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Synthetic and Theoretical Studies on Group-Transfer Imidoylation of Organotellurium Compounds. Remarkable Reactivity of Isonitriles in Comparison with Carbon Monoxide in Radical-Mediated Reactions

Shigeru Yamago,* Hiroshi Miyazoe, Ryuta Goto, Masahiro Hashidume, Takashi Sawazaki, and Jun-ichi Yoshida*

Contribution from the Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan

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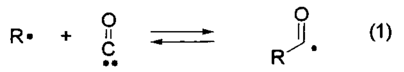
Abstract: Imidoylation of organotellurium compounds with isonitriles has been investigated in conjunction with the radical-mediated C1 homologation reaction by using CO and isonitriles. Carbon-centered radicals generated photochemically or thermally from organotellurium compounds react with isonitriles in a group-transfer manner to give the corresponding imidoylated products. Organotellurium compounds have been found to serve as effective precursors of a wide variety of stabilized radicals, namely benzyl, α-alkoxy, α-amino, and acyl radicals, which take part in the imidoylation with high efficiency. The reactions are compatible with various functional groups, and can be carried out in various solvents including environmentally benign water. The reactivity of isonitriles has been compared with that of CO through competition experiments, and the results indicate that isonitriles are superior to CO as radical acceptors in reactions with stabilized radicals. The origin of the differences has been addressed in theoretical studies with density functional theory calculations using the B3LYP hybrid functional. The calculations suggest that both carbonylation and imidoylation proceed with low activation energies, and that there are virtually no differences in the kinetic sense. Instead, it indicates that thermodynamic effects, namely differences in the stability of the acyl and the imidoyl radicals, control the overall course of the reactions.

1. Introduction

Carbonylations and imidoylations have found enormous application in organic synthesis.[1,2] Many industrially important processes have been developed as exemplified in Monsanto's acetic acid synthesis, and the reactions have been applied to the synthesis of a variety of organic molecules, including polymers and biologically active compounds. While the reaction has been predominantly catalyzed or mediated by transition metals, the radical-mediated carbonylation has been recognized as an important synthetic transformation since its rediscovery by Ryu and Sonoda in 1989.[3,4]

The success of the radical-mediated carbonylation depends on the addition of free radicals to generate acyl radicals (eq 1).[5] This process is well-known to be reversible, and the success of the carbonylation relies on the increase of the equilibrium constant to the acyl radical by applying high CO pressure. The kinetics of the reverse reaction, namely decarbonylation, has been extensively studied, and the rate constants depend strongly on the nature of the substituent R.[3,6] These studies revealed that the rate of the decarbonylation becomes faster as the decarbonylated radical R becomes more stable. Therefore, it is not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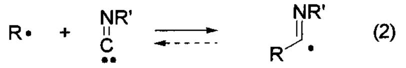
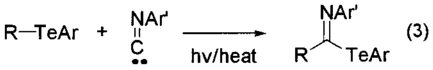
surprising that the reported carbonylations have been limited to radicals which do not possess radical stabilizing groups, e.g., simple aryl and alkyl radicals. Thus, the difficulty in trapping CO by stabilized radicals, e.g., α-phenyl, α-carbonyl, α-alkoxy, and α-amino radicals, is one of the major synthetic drawbacks. Moreover, while the addition of simple alkyl radicals to CO is exothermic, the atom-transfer carbonylation of alkyl iodides has been suggested to be endothermic.[4f] Therefore, further elucidation of the mechanism of each elemental step is highly desirable. Although a detailed reaction mechanism of the addition of carbon-centered radicals to alkenes has been demonstrated by using theoretical investigations,[7] no similar study for carbonylations has been done.[8]

Isonitriles are isoelectronic with CO and thus have sometimes been used as a substitute for CO, especially in transition-metal-catalyzed reactions. It is also known that the addition of free radicals to isonitriles generates imidoyl radicals (eq 2), a process equivalent to the acyl radical formation with CO.[2a,9] The imidoyl radicals thus formed are known empirically to be stable toward the reverse reaction. Instead, they undergo elimination of the R' radical to form nitriles or addition to C−C unsaturated bonds. These types of reactions have been applied to the synthesis of a variety of imidoylated products and nitrogen-containing organic compounds.[10] While the features and benefits of atom and group transfer reactions with C−C multiple bonds are well recognized,[3b] only one example has been reported thus far on the atom transfer imidoylation: the addition of a perfluoroalkyl iodide to isonitriles.[11] Therefore, the synthetic scope, as well as the detailed mechanism of this type of reaction, remains unknown.[12]



To clarify the utility of isonitriles as a C1 unit in radical-mediated reactions, we undertook a detailed study of the group transfer imidoylation from both synthetic and mechanistic viewpoints. Because of their availability and the parallel reactivity of chalcogen group transfer reactions with halogen atom transfer reactions,[13] we selected organotellurium compounds as precursors for carbon-centered radicals.[14,15] In this work, we found the first example of the group-transfer imidoylation of organotellurium compounds with isonitriles, as shown in eq 3. Preliminary results have already been reported.[16] We now report the full details of this study, together with experimental and theoretical studies, to elucidate the origin of the reactivity difference between isonitriles and CO. The current results clearly show that isonitriles are not simple substitutes for CO but instead valuable supplements and complements in the radical-mediated C1 homologation reactions.



2. Results and Discussion

2-1. Imidoylation of Organotellurium Compounds. Detailed reaction conditions were examined by using telluroglycoside **1a** (P = Ac), *N*-phthalimide derivative **3**, and acyl telluride **5** as model compounds. We first examined the effects of light, because irradiation is known to accelerate the generation of radicals from organotellurium compounds.[14h,g] Thus, when a solution of **1a** and 2,6-xylylisonitrile (2.0 equiv) was heated at 100 °C under UV lamp irradiation (4.5 W × 8) for 10 h, the desired imidoylated product **2a** was formed in 65% yield (Table 1, entry 1). The use of an intense light (250 W Hg lamp) considerably shortened the reaction time, and the desired product was obtained in 74% yield after 4 h of irradiation (Table 1, entry 2). Although the reaction took place even in the dark, a higher temperature (140 °C) and longer reaction time were required. In this case, the yield of **2a** was lower, probably due to the instability of the product under the reaction conditions (Table 1, entry 3). The same trend was also observed for **3**, which gave the imidoylated product **4** in good to excellent yield under Hg lamp irradiation. For the imidoylation of **5**, however, the better result was obtained in the dark rather than under irradiation. Since the consumption of **5** was accelerated by UV

