

Reactions of Biphenyl, Diphenylmethane, and Bibenzyl with Acetyl Hypoiodite

By **Y. Ogata**,* **I. Urasaki**, and **T. Ishibashi**, Department of Applied Chemistry, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya, Japan

The iodination of biphenyl with acetyl hypoiodite gave only products iodinated in the *p*-position; reactions with diphenylmethane and bibenzyl gave both *o*- and *p*-iodides in ratios of 0.14:1 and 0.28:1, respectively, probably because of the smaller steric effect for *ortho* substitutions. Study of competitive reactions gave the following relative reactivities for *para* iodination: 100 for biphenyl, 57 for diphenylmethane, and 97 for bibenzyl. This reflects the resonance and inductive effects of the phenyl group. Further, α -acetoxy- and/or α -hydroxy-derivatives were formed with diphenylmethane and bibenzyl under the same conditions. A mechanism involving a radical attack on the methylene group is suggested. The effects of sulphuric acid and water on the iodination and/or α -substitution are discussed in terms of the intermediacy of protonated acetyl hypoiodite.

IN a previous report¹ on the iodination of aromatic compounds such as benzene, naphthalene, acenaphthene, and fluorene with iodine-peracetic acid, acetyl hypoiodite (AcOI) or protonated acetyl hypoiodite (AcOIH⁺) was suggested as a probable attacking species.¹ Recently, the formation of acetyl hypoiodite in the reaction of

iodine with peracetic acid in acetic acid was supported by the detection of carbon dioxide, methyl iodide, and methyl acetate in the mixture.² We have extended our

¹ (a) Y. Ogata and K. Nakajima, *Tetrahedron*, 1964, **20**, 43, 2751; (b) Y. Ogata and K. Aoki, *J. Amer. Chem. Soc.*, 1968, **90**, 6187; (c) Y. Ogata and I. Urasaki, *J. Chem. Soc. (C)*, 1970, 1687.

² Y. Ogata and I. Urasaki, *J. Org. Chem.*, 1971, **36**, 2164.

studies on the reactivity of acetyl hypoiodite, to its reactions with biphenyl, diphenylmethane, and bibenzyl.

RESULTS

Iodination of Biphenyl.—Treatment of biphenyl with acetyl hypoiodite gave 4-iodo- (I) and 4,4'-di-iodo-biphenyl (II) together with small amounts of unidentified products, probably formed by oxidation of biphenyl (see Table 1). The 2-iodo-derivative could not be detected.

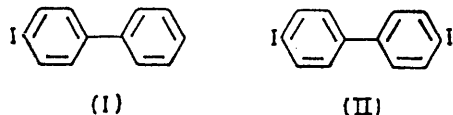


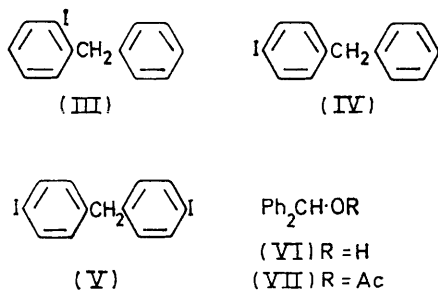
TABLE 1

Iodination of biphenyl with acetyl hypoiodite in acetic acid at 50°^a

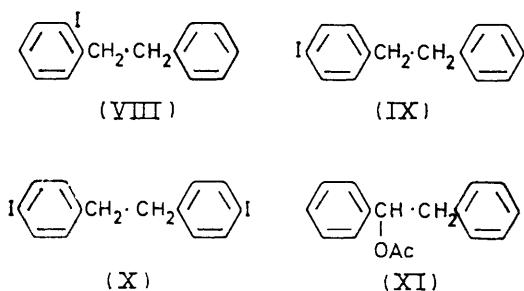
Ph ₂ (mmol)	CH ₃ ·CO ₂ H (mmol)	I ₂ (mmol)	t/h	Products (% yield)	
				(I)	(II)
40	20	20	3.5	62.0	4.6
40	40	40	3.5	67.5	23.1
20	40	40	4.5	54.3	43.8

^a Peracetic acid was slowly added to the acetic acid solution of biphenyl and iodine.

