TABLE I

Preparation of Coumarins by Ether Cleavage

Acid or Acid Chloride	M.P.	M.P., Lit.	Cyclization Product	M.P.	M.P., Lit.	Yield, %
o-Methoxcinnamic acid[a]	188–189	182–183[b]	Coumarin	69.5–70	67–67.5[c]	4
o-Ethoxycinnamic acid	131–132	133–134[d]	Coumarin	69–70	67–67.5[c]	4
2,3-Dimethoxycinnamic acid[a]	182–183	180[e]	8-Methoxycoumarin	88–89	87–89[f]	3
2,3-Dimethoxycinnamoyl chloride	81–82	[g]	8-Methoxycoumarin	88–89	87–89[f]	6
2,4-Dimethoxycinnamic acid[a]	182–183	184[h]	7-Methoxycoumarin	114–115	114[i]	3
2,5-Dimethoxycinnamic acid	146–148	147[j]	6-Methoxycoumarin	102–103.5	103[k]	12
o-Methoxy-α-methylcinnamic acid[a]	92–94[l]	102,[h] 107[m]	3-Methylcoumarin	88–89	90[n]	80
o-Methoxy-α-methylcinnamoyl chloride	B.p. 120/ 0.2	[o]	3-Methylcoumarin	88–89	90[n]	95
o-Ethoxy-α-methylcinnamic acid	131–132	130–133[p]	3-Methylcoumarin	88–89	90[n]	28
o-Methoxy-α-ethylcinnamic acid	107–108	105[q]	3-Ethylcoumarin	72–73	72[r]	48
o-Ethoxy-α-ethylcinnamic acid	113.5–114	[s]	3-Ethylcoumarin	72–73	72[r]	30
o-Methoxy-α-cyanocinnamic acid	211–212	211–212[t]	No coumarin[u]			
o-Methoxy-α-cyanocinnamoyl chloride	128	[v]	No coumarin[w]			
2-Methoxy-5-chlorocinnamic acid	203–204	191[h]	6-Chlorocoumarin	161–162	161–162[x]	8
2-Methoxy-5-nitrocinnamic acid	226	238[y]	No coumarin[z]			
2-Methoxy-5-methylcinnamic acid	114–115	[aa]	6-Methylcoumarin	74–76	73–74[bb]	9

[a] Obtained from Aldrich Chemical Co. [b] W. H. Perkin, *J. Chem. Soc.*, **31,** 414 (1866). [c] W. H. Perkin, *J. Chem. Soc.*, **21,** 56 (1856). [d] R. C. Gupta and K. C. Pandya, *J. Indian Chem. Soc.*, **25,** 148 (1948). [e] W. H. Perkin, Jr., and R. Robinson, *J. Chem. Soc.*, **105,** 2387 (1918). [f] M. Crawford and J. A. M. Shaw, *J. Chem. Soc.*, 3435 (1953). [g] *Anal.* Calcd. for $C_{11}H_{11}O_3Cl$: C, 58.29; H, 4.89. Found: C, 58.60; H, 4.99. [h] D. Chakravarti and B. Majumdar, *J. Indian Chem. Soc.*, **16,** 389 (1939). [i] F. Tiemann and C. L. Reimer, *Ber.*, **12,** 996 (1879). [j] H. Kauffman and K. Burr, *Ber.*, **40,** 2355 (1907). [k] F. Tiemann and W. H. M. Muller, *Ber.*, **14,** 1996 (1881). [l] All attempts to raise this m.p. by recrystallization of a commercial[a] or synthetic sample failed. [m] W. H. Perkin, *J. Chem. Soc.*, **39,** 429, 432 (1874). [n] W. H. Perkin, *J. Chem. Soc.*, **28,** 12 (1863). [o] Impossible to obtain completely free of traces of 3-methylcoumarin which formed during distillation. [p] G. Werner, *Ber.*, **28,** 2001 (1895). [q] W. H. Perkin, *J. Chem. Soc.*, **39,** 447 (1874). [r] T. Nakabayashi, E. Hori, and N. Okamurs, *J. Pharm. Soc. Japan*, **74,** 250 (1954). [s] *Anal.* Calcd. for $C_{13}H_{16}O_3$: C, 70.88; H, 7.32. Found: C, 70.86; H, 7.28. [t] W. Baker and C. S. Howes, *J. Chem. Soc.*, 119 (1953). [u] The acid chloride was the only product isolated. [v] *Anal.* Calcd. for $C_{11}H_8NO_2Cl$: C, 59.56; H, 3.64. Found: C, 59.54; H, 3.45. [w] Acid chloride recovered with slight decomposition. [x] A. Clayton, *J. Chem. Soc.*, **93,** 2022 (1906). [y] A. Schnell, *Ber.*, **17,** 1383 (1884). [z] Only decomposition products were obtained. [aa] *Anal.* Calcd. for $C_{11}H_{12}O_3$: C, 68.73; H, 6.30. Found: C, 68.73; H, 6.46. [bb] T. J. Thompson and R. H. Edee, *J. Am. Chem. Soc.*, **47,** 2556 (1925).