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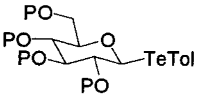
Table 1. Imidoylation under Various Conditions[a]

entry	substrate	solvent	$h\nu$[b]	temp (°C)	time (h)	product	yield (%)
1	**1a**	C_6D_6	A	100	10	**2**	65 (95)[c]
2	**1a**	C_6H_6	B	100	4	**2**	74
3	**1a**	C_6D_6	dark	140	50	**2**	43
4	**3**	C_6H_6	A	60	50	**4**	85
5	**3**	C_6H_6	B	80	2	**4**	91
6	**3**	C_6H_6	C	80	3	**4**	90
7	**3**	C_6H_6	C	80	6	**4**	91
8	**3**	hexane	C	80	3	**4**	67
9	**3**	$(CH_2Cl)_2$	C	80	3	**4**	85
10	**3**	THF	C	80	3	**4**	84
11	**3**	DMF	C	80	3	**4**	86
12	**3**	pyridine	C	80	3	**4**	80
13	**3**	CH_3OH	C	80	3	**4**	73
14	**5**	C_6D_6	A	100	12	**6**	74
15	**5**	C_6D_6	B	100	12	**6**	41
16	**5**	C_6D_6	dark	100	12	**6**	87
17	**5**	hexane	dark	100	12	**6**	83
18	**5**	CD_3CN	dark	100	12	**6**	73
19	**5**	EtOH	dark	100	12	**6**	80
20	**5**	H_2O	dark	100	12	**6**	87

[a] Two equivalents of xylylisonitrile were used except in entry 7, where 1.2 equiv of the isonitrile was used. [b] A: Rayonet RMR600 reactor equipped with a RMR-3500 Å lamp (4.5 W x 8) was used. B: USHIO Optical Modulex reactor equipped with a 250 W Hg lamp was used. C: a 100 W Hg lamp was used. [c] Yield based on the converted substrate.

irradiation, the observed result was presumably due to the instability of the product under UV irradiation (Table 1, entries 14−16).



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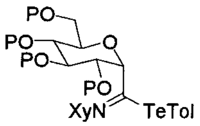
a: P = Ac
b: P = Bz
c: P = Bn



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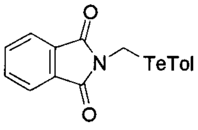

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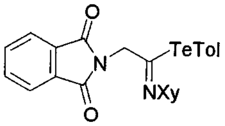

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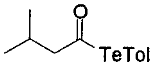

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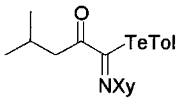

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We next examined the effect of the solvent. If the transition state or the intermediate has polar character, the efficiency of the reaction may be affected by the polarity of the reaction medium. However, contrary to our expectations, the solvent was found to have only a marginal effect on the yield of the product and the rate of the reaction. The reaction could be carried out in various nonpolar and polar solvents including hexane, benzene, tetrachloroethane, THF, DMF, EtCN, pyridine, alcohols, and water (Table 1, entries 7−20).[17] Although α-addition reactions of nucleophiles[18] or electrophiles[19] to isonitriles by ionic mechanisms are well-known, the negligible solvent effects and the insensitivity to basic and protic solvents suggest a radical mechanism. It is also worth noting that the negligible solvent effect indicates that consideration of the reaction medium is not necessary in theoretical studies of the present reaction.

Finally, we briefly investigated the substituent effect of isonitriles, and found that *N*-aryl-substituted isonitriles are more reactive than *N*-alkyl-substituted ones; alkyl-substituted isonitriles, e.g., *n*-octyl- and *cyclo*-hexylisonitrile, gave the desired products in only 5−10% yield under identical conditions. Therefore, in the following sections, we routinely used 2 equiv of an aromatic isonitrile, usually 2,6-xylylisonitrile, but the reaction was also successful when a slight excess of the isonitrile was used, although a longer reaction time was required (Table 1, entry 7).

2-2. Synthetic Scope of the Imidoylation. The scope of the current imidoylation was investigated by using various organotellurium compounds with 2,6-xylylisonitrile, and the results are summarized in Table 2. We focused on the reaction of organotellurium compounds that are expected to generate stabilized radicals, because, as far as we know, there has been no report on the carbonylation of such radicals. We were pleased to find that a variety of stabilized carbon-centered radicals, namely benzyl, α-amino, α-alkoxy, α-carboalkoxy, and acyl radicals, generated from the corresponding organotellurium compounds are effectively trapped by the isonitrile (Table 2, entries 1−21). The successful imidoylation of α-carbomethoxy and acyl radicals is worth mentioning, because the corresponding carbonylation does not take place even under drastic conditions.[20] It is also worth noting that the reaction proceeds with complete stereoselectivity. A single isomer, namely the *syn* isomer with respect to the imidoyl telluride moiety, was formed in all cases (see Supporting Information for the stereochemical assignment). The observed stereoselectivity indicates that the *anti*-imidoyl radical plays a significant role in the current reaction.

We also investigated the imidoylation of nonstabilized radicals and found that the progress of the reaction was slow and required a longer reaction time. Addition of radical initiators, however, slightly increased the efficiency of the reaction. The reaction in the presence of 10 mol % of 1,1′-azobis(cyclohexane-1-carbonitrile) (V-40) resulted in the clean formation of the desired products in moderate to good yields (Table 2, entries 12−14).

The results obtained above are consistent with the well-known radical chain mechanism of the group-transfer reaction. As shown in Scheme 1, the radical R, which is generated by the direct photolysis or thermolysis of organotellurium compounds, or by the reaction with radical initiators, adds to the C−N bond of the isonitrile. The resulting imidoyl radical undergoes a homolytic substitution reaction with the starting organotellurium compound to give the product, together with the regeneration of the radical R (path a). The moderate effect of the radical initiator indicates that the chain length of the current reaction is short. Since a small amount of diaryl ditelluride is usually produced as a side product, the chain may be terminated by the reaction of the imidoyl radical with the diaryl ditelluride (path b).

