NOTES Bull. Chem. Soc. Jpn., 64, 1419—1421 (1991)

Reactions of 1,1-Diphenyl-2-methylpropene Cation Radicals with Methanol. Ketone Formation Involving Carbocation Rearrangement

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(Received November 26, 1990)

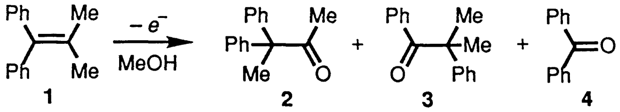
Synopsis. Anodic oxidation of 1,1-diphenyl-2-methylpropene (**1**) in an acetonitrile–methanol mixture under argon gave 3,3-diphenyl-2-butanone (**2**) in high yield together with small amounts of 1,2-diphenyl-2-methyl-1-propanone (**3**) and benzophenone (**4**). Similar anodic oxidation of **1** in the presence of oxygen was also carried out, and the mechanisms for the novel ketone forming reactions are discussed.

Photoinduced electron transfer generating cation radicals has gathered sustained interest during the last decade.[1] Among the cation radicals which have so far been studied, olefin cation radicals have attracted continuing interest. Reactions of the olefin cation radicals with nucleophiles such as methanol have been studied by electrochemical generation of the cation radicals as well as by photoinduced electron transfer. For example, it is well-known that the photochemically generated cation radicals of aromatic olefins react with methanol to give anti-Markovnikoff adducts.[2] In contrast, electrochemical oxidation of olefins in methanol usually gives dimethoxylated monomeric or dimeric products.[3–6]

During the course of our investigation of photosensitized oxygenation of 1,1-diphenyl-2-methylpropene (**1**) in acetonitrile,[7] we have found that electrochemical oxidation of **1** in the presence of methanol gives almost exclusively a skeletally rearranged product, 3,3-diphenyl-2-butanone (**2**). This is a novel example demonstrating that the electrochemically generated aromatic olefin cation radical reacts with methanol to give the skeletally rearranged carbonyl compounds instead of the usually observed dimethoxylation products, although similar skeletal rearrangement was observed in photosensitized electron transfer reaction of styrylcyclopropane in methanol.[8] We have also carried out electrochemical oxidation of **1** in the presence of oxygen in acetonitrile/methanol mixed solvents in order to compare the reactivities of the olefin cation radical toward oxygen and methanol.

Results and Discussion

Controlled-potential electrolysis of **1** (45.4 mg, 0.22 mmol) in acetonitrile/methanol (4:1) under argon at 1.6 V/SCE for 3.2 h gave **2** in 79% yield together with small amounts of 1,2-diphenyl-2-methyl-1-propanone (**3**, 4%) and benzophenone (**4**, 4%). The yields of the products were monitored as a function of the electricity passed, and are shown in Fig. 1. The results show that the reaction involves two one-electron oxidation processes as shown in Scheme 2. Thus, electrochemical oxidation of **1** generates the cation radical of **1**, $1^{+\cdot}$, which is captured by methanol to afford a β-alkoxy radical, **5**. Radical **5** is further oxidized electrochemically to produce a carbocation **6**. Rapid 1,2-migration of a methyl group followed by addition of methanol gives an acetal, **7**, which will be hydrolyzed



Scheme 1.

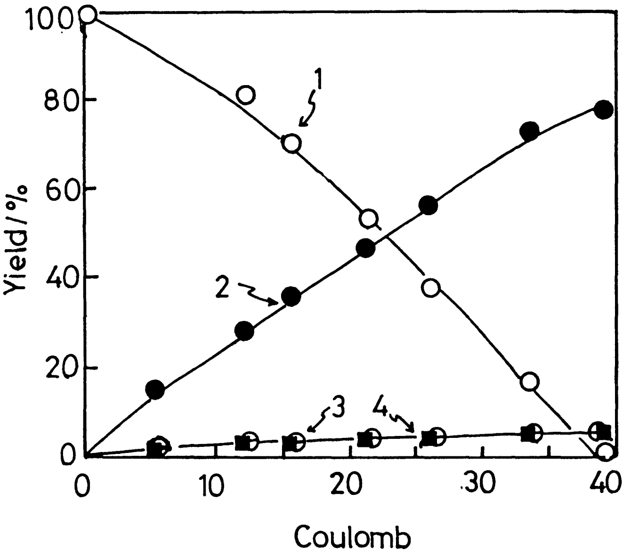
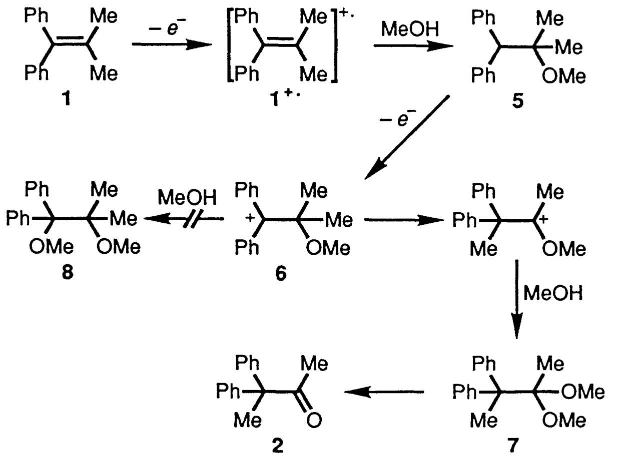


