New oxidative transformations of alkenes and alkynes under the action of diacetoxyiodobenzene

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Treatment of alkenes and alkynes with diacetoxyiodobenzene activated by mineral and organic acids predominantly results in oxidative rearrangement. 1,4-Diphenylbutadiene in MeOH gives 3,4-dimethoxy-1,4-diphenylbut-1-ene.

Key words: polyvalent iodine compounds, diacetoxyiodobenzene, alkenes, alkynes, oxidative rearrangement.

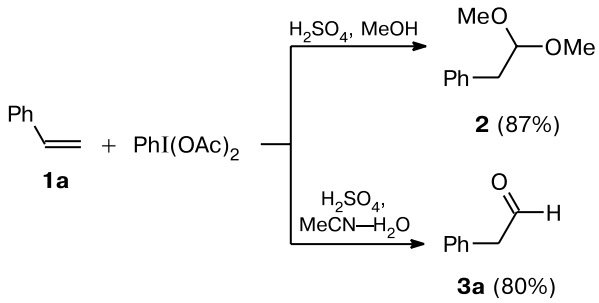
Diacetoxyiodobenzene (DIB) is one of the most accessible, stable, and popular compounds of polyvalent iodine.[1—7]. In contrast to the majority of related compounds, DIB is weakly electrophilic and does not react with most alkenes and alkynes. However, more nucleophilic unsaturated compounds such as cyclopentadiene and cycloocta-1,5-diene in boiling AcOH afford mixtures of bisacetoxylation products.[2,8] The electrophilicity of DIB can be enhanced by activators (I_2, HBF_4, Ph_4PI, Et_4NBr, Me_3SiN_3, PhSeSePh, and $LiClO_4$), which affect, in one way or another, the direction of the reaction and the nature of the final products.[9—16]

Recently,[17] we found that DIB activated by H_2SO_4 reacts with various alkenes to give rearrangement or addition products. In the present work, we performed a more detailed study of the factors affecting the reactions of DIB with alkenes in the presence of mineral or organic acids in the temperature range from −20 to 25 °C (Table 1).

The reaction of styrene (**1a**) with DIB in MeOH in the presence of H_2SO_4 was complete in 20 min to give phenylacetaldehyde dimethyl acetal (**2**) in 87% yield. The same reaction in MeCN + 50% aqueous H_2SO_4 afforded phenylacetaldehyde (**3a**) in 80% yield (Scheme 1).

The yields of products **2** and **3a** were found to depend on the reaction temperature and the isolation procedure (see Table 1, entries *1*—*8*). The best results were achieved at $T \le -20$ °C with neutralization of H_2SO_4 with 10% $NaHCO_3$ and column chromatography on Al_2O_3 (see Table 1, entry *1*). Otherwise, the yield of product **2** was 10—15% lower (see Table 1, entries *2*—*5*). According to GLC/MS data, phenylacetic acid (**4**), methyl phenylacetate **5**, and benzaldehyde (**6**) were the by-products.

Scheme 1



In addition to H_2SO_4, toluene-*p*-sulfonic acid (TsOH) and the cation-exchange resin KU-2-8 (H^+) were assayed as activators (see Table 1, entries *6*, *7*).

The use of the cation-exchange resin seems to be preferred: the yield of acetal **2** increases to 92% and the catalyst can be removed simply by filtration (see Table 1, entry *7*).

The oxidative rearrangement of α-methylstyrene (**1b**) under the action of DIB and H_2SO_4 gave ketone **3b** rather than its acetal in 20 min (Scheme 2).

Scheme 2

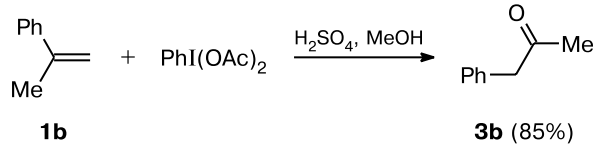


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Table 1. Oxidation of compounds **1a—c**, **13**, **14a,b**, **18**, **20**, **23**, and **26a** (1 mmol) with DIB (1.0—1.1 mmol) (*T* is the reaction temperature and *t* is the reaction time)

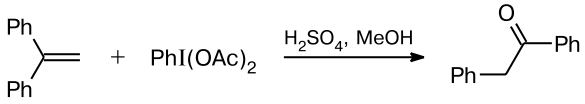
Entry	Substrate	Activator	Solvent[a]	*T*/°C	*t*/min	Product	Yield[b] (%)
1	**1a**	H_2SO_4	MeOH	−20	20	**2**	87 [c]
2	**1a**	H_2SO_4	MeOH	−20	20	**2**	69 [d]
3	**1a**	H_2SO_4	MeOH	−10	20	**2**	76 [c]
4	**1a**	H_2SO_4	MeOH	0	20	**2**	72 [c]
5	**1a**	H_2SO_4	MeOH	−20	20	**2**	70 [e]
6	**1a**	TsOH[f]	MeOH	20	120	**2**	84
7	**1a**	KU-2-8[g]	MeOH	20	720	**2**	92
8	**1a**	H_2SO_4	MeCN	−20	20	**3a**	80 [h]
9	**1b**	H_2SO_4	MeOH	−20	20	**3b**	85 [h]
10	**1b**	H_2SO_4	MeOH	−10	20	**3b**	50 [h]
11	**1c**	H_2SO_4	MeOH	−15	30	**3c**	94
12	**1c**	H_3PO_4[i]	MeCN	20	120	**3c**	90
13	**13**	H_2SO_4	MeCN	20	120	**12b**	32
14	**13**	H_2SO_4	MeOH	20	900	**12b**	24
15	**13**	H_2SO_4	AcOH	60	1200	**12b**	32
16	**14a**	H_2SO_4	MeOH	−15	140	**15a**	42 [h]
17	**14a**	H_2SO_4	MeCN	−15	140	**15a**	39 [h]
18	**14b**	H_2SO_4	MeOH	−15	140	**15b**	22 [h]
19	**18**	H_2SO_4	MeOH	20	120	**19**	59
20	**20**	H_2SO_4	MeOH	20	120	**21**	90
21	**20**	H_3PO_4[i]	MeCN	40	120	**21**	90
22[j]	**23**	H_2SO_4	MeOH	20	240	**24**	52
23 [k]	**23**	H_2SO_4	MeOH	20	300	**24**	10
						25	32
24	**26a**	H_2SO_4	MeOH	20	4320	**4**	53
25	**26a**	KU-2-8[l]	MeOH	20	4320	**4**	50