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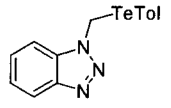
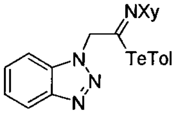
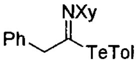
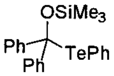
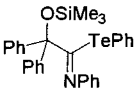
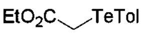
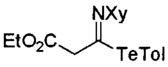
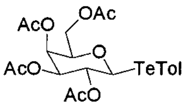
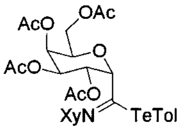
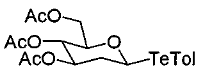
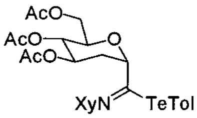
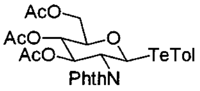
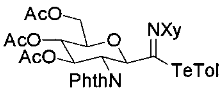
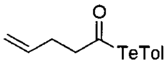
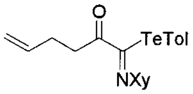
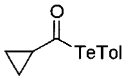
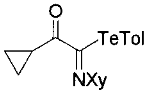
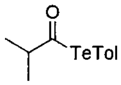
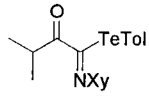
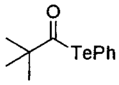
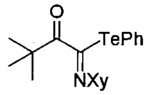
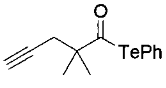
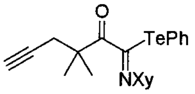
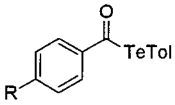
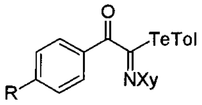
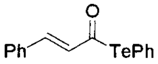
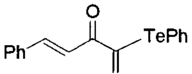
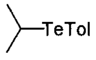
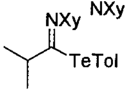
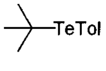
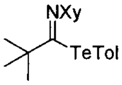
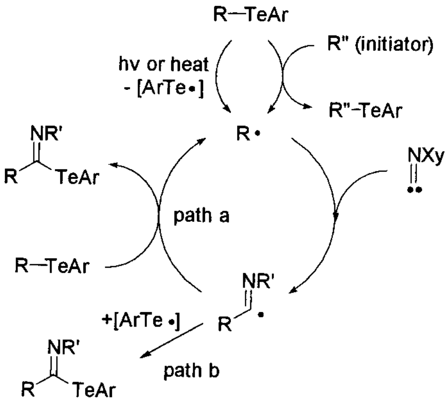
Table 2. Imidoylation of Organotellurium Compounds[a]

entry	substrate	conditions (°C/h)	product	%yield[b]
1	**3**	80/3	**4**	90
2		100/3		78
3		100/3		51[c]
4		100/12[d]		92
5		100/7		66
6	**1a**	100/5[d]	**2a**	75
7	**1b**	100/40	**2b**	76 (97)[e]
8	**1c**	100/20	**2c**	71
9		100/40		80 (100)[e]
10		100/8		81[f]
11		100/40		40 (69)[e]
12	**5**	100/12[d]	**6**	87
13		100/7[d]		78
14		100-120/19[d]		73
15		100/12[d]		26[g]
		100/12[d]		87[h, i]
16		100/12[d]		0[j]
		100/12[d]		73[h, k]
17		100/12[d]		61[h]
18				
	R = Cl	100/6[d]		52
19	R = H	100/6[d]		48
20	R = OMe	100/6[d]		50
21		100/6[d]		52
22		100/9		40[l]
23		100/4		50[l]

[a] The reaction was carried out with 2 equiv of 2,6-dimethyl-phenylisonitrile in C_6D_6 or C_6H_6 in a Pyrex vessel with UV irradiation. A 250 W high-pressure Hg lamp was used except for 7 and 9, wherein a RMR-3500 Å lamp (4.5 W x 8) was used. [b] Isolated yield. [c] 1,2-Diphenylethane formed in 30% yield. [d] The reaction was carried out in the dark. [e] Yield based on the converted substrate. [f] 3,4,5-Tri-*O*-acetylglycal formed in 13% yield [g] Isopropyl tolyl telluride formed in 22% yield. [h] The reaction was carried out under CO pressure (50 atm). [i] Isopropyl tolyl telluride formed in 4% yield. [j] *tert*-Butyl tolyl telluride formed in 78% yield. [k] *tert*-Butyl tolyl telluride formed in 7% yield. [l] Radical initiator (V-40, 10 mol %) was added.

Scheme 1



From a synthetic viewpoint, imidoylation of telluroglycosides and acyl tellurides is particularly rewarding. The imidoylation of the 1-glycosyl radicals provides a new synthetic route to 1-imidoyl and 1-acyl glycosides, which belong to an important class of biologically active sugar derivatives.[21] The stereoselectivity is excellent with respect not only to the imidoyl moiety but also to the anomeric moiety. The α-isomers were formed selectively (>97% selectivity), except for a single case (Table 2, entry 11), where the β-isomer was formed exclusively.[22]

The imidoylation of acyl radicals also opens a new synthetic route to α-acyl carbonyl compounds, which have attracted great

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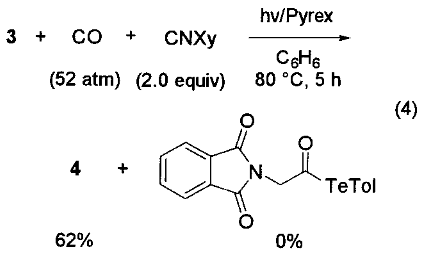
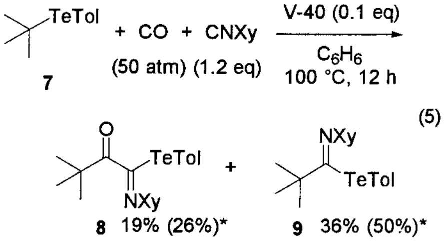
(21) *Glycoscience*; Driguez, H., Thiem, J., Eds.; Springer: Berlin, 1997.

(22) The formation of the α-isomer can be explained by considering the anomeric effect of the glycos-1-yl radicals, wherein the reaction at the α-radical is kinetically more reactive than that of the β-radical due to the interaction of the SOMO and the n-orbital of the neighboring oxygen. On the other hand, the origin of the observed β-selectivity in entry 12 is not clear at the present time. One possible explanation may be an involvement of an intramolecualr participation of the polar C-2 phthaloyl group with the 1-glycosyl radical to shield the α-face, because such an acyloxy group participation and rearrangement have been reported already. See: Giese, B.; Dupuis, J.; Gröninger, K.; Hasskerl, T.; Nix, M.; Weizel, T. In *Substituent Effects in Radical Chemistry*; Viehe, H. G., Janousek, Z., Merényi, R., Eds.; D Reidel Publishing Company: Dordecht, The Netherlands, 1986; p 283. See also: Zipse, H. *J. Am. Chem. Soc.* **1997**, *119*, 1087 and references therein.

interest as versatile building blocks in organic synthesis and as biologically active compounds.[23] In the reaction of acyl tellurides bearing secondary and tertiary alkyl carbon residues, the decarbonylation of CO from the acyl radical competed with the imidoylation (Table 2, entry 15) or the decarbonylation took place exclusively (Table 2, entry 16).[24] However, the decarbonylation was avoided by carrying out the reaction under CO pressure (50 atm). The acyl telluride bearing olefin and acetylene moieties also afforded the simple imidoylated product without intramolecular radical cyclization of the imidoyl radical intermediates (Table 2, entries 13 and 17).

