

## 1,2-Dihydrobenzocyclobutene ('Benzocyclobutene'): Lithiation, and the Preparation of Some 3-Substituted Derivatives

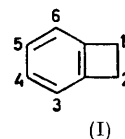
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Treatment of 1,2-dihydrobenzocyclobutene ('benzocyclobutene') with *n*-butyl-lithium-tetramethylethylenediamine in ether gives a mixture of the 1-, 3-, and 4-lithio- and 1,2-dilithio-species; initially the 1- and 3-lithio-species are mainly formed, in roughly equal amounts, but if the reaction is prolonged the 3-lithio-derivative predominates. Treatment of the mixture with chlorotrimethyl-silane or -stannane has given samples of 1- and 3-trimethylsilyl- and -stannyl-1,2-dihydrobenzocyclobutene and 1,2-bis(trimethylsilyl)-1,2-dihydrobenzocyclobutene. Cleavage of the 3-trimethyl-silyl- and -stannyl derivatives with bromine and with iodine monochloride has given 3-bromo- and 3-iodo-1,2-dihydrobenzocyclobutene, and cleavage of the 3-trimethylsilyl compound with mercury-(ii) acetate has given the 3-acetoxymercuri-compound.

ELECTROPHILIC substitution in 1,2-dihydrobenzocyclobutene † (I), which is complicated by ring opening, occurs predominantly or exclusively at the 4-position;<sup>2</sup> for example, if the 3-nitro-derivative is formed at all in nitration, it must be to the extent of less than 5%.<sup>3</sup> The only 3-substituted derivatives known are the 3-carboxy- (made in 6% yield by metallation of the hydrocarbon with *n*-pentylsodium in pentane, followed by carboxylation),<sup>4</sup> the 3-chloro- (made by forming the ring system with the chlorine already attached to the appropriate carbon atom),<sup>1</sup> and the 3-trimethylsilyl derivative (made from the 3-chloro-compound).<sup>1</sup> We have previously pointed out that metallation of the

† This is the correct I.U.P.A.C.-*Chem. Abs.* name for the compound usually referred to as benzocyclobutene (*cf.* ref. 1). The numbering is shown in formula (I).

hydrocarbon, which seemed to occur virtually exclusively at the 3-position,<sup>4</sup> followed by coupling with chlorotri-



methyl-silane or -stannane to give 3-(Me<sub>3</sub>M)C<sub>8</sub>H<sub>7</sub> compounds, and demetallation of the latter with electrophilic reagents, might provide a route to a range of

<sup>1</sup> A. R. Bassindale, C. Eaborn, and D. R. M. Walton, *J. Chem. Soc. (B)*, 1969, 12.

<sup>2</sup> I. L. Klundt, *Chem. Rev.*, 1970, **70**, 471.

<sup>3</sup> J. B. F. Lloyd and P. A. Ongley, *Tetrahedron*, 1964, **20**, 2185.

<sup>4</sup> R. A. Finnegan, *J. Org. Chem.*, 1965, **30**, 1333.

3-substituted derivatives.<sup>1</sup> In the brief pilot study described below we have found that such a route is practicable,<sup>5</sup> although the metallation of the hydrocarbon is, at least under our conditions, more complex than the one previous investigation had suggested.<sup>4</sup>

#### RESULTS AND DISCUSSION

**Lithiation.**—The *n*-butyl-lithium tetramethylethylenediamine complex in ether was used for the metallation. When samples of the reaction mixture were withdrawn at various times and treated with chlorotrimethylsilane, g.l.c. analysis showed that initially three monolithio-species were present, and later a dilithio-species appeared. The variations in the relative proportions of these species are apparent from the Table.

