Electronic Effects in the Reaction of Carbonyl Oxides with Aldehydes[1,2]

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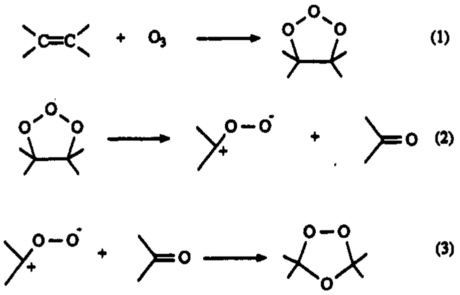
Electronic effects in the third step of the Criegee mechanism of ozonolysis, i.e., the reaction of a carbonyl oxide with a carbonyl compound, were studied by using a non-ozone source of carbonyl oxides as well as by an ozonolysis method. Benzophenone oxide, produced by photosensitized oxidation of diphenyldiazomethane or ozonolysis of tetraphenylethylene, was reacted with a series of para-substituted benzaldehydes. The relative rates of triaryl ozonide formation were treated with the Hammett relationship to give $\rho = 0.48$ or 0.76, respectively, for the photooxidation and ozonolysis reactions. These results indicate that electron-withdrawing substituents in the aldehyde increase the rate of ozonide formation and are consistent with those reported earlier by Kuczkowski and co-workers for stilbene ozonide and with the long held view that ozonide formation involves reaction of a dipolar carbonyl oxide with the carbonyl partner.

Introduction

The mechanism of ozonolysis is generally described in terms of three separate reaction steps (Scheme I).[3,4] This general scheme is now well supported by experimental data. A large number of additional questions can be raised about the details of this overall scheme and, indeed, much experimentation has been directed at these additional questions. Two such additional questions are those pertaining to concertedness in each of these reaction steps and the electronic nature of each of the steps. The available data[4] indicate that steps 1 and 2 are almost certainly concerted. Obtaining evidence on the concertedness question for step 3 has been more difficult. Kuczkowski and co-workers have carried out[5,6] some elegant isotope effect studies that are consistent with concertedness in the carbonyl oxide-carbonyl recombination reaction (step 3) for the systems studied. On the other hand, data have been obtained in other systems, which would seem to require a stepwise recombination reaction in step 3. These data include polyozonide formation[7,8] and an apparent non-ozonide-forming pathway[9] for an adduct between a carbonyl oxide and a ketone.

The electronic requirements in each of the three steps have been studied by means of kinetics and/or the use of linear free energy relationships. The available kinetic data indicate that step 1 involves electrophilic attack of the ozone on the alkene.[4] The electronic requirements in this step have also been studied with the aid of the Hammett linear free energy relationship. Fliszár and co-workers have reported that ozonization of a series of olefins containing aromatic substituents gives a negative ρ value, indicating electrophilic attack of the ozone.[10-12] Application of the Hammett relationship in the ozonolysis of alkyl-substituted olefins has given conflicting results. Two groups have described such studies in which negative ρ values were found.[13,14] A similar study by Fliszár and co-workers[15] gave a positive ρ value. The latter results were explained by postulating a two-step ozone attack. An electrophilic first step to give an ozone-alkene complex, followed by a rate-determining nucleophilic second step to give a 1,2,3-trioxolane, was proposed as consistent with the positive ρ value.

Scheme I



The Hammett relationship has also been used to study step 2 of the overall ozonolysis mechanism. For olefins with aromatic substituents, the results[16,17] indicate that the initially formed 1,2,3-trioxolane cleaves in a manner that favors the carbonyl oxide bearing substituents which stabilize the positive charge in the carbonyl oxide. The Taft relationship has been used[18] to study the decomposition of alkyl-substituted 1,2,3-trioxolanes. In this case the preferred carbonyl oxide was that predicted by inductive effect stabilization.

When this work was initiated there were no literature reports on the application of a linear free energy relationship to step 3 of the mechanism. In part this may be due to the difficulty in isolating kinetic effects in step 3 from the preceding steps. Kuczkowski and co-workers have described[19] a clever way of accomplishing such a study in the ozonolyses of a series of para-substituted styrenes in the presence of similarly substituted benzaldehydes. Such ozonolyses give three different ozonides, i.e., ethylene ozonide, the parent ozonide of the styrene used, and the diaryl-substituted ozonide resulting from cross-recombination of the aryl-containing carbonyl oxide with the added benzaldehyde. The necessary kinetic data for constructing

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[2] Taken, in part, from the Ph.D. Dissertation of Michael M. Morgan, Jan 1989.

