Rearrangements in the halogenation of tetraalkylethylenes with N-halosuccinimides and tert-butyl hypochlorite

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gel with chloroform–acetonitrile (70:30). This affords 0.66 mmol (0.170 g, 38%) of 2 and 0.76 mmol (0.185 g, 38%) of 18. Additional treatment of 18 with an equivalent amount of CHCl₃ in dry ether affords quantitatively the product 2: IR (CHCl₃) 1705, 1620 cm⁻¹; NMR (CDCl₃, 200 MHz) δ 1.35 (t, 3 H, OCH₂CH₃), 1.42 (d, 3 H, 8-CH₃), 1.98 (dd, 1 H, J₆A11 = 7.6 Hz, J₁₁B₁₁ = 11 Hz, 11-H), 2.12 (dd, 1 H, J₆B₁₁ = 7.6 Hz, J₆₁₁ = 11 Hz, 11-H), 2.37 (s, 3 H, 2-OCH₃), 4.73 and 4.82 (ABX₂ pattern, 2 H, J₆₁₁ = 7.5 Hz, OCH₂CH₃), 4.51 (dd, 1 H, J₆₁₁ = 11.5 Hz, J₆₁₁ = 7.6 Hz, 5,5-H), 7.2-7.5 (m, 3 H, 1-H, 3-H, 4-H); ¹³C NMR (CDCl₃, 20.1 MHz) 14.9 (OCH₂CH₃), 21.6 (8-CH₃), 41.7 (5-CH₂), 45.4 (4b-CH), 55.2 (11-C), 55.9 (2-OCH₃), 58.9 (5a-C), 62.1 (OCH₂CH₃), 68.9 (8-CH₂), 105.8 (1-C), 125.5 (5-CH), 126.4 (4-CH), 138.4 (a-C), 145.6 (10a-C), 155.8 (6-NCO), 160.7 (2-C), 204 (CO); mass spectrum, m/e (relative intensity) 330 (63), 257 (10), 215 (22), 214 (24), 200 (100); calcd for M⁺/m/e 258.1368, found m/e 258.1368.

6-Carbethoxy-6,7-diaza-2-methylcyclo[10]bicyclo[5.2.0]nonane (9). Compound 2 (1 mmol, 0.258 g, 1 mmol (0.108 g) of CICOOEt, and 1 mmol (0.104 g) of NEt₃, are dissolved in 15 mL of dry CH₂Cl₂. The solution is stirred for 3 h at room temperature. The mixture is filtered, and the filtrate is evaporated in vacuo. The residue is purified by preparative TLC on silica gel with chloroform–acetonitrile (70:30). This affords 0.66 mmol (0.170 g, 33%) of 9 (2.170 g, 33%) of 18. Additional treatment of 18 with an equivalent amount of CHCl₃ in dry ether affords quantitatively the product 2: IR (CHCl₃) 1705, 1620 cm⁻¹; NMR (CDCl₃, 200 MHz) δ 1.35 (t, 3 H, OCH₂CH₃), 1.42 (d, 3 H, 8-CH₃), 1.98 (dd, 1 H, J₆A11 = 7.6 Hz, J₁₁B₁₁ = 11 Hz, 11-H), 2.12 (dd, 1 H, J₆B₁₁ = 7.6 Hz, J₆₁₁ = 11 Hz, 11-H), 2.37 (s, 3 H, 2-OCH₃), 4.73 and 4.82 (ABX₂ pattern, 2 H, J₆₁₁ = 7.5 Hz, OCH₂CH₃), 4.51 (dd, 1 H, J₆₁₁ = 11.5 Hz, J₆₁₁ = 7.6 Hz, 5,5-H), 7.2-7.5 (m, 3 H, 1-H, 3-H, 4-H); ¹³C NMR (CDCl₃, 20.1 MHz) 14.9 (OCH₂CH₃), 21.6 (8-CH₃), 41.7 (5-CH₂), 45.4 (4b-CH), 55.2 (11-C), 55.9 (2-OCH₃), 58.9 (5a-C), 62.1 (OCH₂CH₃), 68.9 (8-CH₂), 105.8 (1-C), 125.5 (5-CH), 126.4 (4-CH), 138.4 (a-C), 145.6 (10a-C), 155.8 (6-NCO), 160.7 (2-C), 204 (CO); mass spectrum, m/e (relative intensity) 330 (63), 257 (10), 215 (22), 214 (24), 200 (100); calcd for M⁺/m/e 258.1368, found m/e 258.1368.