TABLE

Analysis of the products obtained on treatment of 1,2-dihydrobenzocyclobutene-*n*-butyl-lithium-tetramethylethylenediamine mixtures with chlorotrimethylsilane; peak heights in cm ( $\pm 0.1$  cm) relative to those of the internal standard, tridecane

Time (h)	C <sub>8</sub> H <sub>8</sub>	Me <sub>3</sub> SiC <sub>8</sub> H <sub>7</sub>			(Me <sub>3</sub> Si) <sub>2</sub> C <sub>8</sub> H <sub>6</sub>
		1-	3-	4-	
0.5	6.0	0.7	0.5	0.2	0
1	5.5	1.3	1.3	0.3	0
2	5.0	1.1	1.5	0.4	0
4	4.0	0.9	1.7	0.5	0.3
6	3.7	0.7	1.7	0.4	0.3
8	3.3	0.6	1.9	0.4	0.4
12	2.5	0.5	1.5	0.4	0.4

Initially 1-lithiation is at least equal in extent to 3-lithiation, but later the amount of the 1-lithio-derivative decreases markedly, some of it being converted into the dilithio-derivative. After about 4 h the total amount of mono- and di-metallated species falls, possibly mainly because of decomposition and/or interaction with the solvent, but perhaps also because tri- and other poly-lithio-species are formed. [These would give rise to a range of poly(trimethylsilyl) compounds not detected in the g.l.c. analysis.] A noteworthy feature is that if, as seems likely, the peak heights shown in the Table reflect the proportions of isomers with reasonable accuracy, the ratio of 3- to 4-metallation never exceeds 5 : 1, this is reasonably consistent with an approximate ratio of 7 : 1 observed for protodetrithiation of the 3- and 4-positions of the hydrocarbon with lithium cyclohexylamide in cyclohexylamine.<sup>6</sup> It is a markedly smaller ratio than that for the corresponding 1- and 2-metallations of biphenylene, which is in the region of 20 : 1.<sup>7</sup>

The n.m.r. spectrum of the isolated bis(trimethylsilyl)-compound indicated that it was the 1,2-derivative. The 1,2-dilithio-1,2-dihydrobenzocyclobutene would be expected to have some enhanced stability by virtue of the

<sup>5</sup> C. Eaborn, A. A. Najam, and D. R. M. Walton, *J.C.S. Chem. Comm.*, 1972, 840.

<sup>6</sup> A. Streitwieser, jun., G. R. Ziegler, P. C. Mowery, A. Lewis, and R. G. Lawler, *J. Amer. Chem. Soc.*, 1968, **90**, 1357.

<sup>7</sup> W. Baker, A. J. Boulton, C. R. Harrison, and F. W. McOmie, *Proc. Chem. Soc.*, 1964, 414.

<sup>8</sup> C. Eaborn, A. A. Najam, and D. R. M. Walton, *J. Organometallic Chem.*, 1972, in the press.

<sup>9</sup> C. Eaborn, Z. S. Salih, and D. R. M. Walton, *J.C.S. Perkin II*, 1972, 172, and references therein.

Huckel-rule aromaticity associated with the 1,2-dianion, and Finnegan foresaw the likelihood that the 1-lithio-compound might, for this reason, be converted fairly readily into the 1,2-dilithio-derivative.<sup>4</sup>

**Preparation of Trimethylsilyl and -stannyl Species.**—Lithiation of 1,2-dihydrobenzocyclobutene (0.2 mol scale) followed by treatment with chlorotrimethylsilane and fractionation of the products gave main fractions as follows: (A) unchanged 1,2-dihydrobenzocyclobutene (46%); (B) the pure 1-trimethylsilyl derivative (19% yield based on the hydrocarbon consumed); (C) a mixture (15%) of the 1- and 3-trimethylsilyl derivatives; (D) the pure 3-trimethylsilyl derivative (18%); (E) a mixture (27%) of the 3- and 4-trimethylsilyl derivatives; and (F) 1,2-bis(trimethylsilyl)-1,2-dihydrobenzocyclobutene (4.4%). The positions of the two trimethylsilyl groups in the last compound were deduced from the n.m.r. spectrum, which showed only a singlet, at  $\tau$  7.32, in the region associated with the methylene protons; we did not investigate the stereochemistry, and the product could be *cis* or *trans* or a mixture of both.

Fraction (C) was treated with a mixture of dimethyl sulphoxide and aqueous potassium hydroxide, under conditions chosen (on the basis of a separately reported kinetic study<sup>8</sup>) to effect cleavage of the 1-substituted compound without significant reaction of the 3-derivative; subsequent fractionation gave the expected 1,2-dihydrobenzocyclobutene and the pure 3-trimethylsilyl derivative. Fraction (E), on the other hand, was treated with aqueous methanolic perchloric acid, to effect preferential cleavage of the 4-substituted derivative (*cf.* ref. 1), and so produce 1,2-dihydrobenzocyclobutene and the 3-substituted derivative.