Fig. 1. Correlations of product yields with the electricity passed on electrochemical oxidation of **1** in CH_3CN/CH_3OH under argon.



Scheme 2.

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during work-up to afford **2**. Attempts to isolate the acetal were unsuccessful, although similar conversion of an acetal was observed in 9,10-dicyanoanthracene-sensitized electron-transfer reactions of styrylcyclopropane in methanol.[8)]

The mechanism shown in Scheme 2 is supported by coulometric studies, which indicated that the electricity of 2 F mol^{-1} was required for 99% consumption of **1**. The formation of **3** can be similarly explained by 1,2-migration of a phenyl group in the carbocation formed by addition of methanol to **1**$^{+\cdot}$ at the phenylated carbon. Benzophenone **4** may be afforded by the reaction of **1**$^{+\cdot}$ with residual oxygen (vide infra).[9)]

In order to get further insight into the reactivity of **1**$^{+\cdot}$, we have also carried out electrochemical oxidation of **1** in the presence of oxygen in acetonitrile/methanol. Thus, as in the case under argon, **1** (45.1 mg, 0.22 mmol) was oxidized at 1.6 V/SCE for 3.7 h in acetonitrile/methanol under an oxygen stream to give **2**, **3**, and **4** in 67, 6, and 22% yields, respectively. A plot of the yields of the products as a function of the electricity passed (Fig. 2) indicates that the presence of oxygen significantly decreases the yield of **2** but enhances that of **4**, suggesting that **1**$^{+\cdot}$ reacts competitively with methanol and oxygen. The mechanism for formation of **4** was previously explained in terms of the decomposition of a dioxetane afforded by a reaction of **1**$^{+\cdot}$ with molecular oxygen followed by the reduction by the electrode and/or **1** (ECbE mechanism).[9)] The decrease of the total current (10%) passed in the presence of oxygen is not inconsistent with the ECbE mechanism for the formation of **4**.

The above result that the skeletal rearrangement product **2** is formed in a good yield is in contrast with electrochemical oxidation of olefins usually giving dimethoxylation products.[3–6)] The formation of **2** in high yield and the complete absence of dimethoxylated products in **1** indicate that **1**$^{+\cdot}$ is reluctant to undergoing self-dimerization or addition to **1**, and that the resulting **5** does not dimerize but is rapidly oxidized at the electrode to give carbocation **6**. Rapid rearrangement of **6** followed by the addition of methanol prevents 1,2-addition of methanol.

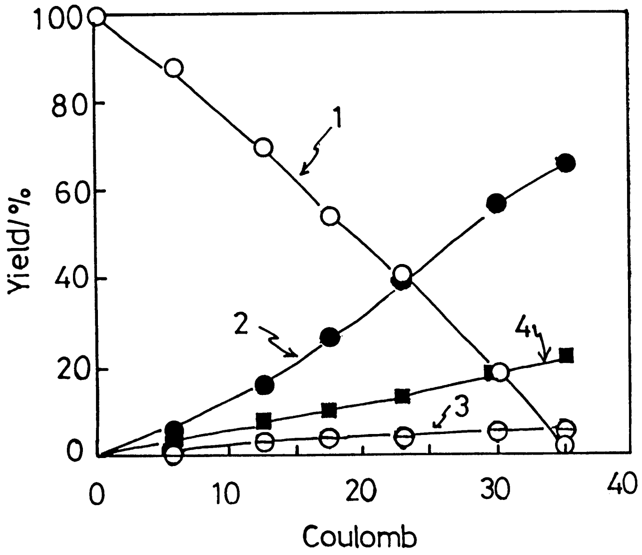

Fig. 2. Correlations of product yields with the electricity passed on electrochemical oxidation of **1** in CH_3CN/CH_3OH in the presence of oxygen.

