This article is dedicated to Professor Satoshi Ōmura in celebration of his 2015 Nobel Prize.

Note

Acceleration of Acid-Catalyzed Hydrolysis in a Biphasic System by Sodium Tetracyanocyclopentadienides

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The hydrolysis of *tert*-butyldimethylsilyl L-menthyl ether (**3**) in a CH_2Cl_2 –1 M HCl biphasic solvent system was accelerated by the addition of sodium tetracyanocyclopentadienides **1**. Particularly, the reaction rate was enhanced using sodium salt **1a–c** with a lipophilic substituent on the cyclopentadienide ring. From the results obtained by a triphasic experiment, hydrolysis proceeds *via* the formation of hydronium ion **2** in the aqueous phase by ion exchange, followed by the transfer of **2** to the CH_2Cl_2 phase.

Key words phase-transfer reaction; hydrolysis; tetracyanocyclopentadienide; acid-catalyzed reaction

Phase-transfer reactions have garnered increasing attention in organic chemistry because of their mild, sustainable conditions.¹⁾ Phase-transfer catalysts (PTCs) enhance the reactivity of anionic reagents by forming a lipophilic ion pair, mediating a reaction in the organic phase or at the interface between two phases. Enantioselective phase-transfer reactions catalyzed by chiral quaternary ammonium salts are one of the representative methods for synthesizing optically active molecules.^{2,3)} Anionic PTCs have also been developed for reactions where lipophilic anions enhance the solubility of the reactive cationic species, thereby promoting the reactions. Kobayashi *et al.* have reported the first anionic phase-transfer reaction using tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (TFPB) anion.^{4–6)} Recently, asymmetric anionic phase-transfer reactions^{7,8)} have been reported using chiral phosphates with an aziridinium cation⁹⁾ and *N*-haloammonium cations.^{10–18)} However, a limited number of studies have been reported about anionic PTCs. Weakly basic anions are candidates for anionic PTCs because they barely undergo protonation or react with other cationic species. Tetracyanocyclopentadienides ($\text{C}_5\text{R}(\text{CN})_4^-$)^{19–21)} are weakly basic anions; their conjugate acids exhibit very small $\text{p}K_{\text{a}}$ values as superacids, *e.g.*, perchloric acid.^{22,23)} Recently, we have efficiently synthesized

various $\text{Na}[\text{C}_5\text{R}(\text{CN})_4]$ salts **1a–f** from tetracyanothiophene and sulfones and achieved direct functionalization at a substitution position R (Fig. 1).²⁴⁾ During our previous study, we noticed that salts **1a–f** are miscible in polar organic solvents (MeCN, tetrahydrofuran (THF), EtOAc) and can be extracted with organic solvents by partitioning between EtOAc and H_2O , despite the absence of large hydrophobic functional groups. Such unique lipophilic behavior exhibited by the $\text{C}_5\text{R}(\text{CN})_4^-$ salts **1a–f** stimulated us to explore their catalytic activities in a biphasic solvent system.

We envisaged that $\text{Na}[\text{C}_5\text{R}(\text{CN})_4]$ **1** could serve as a carrier of hydronium cations in the organic phase of the CH_2Cl_2 – H_2O biphasic system (Fig. 2). In the aqueous phase of the biphasic system, HCl dissociates, forming a hydronium cation (H_3O^+) and chloride anion (Cl^-). The addition of **1** to the aqueous phase forms hydronium salt $\text{H}_3\text{O}^+[\text{C}_5\text{R}(\text{CN})_4]^-$ **2** by ion exchange, which is a hydronium ion that is “masked” by the lipophilic tetracyanocyclopentadienide group; it can be extracted into the CH_2Cl_2 phase. This working hypothesis

Fig. 1. Sodium Tetracyanocyclopentadienides $\text{Na}[\text{C}_5\text{R}(\text{CN})_4]$ **1a–f**

Fig. 2. Role of $\text{C}_5\text{R}(\text{CN})_4^-$ Anion in the H_2O – CH_2Cl_2 Biphasic System

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Table 1. Effect of Catalyst and Aqueous Phase Acidity on the Hydrolysis of TBS Ether **3**