Reaction with Diphenylmethane.—Diphenylmethane reacted with an equimolar amount of acetyl hypoiodite in acetic acid at 70° for 7.5 h to give 2-iodo- (III) (10.3%), 4-iodo- (IV) (57.0%), and bis-4-iodo-diphenylmethane (V) (4.2%), together with diphenylmethanol (VI) (2.8%) or diphenylmethyl acetate (VII) (12.9%). Oxidation of diphenylmethane with peracetic acid alone in acetic acid under the same conditions gave only a 0.5% yield of the alcohol (VI).



Reaction with Bibenzyl.—The products from bibenzyl at 60° after 5 h were similar to those from diphenylmethane



except no α -hydroxy-derivative was detected: 2-iodo- (VIII) (13.2%), 4-iodo- (IX) (34.0%), 4,4'-di-iodo- (X)

(11.0%), and α -acetoxy-bibenzyl (XI) (8.7%). Bibenzyl was stable against peracetic acid alone. The 2,4'- and 2,2'-di-iodo-derivatives could not be detected.

Effects of Sulphuric Acid, Water, and Iodine on the Reaction of Diphenylmethane with Acetyl Hypoiodite in Acetic Acid.—The addition of sulphuric acid apparently raises the yield of iodo-compounds, lowering those of diphenylmethyl acetate (VII) and diphenylmethanol (VI), which was not detected. On the other hand, the iodination was not favoured in aqueous 90% acetic acid, when more (VI) and (VII) were formed. Further, the yield of (VII) as well as of iodo-compounds was increased with increasing concentration of iodine (see Table 2).

TABLE 2

The effects of sulphuric acid, water, and iodine on the reaction of diphenylmethane with acetyl hypoiodite in acetic acid at 50° for 5 h

PhCH ₂ Ph (mmol)	I ₂ (mmol)	CH ₃ ·CO ₂ H (mmol)	H ₂ SO ₄ (mmol)	Products (% yield)			
				(III)	(IV)	(VI)	(VII)
4.0	2.0	2.0		1.0	5.8		10.8
4.0	2.0	2.0	9.0	3.9	19.7		0.2
4.0	2.0	2.0	18.0	4.5	30.0		0.4
4.0	2.0	2.0		0.3	1.9	6.5	19.2 ^a
4.0		2.0				0.13	
4.0	0.06	2.0				0.06	0.17
4.0	0.20	2.0			0.3		1.7

^a With aqueous 90% acetic acid as solvent.

Relative Reactivity.—Since the rate-determining step of the iodination is the formation of acetyl hypoiodite,^{1a} we employed a competitive reaction to estimate the relative reactivities of the substrates. Accordingly, to the reaction mixture was added sulphuric acid, which favours the iodination alone (see Table 2). Results are shown in Table 3

TABLE 3

Relative yields of iodo-aromatic compounds in the competitive iodination of biphenyl and diphenylmethane or bibenzyl with acetyl hypoiodite in acetic acid at 50°^a

t/h	Biphenyl vs. diphenylmethane		
	Products (% yield) (ratio)		
	(I)	(III)	(IV)
1	17.1 (1.00)	1.8 (0.106)	10.1 (0.582)
2	25.8 (1.00)	2.3 (0.089)	15.4 (0.591)
3	34.0 (1.00)	3.3 (0.093)	22.4 (0.614)

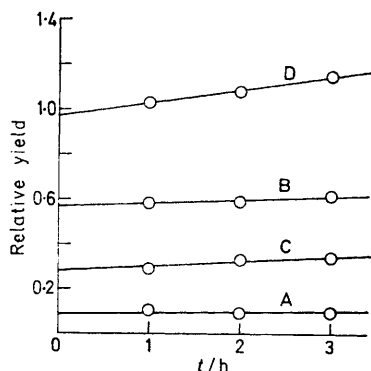
t/h	Biphenyl vs. bibenzyl		
	Products (% yield) (ratio)		
	(I)	(VIII)	(IX)
1	19.0 (1.00)	5.6 (0.29)	19.9 (1.03)
2	23.7 (1.00)	8.0 (0.33)	26.0 (1.08)
3	28.8 (1.00)	10.5 (0.34)	37.0 (1.15)

^a Initial concentration of each reactant was 0.065M; concentration of sulphuric acid was 1.1N.

and the Figure. As seen in the Figure, the initial relative yields (which correspond to the relative reactivities) of iodo-aromatic compounds compared with 4-iodobiphenyl for the formation of 2- and 4-iododiphenylmethane and 2- and 4-iodobibenzyl are 0.08, 0.57, 0.28, and 0.97, respectively. From these values *o* : *p*-ratios were calculated to be 0.14 : 1 for diphenylmethane and 0.28 : 1 for bibenzyl.