2-3. Competition between Isonitriles and CO. To clarify the difference between the reactivity of CO and that of isonitriles in radical-mediated reactions, we next carried out competition experiments. Prior to this, the reactions of **1** and **3** under high CO pressure (50−100 atm) were examined, but neither gave the desired carbonylated products, and the starting materials were recovered quantitatively. The competition experiments with **3** in the presence of xylylisonitrile (2 equiv) under 50−100 atm of CO gave rise to selective formation of the imidoylated product **4** (eq 4). The result clearly shows the obvious advantage of isonitriles over CO for this type of reaction.

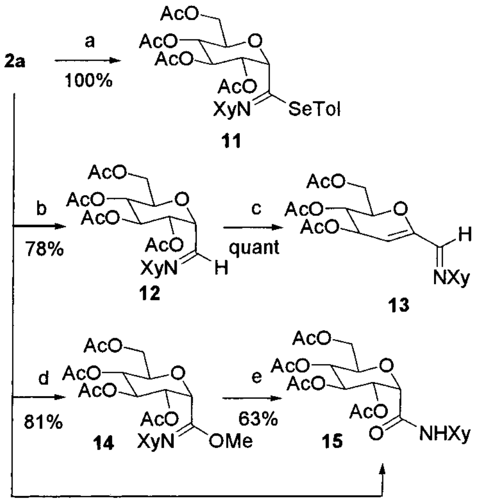




*Yield based on the converted **7**.

We also examined the competition by using *tert*-butyl tolyl telluride (**7**). The reaction afforded the α-acyl imidoyltelluride **8** and the simple imidoylation product **9** in 19% and 36% yield, respectively (26% and 50% yield, respectively, based on the converted **7**, eq 5). The formation of **8** can be ascribed to the carbonylation of the *tert*-butyl radical generated from **7**. The imidoylation of the resulting acyl radical and subsequent group-transfer reaction led to the formation of **8**. The formation of **9** is ascribed to a group-transfer reaction of the *tert*-butyl radical with the isonitrile. The formation of pivaloyl telluride was not detected, but it may undergo imidoylation even if it were formed because the pivaloyl telluride is known to undergo imidoylation under these reaction conditions (Table 2, entry 16). This result suggests that CO and isonitriles possess competitive reactivity toward nonstabilized radicals, e.g., *tert*-butyl radical.

Scheme 2[a]



[a] Reaction conditions; (a) $(TolSe)_2$ (2.1 equiv), C_6H_6, UV lamp (8 W × 6), 100 °C, 43 h, 100%; (b) Bu_3SnH (1.1 equiv), AIBN (0.1 equiv), C_6H_6, 80 °C, 1 h, 78%; (c) −20 °C, 5 days, quant; (d) −e (2.0 F/mol), 0.2 M $LiClO_4$/EtCN, rt, 81%; (e) 1.0 M aqueous HCl/THF (=1/10), rt − 46 °C, 45 h, 63% (f) −e (3.0 F/mol), 0.2 M $LiClO_4$ in H_2O/EtCN (=1/9), rt, 75%.

These competition experiments clearly revealed that isonitriles are superior C1 reagents to CO for this type of group-transfer reaction, especially for reactions involving stabilized carbon radicals.

2-4. Transformations of the Products. The synthetic potential of the imidoylated product is noteworthy, because the carbon−tellurium bond is utilized for several synthetic transformations.[25] We first examined the possibility of an imidoyl radical generation from imidoyl telluride **2a**, which contains a sugar moiety.[26] Thus, the photothermal reaction of **2a** and ditolyl diselenide at 100 °C under Hg lamp irradiation was carried out to obtain the corresponding imidoyl selenide **11** in quantitative yield (Scheme 2). The tin-hydride mediated radical reduction of **2a** took place smoothly in the presence of AIBN to give the glycosyl aldehyde imine **12**, which was further converted to glucal **13** under mild conditions.[27] In both radical-mediated reactions, products derived from the reverse imidoylation were not observed, and the result is consistent with the theoretical prediction (vide infra). The imines **12** and **13** would be useful for further synthetic transformations for the synthesis of new types of *C*-glycosides.

The oxidative transformation of **2a** also provides an important class of *C*-glycosides. Thus, the imidic ester **14** was obtained in good yield by electrochemical oxidation of **2a** in the presence

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[23] Review: Kovács, L. *Recl. Trav. Chim. Pays-Bas* **1993**, *112*, 471. Recent examples: (a) Wasserman, H. H.; Chen, J.-H.; Xia, M. *J. Am. Chem. Soc.* **1999**, *121*, 1401. (b) Wasserman, H. H.; Xia, M.; Petersen, A. K.; Jorgensen, M. R.; Curtis, E. A. *Tetrahedron Lett.* **1999**, *40*, 6163. (c) Singh, R. P.; Kirchmeier, R. L.; Shreeve, J. M. *J. Org. Chem.* **1999**, *64*, 2579. (d) Katritzky, A. R.; Oniciu, D. C.; Ghiviriga, I.; Soti, F. *J. Org. Chem.* **1998**, *63*, 2110. (e) Wasserman, H. H.; Petersen, A. *Tetrahedron Lett.* **1997**, *38*, 953. (f) Baldino, C. M.; Casebier, D. S.; Caserta, J.; Slobodkin, G.; Tu, C.; Coffen, D. L. *Synlett* **1997**, 488.