In all, 57% of the original 1,2-dihydrobenzocyclobutene was recovered, and the total yield of the 3-trimethylsilyl derivative amounted to 38% of the hydrocarbon consumed. Our fractionating column was not very efficient; a higher yield of pure 3-substituted derivative would be obtained directly from the reaction products with a better column.

Similar lithiation of 1,2-dihydrobenzocyclobutene followed by treatment with chlorotrimethylstannane, work-up, and fractionation gave unchanged hydrocarbon (48%), the 1-trimethylstannyl derivative (14%, based on hydrocarbon consumed), and 3-trimethylstannyl-1,2-dihydrobenzocyclobutene (30%, based on hydrocarbon consumed). Intermediate fractions were not examined further.

**Desilylations and Destannylations.**—We have yet to examine the more interesting demetallations (*e.g.*, nitro-,<sup>9</sup> nitroso-,<sup>10</sup> sulpo-,<sup>11</sup> acyl-,<sup>12</sup> sulphonyl-,<sup>13</sup> and

<sup>10</sup> E. H. Bartlett, C. Eaborn, and D. R. M. Walton, *J. Chem. Soc. (C)*, 1970, 1717.

<sup>11</sup> C. Eaborn and T. Hashimoto, *Chem. and Ind.*, 1961, 1081; R. W. Bott, C. Eaborn, and T. Hashimoto, *J. Organometallic Chem.*, 1965, **3**, 442.

<sup>12</sup> C. Eaborn and R. W. Bott, 'Organometallic Compounds of the Group IV Elements,' ed. A. G. MacDiarmid, Dekker, New York, vol. 1, Part 1, pp. 428—431; K. Dey, C. Eaborn, and D. R. M. Walton, *Organometallics in Org. Synth.*, 1970/71, **1**, 151.

<sup>13</sup> S. N. Bhattacharya, C. Eaborn, and D. R. M. Walton, *J. Chem. Soc. (C)*, 1969, 1367.

cyano-demetallation).<sup>14</sup> To illustrate the potential value of the demetallation route to 3-substituted derivatives of 1,2-dihydrobenzocyclobutene we have cleaved the 3-trimethylstannyl compound with bromine and with iodine monochloride in carbon tetrachloride to give the (new) 3-bromo- and 3-iodo-derivatives in 93 and 92% yields, respectively. (We also cleaved the 4-trimethylstannyl compound similarly to give the 4-bromo- and 4-iodo-derivatives.) Analogous cleavages of the 3-trimethylsilyl compound also gave the 3-bromo- and 3-iodo-compounds, and treatment with mercury(II) acetate gave the 3-acetoxymercuri-compound in 83% yield. The availability of the 3-halogeno-compounds by these routes itself makes a range of new functional 3-substituted derivatives accessible through the 3-lithio- or 3-halogenomagnesium-compounds. As an illustration, the Grignard reagent prepared from 3-bromobenzocyclobutene was carboxylated to give the known 1,2-dihydrobenzocyclobutene-3-carboxylic acid in 90% yield.

