was observed on irradiation of the allylic protons (Table I). The positive ion FAB mass spectra of **5** showed relatively abundant fragments corresponding to the intact cations. In this reaction the formation of substituted 1,2,3-triazoles was not observed. Thus the 1,3-dipolar cycloaddition of trimethylsilyl azide[8] to carbon–carbon triple bonds of **1** can not compete with the Michael-type additions yielding the (β-azidovinyl)iodonium salts **5**.

The use of water is essential to the success of this addition reaction. In the absence of water the reaction of decynyliodonium tetrafluoroborate (**1b**) with trimethylsilyl azide led to the considerable carbon–iodine bond cleavage, yielding a complex mixture of products: iodobenzene (48%), 1-iododecyne (12%), (β-azidovinyl)iodonium salt (**5b**, 17%), and **1b** (24%). It should be noted that trimethylsilyl azide is sensitive toward moisture.[9] On the basis of these results, the active species of this Michael-type reaction is most probably hydrazoic acid produced by the hydrolysis of trimethylsilyl azide in situ.

Thus, in contrast to vinyliodonium salts, alkynyliodonium salts serve as a useful Michael acceptor toward nitrogen nucleophiles as well as carbon nucleophiles and produce the (β-azidovinyl)iodonium salts in good yields.

Experimental Section

Physical Data. Melting points were determined with a Yanaco micro melting point apparatus and are uncorrected. IR spectra were recorded on a JASCO A-202 spectrophotometer. NMR spectra were recorded on either a JEOL JNM-FX 100, Varian VXR 200, or JEOL JNM-GX 400 spectrophotometer. Chemical shifts (^1H, ^{13}C) were reported in parts per million (ppm) downfield from internal tetramethylsilane. Mass spectra (MS) were taken on a JEOL JMS-DX 300 spectrometer.

Materials. Alkynyliodonium tetrafluoroborates **1a–c** were prepared from the corresponding alkynyltrimethylsilanes by the reaction with iodosylbenzene and boron trifluoride etherate in dichloromethane in 74–85% yields.[10] (β-*tert*-Butylethynyl)-iodonium tetrafluoroborate (**1d**) was obtained by the reaction of (β-*tert*-butylethynyl)borate with iodosylbenzene and boron trifluoride etherate in dichloromethane in 85% yield.[1e] Trimethylsilyl azide was purchased from Tokyo Kasei Kogyo Co. and distilled from calcium hydride under nitrogen.

General Procedure for Synthesis of (β-Azidovinyl)-iodonium Tetrafluoroborates 5. To a stirred suspension of alkynyliodonium tetrafluoroborate **1** (0.25 mmol) and water (0.30 mmol) in dichloromethane (5 mL) was added trimethylsilyl azide (0.30 mmol) dropwise at −78 °C under nitrogen. The mixture was stirred at −78 °C for 10 min and then allowed to warm to room temperature. Stirring was continued at room temperature until the reaction was complete to TLC (1.5–2.5 h). The mixture was poured into water and extracted with dichloromethane. The organic layer was concentrated under aspirator vacuum to give an oil. Purification of **5** was accomplished by repeated decantation using hexane and/or by recrystallization.

(*Z*)-Phenyl(2-azido-1-propenyl)iodonium tetrafluoroborate (5a): pale yellow oil; IR (film) 3100, 2150, 2125, 1595, 1310, 1070, 1025, 740, and 670 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.99 (m, 2 H), 7.62 (t, J = 7.3 Hz, 1 H), 7.48 (m, 2 H), 6.18 (br s, 1 H), 2.42 (d, J = 1.0 Hz); ^{13}C NMR (25 MHz, CD_2Cl_2) δ 154.2, 135.2, 132.8, 132.6, 112.9, 77.9, 19.1; MS (FAB), m/z 286 [$(M - BF_4)^+$].

