$t_1 = 23.25$, $t_2 = 23.92$, and 4-phenyl-hexan-2-one: $T = 120\,^\circ C$, $t_S = 32.25$, $t_R = 33.32$; b) chiral HPLC Columns: Daicel Chiralcel OD and Chiralpak AD, particle size: $5.0\,\mu m$, column dimensions: 25 cm (length) $\times$ 0.46 cm (i.d.), flow = $1.0\,mL\,min^{-1}$. 1,3-diphenyl-pentan-1-one (Chiralpak AD, 2-PrOH/hexanes = 1/99), $t_S = 20.43$, $t_R = 29.55$; 3-(4-methoxyphenyl)-1-phenyl-pentan-1-one (Chiralpak AD, 2-PrOH/hexanes = 10/90), $t_S = 12.65$, $t_R = 16.83$; 1-(4-methoxyphenyl)-3-phenyl-pentan-1-one (Chiralcel OD, 2-PrOH/hexanes = 10/90), $t_S = 19.80$, $t_R = 22.37$; 3-(4-chlorophenyl)-1-phenyl-pentan-1-one (Chiralpak AD, 2-PrOH/hexanes = 5/95), $t_S = 10.73$, $t_R = 13.87$; and 1-(3-chlorophenyl)-4-phenyl-pentan-1-one. (Chiralpak AD, 2-PrOH/hexanes = 1/99), $t_S = 25.73$, $t_R = 34.97$.

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Catalytic Aerobic Oxidation of Cycloalkanes with Nanostructured Amorphous Metals and Alloys[**]

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The functionalization of unactivated carbon–hydrogen bonds in saturated hydrocarbons has been investigated for both its synthetic and biological interest.[1] Catalytic oxidation of alkanes has been explored using several oxidants,[2] and those reactions with molecular oxygen under mild conditions[3] are especially rewarding goals. The oxidation of cyclohexane turns out to be the least efficient of all major industrial processes.[4]

Typically, cyclohexane is oxidized by air (15 atm) at 160 °C in the presence of cobalt naphthenate as oxidation initiator, giving only 4% conversion with 80% selectivity for cyclohexanone and cyclohexanol.[5] The addition of boric acid to the oxidation mixture allows approximately 10% conversion of cyclohexane with 90% selectivity for cyclohexanone and cyclohexanol.[5] Murahashi et al. have reported the oxidation of cyclohexane with iron powder and observed 11% conversion with 95% selectivity for cyclohexanone and cyclohexanol.[6]

Suslick and co-workers demonstrated the first sonochemical synthesis of amorphous iron particles (10–20 nm) by ultrasonic irradiation of $[Fe(CO)_5]$, and the utility of these particles as an efficient catalyst in the Fischer–Tropsch process.[7] They have extended this sonication synthesis to nanophase amorphous cobalt (20 nm) and an amorphous Co/

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Fe alloy.[8] We have investigated the sonochemical synthesis of amorphous nickel[9] (10 nm) from $[Ni(CO)_4]$ and of amorphous Fe/Ni alloy[10] ($Fe_{20}Ni_{80}$, 25 nm) from a solution of $[Fe(CO)_5]$ and $[Ni(CO)_4]$. The amorphous nature and the particle size were established by X-ray diffraction (XRD) and transmission electron microscopy (TEM) measurements.[11]

Here we report the oxidation of cyclohexane with up to 40% conversion and 80% selectivity[12] for cyclohexanone and cyclohexanol using nanostructured amorphous metals like Fe and Co and an amorphous alloy like $Fe_{20}Ni_{80}$ with oxygen (40 atm) at room temperature (25–28 °C) in the absence of any solvent. In the aerobic oxidation isobutyraldehyde as coreductant and a catalytic amount of acetic acid were used. Initially the oxidations were carried out at room temperature under 1 atm of oxygen, and it was found that oxygen at 40 atm gave better conversion. The results are summarized in Table 1.

