added to a stirred mixture 60 g. (0.6 mole) of methylcyclohexane and 2 g. of aluminum chloride at 4° during 6 min. After being stirred for an additional hour, the product was worked up in the usual manner. There was obtained 5 g. (37%) of isobutylbenzene (V), 3 g. (17%) of the (methylcyclohexyl)-isobutylbenzene (VIII), 5 g. (24%) of unreacted diphenylmethylpropane (VI) which deposited 0.035 g. of crystalline *meso*-2,3-diphenylbutane (XIII) on standing, and 5 g. of higher boiling product.

---

[11] F. C. Whitmore, C. A. Welsberger and A. C. Shabica, Jr., THIS JOURNAL, **65**, 1469 (1943); L. Schmerling and V. N. Ipatieff, *ibid.*, **67**, 1862 (1945).

DES PLAINES, ILLINOIS

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

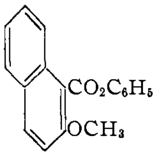
The Reaction of Phenyl 2-Methoxy-1-naphthoate with Grignard Reagents. A New Route to Fluorenones

BY REYNOLD C. FUSON AND F. W. WASSMUNDT[1]

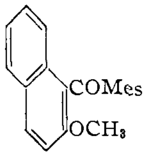
RECEIVED MAY 28, 1956

Phenyl 2-methoxy-1-naphthoate has been found to undergo displacement of the methoxyl group when treated with the phenyl, *o*- and *p*-tolyl and 1- and 2-naphthyl Grignard reagents. The resulting phenyl 2-aryl-1-naphthoates have been cyclized, by the action of cold concentrated sulfuric acid, to the corresponding fluorenones. Benzylmagnesium chloride converts the methoxy ester to phenyl 2-benzyl-1-naphthoate, which undergoes ring closure to give a compound presumed to be 1,2-benzanthrone. Treatment of the impure product with benzoyl chloride converted it to the enol benzoate. Oxidation of the anthrone produced 1,2-benzanthraquinone.

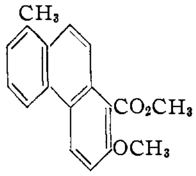
Displacement of nuclear methoxyl groups by the action of Grignard reagents on highly hindered ketones[2] led us to test the effect of such reagents on the corresponding hindered esters. Phenyl 2-methoxy-1-naphthoate I was selected partly because of its convenient melting point and partly because of the great facility with which methoxyl group displacement occurs with the corresponding ketone, II.



I



II



III

It should be mentioned that Richtzenhain and Nippus[3] had suggested a similar possibility with

---

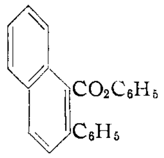
[1] Standard Oil Co. of Indiana Fellow, 1954–1955.

[2] R. C. Fuson and S. B. Speck, THIS JOURNAL, **64**, 2446 (1942).

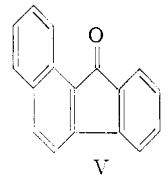
[3] H. Richtzenhain and P. Nippus, *Chem. Ber.*, **82**, 408 (1949).

esters of 2,3-dimethoxybenzoic acid. Also, it seems that Short and Wang[4] may have realized a similar methoxyl group displacement with a related ester, III, since their product was a hydrocarbon. The identity of the hydrocarbon, however, remains uncertain.[5]

When phenyl 2-methoxy-1-naphthoate was treated with Grignard reagents the methoxyl group was replaced in all cases by the hydrocarbon radical of the reagent. Phenylmagnesium bromide, for example, converted the methoxy ester to phenyl 2-phenyl-1-naphthoate (IV) in a yield of 70%. The new ester, IV, could not be hydrolyzed with aqueous sodium hydroxide nor with ethanolic potassium hydroxide. This failure might have been anticipated from the observation of Graebe that these reagents did not hydrolyze the corresponding methyl ester.[6] Confirmation of the structure of phenyl 2-phenyl-1-naphthoate (IV) was obtained by ring closure. Treatment with concentrated sulfuric acid converted it to chrysofluorenone (V).

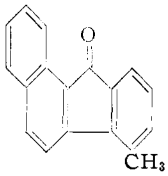


IV

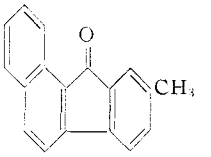


V

When the *o*- and *p*-tolyl Grignard reagents were employed the resulting esters yielded, respectively, 7- (VI) and 9-methyl-chrysofluorenone (VII).