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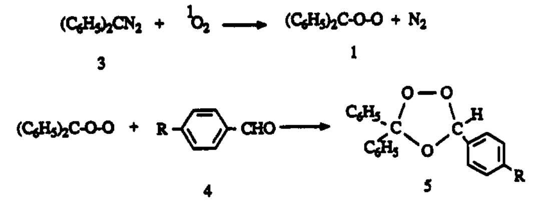
Scheme II



the Hammett plot were obtained by applying a computer program to the observed ozonide yield data. This approach led to a ρ value of +1.4 for the reactions of the aryl-substituted carbonyl oxides with the substituted benzaldehydes. The results are thus consistent with a rate-determining addition of a dipolar carbonyl oxide with the benzaldehyde carbonyl. The rate of this addition reaction is increased by electron-withdrawing groups in both reaction partners. While this dipolar addition reaction had been proposed some time ago,[4] this work[19] appears to be the first experimental evidence on the electronic character of the ozonide-forming reaction step.

In the current work we describe two additional applications of the Hammett relationship to the ozonide-forming step. Two different series of experiments have been carried out. In the first of these the problem of isolating the kinetics of step 3 from the preceding steps has been accomplished by employing a non-ozone source of the carbonyl oxide, benzophenone oxide (1). This approach is made possible by some earlier work[20,21] in which it was shown that oxidation of diazo compounds by singlet oxygen leads to carbonyl oxides. In some cases carbonyl oxides produced in this manner have been reacted with aldehydes to give ozonides.[20,21] In the second series of experiments the same carbonyl oxide, 1, was produced by the ozonolysis of tetraphenylethylene (2). In the case of this symmetrically substituted olefin, only a single carbonyl oxide is possible, thus simplifying the kinetic analysis. In addition, the apparent low reactivity of 1 with the derived carbonyl, benzophenone, effectively eliminates this process as a competitor to the desired reactions of **1b** with the substituted benzaldehydes.

Results

Solutions of diphenyldiazomethane (3) in acetonitrile were oxidized at 2 °C by singlet oxygen in the presence of a series of para-substituted benzaldehydes 4 (Scheme II). The singlet oxygen was produced by using P-Rose Bengal photosensitization. In all cases the total reaction time was 40 min. NMR analyses on the crude reaction mixtures were used in order to measure the true yields of triaryl ozonides 5. Earlier attempts to measure yields using HPLC were complicated by peak overlap between ozonide and other products as the substituent in the benzaldehyde was varied. In the NMR method the reaction solutions were concentrated, a standard amount of an internal standard, 2-phenyl-1,3-dioxolane (6) was added, and the solutions were diluted to a constant volume. The yields of ozonides 5 produced were then determined by integrating the methine hydrogen peaks of the ozonides and the standard. The methine proton of the standard absorbs in the same region as the methine hydrogen of the ozonides but without overlap. The results of these measurements are given in Table I. Since all reactions were run with the same amount of diazo compound and aldehyde (2.5 mmol of each) and for the same time, the yield data can be taken as reflective of the reactive rates of formation of the ozonides 5. A plot of these yield data using Hammett[22] substituent constants gives a ρ value of +0.475 (r = 0.995). Application of the goodness-of-fit analysis suggested by Chapman and Shorter[23] indicates that the relationship is statistically significant at the 99% confidence level.

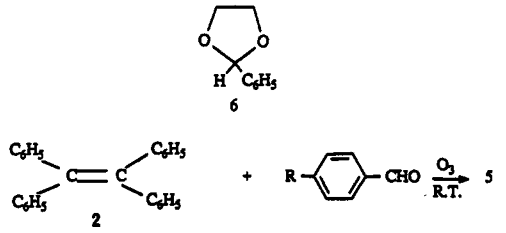
Table I. Triaryl Ozonide Yields in the Reaction of Benzophenone Oxide with Substituted Benzaldehydes

substit	σ value	yield (%) avg	no of runs	std dev	RSD (%)	log
4-OMe	−0.36	21.46	3	0.30	1.41	1.3322
4-tBu	−0.20	24.31	3	0.40	1.66	1.3858
4-Me	−0.17	25.65	3	0.84	3.26	1.4090
H	0.00	30.26	3	0.35	1.17	1.4808
4-F	0.06	34.57	3	1.11	3.20	1.5387
4-Cl	0.37	46.62	3	0.29	0.62	1.6686