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Registry No. 2, 81097-50-9; 3, 55288-51-2; 5a, 81097-51-0; 5b, 81097-52-1; 6, 81097-53-2; 7a, 81120-70-9; 7b, 81097-54-3; 7c, 81097-55-4; 7d, 81097-56-5; 8, 81097-57-6; 13-HCl, 81120-71-6; 15a, 81097-58-7; 15b, 81097-59-8; 18, 81097-60-1; di-tert-butyl azodicarboxylate, 870-50-8; disthyl azodicarboxylate, 1972-28-7; ethyl bromoacetate, 105-36-2; allyl bromide, 106-86-6; ethyl carbonochloridate, 541-41-3.

Rearrangements in the Halogenation of Tetraalkylethylenes with N-Halosuccinimides and tert-Butyl Hypochlorite

E. W. Meijer, Richard M. Kellogg, and Hans Wynberg*

Department of Organic Chemistry, University of Groningen, 8747 AG Groningen, The Netherlands

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The reaction of N-halosuccinimides and tert-butyl hypochlorite with tetraalkylethylenes has been investigated. Halo-cat ion addition to the double bond occurs in a fast reaction, followed by abstraction of an allylic proton, resulting in a double bond shift. In tetraalkylethylenes lacking for structural reasons the possibility of a double bond shift, a homoallylic halogenation occurs to produce the 4(e)-halogeno derivative. The electrophilic halogenation of tetraalkylethylenes with N-halosuccinimides and tert-butyl hypochlorite is compared with the well-known radical-chain allylic halogenation of mono-, di-, and trialkylethylenes with these reagents and the reaction of chlorine with olefins. The halogenations described here are strongly reminiscent of the singlet oxygen one reaction and the causes of this resemblance are discussed.

In this paper we describe the remarkable halogenation of tetraalkylethylenes with N-halosuccinimides and tert-butyl hypochlorite. These reagents are well-known to give allylic halogenation in a radical-chain reaction.⁵ We have found that with tetraalkylethylenes these reagents react cleanly in an ionic manner to give products that deviate in structure from the normally expected halogenation products of N-halosuccinimides and tert-butyl hypochlorite with mono-, di-, and trialkylethylenes. These conclusions were derived from the observations made during the halogenation of adamantylidenadamantane (1). We have found that 1 reacts with chlorine and benzene-sulfonyl chloride to give 4(e)-chloroadamantylidenadamantane (2) via an ionic pathway without any addition to the double bond.⁴⁵ In an attempt to carry out radical chlorination, 1 was treated with 1 equiv of N-chlorosuccinimide (NCS) in boiling CHCl₃ containing a radical initiator. To our surprise the sole product was 2. When this reaction was repeated in CH₂Cl₂ in the absence of radical initiators at room temperature, a rapid (<5 min) reaction occurred and 2 was formed in quantitative yield. The reaction takes place also in CH₂Cl₂, CHCl₃, or CH₂Cl₂/CH₂CO₂H and the rate increases with increasing solvent polarity.⁶ The same product 2 was obtained when

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(6) (a) We observe quantitatively that the reaction rates, in general, increase progressing from eel, to CsHs to CHCl₃ to CH₂C1₂/CH₂CO₂H. In the last two solvents the rates are most often too fast to be measured (b) In an attempt to carry out radical chlorination, 1 was treated with 1 equiv of N-chlorosuccinimide (NCS) in boiling CHCl₃ containing a radical initiator. To our surprise the sole product was 2. When this reaction was repeated in CH₂Cl₂ in the absence of radical initiators at room temperature, a rapid (<5 min) reaction occurred and 2 was formed in quantitative yield. The reaction takes place also in CH₂Cl₂, CHCl₃, or CH₂Cl₂/CH₂CO₂H and the rate increases with increasing solvent polarity. The same product 2 was obtained when
tert-butyl hypochlorite (TBHC) or the combination NaOCl/CH3COOH was used as the chlorinating agent. When the reaction was performed in the presence of a radical inhibitor (hydroquinone), the same rapid conversion took place (Figure 1). With N-bromosuccinimide (NBS), a quantitative yield of 4(e)-bromo-adamantylideneadamantane was obtained, although heating for 12 h at 40 °C was necessary for complete reaction. When N-iodosuccinimide was employed, even in excess and under vigorous conditions, no reaction took place.1