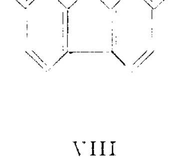
VI



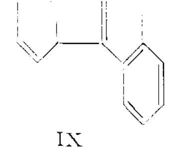
VII

The 2-naphthyl reagent, in a similar way, gave phenyl 2-(2′-naphthyl)-1-naphthoate, which underwent ring closure to yield 1,2,7,8-dibenzofluorenone (VIII).

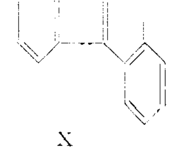
Of especial interest were the results obtained with 1-naphthylmagnesium bromide since the resulting ester IX might be expected to undergo ring closure to give either a 5- or 6-membered ring. Only the 5-membered ring compound X could be isolated. This result is unusual since the closure of a 6-membered ring is generally favored over that of a 5-membered ring. There is at least one recorded example, however, in which the 5-membered cycle is closed preferentially.[7]



VIII

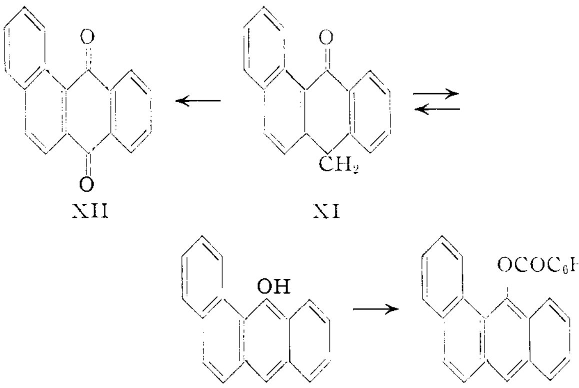


IX



X

Closure of a 6-membered ring was realized, however, with phenyl 2-benzyl-1-naphthoate, obtained by the use of the benzyl Grignard reagent. The ring closure product, presumably the unstable 1,2-benzanthrone XI, was oxidized by a sodium dichromate–acetic acid mixture to 1,2-benzanthraquinone (XII). Also the benzoate XIII of the enolic form of the benzanthrone was prepared.



XII XI

XIII

By analogy with the report of Short and Wang[4] it would appear that the methyl ester, methyl 2-methoxy-1-naphthoate, might undergo methoxyl group displacement with methylmagnesium iodide. The only product that we were able to identify, however, was that formed by 1,2-addition, the methoxycarbinol.

The realization of 1,4-addition reactions of Grignard reagents with α,β-unsaturated acids[8] suggested that methoxyl group displacement might occur if 2-methoxy-1-naphthoic acid were treated with Grignard reagents. Efforts to bring about such a change were unsuccessful, however. Neither phenylmagnesium bromide nor *t*-butylmagnesium chloride, in an ether–benzene solvent, was effective. Methylmagnesium iodide, in the same solvent, brought about demethylation to give 2-hydroxyl-1-naphthoic acid in good yield. The *t*-butyl reagent, in an ether–anisole solvent at 120°, produced a small amount of the hydroxy acid. The use of methylmagnesium iodide as a demethylating agent is well known.[9]

Experimental[10]

1-Bromo-2-methoxynaphthalene.—This compound was made by the procedure described earlier[11]; the reaction mixture was poured into 2.5 l. of ice-water containing a few grams of sodium thiosulfate. The 1-bromo-2-methoxynaphthalene which precipitated was recrystallized from methanol, m.p. 85–85.5°, 94% yield.

2-Methoxy-1-naphthoic Acid.—The procedure was based on that of Bodroux[12] as modified by Bretscher, Rule and

---

[4] W. F. Short and H. Wang, *J. Chem. Soc.*, 2979 (1951).

[5] J. C. Bardhan and D. Nasipuri, *ibid.*, 350 (1956).

[6] C. Graebe, *Ann.*, **335**, 122 (1904).

[7] F. G. Baddar and M. Gindy, *J. Chem. Soc.*, 450 (1941).

[8] J. H. Wotiz, J. S. Matthews and H. Greenfield, THIS JOURNAL, **75**, 6342 (1953).