Table II. Triaryl Ozonide Yields in the Ozonolysis of Tetraphenylethylene in the Presence of Substituted Benzaldehydes

substit	σ value	avg yield (mmol)/mmol ozone consumed	no. of runs	std dev	RSD (%)	log
4-OMe	−0.36	0.1305	3	0.0017	1.33	−0.8845
4-tBu	−0.20	0.1997	3	0.0069	3.46	−0.6997
4-Me	−0.17	0.2128	3	0.0087	4.10	−0.6720
H	0.00	0.3105	3	0.0118	3.90	−0.5208
4-F	0.06	0.2976	3	0.0073	2.46	−0.5263
4-Cl	0.37	0.4898	3	0.0129	2.62	−0.3100

Scheme III



In the second series of experiments, 5 mmol of tetraphenylethylene and 5 mmol of one of the aldehydes, **4**, were dissolved in methylene chloride, and the solution was treated with 2.5 mmol of ozone at room temperature (Scheme III). Methylene chloride was chosen as solvent on the basis of its known[24] tendency to permit escape of the carbonyl oxide from the solvent cage in which it is formed. In the current procedure carbonyl oxide 1 is thus encouraged to react with aldehydes 4 to give ozonides **5**. Yields of the ozonides were determined by the NMR integration method using **6** as the internal standard as before (Table II). Because the amount of ozone absorbed varied slightly from reaction to reaction, the yield data are given on the basis of millimoles of ozonide produced per millimole of ozone absorbed. A crude reaction solution from an unsubstituted benzaldehyde ozonolysis reaction was treated with a small amount of benzoic acid in order to measure the effect, if any, of any benzoic acid produced by aldehyde oxidation. This solution was stored at −18 °C and analyzed after 3 and 30 h. There was no change in the measured ozonide concentration. A plot of these yield data (Figure 1) against Hammett substituent constants gives a ρ value of +0.76 (r = 0.985). Again, application of the goodness-of-fit approach indicates a statistical

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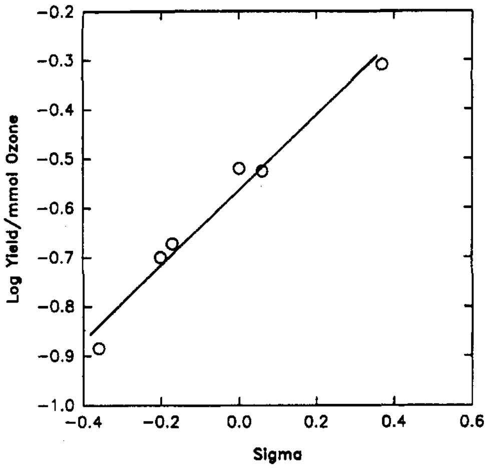

Figure 1. Hammett correlation for triaryl ozonide yields obtained from ozonolysis of tetraphenylethylene in the presence of substituted benzaldehydes.

significance at the 99% confidence level.

All of the triaryl ozonides containing substituents encountered in these two experimental approaches appear to be new compounds. Spectroscopic data for these materials are given in the Experimental Section.

Discussion

The ρ values obtained for the reactions of carbonyl oxide 1 with substituted benzaldehydes 4 in both series of experiments indicate that the ozonide-forming reaction is favored by electron-withdrawing substituents in the aldehyde. This result is consistent with the long held view of the carbonyl oxide as a 1,3-dipole with a negatively charged terminal oxygen. Obtaining positive ρ values in both series of reactions, i.e., with and without using ozone to generate the carbonyl oxide, is reassuring. The difference in magnitude of the two ρ values is presumably largely due to the difference in solvent and temperatures used. The current results confirm the general conclusions arrived at earlier by Kuczkowski and co-workers[19] for the case of the reaction of para-substituted benzaldehyde oxides with para-substituted benzaldehydes. The ρ value (+1.4) obtained in the earlier work is approximately twice that obtained in the present work when ozone was used to generate the carbonyl oxide (+0.76). This difference could indicate an additive effect of the substituents in the earlier work, that is, electron-withdrawing substituents apparently enhance the reactivity of both the carbonyl oxide and the reacting aldehyde in the formation of the stilbene ozonides used in that study.

Experimental Section

Materials. Absolute ethanol and 95% ethanol were purchased from U.S. Industrial Chemical Company, New York, NY. Acetonitrile and deuteriochloroform were obtained from Aldrich Chemical Co., Milwaukee, WI. Tetrachloromethane and dichloromethane (Fischer, Fairlawn, NJ) were purified by distillation from calcium hydride under nitrogen. Acetonitrile and the halogenated solvents were stored over molecular sieves. Benzaldehyde, 4-methoxybenzaldehyde, 4-methylbenzaldehyde, 4-fluorobenzaldehyde, 4-chlorobenzaldehyde, 4-(trifluormethyl)benzaldehyde (Aldrich) and 4-*tert*-butylbenzaldehyde (Lancaster Synthesis, Windham, NH) all were distilled immediately prior to use. Activated manganese dioxide was purchased from Alpha Products, Danvers, MA. P-Rose Bengal was obtained from Hydron Laboratories, New Brunswick, NJ. Benzophenone hydrazone and tetraphenylethylene were obtained from Aldrich Chemical Co., Milwaukee, WI.