In all cases the identity of the coumarins were checked by melting points and infrared and ultraviolet spectra and in most cases by comparison with authentic samples.

EXPERIMENTAL[12]

Reagents. The cinnamic acids used were obtained commercially or were prepared by standard literature methods. Reagent grade thionyl chloride was used.

o-Methoxy-α-methylcinnamic acid with thionyl chloride. A mixture of 4.0 g. of *o*-methoxy-α-methylcinnamic acid and 3.1 ml. of thionyl chloride was refluxed for 0.5 hr. and the excess thionyl chloride removed *in vacuo*. Benzene was added and the mixture was concentrated again. Distillation of the residue gave a white solid, b.p. 170–172° (approx. 60 mm.). Several recrystallizations from benzene or ether gave a solid, m.p., and mixed m.p. with 3-methylcoumarin, 88–89°.

Anal. Calcd. for $C_{10}H_8O_2$: C, 74.98; H, 5.03. Found: C, 75.07; 75.11; H, 5.22, 5.24.

This reaction was repeated under identical conditions. Distillation of the residue gave a liquid, b.p. 126° (2 mm.). This liquid was heated at 170° for 20 min. to yield 3-methylcoumarin, m.p. and mixed m.p. 88–89°.

General reaction of cinnamic acids with thionyl chloride. The cinnamic acid and thionyl chloride (0.6 ml. per g. of acid) were refluxed at 90° in a 3/4″ × 3″ Pyrex tube equipped with a cold-finger condenser. After 45 min., the temperature was raised to 225–250° for a 15- to 20-min. period. The coumarin was collected from the cold finger and recrystallized from an appropriate solvent.

2,3-Dimethoxycinnamoyl chloride. A mixture of 5.0 g. of 2,3-dimethoxycinnamic acid and 3.0 ml. of thionyl chloride was refluxed for 45 min. and the excess thionyl chloride removed *in vacuo* by treatment with benzene. Distillation of the residue gave a solid (90%) b.p. 156° (1 mm.); m.p. 81–82°.

Anal. Calcd. for $C_{11}H_{11}O_3Cl$: C, 58.29; H, 4.89. Found: C, 58.60; H, 4.99.

Heating this solid in the apparatus described above (250°) gave 8-methoxycoumarin, m.p. 88–89°.

o-Methoxy-α-cyanocinnamoyl chloride. Reaction of *o*-methoxy-α-cyanocinnamic acid and thionyl chloride in the general procedure described above gave a 23% yield of solid, m.p. 128°.

Anal. Calcd. for $C_{11}H_8NO_2Cl$: C, 59.56; H, 3.64. Found: C, 59.54; H, 3.45.

Heating this solid at 260° for extended periods of time did not yield any 3-cyanocoumarin.

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[12] Microanalyses by Spang Microanalytical Laboratory, Ann Arbor, Mich., and Drs. Weiler and Strauss, Oxford, England.

Action of Methylmagnesium Iodide on Water

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In connection with an investigation of the reaction of water with carbonyl compounds,[1] we had occasion to determine the number of active hydrogen atoms in carbonyl hydrates which decomposed rapidly into the free carbonyl compounds and water. The method of Zerewitinoff[2] was selected for the determination because it appeared that the techniques had been thoroughly developed,[3] and active hydrogen atoms in carbonyl hydrates had previously been determined successfully by this method.[4,5] However, our experimental results with methylmagnesium iodide in *n*-butyl ether with and without pyridine solvent were difficult to interpret. This was initially attributed to the varying degrees of enolization of the free carbonyl compounds,[6] but it became apparent on further investigation that another factor was important.