[9] V. Grignard and J. Ritz, *Bull. soc. chim. France*, [5] **3**, 1181 (1936); W. S. Johnson, Abstracts, 14th National Organic Symposium, Lafayette, Ind., 1955, p. 88.

[10] All melting points are corrected.

[11] R. C. Fuson and D. H. Chadwick, *J. Org. Chem.*, **13**, 484 (1948).

[12] F. Bodroux, *Compt. rend.*, **136**, 617 (1903); *Bull. soc. chim. France*, [3] **31**, 30 (1904).

Spence.[13] A Grignard reagent was prepared by the slow addition of a solution of 94.8 g. of 1-bromo-2-methoxynaphthalene in a mixture of 300 ml. of ether and 150 ml. of benzene to 10.7 g. of magnesium activated with *n*-butyl bromide. The mixture was stirred for 4 hours under gentle reflux and poured on an excess of crushed solid carbon dioxide. Hydrolysis with 10% sulfuric acid and removal of the solids by filtration were followed by separation of the layers of the filtrate and two ether extractions of the aqueous portion. The solids and the residue from evaporation of the organic solvents were triturated with 160 ml. of 10% aqueous sodium hydroxide and then with 40 ml. of the same alkali. After extraction of the basic solutions with ether, dilute sulfuric acid was added until precipitation began. A gram of Darco was added to the warm mixture which was then stirred for 5 minutes. After filtration, the light yellow solution was acidified with 10% sulfuric acid and cooled. The precipitated 2-methoxy-1-naphthoic acid was washed with cold water. The colorless air-dried product (60.8 g. or 75%) darkens at 170° and melts at 172.5–175°, with the evolution of a gas. Crystallization from a small amount of methanol or from an acetone–toluene mixture provided crystals melting at 175.5–176° dec.

Phenyl 2-Methoxy-1-naphthoate (I).—To 12.6 ml. of thionyl chloride in 40 ml. of benzene was added 30.3 g. of 2-methoxy-1-naphthoic acid; after the initial reaction had subsided, the mixture was heated under reflux for 2 hours. The benzene and excess thionyl chloride were removed under diminished pressure; 15 g. of phenol was added to the cooled purple residue. As the mixture warmed to room temperature, a vigorous evolution of hydrogen chloride occurred. About 200 ml. of methylcyclohexane and 0.5 g. of Darco were added, and the mixture was heated on the steam-bath for 0.5 hour. Filtration of the mixture and cooling of the filtrate yielded 35.9 g. (86%) of a light orange product, m.p. 99.5–101.5°. One recrystallization from the same solvent gave a colorless product, melting at 101.5–102.5°, in 95% recovery. The analytical sample, crystallized from cyclohexane, melted at 103–103.5°.

Anal.[14] Calcd. for $C_{18}H_{14}O_3$: C, 77.68; H, 5.07. Found: C, 78.01; H, 5.29.

The infrared spectrum[15] of this compound contains a band assignable to the ester carbonyl (1749 cm.$^{-1}$), a band assignable to the aralkyl ether (1260 cm.$^{-1}$) and bands assignable to the C–O– stretching vibrations of the ester (1193 and 1212 cm.$^{-1}$).

The phenyl ester could also be prepared, although in lower yield (51%), by the Schotten–Baumann method.

Hydrolysis was effected by heating a mixture of phenyl 2-methoxy-1-naphthoate (278 mg.), 1 g. of potassium hydroxide and 10 ml. of absolute ethanol for 2 hours under reflux. After removal of the solvent, the residue was triturated with benzene. Evaporation of the benzene and crystallization of the residue from methylcyclohexane gave 6 mg. (2%) of the recovered ester, m.p. 101–102.5°. The benzene-insoluble material was dissolved in water, and the resulting solution was acidified. The precipitated 2-methoxy-1-naphthoic acid, after having been washed with water and dried in air, weighed 158 mg. (78%), m.p. 174–175.5° dec. Treatment of the aqueous filtrate and washings with bromine in aqueous potassium bromide afforded 281 mg. (85%) of tribromophenol, m.p. 93–95°.