A tetraalkylethylene closely related to 1 is bicyclo[3.3.1]nonylidenebicyclo[3.3.1]nonane (3). In reaction with NCS, the 4(e)-chloro compound 4 could be isolated as sole product, whereas NBS does not react with 3 under the conditions used for 1 (Figure 2).

These stereoselective homoallylic halogenations are best explained by means of an ionic mechanism. The normal reaction of olefins with NCS, NBS, or TBHC affords halogenation at the allylic position; in 1 and 3 this reaction path is eliminated owing to steric hindrance. These results prompted us to investigate the reaction of these reagents with other tetraalkylethylenes. 2,3-Dimethyl-2-buten (5) reacts spontaneously and quantitatively with NCS and TBHC, forming 3-chloro-2,3-dimethyl-1-buten (6), free from detectable (by 1H NMR) amounts of the thermodynamically more stable allylic isomer, 1-chloro-2,3-dimethyl-2-buten.1,2,10 A tetraalkylethylene, offering both radical initiators (light or peroxides) are needed, resulting in halogenation at the allylic position to form usually the thermodynamically most stable product in excess.1 An exception must be made for the reaction of these reagents in alcoholic solvents and Me2SO–H2O, in which addition to the double bond occurs in an electrophilic fashion.15 Two halogenations with shift of the double bond are known in steroid chemistry, although this shift is favored by the formation of an α,β-unsaturated ketone.16,17 as is shown for the conversion of 16 into 17 (Figure 5).

Whether NCS, NBS, and TBHC react in a radical fashion with an olefin or via an ionic pathway appears to be governed by the electron density of the double bond in question. The radical-chain reaction of olefins with lower electron density at the double bond is well established.12 However, when the olefins are electron rich—as is the case in tetraalkylethylenes and probably also with alkynes such as enol ethers—reagents such as TBHC, NBS, and NCS serve as halo-cation sources to form the halonium ion of the olefin with the base as counterion. The key

The chlorinations reported here and the ene reaction of 1O2 was made with the syn olefin 11 and its anti isomer 12, which have been reported to form, in both cases, the two possible allylic hydroperoxides.13,14 This result was offered as evidence against a concerted mechanism for the ene reaction of 1O2 with alkenes. We have examined the reaction of the same olefins with TBHC; when TBHC was used in C6D6 solution, the only products observed were the allylic chlorides 13 and 14 in a ratio 2:1 as determined by 1H NMR, starting from either 11 or 12. The allylic chlorides 13 and 14 are very sensitive to HCl elimination, yielding 4,4'-di-tert-butyl-1,1'-bicyclohexenyl (15, Figure 4).

**Discussion**

The results presented here provide strong evidence for the ionic reaction of NCS, NBS, and TBHC with tetraalkylethylenes. All products are formed in a very rapid reaction in quantitative yield at room temperature without radical initiators. In contrast, when NCS, NBS, and TBHC are allowed to react with tri-1,2,4,5,6,7-hexaethylpenal, radical initiators (light or peroxides) are needed, resulting in halogenation at the allylic position to form usually the thermodynamically most stable product in excess.1 An exception must be made for the reaction of these reagents in alcoholic solvents and Me2SO–H2O, in which addition to the double bond occurs in an electrophilic fashion.15 Two halogenations with shift of the double bond are known in steroid chemistry, although this shift is favored by the formation of an α,β-unsaturated ketone.16,17 as is shown for the conversion of 16 into 17 (Figure 5).