#### EXPERIMENTAL

*Trimethylsilyl Derivatives.*—*n*-Butyl-lithium (0.60 mol) in ether (50 ml) was added to a stirred solution of 1,2-dihydrobenzocyclobutene (20.8 g, 0.20 mol) and tetramethylethylenediamine (69.6 g, 0.60 mol) in ether (200 ml), maintained below 0° under nitrogen. The mixture was refluxed for 10 h, then cooled. Chlorotrimethylsilane (64.8 g, 0.60 mol) in ether (100 ml) was added carefully with stirring and external cooling, and the mixture was subsequently stirred for 2 h at room temperature then treated with a mixture of crushed ice and dilute hydrochloric acid. The ethereal layer and further ethereal extracts were combined, shaken briefly with 5*M*-hydrochloric acid, then with water, and finally separated and dried (Na<sub>2</sub>SO<sub>4</sub>). Most of the solvent and *n*-butyltrimethylsilane was distilled off, and analysis of a sample by g.l.c. (9 ft column of 5% SE 30 on 100–120 mesh Chromosorb G) showed major peaks corresponding to 1,2-dihydrobenzocyclobutene, the 1-, 3-, and 4-trimethylsilyl derivatives, and the 1,2-bis(trimethylsilyl) derivative. Fractionation through a precision-made 1 m Vigreux column gave fractions as follows: (A) unchanged 1,2-dihydrobenzocyclobutene (9.2 g, 46%), b.p. 150°; (B) the 1-trimethylsilyl derivative (3.8 g, 19% based on hydrocarbon consumed), b.p. 52° at 1.5 mmHg,  $n_D^{20}$  1.5065,  $\tau$  (neat) 3.2–3.6 (m, aryl protons), 7.0–7.7 (m, 1-H and 2-H<sub>2</sub>), and 10.36 (s, Me<sub>3</sub>Si) (Found: C, 75.1; H, 9.1. C<sub>11</sub>H<sub>16</sub>Si requires C, 75.0; H, 9.1%); (C) a mixture (3.0 g, 15%) of the 1- and 3-trimethylsilyl derivatives, b.p. 54–56° at 1.5 mmHg; (D) the 3-trimethylsilyl derivative (3.5 g, 18%), b.p. 58° at 1.5 mmHg,  $n_D^{20}$  1.5150 (lit.,<sup>1</sup> 78° at 2 mmHg,  $n_D^{20}$  1.5020),  $\tau$  (neat) 3.1–3.7 (m, aryl protons), 7.31 (s, CH<sub>2</sub>), and 10.17 (s, Me<sub>3</sub>Si); (E) a mixture (5.4 g, 27%) of the 3- and 4-trimethylsilyl derivatives, b.p. 59–62° at 1.5 mmHg; and (F) 1,2-bis(trimethylsilyl)-1,2-dihydrobenzocyclobutene (1.2 g, 4.4%), b.p. 66–67° at 0.15 mmHg,  $n_D^{20}$  1.4981,  $\tau$  (neat) 2.92–3.32 (m, aryl protons), 7.32 (s, 2 × CH), and 10.0 (s, Me<sub>3</sub>Si) (Found: C, 68.1; H, 9.5. C<sub>14</sub>H<sub>24</sub>Si<sub>2</sub> requires C, 67.7; H, 9.7%). (The fractions were in each case shown by g.l.c. analysis to be either essentially single isomers, or mixtures of isomers, as reported.) A brown residue (5.9 g) remained.

Fraction (C) in dimethyl sulphoxide (5.0 ml) was added to

a rapidly stirred mixture of dimethyl sulphoxide (250 ml) and aqueous 0.2*M*-potassium hydroxide (80 ml) at 80°. After 15 min the mixture was allowed to cool, and water was added. Extraction with ether followed by washing and drying (Na<sub>2</sub>SO<sub>4</sub>) of the extracts and fractionation gave 1,2-dihydrobenzocyclobutene (0.7 g) and the 3-trimethylsilyl derivative (1.4 g).

Fraction (E) in methanol (100 ml) was added rapidly with stirring to a mixture of methanol (300 ml) and 9*M*-hydrochloric acid (160 ml) maintained at 50°. After exactly 10 min cold water (200 ml) was added to the stirred mixture. The organic layer was separated and combined with the ether extracts of the aqueous layer. The ethereal solutions were washed with water, with aqueous sodium carbonate, and with water again, and then dried (Na<sub>2</sub>SO<sub>4</sub>). The ether was carefully distilled off and the residue fractionated to give 1,2-dihydrobenzocyclobutene (1.8 g) and the 3-trimethylsilyl derivative (1.0 g).

The total weight of 1,2-dihydrobenzocyclobutene finally recovered was thus 11.7 g (57%), and the final yield of the 3-trimethylsilyl derivative was 5.6 g (38% based on hydrocarbon consumed).