Phenyl 2-Phenyl-1-naphthoate (IV).—A solution of 2.78 g. of phenyl 2-methoxy-1-naphthoate in 60 ml. of benzene was added dropwise to a Grignard reagent prepared from 6.3 ml. of bromobenzene and 1.22 g. of magnesium in 60 ml. of ether. The reaction mixture was heated under reflux for 2.5 hours, stirred overnight and poured on a mixture of ice and ammonium chloride. The organic phase and three ether extracts of the aqueous portion were combined and washed once with water. Steam distillation removed the organic solvents and a small amount of biphenyl. The residue from the distillation was extracted three times with ether. Evaporation of the solvent left a yellow product which, when crystallized from aqueous acetone, gave 2.26 g. (70%) of colorless crystalline phenyl 2-phenyl-1-naphthoate, m.p. 150–151.5°. The analytical sample melted at 152.5–153°.

Anal. Calcd. for $C_{23}H_{16}O_2$: C, 85.16; H, 4.97. Found: C, 84.95; H, 5.00.

The infrared spectrum exhibits a band assignable to the ester carbonyl (1743 cm.$^{-1}$) and bands assignable to the C–O– stretching vibrations of the ester group (1195 and 1218 cm.$^{-1}$).

11-Chrysofluorenone (V).—A solution of 193 mg. of phenyl 2-phenyl-1-naphthoate in 3 ml. of concentrated sulfuric acid was allowed to stand at room temperature for 2 hours before being poured on ice. The ether solution from three extractions was washed with water, dilute sodium carbonate, and again with water and then dried over calcium chloride. Evaporation of the solvent gave 108 mg. (79%) of 11-chrysofluorenone melting at 131.5–132.5°. Crystallization from methanol afforded orange needles, m.p. 132.5–133°.[16]

The carbonyl absorption band of this compound appears at 1707 cm.$^{-1}$ in the infrared.[17,18]

The oxime crystallized from benzene as clusters of yellow needles, m.p. 202.5–203° dec.[19]

The acidified washes of the ether solution of 11-chrysofluorenone, when treated with bromine vapors, gave a few milligrams of a yellow precipitate. This substance, after crystallization from aqueous methanol, yielded slightly yellow crystals of tribromophenol, m.p. 93–95°.

Attempts to effect the cyclization with polyphosphoric acid at 100° failed; major portions of the starting material were recovered in each experiment. The time of the treatment varied from 15 minutes to 24 hours.

Phenyl 2-(2′-Naphthyl)-1-naphthoate.—A solution of 2.78 g. of phenyl 2-methoxy-1-naphthoate in a mixture of 30 ml. of benzene and 30 ml. of ether was added to a Grignard reagent prepared from 12.4 g. of 2-bromonaphthalene and 1.22 g. of magnesium in an equal amount of the same solvent mixture. The reaction mixture was heated under reflux for 3 hours and poured on a mixture of ice and ammonium chloride. The organic phase and three ether extracts were combined and steam distilled. The residue was extracted four times with ether, washed with water and dried over magnesium sulfate. Evaporation of the ether gave a gummy residue which was boiled with 80 ml. of ethanol. Decantation of the hot ethanol solution from the insoluble 2,2′-binaphthyl and cooling deposited 2.12 g. (57%) of slightly yellow phenyl 2-(2′-naphthyl)-1-naphthoate melting at 115–120°. Crystallization of the compound from aqueous acetone raised its melting point to 120.5–121°. An additional 72 mg. (2%) could be obtained from the binaphthyl by fractional crystallization from aqueous acetone.

Anal. Calcd. for $C_{27}H_{18}O_2$: C, 86.61; H, 4.85. Found: C, 86.24; H, 4.79.

The infrared spectrum of this compound shows a band assignable to the ester carbonyl group (1743 cm.$^{-1}$) and bands assignable to the C–O– stretching vibrations of the ester function (1194 and 1216 cm.$^{-1}$).

13H-Dibenzo[a,i]fluoren-13-one (VIII).—A solution of 94 mg. of phenyl 2-(2′-naphthyl)-1-naphthoate in 1 ml. of concentrated sulfuric acid was allowed to stand at room temperature for one hour and poured on ice. The mixture was boiled for 5 minutes, cooled and filtered. The product crystallized from glacial acetic acid to give 11 mg. (16%) of the dark red ketone, m.p. 263.5–266° (sealed tube).