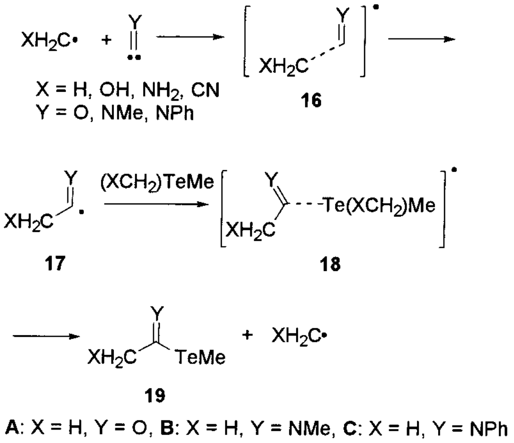
[24] It is noteworthy that decarbonylation did not take place in the cyclopropyl-substituted acyl telluride (entry 14). This is probably because cyclopropyl radicals, which possess sp^3 radical character, are less stable than the conformationally unrestrained secondary alkyl radicals, since the rate of the decarbonylation becomes faster when the decarbonylated radical becomes more stable. For the stability of cyclopropyl radicals, see; Walborsky, H. M. *Tetrahedron* **1981**, *37*, 1625.

[25] Petragnani, N. *Tellurium in Organic Synthesis*; Academic Press: London, 1994.

[26] Leardini, R.; Nanni, D.; Pareschi, P.; Tundo, A.; Zanardi, G. *J. Org. Chem.* **1997**, *62*, 8394 and references therein. Bachi, M. D.; Denenmark, D. *J. Am. Chem. Soc.* **1989**, *111*, 1886. Bachi, M. D.; Denenmark, D. *J. Org. Chem.* **1990**, *55*, 3442. Bachi, M. D.; Melman, A. *J. Org. Chem.*, **1995**, *60*, 6242. Hofmann, J.; Schulz, K.; Zimmermann, G. *Tetrahedron Lett.* **1996**, *37*, 2399.

[27] Clive, D. L. J.; Chittattu, G. J.; Farina, V.; Kiel, W. A.; Menchen, S. M.; Russell, C. G.; Singh, A.; Wong, C. K.; Curtis, N. J. *J. Am. Chem. Soc.* **1980**, *102*, 4438.

Scheme 3



of MeOH (LiClO$_4$ solution of MeOH/EtCN).[28] The imidic ester **14** was further hydrolyzed to 1-carbamoylglycoside **15** by acidic treatment. Alternatively, the same transformation from **2a** to **15** was achieved in a single step by the electrolysis of **2a** in aqueous EtCN.

2-5. Theoretical Model. Theoretical calculations were carried out to understand carbonylations and imidoylations, especially in terms of the differences in the reactivity of CO and isonitriles toward radicals. Addition of substituted-methyl radical (XCH$_2$ radical) to CO and methylisonitrile (CNMe) was used as a model reaction (Scheme 3). The addition of the XCH$_2$ radical to CO or isonitriles generates the acyl or imidoyl radicals **17** by way of transition states **16**, and they undergo homolytic substitution with (XCH$_2$)TeMe via transition states **18** to produce the acyl or imidoyl telluride **19** with generation of the XCH$_2$ radical. We also investigated the reaction pathway of methyl radical addition to phenylisonitrile (Y = NPh) to understand the effect of the substituent on the nitrogen atom.

All theoretical calculations were carried out with Gaussian 94 and Gaussian 98 programs.[29] Geometry optimizations were performed with the hybrid B3LYP density functional[30] with a Hey−Wadt effective core potential (ECP) and the outermost valence electron basis set[31] for tellurium and the 6-31G(d)[32] basis set for the rest (denoted as B3LYP/631HW). Single-point energy calculations were performed with the hybrid B3LYP density functional with a Hey−Wadt ECP and the outermost valence electron basis set for tellurium and the 6-311+G(2df,2p) basis set for the rest (denoted as B3LYP/6311HW). Details are described in the Supporting Information.

2-6. Addition of methyl radical to CO and isonitriles. The geometry and energies of the transition state (TS) **16A** for the methyl radical addition to CO and the acyl radical **17A** (X = H, Y = O) were calculated, and the results are summarized in Figure 1. TS **16A** is calculated to be very early as judged by the small structural changes from the reactants, the long newly forming C−C bond length, and the lack of atomic spin density at the CO moiety. TS **16A** leads to the formation of the σ-type acyl radical **17A**, whose O−C−C bent angle (127.9°) agrees with the proposed structure from ESR studies[33] and previous computational studies.[8,34] The calculated activation energies of the forward reaction (carbonylation) are 10.2 and 18.4 kJ/mol by B3LYP/631HW and B3LYP/6311HW//B3LYP/631HW, respectively, values which are in good agreement with the experimental ones (13−18 kJ/mol).[35] The calculated activation energies of the reverse reaction (decarbonylation) are 73.1 and 70.2 kJ/mol by B3LYP/631HW and B3LYP/6311HW//B3LYP/631HW, respectively, values which are also in good agreement with the experimental value (72 kJ/mol).[35b] The Gibbs free energies are also calculated at 298.15 K under 1 atm of pressure by B3LYP/631HW. The results suggest that the entropic term considerably destabilizes both the TS and the product by ca. 26.8 and 33.6 kJ/mol, respectively. The Mulliken charge does not change significantly during the course of the reaction, but the C−O bond becomes slightly polarized as the reaction progresses. This change may account for the observed small solvent effects in the decarbonylation.[36]

The geometry and energies of the TSs and products for the imidoylation were also obtained by calculations and the results are summarized in Figure 2. TSs **16B** and **16C** are also very early, and the C−N−C bent angles remain almost 180°. TS **16B** leads to *syn*-**17B**, which further isomerizes to the energetically more stable *anti*-**17B**, although there is no direct pathway to the *anti*-isomer from the reactants.[37] In sharp contrast to the reaction with methyl isonitrile, the reaction of phenyl isonitrile directly gives the *anti*-imidoyl radical **17C** via TS **16C**. These results are consistent with the experimental results showing that the *syn*-imidoyl tellurides were formed exclusively from the *anti*-imidoyl radicals. The overall energetics from the reactants to *anti*-**17B** and **17C** is very similar regardless of the nature of the substituent on the nitrogen. It should be emphasized that the imidoylation is far more exothermic than the carbonylation, whereas the activation energies of the imidoylation are slightly

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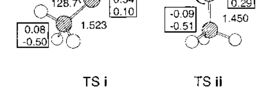
[37] Two transition structures for the isomerization were obtained in close activation energies. The TS **i**, which is corresponding to the isomerization of the nitrogen substituent, is found to be slightly lower in energy than the TS **ii** corresponding to the isomerization of the carbon imidoyl carbon substituents.