(*Z*)-Phenyl(2-azido-1-decenyl)iodonium tetrafluoroborate (5b): colorless needles (recrystallized from dichloromethane–diethyl ether), mp 60–60.5 °C; IR (KBr) 3050, 2930, 2110, 1595, 1310, 1070, and 725 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 7.4 Hz, 2 H), 7.61 (t, J = 7.4 Hz, 1 H), 7.47 (t, J = 7.4 Hz, 2 H), 6.18 (s, 1 H), 2.68 (t, J = 7.5 Hz, 2 H), 1.61 (quint, J = 7.5 Hz, 2 H), 1.4–1.2 (10 H), 0.87 (t, J = 7.0 Hz, 3 H); ^{13}C NMR (25 MHz, $CDCl_3$) δ 157.4, 135.0, 132.5, 132.3, 111.7, 77.8, 33.4, 31.8, 29.1, 28.8, 27.1, 22.6, 14.0; MS (FAB), m/z 384 [$(M - BF_4)^+$]. Anal. Calcd for $C_{16}H_{23}BF_4IN_3$: C, 40.79; H, 4.92; I, 26.94; N, 8.92. Found: C, 40.60; H, 4.73; I, 26.82; N, 8.94.

(*Z*)-Phenyl(2-azido-3-cyclopentyl-1-propenyl)iodonium tetrafluoroborate (5c): pale yellow oil; IR (film) 3100, 2950, 2875, 2125, 1590, 1445, 1310, 1065, 1030, 740, and 670 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.98 (m, 2 H), 7.61 (t, J = 7.5 Hz, 1 H), 7.47 (t, J = 7.5 Hz, 2 H), 6.20 (s, 1 H), 2.69 (d, J = 7.3 Hz, 2 H), 2.08 (septet, J = 7.3 Hz, 1 H), 1.85–1.1 (8 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 156.8, 134.8, 132.4, 132.2, 111.7, 77.9, 39.2, 37.7, 32.2, 24.8; MS (FAB), m/z 354 [$(M - BF_4)^+$].

(*Z*)-Phenyl(2-azido-3,3-dimethyl-1-butenyl)iodonium tetrafluoroborate (5d): colorless needles (recrystallized from dichloromethane–hexane), mp 89–91 °C; IR (KBr) 3050, 2990, 2135, 1570, 1320, 1060, and 730 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.99 (m, 2 H), 7.66 (t, J = 7.5 Hz, 1 H), 7.51 (t, J = 7.5 Hz, 2 H), 6.12 (s, 1 H), 1.38 (s, 9 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 161.6, 135.1, 132.5, 132.3, 111.0, 81.3, 40.5, 28.0; MS (FAB), m/z 328 [$(M - BF_4)^+$]. Anal. Calcd for $C_{12}H_{15}BF_4IN_3$: C, 34.73; H, 3.64; N, 10.13. Found: C, 34.46; H, 3.71; N, 9.98.

Registry No. **1a**, 105502-68-9; **1b**, 102987-32-6; **1c**, 105502-63-4; **1d**, 115505-36-7; **5a**, 117371-21-8; **5b**, 117371-23-0; **5c**, 117371-25-2; **5d**, 117371-27-4; $MeC{\equiv}CSiMe_3$, 6224-91-5; $C_8H_{17}C{\equiv}CSiMe_3$, 54559-17-0; $c\text{-}C_5H_9CH_2C{\equiv}CSiMe_3$, 72097-00-8; iodosylbenzene, 536-80-1; (β-*tert*-butylethynyl)borate, 117407-49-5; trimethylsilyl azide, 4648-54-8.

(8) Birkofer, L.; Wegner, P. *Chem. Ber.* **1966**, *99*, 2512.
(9) West, R.; Thayer, J. S. *J. Am. Chem. Soc.* **1962**, *84*, 1763.
(10) Ochiai, M.; Kunishima, M.; Sumi, K.; Nagao, Y.; Fujita, E. *Tetrahedron* Lett. **1985**, *26*, 4501.