It had been assumed in the carbonyl hydrate work that free water liberates two equivalents of methane on treatment with methylmagnesium iodide because most references state that water reacts with Grignard reagents as if it contained two active hydrogen atoms.[3,7-9] This behavior was first reported by Zerewitinoff who found that the water of hydration of some sugars and water alone liberated two equivalents of methane in pyridine solvent at 18°.[10] Evans and co-workers also reported similar findings when they treated water with methylmagnesium iodide in isoamyl ether.[11] The reaction went to completion in one hour at 25° although much less than two equivalents of methane (as low as 81.7% of the theory for one active hydrogen) were liberated in other experiments. Zerewitinoff and Evans explained their results by postulating that the intermediate magnesium hydroxy iodide reacts with a second mole of Grignard reagent as shown in the accompanying equations.

$$CH_3MgI + H_2O \longrightarrow CH_4 + Mg(OH)I$$

$$CH_3MgI + Mg(OH)I \longrightarrow CH_4 + MgO + MgI_2$$

Our experimental results with carbonyl hydrates could only be explained on the basis of one active hydrogen per molecule of water. Hence, a few experiments were conducted with water alone to determine its reactivity under the conditions used with the carbonyl derivatives. The results of these experiments are summarized in Table I. It is apparent from the results of runs 1 and 2 that water liberates considerably less than two equivalents of methane on treatment with excess methylmagnesium iodide in pyridine solvent at room temperature. Since low results have been reported to be caused by the high solubility of methane in pyridine solvent,[12] run 3 was conducted without solvent. Slightly more than one equivalent of methane was evolved after two weeks at room temperature. Similar experiments carried out with a stable carbonyl hydrate, chloral hydrate, resulted in the liberation of two equivalents of methane.

It now appears that free water reacts with the evolution of one equivalent of methane under the usual conditions of the Zerewitinoff determination. Zerewitinoff carried out his studies of the action of methylmagnesium iodide on water with aqueous pyridine solutions of known water content,[10] whereas the first two runs of Table I were conducted by first adding the Grignard reagent in *n*-butyl ether to pyridine solvent, and then treating the water sample with this mixture. Since the latter procedure would allow the formation of pyridine-Grignard reagent complex first,[2] it is possible that Zerewitinoff observed the liberation of two equivalents of methane because methylmagnesium iodide etherates react more rapidly with water than with pyridine, while in our experiments, the complex reacts slowly with water. This explanation does not seem likely however in view of the results of run 3. Only one equivalent of methane is liberated rapidly. It is not clear why the work of Evans has been interpreted to support the findings of Zerewitinoff[15] since only one of four experiments carried out at room temperature by Evans indicated two active hydrogen atoms per molecule of water. The other three experiments resulted in values of 0.82, 0.99, and 1.07 active hydrogen atoms. Even experiments conducted by Evans at 100° did not result in the evolution of two equivalents of methane; values ranging from 1.19 to 1.88 active hydrogen atoms were reported.

EXPERIMENTAL

The apparatus and procedure described by Roth[14] were used with minor modifications. A 50-ml. gas burette was substituted for the micro burette so that larger samples could be analyzed, the stopcock was connected directly to one neck of the Y-shaped reaction vessel, a serum stopper was connected to the stopcock to facilitate introduction of the Grignard reagent with a hypodermic syringe, and a glass ball was

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[1] This work will be published shortly.

[2] T. Zerewitinoff, *Ber.*, **47**, 2417 (1914).

[3] J. Mitchell, Jr., *et al.*, *Org. Anal.*, Interscience, New York, 1953, Vol. I, p. 155.

[4] H. Hibbert and J. J. Sudborough, *J. Chem. Soc.*, 933 (1904).

[5] H. Hibbert, *J. Chem. Soc.*, 341 (1912).

[6] J. A. Krynitsky, J. E. Johnson, and H. W. Carhart, *J. Am. Chem. Soc.*, **70**, 486 (1948).

[7] F. Pregl, *Die Quantitativ Organische Microanalyse.*, ed. 4, J. Springer, Berlin, 1935, p. 194.

[8] J. B. Niedrel and V. Niedrel, *Micromethods of Quantitative Organic Analysis*, ed. 2, Wiley, New York, 1942, p. 263.

[9] S. Siggia, *Quantitative Organic Analysis via Functional Groups*, Wiley & Sons, Inc., New York, 1949, p. 41.

[10] T. Zerewitinoff, *Ber.*, **40**, 2023 (1907).

[11] R. N. Evans, J. E. Davenport, and A. J. Revukas, *Ind. Eng. Chem., Anal. Ed.*, **12**, 301 (1940).