DISCUSSION

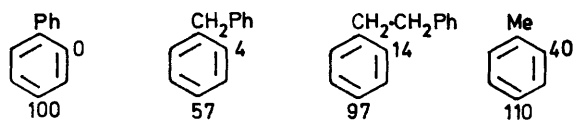
ortho:*para* Ratio and Relative Reactivity.—Biphenyl gave no 2-iodo-derivative, as has been observed with other iodinating agents.^{3,4} This is a typical difference from chlorination where considerable amounts of *ortho* products are obtained;⁵ this is explained by steric hindrance



Extrapolation of relative yields of iodo-aromatic compounds compared with 4-iodobiphenyl *vs.* reaction time in the competitive iodination of biphenyl and diphenylalkanes with acetyl hypoiodite in acetic acid at 50°; initial concentration of each reactant: 0.065M; concentration of sulphuric acid: 1.1N; (A) 2-iododiphenylmethane; (B) 4-iododiphenylmethane; (C) 2-iodobibenzyl; (D) 4-iodobibenzyl

by an adjacent phenyl group to *ortho* attack of the large iodinating species.

ortho-Iodination can occur when a methylene group is inserted between the phenyl groups. However, the *o*:*p*-ratios of diphenylmethane (0.14) and bibenzyl (0.28) are still much smaller than those in chlorination,⁵ where the values are 1.16:1 for diphenylmethane and 0.80:1 for bibenzyl. Molecular models of diphenylmethane and bibenzyl show that there is only a small space for the formation of transition state in *ortho*-iodination, implying that a considerable steric hindrance still exists.



The competitive iodination (see Figure) gave the partial rate factors as shown, based on the *para*-position of biphenyl for the iodination with acetyl hypoiodite, indicating the electrophilic nature of the reagent. The values for toluene are taken from the results of the competitive iodination of biphenyl and toluene reported previously, *i.e.* the ratio of iodinated products of biphenyl and toluene is 1:0.95, and the *o*:*p*-ratio of iodo-toluene is 0.73:1.^{1b} The data are comparable with the partial rate factors for the chlorination in acetic acid at 25°⁵ except for the *o*-position of diphenylmethane.

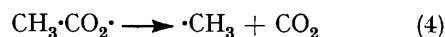
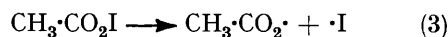
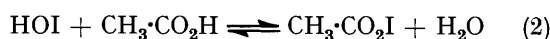
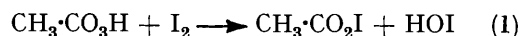
³ P. S. Varma, *J. Indian Chem. Soc.*, 1937, **14**, 156 (*Chem. Abs.*, 1937, **31**, 7410°).

⁴ H. O. Wirth, O. Königstein, and W. Kern, *Annalen*, 1960, **634**, 84.

⁵ P. B. D. de la Mare, E. A. Johnson, and J. S. Lomas, *J. Chem. Soc.*, 1965, 6893.

The substituent effects of benzyl and phenethyl groups as well as of a methyl group on the *para*-position of the phenyl nucleus can usually be explained by using Taft's σ^* constant, because the resonance and steric effects of these groups are almost negligible, whereas phenyl group has a large resonance effect. However, when logarithms of partial rate factors for the *para*-position (excluding biphenyl) were plotted against σ^* , the linearity was unsatisfactory, probably because of the uncertainty of the data for toluene. The negative ρ -value of -1.6 calculated from this plot was a little smaller than that for chlorination ($\rho -2.5$),⁵ where a good linearity was obtained.