Whether NCS, NBS, and TBHC react in a radical fashion with an olefin or via an ionic pathway appears to be governed by the electron density of the double bond in question. The radical-chain reaction of olefins with lower electron density at the double bond is well established.12 However, when the olefins are electron rich—as is the case in tetraalkylethylenes and probably also with alkynes such as enol ethers—reagents such as TBHC, NBS, and NCS serve as halo-cation sources to form the halonium ion of the olefin with the base as counterion. The key

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Halogenation of Tetraalkylethylenes

Figure 4.

Figure 5.

Figure 6.

intermediate 18 is shown here in a symmetrically bridged structure (Figure 6). The base, succinimide-, tert-but oxide-, or hydroxide-anion is capable of abstracting a proton. When an active allylic proton is present, as in 5, 7, 11, and 12, proton abstraction occurs at this position (see intermediate 19). The result is the formation of an allylic halide 20 in which the double bond is shifted relative to the starting olefin. This reaction is strongly reminiscent of the reaction of chlorine with olefins in the liquid state in which substitution competes with addition. This substitution by chlorine in tetra- and trialkylethylenes is almost completely ionic; but for mono- and dialkylethylenes there is a competition between ionic and radical mechanisms. Noteworthy is the high yield of 6 from 5 under these conditions.

In tetraalkylethylenes 1 and 3 a double bond shift cannot occur. In these cases, therefore, a homoallylic proton is abstracted by the base (see intermediate 21), furnishing an α-halocyclopropane 22. The latter rearranges easily to the stable 23, in which the halide occupies the equatorial position. Evidence for the electrophilic mechanism (see intermediates 21 and 22) is the formation of the bromonium ion of 1 when 1 and NBS are allowed to react in the presence of strong acids. In addition, the major product in the bromination of norbornene in Me2So with NBS is an α-bromocyclopropane derivative. The formation of a cyclopropane in the adamantane skeleton and the stereoselective addition to this dehydroadamantane have been reported previously. Moreover the rearrangement of 22 into 23 probably takes place via a not completely free carbonium ion since otherwise acetal formation would have occurred in the presence of acetic acid as cosolvent. Two other routes to 2 have been reported. The decomposition of the chloronium ion of 1 affords 2 in moderate yield. This chlorination probably takes place via the same mechanism as described for NCS, TBHC, and HOC1 and not via the Wagner–Meerwein type rearrangements published earlier. Secondly, the interaction of benzenesulfonyl chloride with 1, furnishing 2 in high yield (85%), is explained on the basis of a dehydroadamantane intermediate.

Noteworthy is the striking resemblance of these chlorinations to the singlet oxygen (\(^{1}O_2\)) additions. The structural consequence—introduction of a heteroatom with shift of the double bond—is identical. Moreover the stereochemical aspects of the \(^{1}O_2\) ene reaction and the chlorinations described here are clearly related as outlined for the syn and anti olefins 11 and 12. This similarity needs stressing in view of the "one of a kind" discussions often encountered in analysis of the mechanism of \(^{1}O_2\) reactions. Central in these discussions are often the perepoxide or the open zwitterionic intermediates. In halonium ion chemistry in which the structures could be studied by \(^1\)H and \(^13\)C NMR spectroscopy, a bridged structure is pro-
posed for a symmetrically substituted olefin (in terms of 
$O_2$ chemistry: the peroxide). An "open" $\alpha$-halo cation 
has been established for an unsymmetrically substituted 
olefin (in terms of $O_2$ chemistry: the zwiterionic per-
oxide). The electronic properties of the substituents
determine the extent of the bridging. In these terms an 
explanation can be found for the observation that only an 
open zwiterionic peroxide is quenched in the reaction of 
$O_2$ with (silyl)enol ethers.\(^{28}\) An analogy to the homoallylic halogenation may also exist in $O_2$ chemistry, namely, in the 
remarkable rearrangement in the $O_2$ addition to tet-
raalkylethylene 24 found by McCrapa.\(^{29}\) This rear-
arrangement furnishes a dioxolane, which can be formed 
by a homoallylic proton abstraction followed by a cyclo-
propane ring-opening (Figure 7). This suggestion does not 
preclude, of course, the earlier proposed mechanism via 
Wagner–Meerwein shifts.