Reaction of Pyridine with Phosgene: A Structural Reevaluation

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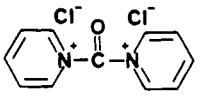
Received June 23, 1988

Several papers dealing with the reaction of tertiary amines with phosgene have appeared in the chemical literature.[1,2] Although both the 1:1 and the 1:2 adducts of phosgene with tertiary amines have been reported, no structural data indicative of the 1:2 configuration for the parent pyridine has been published; the originally proposed 1:2 structure (**1**) was deduced by analogy to the commonly observed 1:1 pyridinium salt.[1]



1

Results and Discussion

The reaction of excess pyridine with phosgene in an aprotic medium is found to yield a canary-yellow flocculent material. Isolation of this precipitate, followed by drying under high vacuum, yielded a light yellow microcrystalline powder. This material is found to be sparingly soluble in most aprotic organic solvents other than methylene chloride and acetonitrile. The isolated salt is observed to be exceedingly hygroscopic and slightly photosensitive. On the basis of elemental analysis, the stoichiometric composition of this material corresponded to a 2:1 adduct of pyridine with phosgene.[3] Previously, Scholtissek[1] had

(1) Scholtissek, C. *Chem. Ber.* **1956**, *89*, 2562.
(2) (a) Goubeau, J.; Winkelmann, G. *Z. Anorg. Allg. Chem.* **1953**, *271*, 235. (b) Johnson, C. K. *J. Org. Chem.* **1967**, *32*, 1508. (c) Weiss, R.; Roth, R. *Synthesis* **1987**, 870.
(3) As noted in ref 1, the material occludes excess pyridine. Drying the material under vacuum (1–30 mmHg) for several hours removes the occluded material.

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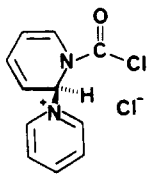
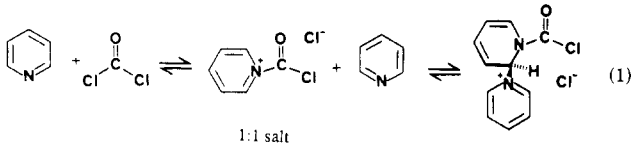
assigned structure **1** to this material on the basis of elemental analysis and its reaction chemistry. We now assign structure **2** to this isolated material.



2

The equilibria involved are shown in eq 1. The 1:2 salt could easily be isolated by condensing the reagents in any nonpolar aprotic medium (e.g., pentane, toluene, or ether). At dilute concentrations at temperatures above −30 °C, the diadduct is observed to undergo a facile reversion to its components. Under these reaction conditions, the formation of the simple 1:1 salt was never observed spectroscopically.



1:1 salt 2 - DHPP (1)

The unique dihydropyridine–pyridinium structure **2** (2-DHPP) can be readily deduced from its low-temperature solution and solid-state spectra. At room temperature, one sees only the carbon resonances indicative of an uncomplexed pyridine (149.9, 135.9, and 123.8 ppm). When this solution is cooled, a set of nine new resonances are observed in the spectrum (147.5, 146.4, 144.1, 129.3, 128.8, 127.8, 107.4, 106.3, and 64.3 ppm). Seven of the new signals are indicative of either olefinic or aromatic sp^2 carbons while one signal is from a carbamoyl chloride moiety. A unique resonance appears at 64.3 ppm. The appearance of a signal at this position can be used as the signature for the point of attachment of the pyridinium ring to the dihydropyridine moiety.[4] The appearance of nine carbon resonances indicates the dihydropyridine ring to be unsymmetrical: three signals for the pyridinium ring, one signal for the carbonyl, and five for the dihydropyridine ring. The off resonance decoupled $^{13}C(^1H)$ spectrum indicates that all the carbons, except the carbonyl carbon (147.3 ppm), have one and only one hydrogen attached to them.

The solid-state ^{13}C CP/MAS spectrum is superimposable on that of the low-temperature ^{13}C NMR solution spectrum. The solid-state resonances are broad and lack fine structure relative to the solution spectrum, but the chemical shifts of the peaks are the same; the absorption bands for the solid-state spectrum occur at 146, 130, 108, and 64 ppm. Hence, the isolated microcrystalline powder appears indistinguishable from the low-temperature solution structure.