The infrared carbonyl absorption band of this compound (potassium bromide pellet) appears at 1691 cm.$^{-1}$[17,20]

Phenyl 2-(1′-Naphthyl)-1-naphthoate (IX).—The procedure for the preparation and partial purification of this compound was identical to that described for phenyl 2-(2′-naphthyl)-1-naphthoate except that 8.4 ml. of 1-bromonaphthalene was employed as the halide. After the steam

---

[13] E. Bretscher, H. G. Rule and J. Spence, *J. Chem. Soc.*, 1493 (1928).

[14] The microanalyses were performed by Mrs. R. Maria Benassi, Mrs. Lucy Chang, Mrs. Esther Fett, Mr. Joseph Nemeth and Mr. R. J. Nesset.

[15] Infrared analyses by Mrs. M. Louise Griffing and Mr. James J. Brader. Unless otherwise indicated, all spectra were observed in dilute solutions of carbon disulfide.

[16] E. Bamberger and C. Burgdorf, *Ber.*, **23**, 2433 (1890).

[17] E. D. Bergmann and S. Pinchas, *J. Chem. Phys.*, **49**, 537 (1952).

[18] M. L. Josien and N. Fuson, *Compt. rend.*, **236**, 1879 (1953).

[19] C. Graebe, *Ann.* **335**, 122 (1904); P. Baumgarten and J. Olshausen, *Ber.*, **64**, 925 (1931); *cf.* W. J. P. Neish, *J. Org. Chem.*, **16**, 694 (1951).

[20] E. D. Bergmann and S. Pinchas, *Bull. Research Council Israel*, 1, 87 (1952).

distillation, the tan residue was taken up in hot aqueous acetone. When cooled, the solution deposited 2.91 g. (78%) of slightly colored material melting at 145.5–148°. Two recrystallizations from the same solvent mixture afforded analytically pure phenyl 2-(1′-naphthyl)-1-naphthoate, m.p. 148.5–149.5°.

Anal. Calcd. for $C_{27}H_{18}O_2$: C, 86.61; H, 4.85. Found: C, 86.59; H, 4.69.

Its infrared spectrum has a band ascribable to the ester carbonyl group (1742 cm.$^{-1}$) and bands ascribable to the C–O– stretching vibrations of the ester function (1193 and 1217 cm.$^{-1}$).

13H-Dibenzo[a,g]fluoren-13-one (X).—A solution of 258 mg. of phenyl 2-(1′-naphthyl)-1-naphthoate in 10 ml. of concentrated sulfuric acid was allowed to stand at room temperature for 2 hours and then poured on ice. The air-dried product weighed 164 mg., m.p. 155–160°.

Estimation by comparison of carbonyl absorption peaks with that of a pure sample indicated the presence of at least 84% of the fluorenone in the crude product, or a 71% yield. The fluorenone could be separated from an apparently polymeric residue by solution in carbon disulfide. Crystallization of the fluorenone from ethyl acetate gave 126 mg. (65%) of dark red plates of 13H-dibenzo[*a,g*]fluoren-13-one, m.p. 166–166.5° (lit.[21] 164–165°). The infrared carbonyl absorption band appears at 1704 cm.$^{-1}$.

Phenyl 2-(*o*-Tolyl)-1-naphthoate.—A solution of 2.78 g. of phenyl 2-methoxy-1-naphthoate in 60 ml. of benzene was added dropwise to a Grignard reagent prepared from 7.3 ml. of *o*-bromotoluene and 1.22 g. of magnesium in 60 ml. of ether. The reaction mixture was heated under gentle reflux for 3 hours. Hydrolysis, extraction and steam distillation were the same as for the preparation of phenyl 2-phenyl-1-naphthoate. The residue remaining after the distillation was separated by filtration and taken up in hot aqueous acetone. When the supernatant solution, which was decanted from a red oil, was cooled, it deposited 1.83 g. (54%) of a slightly yellow product melting at 121–122.5°. An additional 0.30 g. (9%) of the same substance could be obtained from the trituration residue by fractional crystallizations from ethanol and aqueous acetone. Analytically pure phenyl 2-(*o*-tolyl)-1-naphthoate melts at 123.5–124°.

Anal. Calcd. for $C_{24}H_{18}O_2$: C, 85.18; H, 5.36. Found: C, 85.07; H, 5.40.

The infrared spectrum exhibits bands ascribable to the ester carbonyl (1741 cm.$^{-1}$) and to the ester C–O– stretching vibrations (1194 and 1218 cm.$^{-1}$).