The dominant formation of **2** over **3** shows that the addition of methanol to **1**$^{+\cdot}$ takes place preferentially at the ethenyl carbon with the methyl groups. It is of particular interest to point out that the observed orientation is seemingly contradicting to that expected from the distribution of the spin density and positive charge in **1**$^{+\cdot}$; recent ESR[10)] and CIDNP[11)] studies indicate that the spin density is higher at the methylated carbon than at the phenylated one, and that the latter is more positively charged than the former. Therefore, assuming that steric effects by phenyl and methyl groups are similar at each olefinic carbon, the present findings suggest that the regiochemistry of addition of nucleophiles such as methanol to olefin cation radicals is not governed by the distribution of positive charge on the ethenyl carbons but by the stability of the resulting free radicals; **5** is more stable than the other species $\cdot CMe_2CPh_2OMe$. This trend is parallel to the orientation often observed in the addition of atoms or free radicals and electrophiles to olefins giving free radicals and carbocations, respectively.

Once **6** is produced from **5**, only a methyl group can migrate to give the final product. This situation is consistent with the result of pinacol rearrangement of a glycol of **1**, $Ph_2C(OH)CMe_2OH$,[12)] where the dehydration takes place exclusively from the phenylated carbon to give a more stabilized cation, $^{+}CPh_2CMe_2OH$. This carbocation results in the migration of a methyl group affording **2** finally as a sole product though the absolute migratory aptitude is much higher for a phenyl group than for a methyl group in pinacol rearrangement.[13)]

In conclusion, we have shown that the electrochemically generated **1**$^{+\cdot}$ reacts with methanol to give the skeletally rearranged ketone **2**. This is unusual since the electrochemical oxidations of aromatic olefins in methanol usually give dimethoxylated monomeric or dimeric products. It should be also emphasized that the present study revealed that **1**$^{+\cdot}$ reacts competitively with molecular oxygen as a radical and methanol as a cation in solution.

Experimental

General. Nuclear magnetic resonance spectra were taken on a JEOL MH-100 or a JEOL FX-100 FT NMR spectrometer at room temperature in $CDCl_3$. IR spectra were measured with a Hitachi 215 infrared spectrophotometer. Gas chromatographic analyses were performed with a Shimadzu GC-4CM-PF gas chromatograph with an FID. Acetonitrile was distilled over phosphorus pentaoxide and then over potassium carbonate. Commercially available methanol was distilled once and stored over molecular sieve (Waco synthetic zeolite A-3).

Materials. 1,1-Diphenyl-2-methylpropene (**1**),[14)] 3,3-diphenyl-2-butanone (**2**)[15)] and 1,2-diphenyl-2-methyl-1-propanone (**3**)[16)] were prepared by the published procedures, and their IR, ^1H, and ^{13}C NMR spectra were consistent with their structures.

Preparative Electrolysis. Preparative electrolyses were done in a three-compartment cell separated with glass frits (G-3.5). The working and counter electrodes were platinum wire, and the reference electrode was an SCE. Preelectrolysis of the solvent containing a supporting electrolyte under argon was carried out to remove possible electroactive impurities before the substrate was injected into the solvent. A Hokuto HA-201 potentiostat, a Hokuto HB-104 function generator, and a Rika Denki RE-11 X-Y recorder were employed.

Typically, 45.4 mg (0.22 mmol, 4×10^{-3} M, 1 M=1 mol dm^{-3}) of **1** was dissolved in the preelectrolyzed acetonitrile/methanol mixed solvent with tetrabutylammonium perchlorate (TBAP, 0.1 M) as a supporting electrolyte, and the solution was electrolyzed at 1.6 V/SCE for 3.2 h until **1** ,was almost consumed (99%). The progress of the reaction was monitored by taking aliquots periodically from the reaction mixture and examining them by GLC. The GLC analyses of the reaction mixture indicated the formation of 3,3,-diphenyl-2-butanone **2**, 1,2-diphenyl-2-methyl-1-propanone **3**, and benzophenone **4** in 79, 5, and 5% yields, respectively. For isolation of the products, the reaction mixture was poured into water and then extracted with benzene to remove TBAP. The resulting benzene solution was then subjected to TLC separation. The products were identified by comparing their NMR and IR spectra with those of authentic samples.

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