Mechanism for α -Substitution.—The formation of α -acetoxy- and/or α -hydroxy-derivatives from the reactions of diphenylmethane and bibenzyl with iodine-peracetic acid in acetic acid is interesting mechanistically. Table 2 shows that α -acetoxybibenzyl (VII) is produced only in the presence of both peracetic acid and iodine, which implies that acetyl hypoiodite may be necessary for the formation of (VII). A suppressing effect by the radical scavenger, *m*-dinitrobenzene, on the formation of (VII) was observed (see Table 4), indicating a radical mechanism. The formation of radicals from acetyl hypoiodite [equations (1—4)] was confirmed in our previous paper.² Therefore, acetoxy or methyl radical must be the hydrogen abstractor, but since



atomic iodine is known to be a weak hydrogen abstractor,⁶ it may not be involved. The resulting diphenylmethyl radical ($\text{Ph}\dot{\text{C}}\text{HPh}$) (XII) can give (VII) by com-

TABLE 4

The effect of the radical scavenger, *m*-dinitrobenzene, on the acetoxylation of diphenylmethane in acetic acid at 50° for 5 h^a

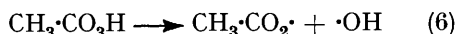
<i>m</i> -Dinitrobenzene (mmol)	Products (% yield)		
	(III)	(IV)	(VII)
0.4	2.7	13.4	13.0
4.0	2.1	13.1	8.8
4.0	2.4	14.9	8.2

^a With diphenylmethane (4 mmol), iodine (2 mmol), and peracetic acid (2 mmol).

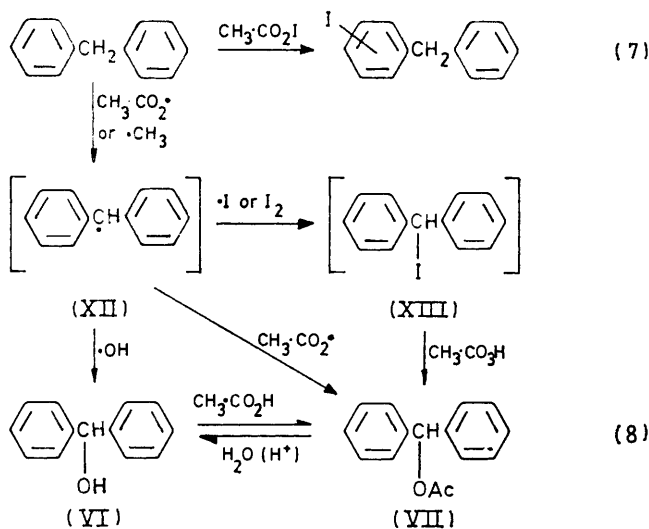
ination with an acetoxy radical, and (VI) by combination with an hydroxyl radical, which may be formed by the decomposition of hypoiodous or peracetic acid [equations (5) and (6)]. The radical (XII) may also re-

⁶ (a) H. J. Schumacher and E. O. Wüg, *Z. phys. Chem. (Leipzig)*, 1931, **B11**, 45; (b) H. J. Schumacher and G. Stieger, *ibid.*, 1931, **B12**, 348; (c) R. E. DeRight and E. O. Wüg, *J. Amer. Chem. Soc.*, 1935, **57**, 2411; (d) Y. Nagai, in 'Chemistry of Free Radicals,' eds. H. Sakurai and K. Tokumaru, Nankodo, Tokyo, 1967, p. 87.

act with atomic or molecular iodine to give diphenyl-



methyl iodide (PhCHIPh) (XIII), which is, however, unstable in the presence of peracetic acid, thus readily giving diphenylmethyl acetate (VII) as reported previously for other alkyl iodides.⁷ Hence, the path *via* iodide (XIII) is also a probable route to (VII). Besides, there should be an equilibrium between (VII) and (VI) in the presence of sulphuric acid, because the yield of (VI) is increased on addition of water (Table 2).



SCHEME

The above discussion leads to the over-all mechanism shown in the Scheme. Here, the iodination [equation (7)] may compete with the acetoxylation or hydroxylation [equation (8)]. In terms of this mechanism, the predominance of the iodination over the acetoxylation on addition of sulphuric acid is explained as follows. Protonated acetyl hypiodite is a more effective electrophile for iodination, as reported previously,^{1a} whereas the formation of radicals from it may be difficult. Further, the reverse effect of addition of water, which leads to an increase of polarity and basicity of the solvent, may be explained by the relatively low concentration of protonated acetyl hypiodite compared with that of the unprotonated compound which should be more effective for acetoxylation but less so for iodination. Moreover, the difference in the yields of acetoxyderivatives of diphenylmethane and bibenzyl can also be explained in terms of the stability of the diphenylmethyl radical (XII) compared with that of the 1,2-diphenylethyl radical.