1- and 3-*Trimethylstannyl*-1,2-dihydrobenzocyclobutene.—A similar reaction was carried out, but with chlorotrimethylstannane in place of the corresponding silicon chloride. Fraction gave 1,2-dihydrobenzocyclobutene (10 g, 48%), the 1-trimethylstannyl derivative (3.8 g, 14% based on hydrocarbon consumed), b.p. 58° at ca. 0.3 mmHg,  $n_D^{20}$  1.5650,  $\tau$  (neat) 2.9–3.4 (m, aryl protons), 6.5–7.3 (m, 1-H and 2-H<sub>2</sub>), and 10.0 (s, Me<sub>3</sub>Sn) (Found: C, 49.8; H, 5.8. C<sub>11</sub>H<sub>16</sub>Sn requires C, 49.5; H, 6.1%), and the 3-trimethylstannyl derivative (8.3 g, 30%), b.p. 66° at ca. 0.2 mmHg,  $n_D^{20}$  1.5510,  $\tau$  (CCl<sub>4</sub>) 2.7–3.25 (m, aryl protons), 6.89 (s, CH<sub>2</sub>), and 9.75 (s, Me<sub>3</sub>Sn) (Found: C, 49.3; H, 5.9%). Each of the products was shown by g.l.c. to be free of other isomers.

4-*Trimethylsilyl*- and -*stannyl*-1,2-dihydrobenzocyclobutene.—4-Bromo-1,2-dihydrobenzocyclobutene<sup>3</sup> was converted into the Grignard reagent in ether; treatment with chlorotrimethylsilane gave 4-trimethylsilyl-1,2-dihydrobenzocyclobutene (75%), b.p. 117.5° at 20 mmHg,  $n_D^{20}$  1.5010 (lit.,<sup>1</sup> b.p. 118° at 20 mmHg,  $n_D^{20}$  1.5005).

Analogously, from chlorotrimethylstannane was obtained the 4-trimethylstannyl compound (68%), b.p. 70° at ca. 0.2 mmHg,  $n_D^{20}$  1.5679,  $\tau$  (neat) 2.85–3.4 (m, aryl protons), 7.15 (s, CH<sub>2</sub>), and 9.93 (s, Me<sub>3</sub>Sn) (Found: C, 49.2; H, 6.2. C<sub>11</sub>H<sub>16</sub>Sn requires C, 49.5; H, 6.1%).

*Cleavage of 3- and 4-Trimethylstannyl Derivatives.*—(i) Bromine (3.2 g, 0.020 mol) in carbon tetrachloride (10 ml) was added dropwise with stirring under nitrogen to a solution of 3-trimethylstannyl-1,2-dihydrobenzocyclobutene (5.3 g, 0.020 mol) in carbon tetrachloride (20 ml) maintained at ca. –35°. Initially the colour of the bromine disappeared immediately on mixing, but towards the end of the addition (ca. 20 min) a faint orange colour persisted. The mixture was brought to room temperature during 15 min with stirring; g.l.c. analysis then showed that no trimethylstannyl-1,2-dihydrobenzocyclobutene remained. Fractionation gave 3-bromo-1,2-dihydrobenzocyclobutene (3.4 g, 93%), b.p. 40° at ca. 0.2 mmHg,  $n_D^{20}$  1.5730 (Found: C, 52.7; H, 3.8. C<sub>8</sub>H<sub>7</sub>Br requires C, 52.5; H, 3.8%),  $\tau$  (neat) 3.0–3.5 (m, aryl protons) and 7.3 (s, CH<sub>2</sub>),  $\tau$  (CCl<sub>4</sub>) 2.75–3.2 (m) and 6.9 (s). Only one peak was obtained on g.l.c.

<sup>14</sup> E. H. Bartlett, C. Eaborn, and D. R. M. Walton, U.S. Clearinghouse Fed. Sci. Tech. Inform. AD, 1969, 701102 (*Chem. Abs.*, 1970, **73**, 35473r).

(ii) Analogously, but with use of a solution of iodine monochloride (0.020 mol) in carbon tetrachloride (25 ml), was obtained 3-iodo-1,2-dihydrobenzocyclobutene (4.2 g, 92%), b.p. 73–75° at *ca.* 0.9 mmHg,  $n_D^{20}$  1.6325 (Found: C, 42.0; H, 3.1.  $C_8H_7I$  requires C, 41.8; H, 3.1%),  $\tau$  (neat) 2.5–3.25 (m, aryl protons) and 7.05 (s,  $CH_2$ ).