Entry	Sodium salt	Aqueous phase	Time (h)	L-Menthol (%)
1	Na[C ₅ (CO ₂ Menthyl)(CN) ₄] 1a	H ₂ O	24	0
2	Na[C ₅ (CO ₂ Menthyl)(CN) ₄] 1a	pH 4 buffer	24	0
3	Na[C ₅ (CO ₂ Menthyl)(CN) ₄] 1a	0.03 M HCl	20	89
4	Na[C ₅ (CO ₂ Menthyl)(CN) ₄] 1a	1.0 M HCl	2	92
5	NaClO ₄	1.0 M HCl	24	0
6	NaBF ₄	1.0 M HCl	24	0
7	—	1.0 M HCl	24	0

Fig. 3. NMR Study for the Reaction Rate for the Hydrolysis of **3** Catalyzed by **1** in (A) 1 M HCl–CD₂Cl₂ or (B) 1 M HCl–CDCl₃

could be verified by investigating the hydrolysis of *tert*-butyldimethylsilyl (TBS) ether **3** to L-menthol in CH₂Cl₂ catalyzed by hydronium salt **2**.

The reaction rate for the hydrolysis of the TBS group was significantly affected by acid strength. We examined the effects of sodium salt **1a** and acidity of the aqueous phase on the biphasic hydrolysis of **3** (Table 1). Hydrolysis did not proceed in water–CH₂Cl₂ and in a pH 4 buffer solution–CH₂Cl₂ two-phase system (entries 1, 2, respectively). By using 0.03 M

HCl, the TBS group was eliminated, albeit very slowly (entry 3). Furthermore, with increasing acid concentration to 1.0 M, the hydrolysis rate increased, and desilylation was completed within 2 h (entry 4). By contrast, in the absence of **1a**, the hydrolysis of **3** did not occur even when using 1.0 M HCl as the aqueous phase (entries 5–7). For comparison with representative superacid salts, NaClO₄ and NaBF₄ were examined. However, the desilylation was not induced because they could not be partitioned into the organic phase, attributed to the lack of lipophilicity (entries 5, 6, respectively).

Next, the effect of substitution of C₅R(CN)₄ salt **1** on the hydrolysis of **3** in a 1 M HCl and CD₂Cl₂ biphasic solvent system was investigated by ¹H-NMR (Fig. 3(A)). Tetracyanocyclopentadienides **1a**–**c** with less polar substituents (R = CO₂menthyl (◆), CH₂CH₂OBn (■), and Ph (▲), respectively) significantly accelerated hydrolysis, while those with polar substituents **1d**–**f** (R = CO₂Et (●), CN (×), and CH₂OH (*), respectively) resulted in slow reactions. These results suggest that more hydrophobic anions increase the amount of hydronium salt **2** dissolving in CD₂Cl₂. The hydrolysis of the TBS group in a 1 M HCl–CDCl₃ biphasic system was slower than that in 1 M HCl–CD₂Cl₂ (Fig. 3(B)). The decreased reaction rate in CDCl₃ is attributed to a lower solubility of hydronium salt **2** in CDCl₃ than in CD₂Cl₂.²⁵ The electron-withdrawing power of the substituent R of C₅R(CN)₄ anion did not affect the hydrolysis rate, as indicated by the moderate reaction rates of **1d**–**f**.

Other acid-catalyzed reactions by **1** were examined under the same biphasic system. A hydrolysis of acetal **5** provided diol **6** in only 22% yield after 23 h in the absence of catalyst **1**. The addition of catalyst **1c** to the biphasic system markedly enhanced the reaction rate, and diol **6** was obtained in 73% yield after 2 h (Eq. 1). As an example of a different type of reaction, we demonstrated an acid-catalyzed rearrangement of

cis-stilbene oxide (**7**) to aldehyde **8**, induced by addition of **1c** (Eq. 2).