⁷ Y. Ogata and K. Aoki, *J. Org. Chem.*, 1969, **34**, 3974.

⁸ W. W. Hartman and R. Phillips, *Org. Synth.*, 1943, Coll. vol. II, p. 232.

⁹ H. A. Smith, D. M. Alderman, D. D. Shacklett, and C. M. Welch, *J. Amer. Chem. Soc.*, 1949, **71**, 3772.

¹⁰ F. Y. Wiselogle and H. Sonneborn, *Org. Synth.*, 1941, Coll. vol. I, p. 90.

EXPERIMENTAL

Materials.—Commercial biphenyl of reagent grade was used without further purification (m.p. 70.2–70.7°). Diphenylmethane was distilled under reduced pressure; b.p. 90–95° at 3 mmHg (lit.,⁸ 125–130° at 10 mmHg). Bibenzyl was recrystallised from methanol; m.p. 50.5–51.0° (lit.,⁹ 52.5°). Peracetic acid was used as a *ca.* 2.0M-solution in acetic acid. Commercial acetic acid (99.5%) and iodine (reagent grade) were used without further purification. Diphenylmethanol was recrystallised from light petroleum (b.p. 100–125°); m.p. 66° (lit.,¹⁰ 68°). Diphenylmethyl acetate was recrystallised from methanol; m.p. 40.5–41.0° (lit.,¹¹ 41°). Crude α -acetoxybibenzyl,¹² purified by chromatography on silica gel in benzene, was a liquid, ν_{max} 1740 (C=O) and 1200–1300 cm^{-1} (CO–O–C).

Iodination of Biphenyl.—An acetic acid solution (10 ml) of 2.0M-peracetic acid (0.02 mol) was slowly dropped into a stirred solution of biphenyl (6.2 g, 0.04 mol) and iodine (5.1 g, 0.02 mol) in acetic acid (130 ml) at 50° during 3.5 h. The precipitate was filtered off and washed with aqueous 5% sodium hydrogen carbonate and then with water. Fractional crystallisation of the precipitate from methanol gave 4-iodo- and 4,4'-di-iodo-biphenyls. 4-Iodobiphenyl was also obtained from the filtrate of the mixture, which was diluted with water and extracted with chloroform. The extract was washed with aqueous potassium iodide, sodium thiosulphate, sodium hydrogen carbonate, and water, dried (Na_2SO_4), and evaporated. The yields of the products were determined by u.v. spectrophotometry (see Table 1): 4-iodobiphenyl (I), m.p. 109–111° (from methanol) (lit.,¹³ 113°), and 4,4'-di-iodobiphenyl (II), m.p. 204–205° (from carbon tetrachloride) (lit.,¹⁴ 205.5°). Both (I) and (II) were identified also by elemental analyses and i.r. and n.m.r. spectroscopy.

Reaction of Diphenylmethane.—A solution of 2.0M-peracetic acid in acetic acid (20 ml, 0.04 mol) was added dropwise to a stirred solution of diphenylmethane (6.7 g, 0.04 mol) and iodine (10.2 g, 0.04 mol) in acetic acid (250 ml) at 70° during 7.5 h. No precipitate was obtained from the cooled mixture, which was extracted with chloroform and worked up as for biphenyl. The products were dissolved in chloroform and analysed by g.l.c. [Yanagimoto model GCG 550 F instrument, flame ionisation detector, 1.5 m \times 3 mm column of 15% Apiezon L on Celite 545 (80–100 mesh), nitrogen as a carrier (30–45 ml min^{-1}) at 80–200° (6° min^{-1}), hydrogen flow rate 30–40 ml min^{-1} , injection temperature 200–230°, detector temperature 230–270°]. Diphenylmethanol and its acetate were identified on the basis of comparison of retention times with those of authentic samples. Diphenylmethyl acetate was isolated by t.l.c. with benzene as eluant. The i.r. spectrum was identical with that of an authentic sample.