7-Methyl-11-chrysofluorenone (VI).—A solution of 710 mg. of phenyl 2-(*o*-tolyl)-1-naphthoate in 10 ml. of concentrated sulfuric acid was allowed to stand at room temperature for 2 hours and then poured on ice. The solids, separated by filtration, were combined with the residue from evaporation of three ether extracts of the aqueous filtrate. Crystallization of this substance from ethanol yielded 378 mg. (74%) of an orange product melting at 143–144°; analytically pure material melts at 145.5–146°.

Anal. Calcd. for $C_{18}H_{12}O$: C, 88.50; H, 4.95. Found: C, 88.50; H, 4.97.

The infrared carbonyl absorption band of this compound appears at 1700 cm.$^{-1}$.

The oxime, m.p. 183.5–184 dec., separated from aqueous ethanol as yellow crystals.

Anal. Calcd. for $C_{18}H_{13}ON$: C, 83.37; H, 5.05; N, 5.40. Found: C, 83.20; H, 5.28; N, 5.26.

Phenyl 2-(*p*-Tolyl)-1-naphthoate.—A solution of 2.78 g. of phenyl 2-methoxy-1-naphthoate in 60 ml. of benzene was added dropwise to a Grignard reagent prepared from 7.4 ml. of *p*-bromotoluene and 1.22 g. of magnesium in 60 ml. of ether. The remainder of the procedure was the same as that described for the *o*-tolyl analog. The total yield of phenyl 2-(*p*-tolyl)-1-naphthoate, m.p. 119.5–120°, was 2.15 g. (63%).

Anal. Calcd. for $C_{24}H_{18}O_2$: C, 85.18; H, 5.36. Found: C, 84.95; H, 5.66.

The infrared spectrum exhibits bands attributable to the ester carbonyl (1743 cm.$^{-1}$) and to the ester C–O– stretching vibrations (1195 and 1215 cm.$^{-1}$).

9-Methyl-11-chrysofluorenone (VII), m.p. 142–142.5°, was prepared in 60% yield by the procedure described for 7-methyl-11-chrysofluorenone.

Anal. Calcd. for $C_{18}H_{12}O$: C, 88.50; H, 4.95. Found: C, 88.23; H, 4.73.

The carbonyl absorption band of 9-methyl-11-chrysofluorenone appears at 1704 cm.$^{-1}$ in the infrared.

The oxime, m.p. 177–177.5° dec., separated from aqueous ethanol as yellow crystals.

Anal. Calcd. for $C_{18}H_{13}ON$: C, 83.37; H, 5.05; N, 5.40. Found: C, 83.85; H, 5.24; N, 5.87, 5.21.

Phenyl 2-Benzyl-1-naphthoate.—A solution of 1.39 g. of phenyl 2-methoxy-1-naphthoate in 30 ml. of benzene was added over a period of one hour to a Grignard reagent prepared from 3.5 ml. of benzyl chloride and 0.61 g. of magnesium in 30 ml. of ether. The reaction mixture was heated under reflux for one hour and then was hydrolyzed with ice and ammonium chloride. The organic layer and three ether extracts of the aqueous portion were combined and washed once with water. Steam distillation removed the organic solvents and some bibenzyl. The residue from the distillation was extracted three times with ether; evaporation of this solvent gave slightly green material. Treatment with Darco and crystallization from aqueous acetone yielded 1.37 g. (81%) of crystalline phenyl 2-benzyl-1-naphthoate, m.p. 116–117.5°. The analytical sample melted at 118.5–119°.

Anal. Calcd. for $C_{24}H_{18}O_2$: C, 85.18; H, 5.36. Found: C, 85.32; H, 5.31.

The infrared spectrum contains bands assignable to the ester carbonyl (1746 cm.$^{-1}$) and to the C–O– stretching vibrations of the ester (1193 and 1208 cm.$^{-1}$).