Next, we focused on the phase transfer ability of hydronium cation **2**. Initially, we attempted to isolate the hydronium salt **2**, an ion pair formed from $\text{Na}[\text{C}_5\text{Ph}(\text{CN})_4]$ (**1c**) and a hydronium cation, using a separating funnel. However, the CH_2Cl_2 extract of a solution of **1c** in 1 M HCl did not afford enough tetracyanocyclopentadienide salt for detection by ^1H -NMR and TLC. Then, another experiment was planned for determining the presence of **2** in CH_2Cl_2 phase using a right-angled U-tube, where two independent aqueous phases were separated by an organic phase (Fig. 4). A U-tube apparatus was equipped with a stir bar and two glass sticks, and another two stir bars were placed on the top of each glass stick. The U-tube was filled with CH_2Cl_2 right up to the upper level of the glass sticks, and an aqueous phase was added over the CH_2Cl_2 phase in both arms (Phases A, B). After adding **1c** to phase A, the whole system was stirred for the indicated time.²⁶⁾ The percentages of the amount of the remaining **1c** in phase A and the transferred amount to phase B were measured on the basis of the initial amount of **1c**.

In the case where both phases A and B were water, the transfer of the $\text{C}_5\text{Ph}(\text{CN})_4$ anion from phase A to phase B was not observed regardless of the additive ether in the CH_2Cl_2 phase (Table 2, entries 1, 2, respectively). On the other hand, by changing the phases A and B from water to 1 M HCl, the slow transfer of the $\text{C}_5\text{Ph}(\text{CN})_4$ anion was induced from phase A to phase B *via* the middle organic phase (entry 3). These results supported our hypothesis that $\text{H}_3\text{O}^+[\text{C}_5\text{Ph}(\text{CN})_4]^-$ (**2**),

formed from $\text{H}_3\text{O}^+\text{Cl}^-$ and **1**, is partitioned between the organic and aqueous phases. The addition of hydrophobic **3** and *L*-menthol accelerated the rate of transfer from phase A to phase B (entries 5, 6, respectively),²⁷⁾ while with the addition of diethyl ether as an additive into the CH_2Cl_2 phase, the transfer rate of the $\text{C}_5\text{Ph}(\text{CN})_4$ anion was slightly affected (entry 4). The acceleration effect of the former additives was attributed to the formation of a hydrophobic oxonium specie such as **4** shown in Fig. 2, which enhances the solubility of the $\text{C}_5\text{Ph}(\text{CN})_4$ salt into the CH_2Cl_2 phase.

The hydronium cation carrier ability of **1** was also confirmed by pH measurements (Fig. 5). A similar experiment as shown in Table 2 was conducted using a U-tube apparatus charged with 1 M HCl for phase A and H_2O for phase B. The change of pH in phase B was measured at the indicated times. In the absence of **1c**, the pH of phase B slowly decreased from 7.0 to 5.3 after 24 h (●). The addition of sodium salt **1c** accelerated the decrease of pH, attaining pH 2.8 after 24 h (▲). The synergetic effect of an additive and salt **1c** on the decrease of pH was also observed for the $\text{C}_5\text{Ph}(\text{CN})_4$ anion transfer experiment summarized in Table 2 (entries 4–6). The addition of diethyl ether to the CH_2Cl_2 phase did not change the rate (◆), while hydrophobic **3** or *L*-menthol significantly accelerated the pH decrease of phase B (× and +). When NaBF_4 was employed instead of **1c**, the rate of pH decrease was much slower than when **1c** was used (■), consistent with the result of the hydrolysis reactions shown in Table 1, entry 6.

In conclusion, we discovered that tetracyanocyclopenten-

Fig. 4. Apparatus for the Measurement of the Phase-Transfer Rate

(A) Schematic; (B) Photograph of the apparatus; (C) Photograph of the glass stick.

a) $\text{Na}[\text{C}_5\text{Ph}(\text{CN})_4]$ (**1c**) was not added in phase A. b) NaBF_4 was used instead of **1c**.