In summary we emphasize that the present results 
provide additional support for the electrophilic character 
of the halogenation of tetraalkylethylenes with $N$-
halosuccinimides on tert-buty hypochlorite. These reactions 
are carried out at room temperature in a high yield 
with water and a saturated $Na_2SO_4$ solution. The organic layer was 
dried over $MgSO_4$ and evaporated. The yield of 4(e)-bromo-
adamantylidenadamantane was 97% (97%). An analyti-
cally pure sample was obtained by crystallization from acetone and 
inubination [115 °C (0.002 mm)]: $mp$ 305.0–315.5 °C; \(^{13}C \) NMR (CDC$_3$) $\delta$ 4.4 (br s, 1 H), $3.05$ (br s, 1 H), $2.8$ (br s, 3 H), $2.6$–$1.5$ (br, 22 H); \(^3\)N NMR (CDC$_3$) $\delta$ 136.9 (s), 129.7 (s), $66.8$ (d), and 12 signals between $39.9$ and $27.6$; mass spectrum, $m/e$ 346/348 (1:1). Anal. Calcd: C, 69.16; H, 7.84; Br, 23.01. Found: C, 69.21; H, 7.82; Br, 22.99.

4(e)-Bromo[3.3.1]nonylidenecyclo[3.3.1]nonane. To a solution of 200 mg (0.82 mmol) of bicyclo[3.3.1]-
onylenedicyclo[3.3.1]nonane in 20 mL of CH$_2$Cl$_2$ was added $6.6$ mmol (1.175 g) of N-bromosuccinimide. 
The reaction mixture was refluxed and stirred for 12 h. The reaction mixture was diluted with CH$_2$Cl$_2$ in a high yield 
with water and a saturated $Na_2SO_4$ solution. The organic layer was 
dried over Mg$SO_4$ and evaporated. The yield of 4(e)-bromo-
adamantylidenadamantane was 97% (97%).}

Experimental Section

Instrumentation. Melting points were determined on a 
Mettler FP2 melting point apparatus. IR spectra were recorded on a 
Unicam (SP-200) spectrophotometer. $^1H$ NMR spectra were recorded at 60 MHz (Varian A-60 or Hitachi Perkin-Elmer R-24
B). $^1H$ chemical shifts are reported in $\delta$ units (parts per million) 
relative to CDCl$_3$ and converted to $\delta Me$_4Si values, using $\delta (CHC$_3$) 
= 7.25 ppm. $^{13}C$ NMR spectra were recorded at 25 MHz (Varian 
XL-100) and $^{13}C$ chemical shifts are denoted in $\delta$ units (parts per million) 
relative to the solvent CDCl$_3$ and converted to $\delta Me$_4Si values, using $\delta (CDCl$_3$) 
= 76.9 ppm. Mass spectra were recorded on an AEI MS-902 spectrometer. Elemental analyses were performed in the 
microanalytical section of this department.

Solvents. All solvents used were purified according to standard 
procedures.

Chlorinating Agents. The chlorination agents NCS, NBS, 
$N$-iodosuccinimide, and NaCl/CH$_2$COOH were obtained 
commercially and used as such. TBHC was prepared according to 
a published procedure.\(^{30}\)

Tetraalkylethylenes. The tetraalkylethylenes, adamantyliden-
adamantane (1),\(^{31}\) bicyclo[3.3.1]nonylidenecyclo[3.3.1]-
nonane (3),\(^{32}\) 2-adamantylidenepropene (7),\(^{11}\) $syn$- and anti-
4,4-'di-tert-butylicyclohexylidene-1,3-cyclohexane (11 and 12)\(^{14}\) were 
prepared by known procedures. In our hands 7 is a crystalline 
compound, mp 34–38 °C, instead of an oil. 2,3-Dimethylbut-2-ene (5) 
was obtained commercially and used without further purifi-
cation.