(iii) Similar cleavage of 4-trimethylstannyl-1,2-dihydrobenzocyclobutene with bromine or iodine monochloride gave 4-bromo- (90%), b.p. 100–101° at 10 mmHg,  $n_D^{20}$  1.5689 (lit.,<sup>3</sup> b.p. 118–119° at 20 mmHg,  $n_D^{20}$  1.5872), and 4-iodo-1,2-dihydrobenzocyclobutene (91%), b.p. 54–56° at *ca.* 0.1 mmHg,  $n_D^{20}$  1.6343 (lit.,<sup>15</sup> b.p. 55° at 0.01 mmHg,  $n_D^{21}$  1.6395).

*Cleavage of 3-Trimethylsilyl-1,2-dihydrobenzocyclobutene.*—

(i) When the 3-trimethylsilyl derivative was used with bromine, in a procedure similar to that followed for the corresponding tin compound, warming to 50° for 30 min was necessary to bring about complete removal of the bromine colour. Fractionation gave the 3-bromo-derivative (76%), b.p. 40° at *ca.* 0.2 mmHg,  $n_D^{20}$  1.5730.

(ii) Similarly, when the 3-trimethylsilyl derivative was treated with iodine monochloride, heating of the mixture at 50° for 30 min was required. An iodine colour in the ethereal extracts was removed with aqueous sodium thiosulphate before the fractionation, which gave the 3-iodo-1,2-dihydrobenzocyclobutene (70%), b.p. 73–75° at *ca.* 0.9 mmHg,  $n_D^{20}$  1.6335.

(iii) Mercury(II) acetate (3.2 g, 0.010 mol) in glacial acetic acid (10 ml) was added dropwise with stirring at room temperature under nitrogen to a solution of 3-trimethylsilyl-1,2-dihydrobenzocyclobutene (1.76 g, 0.010 mol) in a mixture of glacial acetic acid (8 ml) and water (2 ml) (*cf.* ref. 16). The mixture was subsequently stirred for 15 min at room temperature and added to water (50 ml). Extraction with ether, followed by washing and drying ( $Na_2SO_4$ ) of the extracts, and evaporation of the ether left a solid, which was recrystallised from ethanol to give

<sup>15</sup> L. Horner, P. V. Subramaniam, and K. Eiben, *Tetrahedron Letters*, 1965, 247.

needles of 3-(acetoxymercuri)-1,2-dihydrobenzocyclobutene (3.0 g, 83%), m.p. 77–78° (Found: 33.0; H, 2.8.  $C_{10}H_{10}O_2Hg$  requires C, 33.15; H, 2.8),  $\tau$  ( $CDCl_3$ ) 2.8–3.1 (m, aryl protons), 6.9 (s,  $CH_2$ ), and 7.95 (s,  $CH_3$ ).

*1,2-Dihydrobenzocyclobutene-3-carboxylic Acid.*—3-Bromo-1,2-dihydrobenzocyclobutene (1.83 g, 0.010 mol), prepared by cleavage of the 3-trimethylstannyl compound with bromine, was treated with magnesium (0.36 g, 0.15 g atom) in ether (100 ml). Carboxylation and work-up in the usual way, culminating in acidification of the solution in aqueous sodium hydrogen carbonate, gave crystals, which were dried under vacuum and sublimed to give the 3-carboxylic acid (1.3 g, 90.5%), m.p. (sealed tube) 190–192° (lit.,<sup>4</sup> 188–191°).

*Lithiation of 1,2-Dihydrobenzocyclobutene.*—A mixture of 1,2-dihydrobenzocyclobutene (2.08 g, 0.020 mol), tetramethylethylenediamine (2.32 g, 0.020 mol), tridecane (1 ml), and *n*-butyl-lithium (0.030 mol) in ether (50 ml) was boiled under reflux in a nitrogen atmosphere. Samples were removed at appropriate intervals, and each was added to an excess of neat chlorotrimethylsilane; the mixture was stirred for 15 min then treated with 2M-hydrochloric acid, and the organic products were extracted with ether. The ethereal extract was concentrated, and the residue analysed (Pye Series 104 model 64 Chromatograph) with a 9 ft column of 5% SE 30 on 100–120 mesh silanised Chromosorb G at 200°, with nitrogen as carrier gas. Peak heights were recorded relative to those of the tridecane, with the results shown in the Table. The peaks were identified by comparison of retention times with those of authentic samples of the separate components.

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<sup>16</sup> C. Eaborn, Z. Lasocki, and D. E. Webster, *J. Chem. Soc.*, 1959, 3034.