Chromatography Supplies. Preparative TLC glass plates (20 × 20 cm) precoated with 1-mm silica gel with fluorescent indicator (254 nm) were purchased from Analtech Inc., Newark, DE. Analytical TLC plastic plates precoated with 0.1-mm silica gel with fluorescent indicator (254 nm) were purchased from Eastman Kodak Co., Rochester, NY. Alumina, activity 1 (80–200 mesh), and silica gel (80–100 mesh) for column chromatography were purchased from Fischer Scientific, Fairlawn, NJ.

Instrumentation. Infrared spectra for solid ozonides were obtained in KBr pellets. Melting points were determined on a capillary melting point apparatus and are uncorrected. Ozone was obtained in a commercial ozone generator. NMR spectra were measured on a 60- or 300-MHz spectrometer using CCl_4 or deuteriochloroform, respectively, as solvents. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

Preparation of Diphenyldiazomethane. Following the method of Reimlinger,[25] a solution of 30 mmol (5.89 g) of benzophenone hydrazone, 30 mmol (3.61 g) of anhydrous magnesium sulfate, and 60 mL of CH_2Cl_2 was stirred rapidly in an ice bath. To the stirred solution was added 106 mmol (9.22 g) of activated manganese dioxide. Stirring was continued for 2 h at 0 °C and for 1 h at room temperature. The solution was filtered and the solvent removed on the rotary evaporator. The crude compound was purified by recrystallization from ethanol at −18 °C to give red needles of diphenyldiazomethane (4.66 g; 80%), mp 30 °C, lit.[25] mp 35 °C.

Preparation of 2-Phenyl-1,3-dioxolane. To a 500-mL round-bottom flask fitted with a Dean–Stark trap filled with benzene and a reflux condenser were added a solution of benzaldehyde (25 mmol, 2.65 g), 2 mmol (0.47 g) of camphorsulfonic acid in 25 mL of benzene, 25 mmol (1.55 g) of ethylene glycol, and 200 mL of benzene. The solution was refluxed for 16 h and then the solvent removed by rotary evaporation. The 2-phenyl-1,3-dioxolane was separated by fractional distillation at reduced pressure, bp 130 °C (16 mm).

General Photolysis Procedure. The photolysis apparatus consisted of a Pyrex vessel equipped with a jacketed immersion well, a fritted gas inlet at the bottom, a gas outlet fitted with a Dewar condenser, and a side arm stoppered with a rubber septum providing access for introduction of reactants into the vessel. During the photooxidations the vessel was immersed in an ice bath at approximately 2 °C with cooling provided for the lamp by circulating ice water through the jacket of the immersion well. Irradiation was provided by a General Electric DWY 650-W lamp regulated by a DC power transformer at 80% power.

Photooxidation of Diphenyldiazomethane in the Presence of a Substituted Benzaldehyde. A solution of 2.5 mmol of the freshly distilled aldehyde in 40 mL of acetonitrile was placed in the reaction vessel. To this solution was added 0.50 g of P-Rose Bengal[26] (Rose Bengal bound to 200–400-mesh styrene–divinylbenzene copolymer beads). Oxygen was bubbled through the solution via the fritted glass inlet at a rate of 50 mL/min. Diphenyldiazomethane (2.5 mmol, 0.50 g) was dissolved in 10 mL of acetonitrile in a 25-mL round-bottom flask and this solution was placed in a 30-mL glass syringe. The flask was washed with 2 mL of acetonitrile and the wash liquor added to the syringe. The syringe was fitted with a stainless steel stopcock, PE 160 polyethylene tubing, and a 15-gage stainless steel needle. The syringe was placed in a Sage Model 341 A syringe pump and the polyethylene tubing inserted through the septum of the side arm of the reaction vessel. The reaction vessel was immersed in the ice water bath, and 2 mL of the diphenyldiazomethane solution was added rapidly (10 mL/min). The lamp was turned on and the remaining diphenyldiazomethane solution was added to the reaction vessel at a rate of 0.22 mL/min. After addition of the solution of diazo compound was complete (35 min), the syringe and tubing were rinsed with an additional 5 mL of acetonitrile followed by an additional 5 min of irradiation, giving a total irradiation time of 40 min. The reaction solution was filtered through glass wool in order to remove the P-Rose Bengal. The solvent was then removed by rotary evaporation. A 0.10-g portion of the standard, 2-phenyl-1,3-dioxolane, was then added to the residue. The reaction sample was then dissolved in the NMR solvent (CCl_4 for 60 MHz and deuteriochloroform for 300 MHz).