Products with the two longest retention times were isolated by preparative g.l.c. [Yanagimoto model GCG 220 instrument with a thermocouple detector, 1.5 m \times 4.5 mm column of 15% Silicone SE-30 and 3% phosphoric acid on Celite 545 (80–100 mesh), hydrogen as carrier at 200°] and identified as 2- and 4-iododiphenylmethanes by i.r. and

¹¹ N. T. Farinacci and L. P. Hammett, *J. Amer. Chem. Soc.*, 1937, **59**, 2542.

¹² C. R. Hauser, J. C. Shivers, and P. S. Skell, *J. Amer. Chem. Soc.*, 1945, **67**, 409.

¹³ E. Votocěk and J. Köhler, *Ber.*, 1914, **47**, 1219, 1221.

¹⁴ B. Williamson and W. H. Rodebush, *J. Amer. Chem. Soc.*, 1941, **63**, 3018.

n.m.r. spectra and elemental analyses: 2-iododiphenylmethane (III), liquid (lit.,¹⁵ b.p. 182° at 11 mmHg), and 4-iododiphenylmethane (IV), m.p. 41.0—41.5° (lit.,¹⁶ 43—44°).

Bis-4-iododiphenylmethane (V) was isolated by fractional crystallisation from methanol, m.p. 91—93° (lit.,¹⁷ 93°). The data from elemental analysis and i.r. and n.m.r. spectra also support the identification of this compound.

Reaction of Bibenzyl.—The reaction was carried out as described for diphenylmethane except at 60° for 4 h. The precipitate was filtered off after cooling and recrystallised from methanol, giving 4,4'-di-iodobenzyl (X), m.p. 146° (lit.,¹⁸ 152°).

The filtrate was diluted with water and extracted with chloroform as described for biphenyl. G.l.c. analysis showed at least three products in the extract. One of them was isolated by t.l.c. (with benzene); it was identical with authentic α -acetoxybenzyl (i.r. spectrum and g.l.c. retention time). The other two products, isolated by g.l.c. as for the diphenylmethane reaction, were 2-iodobenzyl (VIII), liquid (lit.,¹⁵ b.p. 175° at 0.5 mmHg) and 4-iodobenzyl (IX), m.p. 35—36° (lit.,¹⁹ 44—45°). Identification of compounds (VIII)—(X) was confirmed by elemental analyses and their i.r. and n.m.r. spectra.

Determination of Yields.—The yields of the products in the iodination of biphenyl were determined spectrophotometrically. The u.v. absorption maxima of biphenyl, 4-iodobiphenyl, and 4,4'-di-iodobiphenyl in methanol were

¹⁵ J. Collette, D. McGreer, R. Crawford, F. Chubb, and R. B. Sandin, *J. Amer. Chem. Soc.*, 1956, **78**, 3819.

¹⁶ S. Akagi and T. Iwashige, *J. Pharm. Soc. Japan*, 1954, **74**, 610.

at 246 (ϵ 17,300), 259 (25,700), and 268 nm (34,600), respectively. The yield of each product was calculated from the ratio of biphenyl to 4-iodobiphenyl in the solution and that of 4-iodobiphenyl to 4,4'-di-iodobiphenyl in the precipitate.

The yields of the products in the other reactions were determined by g.l.c. under the conditions described before, with acetophenone (R_t 10 min) as an internal standard. Table 5 shows the retention times and the relative molar sensitivities of various substrates and products.

TABLE 5

Retention time and relative molar sensitivity in g.l.c.

Material	R_t /min	Relative molar sensitivity (acetophenone : sample)
Biphenyl	20	0.59
4-Iodobiphenyl	55	0.84
Diphenylmethane	22	0.63
Diphenylmethanol	27	0.73
Diphenylmethyl acetate	28	0.80
2-Iododiphenylmethane	50	0.54
4-Iododiphenylmethane	60	0.99
Bibenzyl	24	0.60
α -Acetoxybenzyl	30	0.60
2-Iodobenzyl	60	1.01
4-Iodobenzyl	70	1.00

[1/1036 Received, June 22nd, 1971]

¹⁷ A. M. Nastyukov and V. V. Shelyagin, *J. prakt. Chem.*, 1928, [2] **119**, 303.

¹⁸ K. Elbs and A. Jaroslazew, *J. prakt. Chem.*, 1913, [2] **88**, 92.

¹⁹ J. Braun, H. Deutsch, and O. Koscielski, *Ber.*, 1913, **46**, 1511, 1516.