[a] 3—4 mL of solvent per mmol of the substrate.
[b] The yields of the isolated products.
[c] With 10% $NaHCO_3$; column chromatography on Al_2O_3.
[d] With 10% $NaHCO_3$; column chromatography on SiO_2.
[e] Column chromatography on Al_2O_3.
[f] 2.0 mmol.
[g] 120 mg.
[h] Isolated as 2,4-dinitrophenylhydrazone.
[i] Used as a 50% solution in MeOH (0.3 mL).
[j] With 1.05 equiv. of DIB.
[k] With 2.1 equiv. of DIB.
[l] 360 mg.

The yield of compound **3b** depends on the reaction temperature, being high (85%) at −20 °C and <50% at −10 °C (see Table 1, entries *9*, *10*). In this case, benzaldehyde (**6**), benzoic acid (**7**), and acyloin were identified as the by-products (GLC/MS data).

The reaction of 1,1-diphenylethene (**1c**) with DIB in MeOH in the presence of H_2SO_4 (−15 °C, 30 min) proceeds similarly (Scheme 3) to give deoxybenzoin (**3c**) in 94% yield as the result of oxidative rearrangement (see Table 1, entry *11*). However, a temperature jump to 0 °C did not reduce the yield of ketone **3c**. Good yield (90%) was also attained with H_3PO_4 (2 h, 20 °C) (see Table 1, entry *12*).

Scheme 3



1c **3c** (94%)

Based on the GLC/MS data, one can assume that transformations of alkenes **1a—c** proceed in two pathways (Scheme 4). The main pathway is the oxidative rearrangement yielding carbonyl compounds **3a—c** and trace amounts of related products **7**, **8a—c**, and **9a—c**; the side pathway involves oxidation into compounds **10a,b—12a,b**.

Nonterminal alkenes behave in a different way. For instance, the oxidation of (*E*)-stilbene (**13**) with the DIB—H_2SO_4 system was nonselective and gave a mixture of compounds **3c**, **8c**, **9c**, and **10b—12b** (see Table 1, entries *13—15*). This fact is explained by the poor solubility and low nucleophilicity of (*E*)-stilbene.[18,19] Interestingly, the reaction of well soluble (*Z*)-stilbene with a complex of iodosylbenzene with $BF_3 \cdot Et_2O$ in CH_2Cl_2 at −10 °C affords diphenylacetaldehyde (**10b**) in 80% yield as a result of oxidative rearrangement.[20]

Cyclohexenes **14a,b** react with DIB to give mixtures of oxidative rearrangement and addition products (Scheme 5). In the case of cyclohexene (**14a**), rearrangement is a main reaction pathway; the yield of cyclopentanecarbaldehyde (**15a**) reaches 42% (see Table 1, entry *16*). 1-Methylcyclohexene (**14b**) was converted into acetylcyclopentane (**15b**) in a noticeably lower yield of 22% (see Table 1, entry *18*). It should be noted that the ring contraction of cyclohexene (**14a**) was observed earlier[20] with the use of related reagents in CH_2Cl_2.

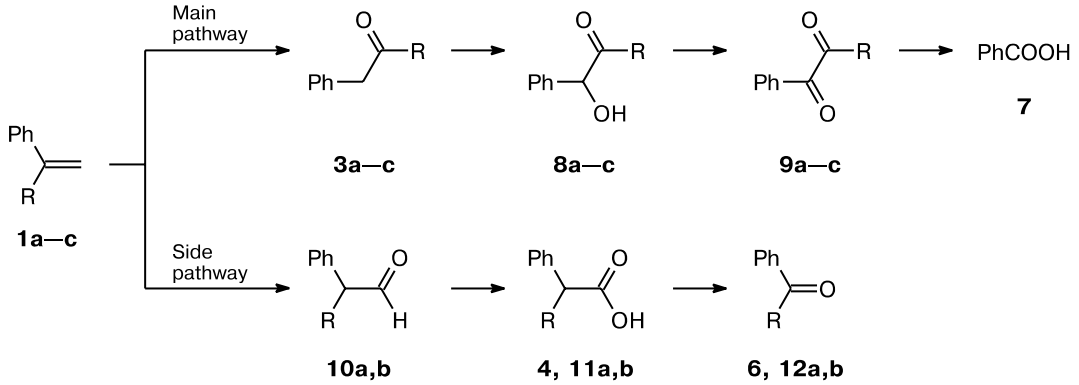
Thus, in contrast to alkenes **1a—c**, oxidative rearrangement of cycloalkenes in the reaction with DIB activated by sulfuric acid is not the main pathway. This agrees well with data on the migration ability of an aryl radical compared to alkyl.[21]

Earlier,[22—24] some alkenes were found to undergo oxidative rearrangement under the action of PhIO in the presence of acids (CF_3SO_3H, FSO_3H, and $BF_3 \cdot Et_2O$) and PhI(OH)OTs (Koser´s reagent) to give products in 18—81% yields.