Table 1. Aerobic oxidation of cyclohexanes using amorphous metals/alloys at 28 °C.[a]

Substrate	Nanometal/ alloy	Particle size [nm]	Conversion [%][b]	one:ol[c]
cyclohexane	Fe	20	40	1:4.5
	Co	20	41	1:5
	$Fe_{20}Ni_{80}$	25	38	1:3.6
methylcyclohexane	Fe	20	32	1:1
	Co	20	38	1:3
	$Fe_{20}Ni_{80}$	25	36	1:2

[a] A mixture of nanometal/alloy (0.025 g), cyclohexane (250 mmol), isobutyraldehyde (50 mmol), and acetic acid (5 mmol) was stirred in a Parr reactor with oxygen (40 atm) at room temperature for 10–15 h. [b] Conversion is defined as the percentage of the starting alkane converted into products. [c] Determined by GC analysis using starting alkane as internal standard and also by isolation of products.

For the oxidation of cyclohexane, use of amorphous cobalt gave the best result at 41% conversion and 80% selectivity for cyclohexanone and cyclohexanol. In a control reaction where the same cycloalkanes were treated with molecular oxygen, isobutyraldehyde, and acetic acid in the absence of amorphous Co, Fe, or alloy as catalyst, no oxidation products were obtained. The oxidation of methylcylohexane under similar conditions occurs only at the secondary and tertiary C–H bonds; primary C–H bonds remain unaffected. In the reaction catalyzed by amorphous cobalt the product was a mixture of methylcyclohexanones and methylcyclohexanols (1:3; 2-one:3-one:4-one = 28:42:30 and 1-ol:2-ol:3-ol:4-ol = 65:9:15:11). When the oxidation of cyclohexane was carried out using nanostructured Co (20 nm) as catalyst at 70 °C under 40 atm of oxygen for 8 h, the conversion had gone up to 67% but there was a change in the ratio of ketone to alcohol (1:2; Table 2).

Table 2. Aerobic oxidation of cyclohexane using amorphous metals/alloys at 70 °C.

Nanometal/alloy	Conversion [%]	one:ol
Fe	62	1:1.5
Co	67	1:2
$Fe_{20}Ni_{80}$	56	1:2

The oxidation of adamantane with various nanometals/alloys was carried out under similar conditions (28 °C, 40 atm O_2), and in general the conversion was in the range of 52–57%; adamantan-1-ol was the major product in all the reactions (Table 3). It is noteworthy that our catalytic system is quite different from the Gif^{II} system.[13] For example, the selectivity for the tertiary or secondary C–H bond on a "per bond" basis for the oxidation of adamantane is 10 for our system and 0.25 for the Gif^{II} system. Interestingly no other oxidation products were observed in our reaction (100% selectivity).

Table 3. Aerobic oxidation of adamantane using amorphous metals/alloys at 28 °C.

Nanometal/alloy	Conversion [%]	1-ol:2-ol:2-one
Fe	56	16:1:3
Co	57	11:1:0.5
$Fe_{20}Ni_{80}$	52	17:2:1

Although we do not have proof for a precise mechanism at the present stage, the reaction can be rationalized by assuming the following pathway, which is similar to that suggested by Murahashi et al.:[6] The reaction of isobutyraldehyde with molecular oxygen[14] in the presence of amorphous metal/alloy and acetic acid would give perisobutyric acid,[15] which subsequently reacts with metal/alloy to afford a metal–oxo species[16, 17] along with isobutyric acid. Abstraction of a hydrogen atom from cyclohexane with the oxo-metal species followed by hydroxy ligand transfer to the resulting radical would give the alcohols. Under the same reaction conditions alcohols can be converted into ketones.

The reactions presented above clearly indicate that the nanostructured amorphous metals/alloys are superior catalysts for aerobic oxidation of cycloalkanes under mild reaction conditions.