Fig. 5. Change of pH in Phase B When 1 M HCl and H_2O Were Used for Phases A and B, Respectively

Table 2. Percentages of the Remaining $\text{C}_5\text{Ph}(\text{CN})_4$ Anion **1c** in Phase A and the Transferred $\text{C}_5\text{Ph}(\text{CN})_4$ Anion to Phase B

Entry	Phase A/Phase B	Additive	Phase A (%) / Phase B (%) ^{a)}			
			2 h	6 h	24 h	48 h
1	$\text{H}_2\text{O}/\text{H}_2\text{O}$	—	101/0	100/0	102/0	—
2	$\text{H}_2\text{O}/\text{H}_2\text{O}$	TBS ether 3	105/0	104/0	104/0	—
3	1 M HCl / 1 M HCl	—	88/2	79/3	81/3	77/11
4	1 M HCl / 1 M HCl	Diethyl ether	93/1	92/8	76/15	73/21
5	1 M HCl / 1 M HCl	TBS ether 3	90/4	68/16	50/32	41/36
6	1 M HCl / 1 M HCl	<i>L</i> -Menthol	79/6	65/13	53/25	43/28

a) Each percentage was calculated on the basis of the initial amount in phase A.

tadienides **1** promote the hydrolysis of TBS ether **3** in a CH_2Cl_2 –1 M HCl biphasic solvent system *via* the formation of lipophilic hydronium salt **2**. The capability of **2** as a phase-transfer catalyst was also demonstrated by experiments conducted using a triphasic system with a right-angled U-tube. Currently, more experiments for verifying the synthetic utility of catalyst **1** is underway in our laboratory.

Experimental

Hydrolysis of TBS Ether **3 in a Biphasic System Using Catalyst **1a** (Table 1, Entry 4)** To a solution of TBS ether **3**²⁸⁾ (100 mg, 0.37 mmol) in CH_2Cl_2 (1.0 mL) was added 1 M HCl (0.50 mL, 0.50 mmol) and tetracyanocyclopentadienide **1a** (7.4 mg, 0.02 mmol) and the reaction mixture was stirred for 2 h. The reaction was quenched with saturated aq NaHCO_3 and the mixture was extracted with EtOAc. The extract was washed with brine, dried over Na_2SO_4 , filtered, and concentrated under reduced pressure. Purification by flash chromatography (20% EtOAc in *n*-hexane) afforded L-menthol (53 mg, 92%). Further elution with EtOAc provided recovered **1a** (6.4 mg, 86% recovered).

L-Menthol. $^1\text{H-NMR}$ (CDCl_3 , 500 MHz) δ : 3.40 (1H, td, $J=10.4$, 4.4 Hz), 2.18 (1H, sptd, $J=7.0$, 2.7 Hz), 1.96 (1H, dtd, $J=12.1$, 3.9, 2.1 Hz), 1.66 (1H, dqd, $J=3.2$, 2.5 Hz), 1.61 (1H, dq, $J=12.9$, 3.2 Hz), 1.56 (1H, brs), 1.42 (1H, tqd, $J=11.5$, 7.0, 3.4 Hz), 1.11 (1H, ddt, $J=12.4$, 9.8, 3.1 Hz), 1.01–0.81 (3H, m), 0.93 (3H, d, $J=7.0$ Hz), 0.91 (3H, d, $J=7.0$ Hz), 0.81 (3H, d, $J=7.0$ Hz).²⁹⁾

Hydrolysis of Acetonide **5 in a Biphasic System Using Catalyst **1c** (Eq. 1)** To a solution of acetonide **5**³⁰⁾ (100 mg, 0.56 mmol) in CH_2Cl_2 (1.5 mL) was added 1 M HCl (0.75 mL) and catalyst **1c** (7.4 mg, 0.028 mmol), and the reaction mixture was stirred for 2 h. The reaction was quenched with saturated aq NaHCO_3 and the mixture was extracted with EtOAc. The extract was washed with brine, dried over Na_2SO_4 , filtered, and concentrated under reduced pressure. Purification by flash chromatography (80% EtOAc in *n*-hexane) afforded diol **6** (53 mg, 92%). Further elution with EtOAc provided recovered **1c** (6.0 mg, 81% recovered).