An equivalent set of variable-temperature experiments were performed with ^{15}N-labeled pyridine. At room temperature, the ^{15}N NMR spectrum indicates that the pyridine is not complexed to the phosgene. Two new resonances appear at lower temperature. The first signal occurs at −144.6 ppm and is indicative of a pyridinium nitrogen. The second signal occurs at −227 ppm, which is consistent with an amide (carbamoyl) nitrogen.[5]

The ^1H NMR spectra lend further support to the proposed mixed dihydropyridine–pyridinium structure. The ambient-temperature proton spectrum shows only "free" pyridine in solution (8.57, 7.64, and 7.25 ppm). Upon lowering of the solution temperature to −55 °C, one observes peaks indicative of a pyridinium ring: δ 9.54 (ortho), 8.43 (para), and 8.03 (meta). The formation of a 1,2-dihydropyridine moiety is apparent: δ 5.55 (C(4)-H), 5.62 (C(6)-H), 7.33 (C(1)-H), 7.46 (C(5)-H), and 7.51 (C(3)-H). The proton–proton positional interrelationships were verified by a homonuclear decoupling experiment ($^1H(^1H)$). The synchronous formation of both fragments of the dihydropyridine–pyridinium unit could be confirmed by comparative integration of the two portions as a function of temperature. The integration ratio of the two fragments was always 1:1; i.e., this ratio was observed to be invariant with temperature. The low-temperature proton and carbon spectra could be completely correlated via a 2D ^1H:^{13}C HETCOR experiment.

The isolated solid material exhibited a carbonyl stretching frequency in the infrared spectrum of 1752 cm^{-1} (KBr). Upon solution in methylene chloride, infrared spectral analysis of the dissolved salt showed only the presence of free phosgene (1807 cm^{-1}). Variable-temperature solution IR showed three new absorptions in the carbonyl region (at −66 °C, CH_2Cl_2, 6.2×10^{-2} M): 1762 (w), 1734 (vs), and 1689 (s) cm^{-1}. These bands indicate the presence of both new C=O and C=C bonds. Furthermore, a shift in the stretching frequency to lower energy upon formation of the 2:1 adduct is consistent with what has been observed previously;[4] conversion of a reactive carboxylate moiety to its corresponding 1:1 pyridinium salt results in an increase in the carbonyl stretching frequency.[4,6]

When the reaction medium was changed from methylene chloride (ε = 9.08 at 20 °C) to a 1:1 mixture of acetonitrile/methylene chloride (ε ≅ 23 at 20 °C),[7] the 4-DHPP adduct was observed to form in solution at low temperature (−65 °C, 7.5×10^{-2} M, 150.2, 144.37, 142.6, 127.15, 125.8, 108.5, and 62.3 ppm).[8] The ratio of 2-DHPP to 4-DHPP is found to be 4:1 under these conditions; at −40 °C, the ratio was 9:1. The unique carbon at 62.3 ppm is indicative of the pyridinium ring's point of attachment to the 4-position of the dihydropyridine moiety. The 3,5-positions of the dihydropyridine ring appear as a single resonance at 108.4 ppm. The observance of seven new signals in the ^{13}C NMR spectrum is consistent with the 4-DHPP structure:[9] three resonances for the pyridinium ring, one signal for the carbonyl, and three for the symmetrical dihydropyridine ring. Under no conditions were

(4) King, J. A., Jr. *J. Am. Chem. Soc.* **1988**, *110*, 5764.

(5) A comprehensive review of general ^{15}N NMR methods and chemical shift data can be found in the following: von Philpsborn, W.; Muller, R. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 383. Also see: Noth, H.; Wrackmeyer, B. *Chem. Ber.* **1974**, *107*, 3070, 3089.

(6) The C=O stretching frequency is strongly coupled to the basicity of the pyridine. For example, the 1:1 salts of DMAP or PPY actually show a decrease in the C=O stretching frequency: (a) Höfle, G.; Steglich, W.; Vorbrüggen, H. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 569. (b) King, J., unpublished results. The simple 1:1 salts of pyridine with reactive carbonyl groups show an increase in the carbonyl stetching band. The latter 1:1 salts are not generally formed (nor observable) in nonpolar, aprotic media at room temperature.

(7) Barton, A. F. M. *Handbook of Solubility Parameters and Other Cohesion Parameters*; CRC: Boca Raton, FL, 1985; Chapter 8, Section 8.5, Table 11.