In our case, the processes appear to be similar. For instance, the reaction of DIB with sulfuric acid gives polyvalent iodine derivatives **A—D** *in situ*, which are more electrophilic than the starting carboxylate (Scheme 6).

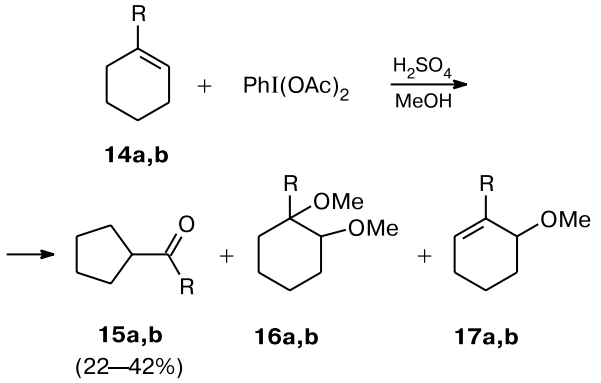
The following mechanism can be proposed for the oxidative rearrangement of alkenes **1a—c** under the action of reagent **A** (Scheme 7).

Scheme 4



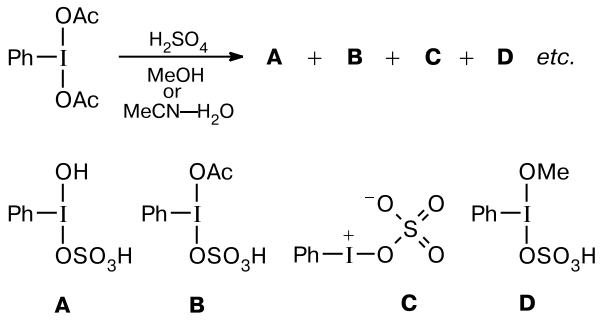
R = H (**1a**, **3a**, **8a**, **9a**, **4**, **6**), Me (**1b**, **3b**, **8b**, **9b**, **10a**, **11a**, **12a**), Ph (**1c**, **3c**, **8c**, **9c**, **10b**, **11b**, **12b**)

Scheme 5

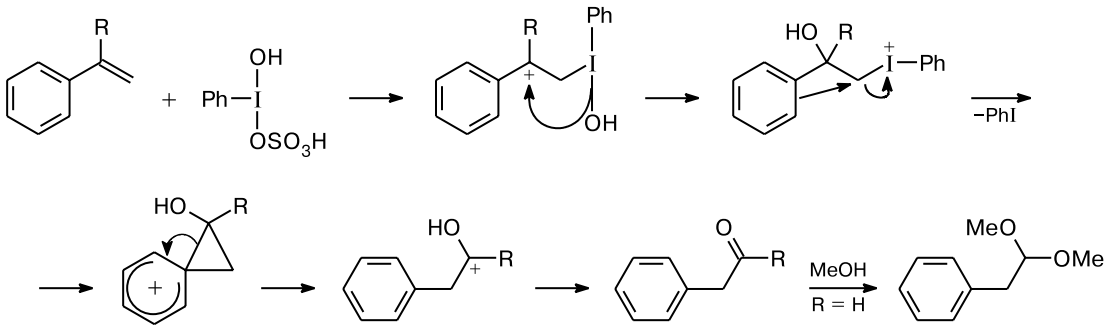


R = H (**a**), Me (**b**)

Scheme 6



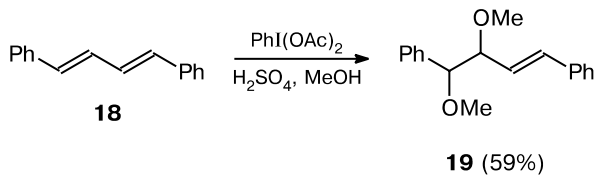
Scheme 7



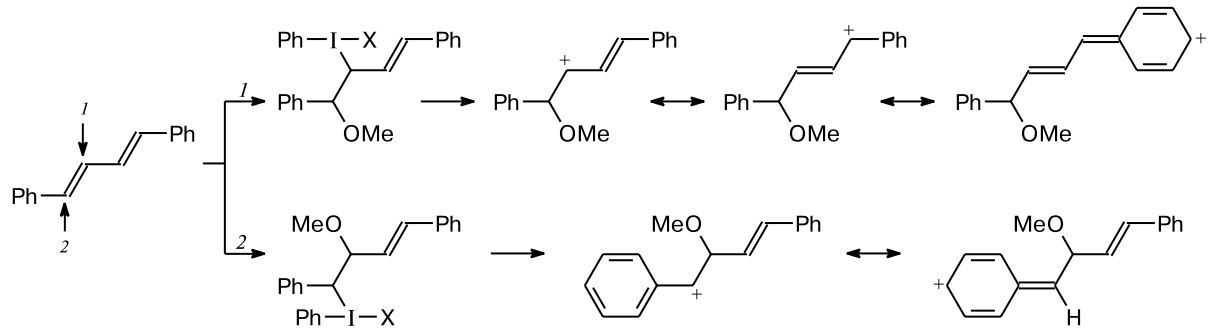
1,4-Diphenylbutadiene (**18**), a representative of conjugated dienes, in the reaction with DIB yielded no oxidative rearrangement products at all. In this case, only dimethoxy derivative **19** was obtained (Scheme 8) in 59% yield (see Table 1, entry *19*).