Diol **6**. $^1\text{H-NMR}$ (CDCl_3 , 500 MHz) δ : 7.36–7.26 (5H, m), 4.81 (1H, dd, $J=8.1$, 3.4 Hz), 3.74 (1H, dd, $J=11.3$, 3.4 Hz), 3.66 (1H, dd, $J=11.3$, 8.1 Hz), 2.88 (1H, brs), 2.44 (1H, brs).²⁹⁾

Acid-Catalyzed Rearrangement of *cis*-Stilbene Oxide (7**) to Aldehyde **8** (Eq. 2)** To a solution of *cis*-stilbene oxide (**7**) (50.0 mg, 0.25 mmol) in CH_2Cl_2 (1 mL) was added 1 M HCl (0.5 mL) and catalyst **1e** (2.9 mg, 0.014 mmol), and the reaction mixture was stirred for 24 h. The reaction was quenched with saturated aq NaHCO_3 and the mixture was extracted with EtOAc. The extract was washed with brine, dried over Na_2SO_4 , filtered, and concentrated under reduced pressure. Purification by flash chromatography (10% Et₂O in *n*-hexane) afforded diol **6** (28.2 mg, 58%). Further elution with EtOAc provided recovered **1e** (1.9 mg, 66% recovered).

Aldehyde **8**. $^1\text{H-NMR}$ (CDCl_3 , 500 MHz) δ : 9.94 (1H, d, $J=2.5$ Hz), 7.40–7.34 (4H, m), 7.30 (2H, tt, $J=7.3$, 1.5 Hz), 7.24–7.20 (4H, m), 4.89 (1H, d, $J=2.5$ Hz).²⁹⁾

General Procedure for the NMR Experiment of the Hydrolysis of TBS Ether **3 in a Biphasic System (Fig. 3)** An NMR tube was charged with a solution of TBS ether **3** (30 mg, 0.11 mmol) and benzene (internal standard, 10 μL) in CD_2Cl_2 (0.6 mL). A solution of tetracyanocyclopentadienide **1**

(0.0055 mmol, 0.05 equiv) in 1 M HCl (0.3 mL) was added, followed by vigorous manual shaking. The mixture was allowed to stand for the indicated time. The yields were calculated on the basis of the integration of the $^1\text{H-NMR}$ signals of L-menthol (0.74 ppm for methyl group) and benzene (7.37 ppm).

General Procedure of the U-Tube Experiment for the $\text{C}_5\text{Ph}(\text{CN})_4$ Salt Solubility in CH_2Cl_2 (Table 2) A right-angled U-tube equipped with two glass sticks and three magnetic stir bars (Fig. 4) was charged with a solution of an additive (0.75 mmol) in CH_2Cl_2 (20 mL). A solution of **1c** (8 mg, 0.03 mmol) in 1 M HCl or H_2O (3 mL) was added to one side of the U-tube (phase A), and 1 M HCl or H_2O (3 mL) was added to the other side (phase B), and the system was stirred at a rate of approx. 1000 rpm. The amount of the $\text{C}_5\text{Ph}(\text{CN})_4$ anion was measured at the indicated time according to the following procedures. A 10 μL sample was collected using a micropipette and diluted with a 0.025% (w/v) phenol aqueous solution in a 5 mL volumetric flask. The resulting solution was analyzed by HPLC (Develosil C30-UG-5, 70% MeOH/25 mM aqueous Na_2HPO_4 , 0.8 mL/min, 254 nm, 5.7 min for phenol and 9.5 min for **1c**), and the percentages of the remaining $\text{C}_5\text{Ph}(\text{CN})_4$ anion in phase A or the transferred $\text{C}_5\text{Ph}(\text{CN})_4$ anion to phase B were calculated on the basis of the initial amount of **1c** in phase A.

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Conflict of Interest The authors declare no conflict of interest.

Supplementary Materials The online version of this article contains supplementary materials.

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- 26) The movie showing the experiment was attached as a supplementary material.
- 27) One referee pointed out that the total concentration of **1c** in the combined aqueous phases A and B reduced to *ca.* 90% based on the initial amount of **1c** in every entry. We consider that it is within the limits of experimental error because the total amount of **1c** in the combined aqueous phases was with the same after 2 and 48 h for entries 3 and 4. In entries 5 and 6, **1c** would be partially dissolved in the CH_2Cl_2 phase after 48 h. A small amount of **1c** was detected by ^1H -NMR analysis of a CH_2Cl_2 extract from **1c** solution in 1 M HCl, when 20 equiv of L-menthol was used as an additive for the extraction.
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