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Enantioselective Single-Crystal-to-Single-Crystal Photodimerization of Coumarin and Thiocoumarin in Inclusion Complexes with Chiral Host Compounds

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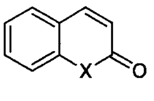
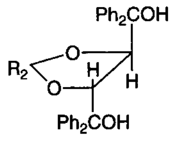
Dedicated to Professor Masazumi Nakagawa on the occasion of his 83rd birthday

Some examples of single-crystal-to-single-crystal photoreactions have been reported,[1–5] but only a few of these involve enantioselective reactions and they are all intramolecular photocyclization reactions.[3–5] For example, the enantioselective photocyclization of *N*,*N*-dibenzyl-1-cyclohexenecarbothioamide to an optically active β-thiolactam has been reported to proceed in a single-crystal-to-single-crystal manner.[4] We have now found that the single-crystal-to-single-crystal enantioselective photodimerization of coumarin (**1a**) or thiocoumarin (**1b**) proceeds efficiently in inclusion complexes with (*R*,*R*)-(−)-*trans*-bis(hydroxydiphenylmethyl)-2,2-dimethyl-1,3-dioxacyclopentane (**2a**) or (*R*,*R*)-(−)-*trans*-2,3-bis(hydroxydiphenylmethyl)-1,4-dioxaspiro[4.4]nonane (**2b**), respectively.



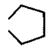
1

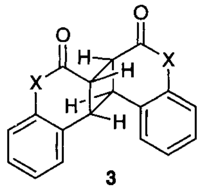
a: X = O
b: X = S



2

a: R_2 = Me_2
b: R_2 =

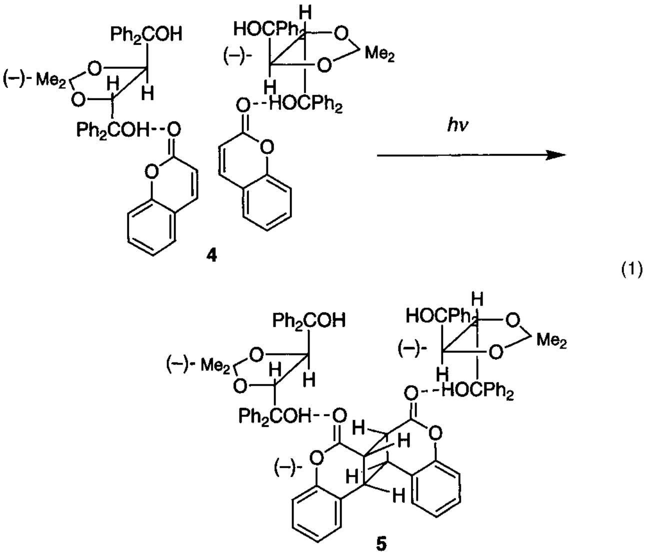




3

a: X = O
b: X = S

When a solution of a 1:1 mixture of **1a** and (−)-**2a** in a mixture of EtOAc and hexane was kept at room temperature for 3 h, a 1:1 inclusion complex (**4**) was obtained as colorless needles.[6] Irradiation of **4** in the solid state with a 400 W high-pressure Hg lamp (Pyrex filter, room temperature, 4 h) gave a 2:1 complex (**5**)[6] of (−)-**2a** with (−)-**3a** [Eq. (1)]. The crystals were still clear after photoirradiation and the reaction proceeded in a single-crystal-to-single-crystal manner throughout the reaction. The (−)-*anti*-head-to-head dimer **3a** was isolated by exchange with DMF. A 1:1 complex of (−)-**2a** with DMF was obtained as colorless needles in 99% yield after recrystallization of the 2:1 complex **5** from DMF/H_2O (5/1). Concentration of the filtrate left the optically pure (−)-*anti*-head-to-head dimer **3a**, which was isolated as colorless prisms in 89% yield. The optical purity of (−)-**3a** was determined by comparison of its $[\alpha]_D$ value to that of enantiomerically pure **3a**.[7] Optically pure (+)-**3a** was obtained when the host compound (+)-**2a** was used instead of (−)-**2a**.



(1)

This result shows that two molecules of **1a** are arranged in chirally related positions, which gives the optically active *anti*-head-to-head dimer **3a** by [2+2] photodimerization. This

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