Apparently, the conjugated structure of the butadiene prevents rearrangement. Stabilization of the carbocation is due to conjugation with either the aromatic ring or the

Scheme 8



Scheme 9

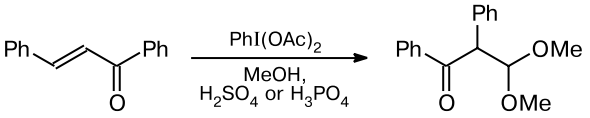


C=C bond (Scheme 9), irrespective of the way in which the polyvalent iodine derivative adds to the double bond.

Previously,[25] the reactions of conjugated dienes with related reagents mainly afforded 1,4-adducts in low yields (12—23%).

The reaction of chalcone (**20**) with DIB under different conditions (see Table 1, entries *20*, *21*) smoothly gave oxo acetal **21** as the result of oxidative rearrangement (Scheme 10). Similar results were obtained earlier[19,26,27] with related reagents; however, our procedure is more convenient and provides higher yields.

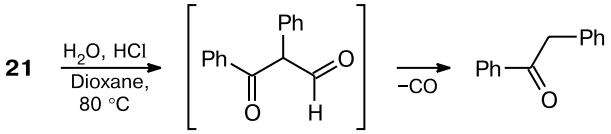
Scheme 10



20 **21** (90%)

At higher reaction temperatures, the reaction mixture contains, in addition to the target dicarbonyl compound, overoxidation and decarbonylation products. Decarbonylation occurred in an attempt to hydrolyze acetal **21** into dicarbonyl compound **22** by heating in aqueous dioxane in the presence of HCl (Scheme 11).

Scheme 11



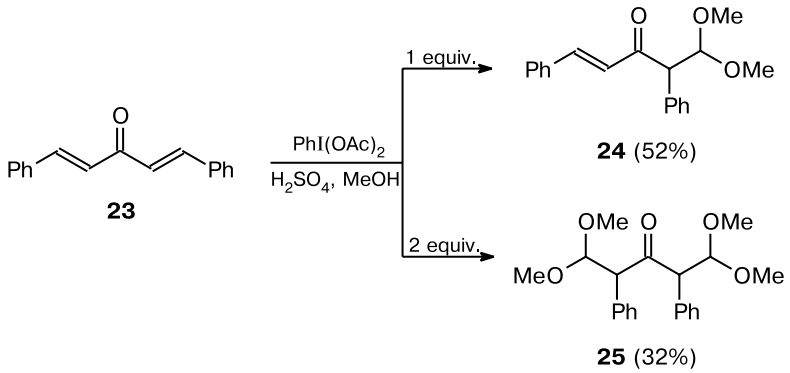
22 **3c** (~100%)

Dibenzylideneacetone (**23**) selectively reacts with the first equivalent of DIB and only then with the second one (see Table 1, entries *22*, *23*). Thus, by varying the amount of the reagent, one can obtain either acetal **24** or diacetal **25** (~1 : 1 mixture of diastereomers) (Scheme 12).

Reactions of alkynes with Koser´s reagent and phenyliodosyl trifluoroacetate[17,20] represent rare examples of functionalization of this kind. We studied the oxidation of phenylacetylene (**26a**), phenyl(propyl)acetylene (**26b**), and diphenylacetylene (tolan) (**26c**) with DIB.

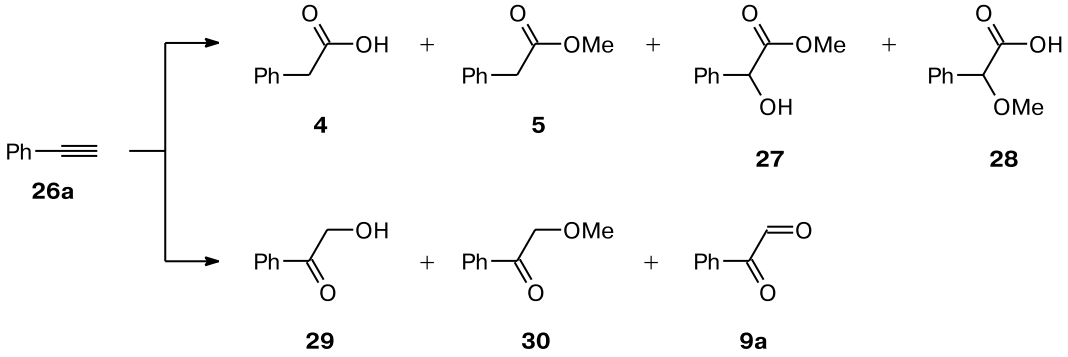
The oxidation of phenylacetylene (**26a**) with DIB in the presence of H_2SO_4 or the cation-exchange resin KU-2-8 (H^+) at ~20 °C was complete in 72 h to give a

Scheme 12



23 **24** (52%) **25** (32%)

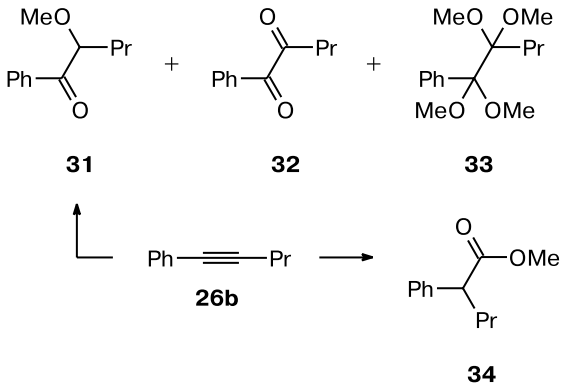
Scheme 13



mixture of compounds **4**, **5**, and **27**—**30** (Scheme 13). Acid **4** was isolated in 53% yield (see Table 1, entries *24*, *25*).