	TS **i**	TS **ii**
δE from **E** (kJ/mol)	37.2^a [32.1]^b (33.3)^c	43.2^a [43.3]^b (41.6)^c

^{a}B3LYP/631HW + ZPE, ^{b} Gibbs free energy at 298.15 K under 1 atmosphere of pressure
^{c}B3LYP/6311HW//B3LYP/631HW + ZPE

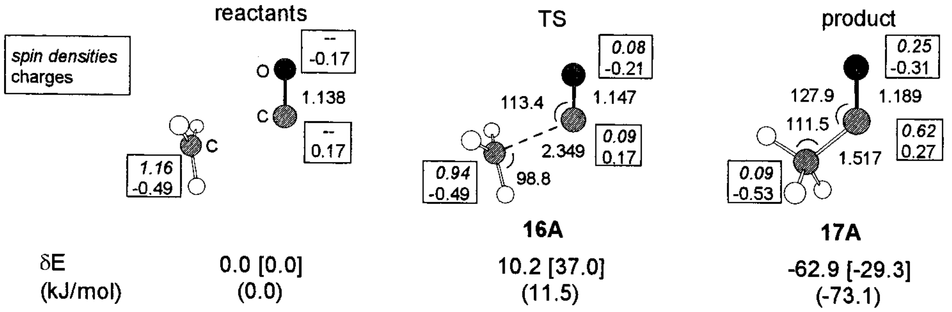


Figure 1. Geometry (A, deg) and relative energies (total energy + ZPE, kJ/mol) of the reactants, TS, and product for the addition of methyl radical to CO obtained by B3LYP/631HW calculations. Mulliken spin densities and charges of the heavy atoms are in boxes. Relative Gibbs energies at 298.15 K under 1 atm of pressure are shown in square brackets. The energies obtained by B3LYP/6311HW//631GHW + ZPE are shown in parentheses.

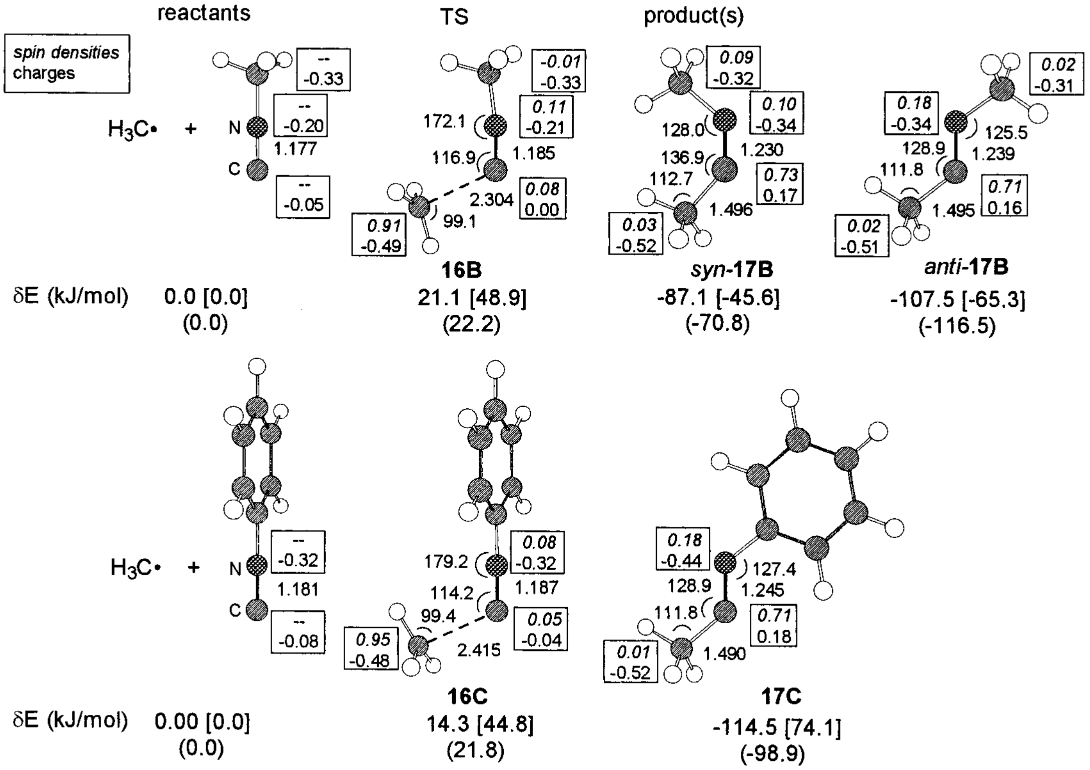


Figure 2. Geometry (A, deg) and relative energies (kJ/mol) of the reactants, TSs, and products for the addition of methyl radical to CNMe and CNPh obtained by B3LYP/631HW calculations. Mulliken spin densities and charges of the selected heavy atoms are in boxes. Relative Gibbs energies at 298.15 K under 1 atm of pressure are shown in square brackets. The energies obtained by B3LYP/6311HW//631GHW + ZPE were shown in parentheses.

higher than those of the carbonylation. Therefore, the net activation energies of the reverse imidoylation from the *anti*-radicals are 121−123 kJ/mol by B3LYP/6311HW//B3LYP/631HW, which are significantly higher than those of the decarbonylation (70 kJ/mol). The trend of the relative Gibbs free energies of the TSs and the products is similar to that of the carbonylation, and the entropic term considerably destabilizes both the TSs and the products.

2-7. Homolytic Substitution Reaction. Homolytic substitution reactions of the acyl radical **17A** and the *anti*-imidoyl radical **17B** with Me_2Te (X = H in Scheme 3) were also analyzed by calculations, and the results are summarized in Figure 3. The reactions were calculated to take place via the T-shaped TSs **18A** and **18B** as shown in Figure 3. While two isomeric TSs with respect to the relative orientation of the acyl and the imidoyl radicals to Me_2Te were obtained for each reaction, only the lower energy TSs are shown here (geometries and energies of all calculated TSs and products are shown in the Supporting Information). Although formation of the hypervalent chalcogen-centered radical intermediate has been proposed for the simple model reaction, no such intermediate could be located by using the present calculations.[38,39]

The overall energetics of the two processes is very similar, and late TSs are obtained in both cases. Thus, the forming C−Te bond is shorter than the cleaving C−Te bond, and the spin density is mainly located on the leaving methyl group. Both processes are endothermic, because the starting acyl and imidoyl radicals are more stable than the forming methyl radical. Analysis of the Gibbs free energies indicates that the entropic

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(39) Homolytic substitution reaction of **17A** and Me_2Te at the MP2-(FU)/631HW level of theory also gave the similar T-shaped transition state. Although the activation energy (57 kJ/mol) was slightly higher than that obtained by B3LYP/631HW, we could not locate the hypervalent intermediate as discussed in ref 38.