(8) Similar solvolytic manipulation has been employed to induce the rearrangement of 1,2- to 1,4-dihydropyridinium adducts; see: (a) Mann, V.; Schneider, G.; Krohnke, F. *Tetrahedron Lett.* **1973**, 683. (b) Duchardt, K.; Krohnke, F. *Chem. Ber.* **1977**, *110*, 2669.

(9) A structurally analogous compound (although an uncharged species) has been characterized in the following: Hilpert, H.; Hoesch, L.; Dreiding, A. S. *Helv. Chim. Acta* **1987**, *70*, 390.

we able to shift the 2-DHPP/4-DHPP equilibrium in solution such that the 4-DHPP isomer became the dominant species. Slowly warming the 2-DHPP/4-DHPP mixture to room temperature resulted in the more facile reversion of the 4-DHPP isomer to its components relative to that of the 2-DHPP isomer. Thus, the formation of the 2-DHPP structure appears to be both the thermodynamic as well as the kinetic product under our reaction conditions.

The 2-DHPP material is noted to darken on prolonged standing at room temperature. The colored material must be present in only trace quantities as it cannot be detected spectroscopically; no loss of chemical reactivity for **2** is observed either. The resulting purple-red color is believed to result from a thermally induced solid-state electrocyclic rearrangement of the dihydropyridine ring. Such a transformation would produce an azaglutaconaldehyde derivative which is expected to be highly colored.[10]

The solution chemistry of **2** mirrors that of traditional phosgene reactions. In aprotic media, **2** can be used to produce carbonates, chloroformates, isocyanates, and ureas in high yield. Furthermore, this material can be used as a highly efficient dehydrating agent; at room temperature, carboxylic acids are converted to their corresponding anhydrides with isolated yields ranging from 80 to 95%. The procedure used for the preparation of the anhydrides is analogous to those published previously.[11]

In conclusion, the reaction of pyridine with phosgene to produce a 2:1 salt generates the 2-DHPP structure, **2**, rather than the previously proposed bis(pyridinium salt), **1**. The 2-DHPP isomer is indicated to be both the kinetically and thermodynamically preferred isomer in solution. Furthermore, this type of diadduct may be common to the chemistry of thiophosgene which is also observed to produce a sensitive yellow crystalline precipitate upon reaction with pyridine.[12] The excellent thermal stability of the solid material (**2**), coupled with its facile reversion to its components in solution, allows this salt to be used as a convenient storage system for phosgene.[13]

Experimental Section

General: ^1H NMR and ^{13}C NMR spectra were obtained on Varian XL 200 and XL 300 spectrometers, respectively. The ^{15}N NMR spectra were obtained on a Varian XL 300 spectrometer. The solid-state ^{13}C CP/MAS spectra were acquired on a Nicolet NT-150 wide-bore spectrometer (^{13}C, 37.7 MHz) at the Colorado State University Regional NMR Center (an USF Regional Instrumentation Facility, Grant No. CHE 8208821).

The solution IR data was acquired on a Nicolet 7198 FTIR spectrometer with a MCT(HgCdTe) detector. The system was outfitted with a class II Imw HeNe laser and a Nicolet IR-80 data processor. The variable-temperature IR cell was a SPECAC P/N 21.000 low-temperature solution cell containing 0.1-mm AgCl windows. All nonvariable-temperature infrared measurements were made by using a Perkin-Elmer Model 598 IR spectrometer.

All manipulations of materials and reaction solutions were carried out under an anhydrous nitrogen atmosphere; whenever possible, a Vacuum Atmospheres Model HE-43-2 DRI-LAB glovebox was used.

The elemental analyses were performed by Galbraith Analytical Laboratories.

General Procedure for Solution Analysis of Pyridinium Salts by IR or NMR. In a typical experiment, the pyridinium salt was weighed out on an analytical balance inside a glovebox under a nitrogen atmosphere. A measured amount of the desired deoxygenated, anhydrous solvent was added to form a homogeneous solution. The resulting solution was partitioned among the various IR cells and precison-bore NMR tubes to be used for study. All tubes and cells were stoppered and sealed before their removal from the glovebox for analysis.