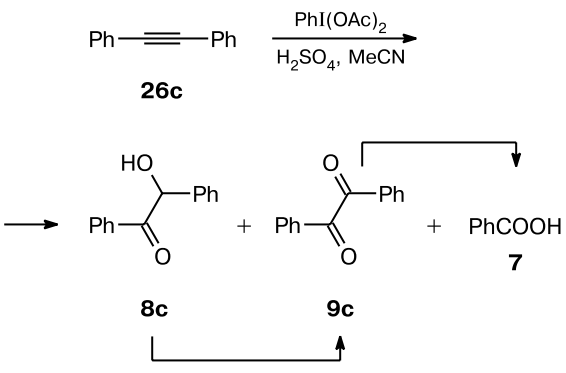
The oxidation of phenyl(propyl)acetylene (**26b**) with this reagent in boiling MeOH occurred in a more complex way yielding an inseparable mixture of compounds **31**—**34** (Scheme 14).

Scheme 14



The oxidation of tolan (**26c**) with DIB—H_2SO_4 in boiling MeOH proceeded very slowly: after 42 h, the degree of conversion of the starting alkyne was only 40%; the major products were benzoic acid (**7**), benzoin (**8c**), and benzil (**9c**) (Scheme 15). In MeCN with a double excess of DIB at 20 °C, the conversion of tolan (**26c**) was nearly 80%, the qualitative composition of the products being the same. The oxidation of tolan (**26c**) into benzoin (**8c**) is a slower step than the oxidation of ketone **8c** into benzil (**9c**) and benzoic acid (**7**).

Scheme 15



Hence, the results obtained extend the area of application of DIB, an accessible polyvalent iodine derivative, in reactions with alkenes and alkynes. New activators of DIB proposed by us favor high-yielding oxidative rearrangement.

Experimental

IR spectra were recorded on a UR-20 spectrophotometer (thin film or KBr pellets). ^{1}H and ^{13}C NMR spectra were recorded on Bruker AC-200 (200 and 50 MHz), AMX-400 (400 MHz), and DRX 500 spectrometers (500 and 125 MHz, respectively) in $CDCl_3$, acetone-d_6, and CCl_4 with Me_4Si as the internal standard. GLC/MS spectra were recorded on a Hewlett Packard 5890/II gas chromatograph with an HP MSD 5971 quadrupole mass spectrometer as a detector (EI, 70 eV); an HP-5 quartz column was used (30 m, copolymer of diphenyl- (5%) and dimethylsiloxane (95%); inner diameter 0.25 mm, thickness of the stationary phase film 0.25 μm). Mass spectra (EI, 70 eV) were recorded on a Finnigan MAT 8200 spectrometer. Elemental analysis was performed with an E.A. 1106 Carlo Erba CHNS-O analyzer. Melting points were measured on a Boetius instrument. Silica gel L 40/100 μm (Chemapol) and alumina (Brockmann activity II, neutral, pH of its aqueous 10% suspension is 9—10) (Reanal) were used for column chromatography. TLC was carried out on Sorbfil (PTSKh-AF-A-UF, PTSKh-P-A-UF) and Silufol UV-254 plates (Kavalier).

Styrene (**1a**), methylstyrene (**1b**), diphenylethene (**1c**), and phenylacetylene (**26a**) were distilled immediately before use. Commercial stilbene (**13**) (m.p. 125 °C), tolan (**26c**) (m.p. 62 °C), toluene-*p*-sulfonic acid monohydrate (m.p. 103—106 °C), KU-2-8 (H^+), 96% H_2SO_4, and 85% H_3PO_4 (reagent grade) were used. Acetic acid (reagent grade) was employed without additional purification; freshly distilled MeCN

and MeOH were used. Cyclohexene (**14a**), 1-methylcyclohexene (**14b**), *trans*,*trans*-1,4-diphenylbuta-1,3-diene (**18**), and 1-phenylpent-1-yne (**26b**) were from Aldrich. Chalcone (**20**) and dibenzylideneacetone (**23**) were prepared by condensation of benzaldehyde with the corresponding ketones.[28]

Synthesis of DIB. A 2-L flask fitted with a mechanical stirrer, a reflux condenser, and a thermometer was immersed in a water bath and charged with Ac_2O (610 mL) and 30% H_2O_2 (140 mL), which were carefully mixed. The bath temperature was elevated to 40 °C and the reaction mixture was vigorously stirred at this temperature for 4 h. Iodobenzene (100 g) was added and stirring was continued for an additional 1.5 h. The reaction mixture was left at ~20 °C for ~12 h and then diluted with a double volume of water with ice. The precipitate that formed was filtered off and dried in air. Recrystallization from a minimum amount of AcOH gave DIB as lustrous crystals. The yield of DIB was 158 g (83%), m.p. 157—159 °C (*cf.* Ref. 29: m.p. 158—159 °C).