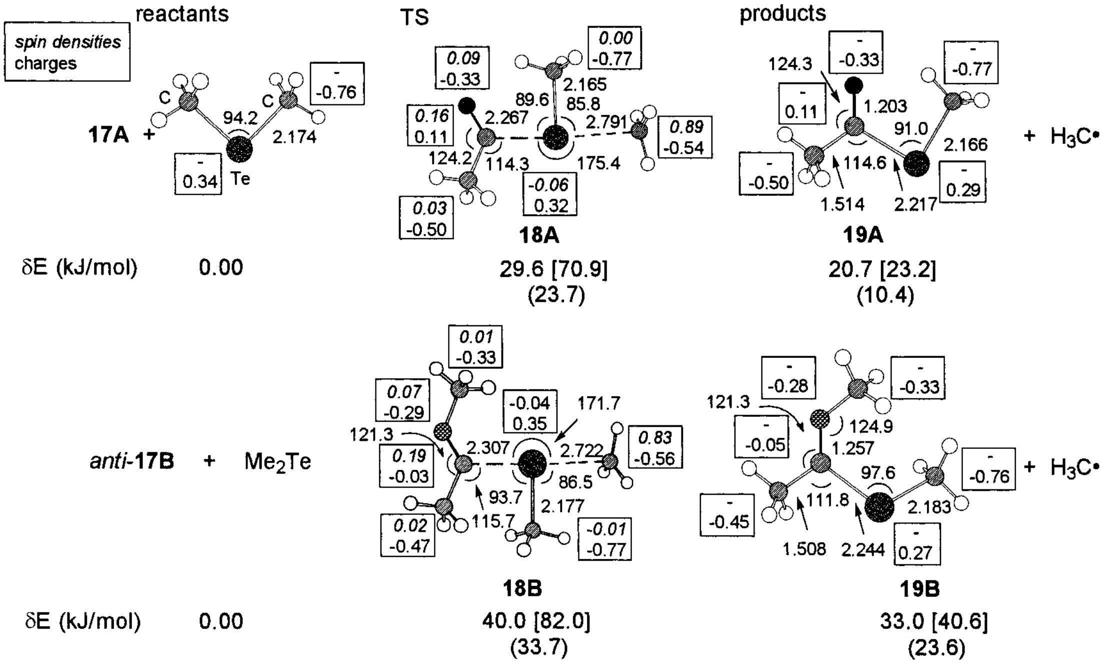

Figure 3. Geometry (A, deg) and relative energies (total energy + ZPE, kJ/mol) of Me_2Te, TSs, and products of the addition of acyl radical **17A** and anti-imidoyl radical **17B** to Me_2Te obtained by B3LYP/631HW calculation. While two isomeric TSs were obtained, only the TSs of lower energy are shown. Mulliken spin densities and charges of the heavy atoms are in boxes. Relative Gibbs energies at 298.15 K under 1 atm of pressure are shown in square brackets. The energies obtained by B3LYP/6311HW//631GHW + ZPE were shown in parentheses.

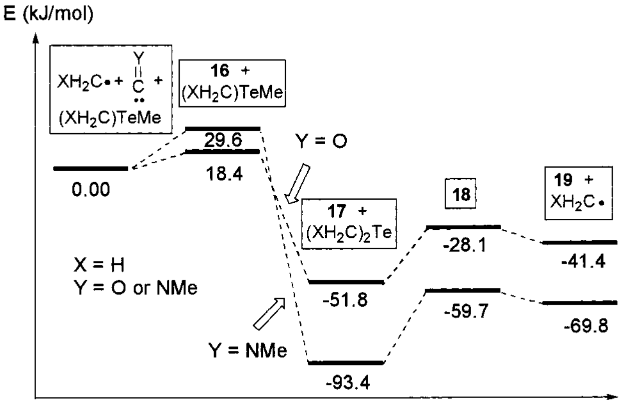

Figure 4. Energy profile of the group-transfer carbonylation and imidoylation reactions of methyl radical (X = H) and CO and methyl isonitrile with Me_2Te (X = H) obtained by B3LYP/6311HW//B3LYP/631HW + ZPE. The energy corresponding to the *anti*-imidoyl radical (*anti*-**17B**) is shown for Y = NMe.

term also significantly destabilizes both the TSs and the products. Mulliken charge analysis indicates a small amount of electron flow from the leaving methyl group to the acyl and the imidoyl carbon. This may be the origin of the reported minor solvent effect in the group transfer reaction.[40]

2-8. Energetics of the Group Transfer Carbonylation and Imidoylation. The energetics of the radical-chain reaction of the methyl radical, Me_2Te, and CO and that of the methyl radical, Me_2Te, and methyl isonitrile (Scheme 3, X = H) obtained by B3LYP/6311HW//B3LYP/631HW is summarized in Figure 4. The initial addition reaction of the methyl radical to CO and methyl isonitrile is highly exothermic to form the acyl and imidoyl radicals **17** via TS **16**, and the subsequent slightly endothermic homolytic substitution reaction affords the products **19** via TS **18**. Figure 4 clearly indicates that the striking differences between the two reactions derive from the first elemental step, and that the imidoylation is more exothermic than the carbonylation due to the formation of the stable imidoyl radicals.

The overall chain cycle is exothermic (41.4 and 69.8 kJ/mol for the carbonylation and the imidoylation, respectively). In addition, since the activation energies of both TSs **16** and **18** are very low, the kinetics, as well as the thermodynamics, suggests that both reactions must take place spontaneously. The competitive carbonylation and imidoylation of the *tert*-butyl radical, as in eq 5, are consistent with the theoretical results.

Conversely, the imidoylation took place exclusively instead of the carbonylation for stabilized radicals as shown in Table 2 and eq 4, and the results cannot be explained by the energy profile shown in Figure 4. Therefore, we next examined the effects of the substituent X, because the energy profiles of the radical addition to CO are well-known to be related to the stability of the starting radicals.