Reaction of Phenyl 2 Benzyl-1-naphthoate with Sulfuric Acid.—A solution of 75 mg. of phenyl 2-benzyl-1-naphthoate in 2 ml. of concentrated sulfuric acid was allowed to stand at room temperature for 2 hours. The dark solution was poured into 50 ml. of ice-water. The solution from three ether extractions was dried over magnesium sulfate a few minutes and evaporated to dryness. The yellow residue, presumably benz[*a*]anthracen-12(7H)-one, decomposes at about 130°; it was heated with 3 ml. of benzoyl chloride at 160° for 20 minutes. The dark brown mixture was poured into water and allowed to solidify; the solid was then leached with cold aqueous sodium bicarbonate. The remaining solids were taken up in ether. The ether solution was washed with sodium bicarbonate, dried over magnesium sulfate and concentrated to a small volume. Cooling the solution to 0° afforded 18 mg. (23%) of colorless crystals of the benzoyl derivative of benz[*a*]anthracen-12-ol (XIII), m.p. 202–203.5° (lit.[22] 201–202°).

Alternatively, a solution of 79.5 mg. of the phenyl ester in 2 ml. of concentrated sulfuric acid was allowed to stand at room temperature for an hour and then poured on ice. The solution from three ether extracts was dried briefly over magnesium sulfate and evaporated to dryness. Sodium dichromate was added to the residue in acetic acid solution at 50° until an excess was visible. After the excess was destroyed with methanol, the reaction mixture was poured into ice-water. Filtration of the precipitate and crystallization from acetic acid afforded 17.2 mg. (28%) of benz[*a*]anthraquinone (XII), m.p. 164.5–166°. Addition of water to the filtrate gave an additional 11.6 mg. (19%) of the quinone. Admixture with authentic quinone, m.p. 168.5–169.5°, prepared from 2-(1′-naphthoyl)-benzoic acid by the method of Oda and Tamura[23] caused no depression of the melting point.

Methyl 2-Methoxy-1-naphthoate.—To the cooled acid chloride, prepared from 10.11 g. of 2-methoxy-1-naphthoic acid and thionyl chloride, was added 3.0 ml. of absolute methanol. After the reaction mixture had been heated under reflux for one hour, the excess alcohol was removed. Crystallization of the residue from toluene–ligroin gave 7.88 g. (73%) of methyl 2-methoxy-1-naphthoate, m.p. 52–53°.[24]

The infrared spectrum shows a band assignable to the ester carbonyl group (1728 cm.$^{-1}$), a band assignable to the aralkyl ether (1261 cm.$^{-1}$) and bands assignable to the C–O– stretching vibrations of the ester (1155 and 1238 cm.$^{-1}$).

---

(21) G. Swain and A. R. Todd, *J. Chem. Soc.*, 674 (1941).

(22) J. W. Cook, *ibid.*, 1087 (1930).

(23) R. Oda and K. Tamura, *Sci. Papers Inst. Phys. Chem. Research Tokyo*, **32**, 263 (1937).

(24) A. Werner and W. Seybold, *Ber.*, **37**, 3658 (1904).

Dimethyl-(2-methoxy-1-naphthyl)-carbinol.—A solution of 2.16 g. of methyl 2-methoxy-1-naphthoate in 60 ml. of benzene was added dropwise to a Grignard reagent prepared from 3.7 ml. of methyl iodide and 1.22 g. of magnesium in 60 ml. of ether. The reaction mixture was heated under gentle reflux for 3 hours and poured into a mixture of ice and ammonium chloride. The organic layer and three ether extracts of the aqueous portion were evaporated in the cold. Crystallization of the residue from aqueous methanol containing a drop of concentrated ammonium hydroxide gave 1.33 g. (61%) of colorless crystals of the tertiary carbinol, m.p. 95–95.5°.

Anal. Calcd. for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.82; H, 7.58.

Reaction of Methylmagnesium Iodide and 2-Methoxy-1-naphthoic Acid.—To the Grignard reagent prepared from 3.7 ml. of methyl iodide and 1.22 g. of magnesium in 80 ml. of ether was added a slurry of 2.02 g. of 2-methoxy-1-naphthoic acid in 50 ml. of benzene. After 20 hours of heating under reflux, the reaction mixture was poured into dilute hydrochloric acid. The organic layer was removed and the aqueous layer was extracted three times with ether. The combined organic layers were extracted three times with 10% aqueous sodium hydroxide. Acidification with concentrated hydrochloric acid caused the separation of 1.51 g. (80%) of a colorless precipitate melting at 123–128° with the evolution of a gas. Repeated crystallization of the material from aqueous acetone did not raise the decomposition point above 124–128° (slow heating). Ferric chloride in methanol produces a dark blue coloration with this compound, which was identified as 2-hydroxy-1-naphthoic acid. The decomposition point given in the literature is 124–128°.[25]

Anal. Calcd. for $C_{11}H_8O_3$: C, 70.21; H, 4.29; neut. equiv., 188. Found: C, 69.95; H, 4.47; neut. equiv., 188.