Solution of 2,4-dinitrophenylhydrazine. 2,4-Dinitrophenylhydrazine (3.0 g) was dissolved in 15 mL of conc. H_2SO_4. The solution was added to a stirred mixture of water (20 mL) and 95% EtOH (70 mL). The resulting solution was thoroughly stirred and filtered.[30]

Oxidation of alkenes 1a—c, 13, 14a,b, and 18 with diacetoxyiodobenzene in acidic media (general procedure). A solution of an alkene (2.0 mmol) in MeOH (6—8 mL) was precooled to the temperature specified in Table 1 and DIB (2.1 mmol) was added. A 50% solution of H_2SO_4 in MeOH (0.45—0.5 mL) was added dropwise with stirring. The reaction mixture was kept at this temperature for the time specified in Table 1 and poured into 10% $NaHCO_3$ (30 mL). The product was extracted with ether (2×30 mL). The extract was washed with water (2×30 mL) and brine (30 mL) and dried with Na_2SO_4. After the ether was removed, the residue was dissolved in benzene and chromatographed on silica gel. Iodobenzene (b.p. 182—185 °C) was eluted with hexane (*cf.* Ref. 28: b.p. 184—186 °C). Further elution with hexane—benzene (4 : 1) gave products **2**, **3c**, **12b**, and **19**. Products **3b** and **15a,b** were isolated as hydrazones by adding a solution of 2,4-dinitrophenylhydrazine (15—18 mL). The crystals that formed were filtered off, washed with ethanol, dried, and recrystallized from the corresponding solvents.

1,1-Dimethoxy-2-phenylethane (2). Oil, b.p. 217—220 °C (750 Torr) (*cf.* Ref. 18: b.p. 219—221 °C (754 Torr)). ^{1}H NMR (200 MHz, $CDCl_3$), δ: 2.78 (d, 2 H, CH_2, J = 9.6 Hz); 3.22 (s, 6 H, OMe); 4.41 (t, 1 H, CH, J = 5.6 Hz, J = 11.2 Hz); 6.99—7.21 (m, 5 H, H arom.). ^{13}C NMR (50 MHz, $CDCl_3$), δ: 35.10 (CH_2), 48.02 (OMe), 100.03 (CH), 121.68, 123.62, 124.88, 132.63 (C arom.).

Phenylacetaldehyde (3a). Diacetoxyiodobenzene (676 mg, 2.1 mmol) was added to a cooled (−20 °C) solution of styrene (**1a**) (204 mg, 2.0 mmol) in 6 mL of MeCN. Then 50% H_2SO_4 (0.45 mL) was added dropwise with stirring. The reaction mixture was kept at this temperature for 20 min and then a solution of 2,4-dinitrophenylhydrazine (18 mL) was added. The crystals that formed were filtered off, washed with cold EtOH, dried, and recrystallized from EtOH to give phenylacetaldehyde 2,4-dinitrophenylhydrazone (192 mg, 80%), m.p. 120—121 °C (*cf.* Ref. 28: m.p. 121 °C).

1-Phenylpropan-2-one (3b) was isolated as 2,4-dinitrophenylhydrazone, m.p. 157—158 °C (*cf.* Ref. 28: m.p. 156 °C).

Deoxybenzoin (3c). M.p. 59—60 °C (*cf.* Ref. 28: m.p. 60 °C). ^{1}H NMR (200 MHz, $CDCl_3$), δ: 4.24 (s, 2 H, CH_2); 7.27—7.28 (m, 5 H, H arom.); 7.42—7.45 (m, 3 H, H arom.); 8.00 (dd, 2 H, H arom., J = 1.6 Hz, J = 7.0 Hz). ^{13}C NMR (50 MHz, $CDCl_3$), δ: 45.26 (CH_2), 126.63, 128.34, 128.44, 129.04, 129.22, 132.66, 134.43, 126.60 (C arom.), 196.32 (CO).

Benzophenone (12b) was isolated as 2,4-dinitrophenylhydrazone, m.p. 236—238 °C (*cf.* Ref. 28: m.p. 236 °C).

Cyclopentanecarbaldehyde (15a) was isolated as 2,4-dinitrophenylhydrazone, m.p. 154—156 °C (*cf.* Ref. 31: m.p. 156—157 °C).

Acetylcyclopentane (15b) was isolated as 2,4-dinitrophenylhydrazone, m.p. 115—116 °C (EtOH). Found (%): C, 53.15; H, 5.76; N, 20.01. $C_{13}H_{16}N_4O_4$. Calculated (%): C, 53.42; H, 5.52; N, 19.17.