1-(2-(Chloroformyl)-2-azacyclohexa-3,5-dienyl)pyridinium Chloride (2). To 48.9 g (0.618 mol) of pyridine in pentane (500 mL) was added 30.7 g (0.309 mol) of phosgene dissolved in pentane (200 mL) over a 15-min time period. The temperature of the reaction solution was maintained at 4 °C (ice–water bath) during the addition time; the reaction was observed to be slightly exothermic. A voluminous yellow-white precipitate formed spontaneously as the phosgene solution was added. After the addition was completed, the reaction mixture was stirred for an additional 30 min and then filtered. The filtrate was washed twice with 500 mL of anhydrous, deoxygenated pentane and then dried under vacuum (~30 mmHg) at room temperature for 3 h. The resulting light yellow material amounted to 73.6 g or a 92.4% yield: mp 84–87 °C dec; IR (KBr) 1752 cm^{-1} (C=O, br); IR (CH_2Cl_2, −66 °C) 1762 (w), 1734 (vs), 1689 cm^{-1}; ^1H NMR (CD_2Cl_2, 200 MHz, −55 °C) δ 9.54 (d, J = 6.2 Hz, 2 H), 8.43 (t, J = 7.65, 7.65 Hz, 1 H), 8.03 (dd, J = 6.2, 7.65 Hz, 2 H), 7.51 (d, J = 9.5 Hz, 1 H), 7.46 (d, J = 8 Hz, 1 H), 7.33 (dd, J = 4.2, 3.5 Hz, 1 H), 5.61 (dd, J = 8, 4.2 Hz, 1 H), 5.55 (dd, J = 9.5, 3.5 Hz, 1 H); ^{13}C NMR (CD_2Cl_2, 75 MHz, −55 °C) δ 147.5, 146.4, 144.1, 129.3, 128.8, 127.8, 107.4, 106.3, 64.3; ^{13}C NMR (solid state, 37.7 MHz) δ 146, 130, 108, 64. Anal. Calcd for $C_{11}H_{10}Cl_2N_2O$: C, 51.39; H, 3.92; N, 10.90; Cl, 27.58. Found: C, 51.60; H, 4.13; N, 11.09; Cl, 27.24.

Acknowledgment. We thank Dr. Peter Codella for help with the solution IR data. The assistance of Drs. J. S. Frye and G. E. Maciel of the Colorado State University Regional NMR Center (funded by National Science Foundation Grant No. CHE-8208821) is gratefully acknowledged for acquiring the solid-state ^{13}C NMR data.

Registry No. 1, 117371-70-7; 2, 117371-69-4; pyridine, 110-86-1; phosgene, 75-44-5.

Supplementary Material Available: Proton and carbon NMR spectra for **2** (4 pages). Ordering information is given on any current masthead page.

(10) Becher, J. *Synthesis* **1980**, 589.

(11) (a) Rinderknecht, H.; Gutenstein, M. *Org. Synth.* **1967**, *47*, 89. (b) Rinderknecht, H.; Ma, V. *Helv. Chim. Acta* **1964**, *47*, 162.

(12) Boyle, F. T.; Hull, R. *J. Chem. Soc., Perkin Trans. 1* **1974**, 1541.

(13) This material can be stored at room temperature for over a year with essentially no loss of chemical reactivity. Rigorous exclusion of moisture is required. This diadduct salt (**2**) has been termed phosgene-in-a-can.

Iejimalides A and B, Novel 24-Membered Macrolides with Potent Antileukemic Activity from the Okinawan Tunicate *Eudistoma* cf. *rigida*

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Received September 6, 1988

Recently, increasing attention has been paid to tunicates, since their metabolites frequently possess interesting pharmacological activities.[2] In our continuing search for bioactive compounds from Okinawan tunicates,[3] we have

(1) (a) Mitsubishi Kasei Institute of Life Sciences. (b) Tohoku University. (c) Meijo University. (d) Kanazawa University.

(2) (a) Faulkner, D. J. *Nat. Prod. Rep.* **1984**, 551. (b) Faulkner, D. J. *Nat. Prod. Rep.* **1986**, 1. (c) Faulkner, D. J. *Nat. Prod. Rep.* **1987**, 539.

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