2-9. Carbonylation and Imidoylation of Substituted Methyl Radicals. The reactions of the substituted methyl radical $XH_2C^\bullet$ (X = H, Me, OH, CN), CO or methyl isonitrile, and $(XH_2C)TeMe$ were calculated, and the relative energies of the TS **16,** radical intermediate **17**, and final product **19** are summarized in Table 3.[41] For the imidoylation, only the *anti*-imidoyl radicals and the *syn*-imidoyl tellurides are shown here, and the energies corresponding to the *syn*-imidoyl radicals are shown in the Supporting Information. We did not calculate TS **18** primarily because of limited computational expenses. The activation energies of the reaction of the substituted derivatives of **17D**−**I** (X = Me, OH, and CN) with $(XH_2C)TeMe$ are expected to be very similar to or lower than those of **17A** and **17B** with Me_2Te, because elimination of the stabilized radicals $XH_2C^\bullet$ (X = Me, OH, and CN) occurs as the reaction progresses.

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[41] For the ethyl radical addition to CO, the activation energies for the forward reaction and the reverse reaction are in good agreement with the experimental data. See ref 35a.

Table 3. B3LYP-Calculated Relative Energies (kJ/mol) and Gibbs Energies (kJ/mol) for TSs and Products Related to $H_2XC^{\bullet}$ Addition Reactions to CO, CNMe, and CNPh

			total energy[a]		Gibbs energy[b]
X	Y	compd	631HW	6311HW	631HW
		transition state **16**			
H	O	**16A**	10.2	18.4	37.0
CH_3[c]	O	**16D**	8.7	16.8	42.9
OH[c]	O	**16E**	3.9	14.1	39.0
CN[c]	O	**16F**	3.9	42.9	68.3
H	NMe	**16B**	21.1	29.6	48.9
CH_3[c]	NMe	**16G**	22.2	31.5	58.3
OH[c]	NMe	**16H**	17.1	29.9	54.7
CN[c]	NMe	**16I**	18.7	28.3	59.1
H	NPh	**16C**	14.3	21.8	44.8
		product **17**			
H	O	**17A**	−62.9	−51.8	−29.3
CH_3[c]	O	**17D**	−52.8	−40.4	−9.4
OH[c]	O	**17E**	−39.0	−26.4	1.9
CN[c]	O	**17F**	2.0	12.5	41.3
H	NMe	*anti*-**17B**	−107.5	−93.4	−65.3
CH_3[c]	NMe	*anti*-**17G**	−95.5	−80.5	−46.4
OH[c]	NMe	*anti*-**17H**	−87.7	−72.3	−41.8
CN[c]	NMe	*anti*-**17I**	−45.0	−38.3	−4.8
H	NPh	*anti*-**17C**	−114.5	−98.9	−74.1
		product **19**			
H	O	**19A**	−42.2	−41.4	−6.1
CH_3	O	**19D**	−49.2	−45.1	−5.2
OH	O	**19E**	−32.9	−29.5	11.6
CN	O	**19F**	−28.2	−23.6	14.8
H	NMe	*syn*-**19B**	−74.5	−69.8	−24.8
CH_3	NMe	*syn*-**19G**	−79.6	−72.6	−28.3
OH	NMe	*syn*-**19H**	−68.6	−62.1	−17.2

[a] $\delta E_a = \delta E + \delta$ZPE. Single-point calculation for 6311HW. [b] Energy obtained at 298.15 K under 1 atm of pressure. [c] Two isomeric stationary points were obtained within close energy differences, and the value is taken from the lowest energy TS. Optimized structures and energies are shown in the Supporting Information.

The nature of the substituent X is found to strongly influence the stability of the products **17** and **19**, while the effect on the TS **16** is small in all cases. The relative total energies of the acyl and imidoyl radicals **17** decreased dramatically as the substituent X changed from H to Me, OH, and CN. Indeed, the carbonylation of CN-substituted methyl radical to form **17F** is calculated to be an endothermic process. Despite the same substitution effects, formation of the imidoyl radicals *anti*-**17G**−**I** is still highly exothermic. The entropic terms considerably destabilize **17**, and the relative Gibbs free energies of the products **17** indicate that the formation of the acyl radicals **17E** and **17F** is an endothermic process, although the formation of the imidoyl radicals *anti*-**17G**−**I** is still exothermic. The substituent effects on the stability of the acyl radicals **17A**−**F** toward decarbonylation are consistent with the previous kinetic experiments in that decarbonylation proceeds more rapidly when the decarbonylated radical becomes more stable.[6] Conversely, the activation energies of deimidoylation are, in all cases, very high (67−123 kJ/mol). These results are also consistent with the fact that imidoyl radicals are stable toward reverse reactions.

The effects of the substituent X on the stability of the product **19** are also noteworthy. The relative total energies of **19** also decreased as the substituent X changed from H to Me, OH, and CN, although the relative total energies were calculated to be exothermic in all cases. Interestingly, formation of the imidoyl tellurides is more exothermic (61−73 kJ/mol) than that of the acyl tellurides (24−45 kJ/mol). The relative Gibbs free energies reveal that carbonylations of nonstabilized radicals (X = H and Me) are slightly exothermic while those of stabilized radicals (X = OH and CN) are endothermic. The calculated results are consistent with the current experimental results in that carbonylation takes place only with nonstabilized radicals but not with stabilized radicals. The relative Gibbs free energies also reveal that the formation of the imidoyl tellurides is exothermic in all cases, as much as 17−28 kJ/mol, suggesting that imidoylation proceeds with both nonstabilized and stabilized radicals.

The substituent effects on the TSs are small for both carbonylation and imidoylation, but more definitive electronic effects are observed in carbonylation. Thus, as the radical becomes electron rich, the activation energy decreases due to the electron-deficient character of CO. For imidoylation, however, no electronic effects are observed, while polar substituent effects have been proposed in the reaction of electrophilic radicals.[12]

3. Conclusion

We have demonstrated that a variety of organotellurium compounds undergo radical-mediated group-transfer reactions with isonitriles. Imidoylation takes place under mild photothermal conditions with complete stereoselectivity to give a single stereoisomer in all cases. The reaction is especially useful when stabilized radicals are formed, because the synthetically equivalent reaction with CO, namely carbonylation, does not take place in such cases. The synthetic utility of the present group-transfer imidoylation is obvious. Theoretical calculations of the carbonylation and the imidoylation processes revealed that both reactions proceed with low activation energies, and that kinetic factors cannot explain the differences in the reactivity between CO and isonitriles. Instead of kinetic factors, the calculations suggest that thermodynamic factors play a crucial role, namely imidoylation is highly exothermic because stable imidoyl radicals are formed. Therefore, isonitriles are not simple substitutes for CO but are useful complements in radical-mediated C1 homologation reactions.

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Supporting Information Available: Crystal date for the imidoylated product (Table 2, entry 2), experimental procedures and characterization of all new compounds, and optimized geometries and energies for the theoretical calculation (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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