3,4-Dimethoxy-1,4-diphenylbut-1-ene (19). M.p. 48—50 °C (MeOH—H_2O). Found (%): C, 80.45; H, 7.50. $C_{18}H_{20}O_2$. Calculated (%): C, 80.56; H, 7.51. IR (2% solution in CCl_4), ν/cm^{-1}: 1108 (C—O—C), 1619 (C=C). ^{1}H NMR (400 MHz, CCl_4—$CDCl_3$ (3 : 1)), δ: 3.24, 3.26 (both s, 3 H each, OMe); 3.78 (dd, 1 H, =CHC<u>H</u>(OMe), J = 4.9 Hz, J = 7.7 Hz); 4.24 (d, 1 H, PhC<u>H</u>(OMe), J = 4.9 Hz); 6.15 (dd, 1 H, PhCH=C<u>H</u>, J = 7.7 Hz, J = 16.1 Hz); 6.40 (d, 1 H, PhC<u>H</u>=CH, J = 16.1 Hz); 7.20—7.37 (m, 10 H, H arom.). ^{13}C NMR (100 MHz, CCl_4—$CDCl_3$ (3 : 1)), δ: 56.75 (OMe), 57.03 (OMe), 85.98 (<u>C</u>HOMe), 86.43 (<u>C</u>HOMe), 126.31 (PhCH=<u>C</u>H), 127.53 (Ph<u>C</u>H=CH), 126.55, 127.64, 127.77, 127.96, 128.32, 128.44, 141.01, 143.80 (C arom.).

3,3-Dimethoxy-1,2-diphenylpropanone (21). A 50% solution of H_2SO_4 (0.3 mL) in MeOH was added dropwise to a stirred solution of chalcone (**20**) (244 mg, 1.08 mmol) and DIB (372 mg, 1.15 mmol) in 5.0 mL of MeOH. The reaction mixture was kept at ~20 °C for 2.0 h and poured into 30 mL of water. The product was extracted with ether (2×30 mL). The extract was washed with brine (30 mL), dried with Na_2SO_4, and concentrated. Hexane (5.0 mL) was added to the residue and the crystals that formed were filtered off and washed again with hexane (2×3 mL) to give compound **21** as colorless crystals (262 mg, 90%), m.p. 95—96 °C (*cf.* Ref. 18: m.p. 94 °C). ^{1}H NMR (400 MHz, $CDCl_3$), δ: 3.20, 3.44 (both s, 3 H each, OMe); 4.83 (d, 1 H, CH, J = 8.5 Hz); 5.06 (d, 1 H, C<u>H</u>$(OMe)_2$, J = 8.5 Hz); 7.27—7.28 (m, 1 H, H arom.); 7.29—7.38 (m, 2 H, H arom.); 7.40—7.41 (m, 4 H, H arom.); 7.41—7.42 (m, 1 H, H arom.); 7.95 (d, 2 H, H arom., J = 7.3 Hz). ^{13}C NMR (100 MHz, $CDCl_3$), δ: 54.16 (OMe), 56.09 (OMe), 57.01 (CH), 106.94 ($CH(OMe)_2$), 127.43, 128.42, 128.56, 128.68, 129.04, 129.08, 132.68, 135.03 (C arom.), 196.91 (CO).

Oxidation of dibenzylideneacetone (23). Procedure *A*. A 50% solution of H_2SO_4 (0.7 mL) in MeOH was added dropwise to a stirred solution of dibenzylideneacetone (**23**) (585 mg, 2.5 mmol) and DIB (837 mg, 2.6 mmol) in 10 mL of MeOH. The reaction mixture was kept at ~20 °C for 4 h and poured into water (30 mL). The product was extracted with ether (2×30 mL). The extract was washed with 10% $NaHCO_3$ (30 mL) and brine (30 mL), dried with Na_2SO_4, and concentrated. The residue was chromatographed on silica gel. Iodobenzene (472 mg, 89%) was isolated by elution in hexane. Further elution in hexane—AcOEt (8 : 1) gave (*E*)-5,5-dimethoxy-1,4-diphenylpent-1-en-3-one (**24**) (384 mg, 52%), m.p. 90—91 °C (hexane). Found (%): C, 77.17; H, 6.73. $C_{19}H_{20}O_3$. Calculated (%): C, 77.00; H, 6.80.

IR (KBr), ν/cm^{-1}: 1094 (C—O), 1684 (C=O). ^{1}H NMR (200 MHz, CCl_4—$CDCl_3$ (3 : 1)), δ: 3.08, 3.36 (both s, 3 H each, OMe); 4.17 (d, 1 H, PhC<u>H</u>, J = 8.7 Hz); 4.92 (d, 1 H, C<u>H</u>$(OMe)_2$, J = 7.7 Hz); 6.61 (d, 1 H, PhCH=C<u>H</u>, J = 16.0 Hz); 7.46 (d, 1 H, PhC<u>H</u>=CH, J = 16.0 Hz); 7.15—7.30 (m, 10 H, H arom.).

Procedure *B*. A 50% solution of H_2SO_4 (0.55 mL) in MeOH was added dropwise to a stirred solution of dibenzylideneacetone (**23**) (234 mg, 1.0 mmol) and DIB (680 mg, 2.1 mmol) in 6.0 mL of MeOH. The reaction mixture was kept at ~20 °C for 5.0 h and poured into water (30 mL). The product was extracted with ether (2×30 mL). The extract was washed with 10% $NaHCO_3$ (30 mL) and brine (30 mL), dried with Na_2SO_4, and concentrated. The residue was chromatographed on silica gel. Iodobenzene (411 mg, 96%) was isolated by elution with hexane. Further elution with hexane—benzene (3 : 1) gave compound **24** (30 mg, 10%), m.p. 90—91 °C. Elution with hexane—benzene (1 : 2) afforded a fraction (115 mg, 32%) which was rechromatographed to yield equal amounts of diastereomers **25´** and **25″**.