---

[25] R. Schmitt and E. Burkard, *Ber.*, **20**, 2699 (1887).

URBANA, ILLINOIS

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

Diels–Alder Reactions of 9-Substituted Anthracenes.[1] II. 9-Cyanoanthracene

BY JOHN S. MEEK, JOHN R. DANN AND BING T. POON

RECEIVED DECEMBER 27, 1955

9-Cyanoanthracene has been found to give *ortho*-type adducts with acrylamide, methyl acrylate and acrylic acid. With allyl alcohol and acrylonitrile both possible isomeric adducts were found. The *ortho*-type adduct predominated with allyl alcohol while the major isomer was the *meta*-type with acrylonitrile.

When 9-anthraldehyde was condensed with acrylic acid, allyl alcohol and acrylonitrile only one of two possible isomeric adducts was isolated in each case.[2] These adducts were all 12-substituted ethanoanthracenes in which the carboxaldehyde group and the functional group coming from the dienophile were located on adjacent carbon atoms (*ortho*-type adduct) rather than on non-adjacent atoms (11-substituted ethanoanthracenes, *meta*-type adducts).

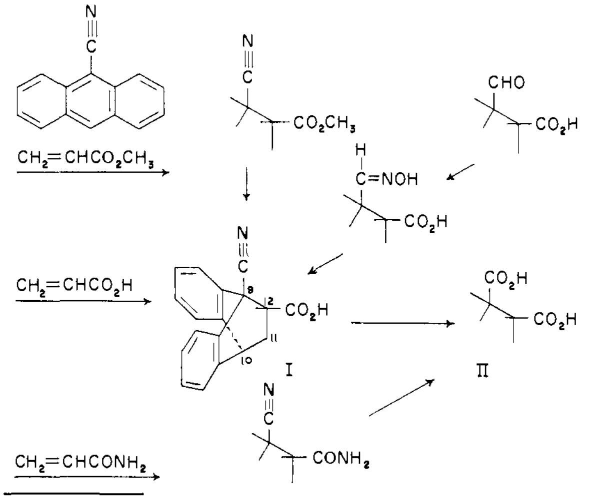
In the present work 9-cyanoanthracene was used as a diene and, with acrylic acid, methyl acrylate and acrylamide, only the *ortho*-type adduct was found.

With allyl alcohol the product was an oil which upon heating with acetic anhydride gave two crystalline acetates. The major acetate was again an *ortho*-type derivative and was formed in about twice the amount of that of the second acetate. Although the adducts of allyl alcohol were not isolated directly it is believed that their relative amounts correspond to those of the acetates and that heating with acetic anhydride did not cause any isomerization. To isomerize adducts which are positional isomers requires a complete reversal of the Diels–Alder reaction. All the adducts of 9-substituted anthracenes which we have so far examined are colorless and even when heated at melting points of above 200° they do not produce the yellow color characteristic of a 9-substituted anthracene.

When acrylonitrile was used as a dienophile both isomeric adducts were formed and the *meta*-type 11-substituted adduct predominated for the first time.

9-Cyanoanthracene can be considered the dibenz analog of the open chain compound *trans*-1-cyano-1,3-butadiene. This latter substance has been reported to give only *cis–ortho*-type adducts with methyl and ethyl acrylate and when condensed with acrylonitrile the adduct formed could not be separated from the dimer of 1-cyano-1,3-butadiene in sufficient quantity for characterization studies.[3] Incorporating the cyanobutadiene system into an anthracene derivative eliminated *cis–trans* isomerism in the adducts as well as dimerization of the diene and simplified our work.

The structure of the acrylic acid adduct I of 9-cyanoanthracene was proved by synthesizing the compound from the known 9-formyl-9,10-ethano-



---

[1] This paper was presented in part at the XIIth International Congress of Pure and Applied Chemistry, September, 1951, and was supported by the Office of Naval Research.

[2] J. S. Meek, B. T. Poon and S. J. Cristol, THIS JOURNAL, **74**, 761 (1952).

[3] H. R. Snyder and G. I. Poos, *ibid.*, **72**, 4104 (1950).