[12] R. A. Lehman and H. Basch, *Ind. Eng. Chem., Anal. Ed.*, **17**, 428 (1945).

[13] F. Pregl, *Quantitative Organic Analysis*, English ed. 3, P. Blakiston's, Philadelphia, 1937, p. 156.

TABLE I

METHANE LIBERATED ON TREATMENT OF WATER WITH EXCESS METHYLMAGNESIUM IODIDE AT ROOM TEMPERATURE

Run	Water, G.	Time from Start	Methane Liberated Standard Conditions, Ml.	Theory for One H, Ml.	%, Theory
1[a]	0.0177	30 min.	11.5	22.0	52.3
		1 hr.	12.5		56.9
		6 days	13.9		63.2
2[a]	0.0199	1.5 hr.	15.8	24.7	64.0
		12 hr.	17.8		72.2
		4 days	19.7		79.8
		7 days	23.7		96.0
		2 weeks	24.9		101
		4 weeks	25.0		101
3[b]	0.0182	4 min.	16.6	22.6	73.5
		7 min.	20.1		89.0
		30 min.	22.3		98.6
		1 hr.	23.5		104
		13 hr.	25.6		113

[a] Anhydrous pyridine used as solvent; pyridine treated with Grignard reagent before bulb broken. [b] No solvent used.

used in the reaction vessel to allow agitation of the reactants and to break the glass bulb containing the sample of water. Methylmagnesium iodide was purchased as a 1.0*N* solution in purified *n*-butyl ether.[14] Four-bed deionized and distilled water of 700,000 ohm-cm. volume resistivity was used for each run. Pyridine solvent, Eastman white label, was dried by distillation from barium oxide.

The general procedure for each experiment was as follows. A thin, dry, tared glass bulb was filled with the sample of water, sealed, cooled, and weighed. The bulb was then placed in one neck of the reaction vessel which had previously been dried in an oven overnight at 110°. The glass ball, also oven-dried, was placed in the other neck of the vessel with 5 ml. of pyridine (runs 1 and 2), and the unit was attached to the apparatus. The apparatus was swept with dry nitrogen for 15 min. and then 10 ml. of methylmagnesium iodide solution was introduced into the neck containing the glass ball and pyridine. The reagent and solvent were allowed to stand for 10 min. to eliminate any error because of traces of moisture in the solvent, and then the entire reaction vessel was brought to room temperature by external cooling in a large beaker of water. The apparatus was again adjusted to atmospheric pressure to compensate for any gas given off on mixing the reagent and solvent, and the determination was then made in the usual manner.[15] The reactants were agitated periodically. The apparatus was tested for leakage during each experiment by application of a positive pressure with the leveling reservoir. No leakage was detected. That an excess of methylmagnesium iodide had been used was determined after each run by observation of gas evolution on addition of water.

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[14] Arapahoe Special Products, Inc., Boulder, Col.

[15] Ref. 3, p. 181.

Studies of Quinoid Structures. VI. A Note on the Action of Arylmagnesium Halides on Anthraquinone Monoanil at Elevated Temperature

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It has been found in these laboratories[1-4] that Grignard reagents add preferentially to the carbonyl group of phenanthrenequinonimine, chrysenequinonimine, phenanthrenequinone monoxime, chrysenequinone monoxime, phenanthrenequinone and chrysenequinone monosemicarbazones, benzil monosemicarbazone, as well as anthraquinone monoanil. We have now allowed anthraquinone monoanil (I) to react with phenyl- and anisylmagnesium bromides in boiling toluene, where both the carbonyl group and the $\rangle C{=}N{-}$ group are attacked by the Grignard reagent, with the ultimate formation of 9,10-diphenyl-9,10-dihydroanthracene-9,10-diol and 9,10-di-(*p*-methoxyphenyl)-9,10-dihydroanthracene-9,10-diol, respectively, according to the following scheme.

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[1] W. I. Awad and A. R. A. Raouf, *J. Org. Chem.*, **22**, 881 (1957).

[2] W. I. Awad and A. R. A. Raouf, *J. Org. Chem.*, **23** 282 (1958).

[3] W. I. Awad, A. R. A. Raouf, and Miss A. M. Kamel, *J. Org. Chem.*, **24**, 1777 (1959).

[4] W. I. Awad, A. K. Fateen, and M. A. Zayed, *J. Org. Chem.*, **25**, 358 (1960).