4(e)-Chloroadamantylidenadamantane. To a solution of 1 
mmol (268 mg) of adamantylidenadamantane in 20 mL of 
CH$_2$Cl$_2$ was added $1.05$ mmol (140 mg) of $N$-chlorosuccinimide. 
The reaction mixture was stirred for 1 h at room temperature, 
diluted with CH$_2$Cl$_2$, and washed twice with water. The organic 
layer was dried over Mg$SO_4$ and evaporated. The yield of 4-
(e)-chboroadamantylidenadamantane was 300 mg (98%): $mp$ 14-
16 (lit.\(^{12}\) $mp$ 14.0–14.5 °C); \(^1H \) NMR (CDCl$_3$) $\delta$ 4.15 (br 
$s, 1 H), 3.05$ (br $s, 1 H), 2.8$ (br $s, 3 H), 2.6–1.5$ (br, 22 H). When 
$0.1$ mmol of hydroquinone is added to the solution, exactly 
the same reaction occurs and the product could be isolated in almost 
the same quantitative yield.

4(e)-Bromoadamantylidenadamantane. To a solution of 3 
mmol (804 mg) of adamantylidenadamantane in 40 mL of 
CH$_2$Cl$_2$ was added $6.6$ mmol (1.175 g) of $N$-bromosuccinimide. 
The reaction mixture was refluxed and stirred for 12 h. The reaction mixture was diluted with CH$_2$Cl$_2$ in a high yield 
with water and a saturated $Na_2SO_4$ solution. The organic layer was 
dried over Mg$SO_4$ and evaporated. The yield of 4(e)-bromo-
adamantylidenadamantane was 97% (97%).

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Thermal Decomposition of Some Perfluoro- and Polyfluorodiacyl Peroxides

Zhao Chengxue, Zhou Renmo, Pan Heqi, Jin Xiangshan, Qu Yangling, Wu Chengjiu,* and Jiang Xikui^1

Shanghai Institute of Organic Chemistry, Academia Sinica, Shanghai 200032, China

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Seven perfluoroacyl peroxides were synthesized, some of them by a new procedure involving the direct interaction of an acyl fluoride with hydrogen peroxide. In the temperature range of 20-40 °C, all these peroxides undergo first-order decomposition in dilute 1,1,2-trichloro-1,2,2-trifluoroethane (Freon-113) solutions (50.02 M). The major decomposition products were separated and characterized as the coupling products of the corresponding radicals, R* + R*. Differing from other perfluoro or polyfluoro radicals, the perfluoro-α-isopropoxyethyl radicals undergo substantial decomposition in dilute solutions, whereas the former decomposes with a more favorable ΔS* term, whereas the former decomposes with lower values of both ΔH* and ΔS*. Thus, weakening of the peroxide bond by H bonding of the peroxide oxygen atom to the acidic α-hydrogen atom seems to be implicated in the decomposition of 9. With a half-life of 51 min at 20 °C, 3 may become a useful low-temperature initiator for free-radical reactions and polymerization.

Both theoretical and practical interests have unceasingly kept the research on diacyl peroxides active for many years. One important theoretical theme has been the mechanistic pathways of their decomposition, whether ionic or free radical or whether concerted or stepwise, in cases where homolysis pertains. Other aspects of interests concern themselves with structural and environmental effects on the rates and mechanistic paths of decomposition. The subject has been comprehensively reviewed by Hiatt and Koenig; the impact of ESR and CIDNP on this branch of research is also well-known. Most of all of the diacyl peroxides which had been investigated are hydrocarbon derivatives. Relatively few fluoro- or perfluorodiacyl peroxides are known, and available kinetic data are few. Since they have been used as initiators for polymerization of fluoro olefins for years and they possess distinct structural characteristics, research on synthetic and mechanistic aspects of these compounds may yield useful information on both basic knowledge and practical applications.

Barium peroxide, sodium peroxide, and hydrogen peroxide have been used for the synthesis of perfluorodiacyl peroxides;^3 the last two reagents were used in this work. In preparing peroxides by the reaction between aqueous sodium peroxide and perfluorocetyl chlorides, we made a preliminary study on the effects of various factors on the yields of the desired products. Among these factors, e.g., the reaction temperature, the amount of water, and the NaO2/RF2COCI molar ratio, the last one appeared rather important, and a value of 0.4–0.5 was preferred. When H2O2 was used in place of NaO2, the procedure became even more convenient for the aqueous–organic two-phase system used. This procedure has been successfully adapted to the syntheses starting from acyl fluorides. All seven

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(1) Formerly spelled Jiang Hsi-Kwei, Chiang Hsi-Kwei, or Stanley Hsi-Kwei Jiang (Chiang).

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