1,1,5,5-Tetramethoxy-2,4-diphenylpentan-3-one (25´). Oil. IR (oil), ν/cm^{-1}: 1108 (C—O), 1696 (C=O). ^{1}H NMR (400 MHz, CCl_4—$CDCl_3$ (3 : 1)), δ: 3.04, 3.08 (both s, 6 H each, OMe); 3.96, 4.79 (both d, 2 H each, CH, J = 8.3 Hz); 7.20—7.28 (m, 10 H, H arom.). ^{13}C NMR (100 MHz, CCl_4—$CDCl_3$ (3 : 1)), δ: 53.48 (OMe), 54.74 (OMe), 61.50 (CH), 105.03 (<u>C</u>H$(OMe)_2$), 127.40, 128.23, 129.50, 134.21 (C arom.), 203.81 (CO). High-resolution MS, found: m/z 358.17901 $[M]^+$. $C_{21}H_{26}O_5$. Calculated: M = 358.17801. MS (EI), m/z (I_{rel} (%)): 358 $[M]^+$ (<1), 252 $[M - C_4H_{10}O_3]^+$ (3), 193 $[M - C_6H_{13}O_5]^+$ (5), 151 $[C_9H_{11}O_2]^+$ (6), 134 $[C_8H_6O_2]^+$ (15), 91 $[C_7H_7]^+$ (16), 77 $[C_6H_5]^+$ (5), 75 $[C_3H_7O_2]^+$ (100), 47 $[CH_2O_2]^+$ (11).

1,1,5,5-Tetramethoxy-2,4-diphenylpentan-3-one (25″). Oil. IR (oil), ν/cm^{-1}: 1108 (C—O), 1696 (C=O). ^{1}H NMR (400 MHz, CCl_4—$CDCl_3$ (3 : 1)), δ: 3.08, 3.40 (both s, 6 H each, OMe); 4.02, 4.82 (both d, 2 H each, CH, J = 8.3 Hz); 6.90—7.09 (m, 10 H, H arom.). ^{13}C NMR (100 MHz, CCl_4—$CDCl_3$ (3 : 1)), δ: 52.98 (OMe), 55.04 (OMe), 62.22 (CH), 105.25 (<u>C</u>H$(OMe)_2$), 127.05, 128.36, 129.45, 134.27 (C arom.), 204.28 (CO). High-resolution MS, found: m/z 358.17901 $[M]^+$. $C_{21}H_{26}O_5$. Calculated: M = 358.17801. MS (EI), m/z (I_{rel} (%)): 358 $[M]^+$ (<1), 252 $[M - C_4H_{10}O_3]^+$ (3), 193 $[M - C_6H_{13}O_5]^+$ (5), 151 $[C_9H_{11}O_2]^+$ (6), 134 $[C_8H_6O_2]^+$ (15), 91 $[C_7H_7]^+$ (16), 77 $[C_6H_5]^+$ (5), 75 $[C_3H_7O_2]^+$ (100), 47 $[CH_2O_2]^+$ (11).

Oxidation of phenylacetylene (26a). A 50% solution of H_2SO_4 (0.3 mL) in MeOH was added dropwise to a stirred solution of alkyne **26a** (162 mg, 1.5 mmol) and DIB (511 mg, 1.5 mmol) in 5.0 mL of MeOH. The reaction mixture was kept at 20 °C for 72 h and then 10% NaOH (10 mL) was added. The resulting mixture was heated at 100 °C for 10 min and poured into water (30 mL). The aqueous layer was washed with ether (2×30 mL) and acidified with HCl. The product was extracted with AcOEt. The solvent was removed to give phenylacetic acid (**4**) (108 mg, 53%), m.p. 75—76 °C (hexane) (*cf.* Ref. 28: m.p. 77 °C).

Oxidation of phenyl(propyl)acetylene (26b). A 50% solution of H_2SO_4 (0.25 mL) in MeOH was added dropwise to a stirred solution of alkyne **26b** (144 mg, 1.0 mmol) and DIB (322 mg, 1.0 mmol) in 5 mL of MeOH. The reaction mixture was heated at 64 °C for 17 h, cooled, and poured into water (30 mL). The product was extracted with AcOEt (2×30 mL). The extract was washed with brine, dried with Na_2SO_4, and concentrated. The residue was analyzed by GC-MS in the following temperature regime: 50 °C (2 min), 50—280 °C (10 deg. min^{-1}), and 280 °C (5 min). The mixture contained the starting alkyne **26b** (9%, t_r 10.92 min), 2-methoxy-1-phenylpentan-1-one (**31**) (30%, t_r 14.36 min), 1-phenylpentane-1,2-dione (**32**) (20%, t_r 13.50 min), (1,1,2,2-tetramethoxypentyl)benzene (**33**) (5%, t_r 15.16 min), and methyl 2-phenylpentanoate (**34**) (10.5%, t_r 12.81 min) as the rearrangement product.

Oxidation of tolan (26c). Aqueous 50% H_2SO_4 (0.55 mL) was added dropwise to a stirred solution of alkyne **26c** (178 mg, 1.0 mmol) and DIB (644 mg, 2.0 mmol) in 5.0 mL of MeCN. The reaction mixture was kept at 20 °C for 72 h and poured into water (30 mL). The product was extracted with AcOEt (2×30 mL). The extract was washed with brine, dried with Na_2SO_4, and concentrated. The residue was analyzed by GC-MS in the following temperature regime: 50 °C (2 min), 50—280 °C (10 deg. min^{-1}), and 280 °C (5 min). The identified products were benzoic acid (**7**) (58%, t_r 10.11 min), benzoin (**8c**) (13%, t_r 16.44 min), and benzil (**9c**) (25%, t_r 18.04 min).

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