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The ^{1}H NMR spectrum of the sample solution was then measured and the region encompassing the methine protons of the ozonide (5.9–6.4 ppm) and the standard (5.8 ppm) was integrated. Each spectrum obtained at 60 MHz was integrated three times and averaged while a single integration was performed on the 300-MHz spectra. The ozonide yields were obtained by comparing the integrations of the ozonides and the internal standard (Table I).

General Procedure for Ozonolysis Reactions. Ozone was produced in a commercial ozone generator and delivered at a rate of 0.17 to 0.22 mol/min. The reaction vessel consisted of a Pyrex impinger equipped with a Dewar condenser. Exhaust gases were passed through a 5% KI solution in gas washing bottles. The ozone rate was determined just prior to each reaction set by passing the ozone stream through a 5% solution of KI for 5 min followed by iodometric titration. The amount of ozone consumed in each reaction was determined by titrating the KI solution in series with the reaction and subtracting the corresponding amount of ozone from that delivered to the reaction vessel.

Ozonolysis of Tetraphenylethylene in the Presence of a Sustituted Benzaldehyde. A solution of 5 mmol (1.66 g) of tetraphenylethylene and 5 mmol of the aldehyde in 50 mL of CH_2Cl_2 was placed in the reaction vessel described above. Ice water was circulated through the Dewar condenser. The reaction solution was sparged with He for 5 min followed by the passage of 2.5 mmol of ozone. The solution was sparged with He for an additional 5 min after completion of ozone passage. The solvent was then removed by rotary evaporation. A 0.10-g portion of the internal standard was added to the reaction residue. The NMR spectra of the product mixtures were then measured and integrations of methine protons carried out as described above. The yields are given in Table II.

Isolation and Analysis of Substituted Ozonides. The solvent was removed from the crude reaction mixture by rotary evaporation. The crude mixture was separated initially by flash column chromatography on 80–100-mesh silica gel using 95:5 pentane/ethyl ether. The fraction containing the ozonide and diperoxide was further separated by preparative TLC on glass plates coated with 0.1 mm of silica gel. The samples were placed on the plates by dissolving in CH_2Cl_2 and spotting in a continuous line 1–1.5 cm from the bottom of the plate with a capillary tube. The plates were developed with 90:10 pentane/ethyl ether and air dried. The ozonide bands were identified with UV light, removed from the plates, and extracted twice with CH_2Cl_2. The solvent was removed by rotary evaporation to give a colorless solid. The solid ozonides were recrystallized from ethanol. Residual solvents were removed by drying in vacuo for 16 h.

Test for Acid Sensitivity of the Crude Reaction Mixtures. The following control reaction was carried out in order to determine whether any acid formed by oxidation of an aldehyde during the ozonolysis could affect the ozonides. A crude reaction mixture was prepared by following the general ozonolysis procedure given above and using benzaldehyde as the aldehyde. A 2-mL aliquot of a 0.001 M solution of benzoic acid in CH_2Cl_2 was added to the crude reaction mixture. This mixture was dissolved in 5 mL of deuteriochloroform and stored at −18 °C. The NMR spectrum of this mixture was recorded after 3 h and 30 h of storage. No decrease in the ratio between the methine protons of the internal standard and the ozonide was observed.

Ozonide Physical Data. 3,3,5-Triphenyl-1,2,4-trioxolane: IR (KBr) 1490, 1450, 1385, 1318, 1255, 1205, 1178, 1040, 1020, 960, 940, 910, 850, 785, 740, 690, 640 cm^{-1}; ^{1}H NMR (60 MHz, $CDCl_3$) δ 7.2–7.7 (m, 15 H), 6.2 (s, 1 H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 130.67, 130.20, 129.48, 128.73, 128.70, 128.48, 128.41, 128.37, 128.34, 127.36, 126.77, 106.0; mp 93 °C, lit.[27] mp 95 °C. Anal. ($C_{20}H_{16}O_3$) C, H.

3,3-Diphenyl-5-(4-methoxyphenyl)-1,2,4-trioxolane: IR (KBr) 2990, 2950, 2900, 2840, 1610, 1595, 1500, 1470, 1440, 1370, 1200, 1170, 1040, 880, 790 cm^{-1}; ^{1}H NMR (60 MHz, $CDCl_3$) δ 7.0–8.0 (m, 14 H), 3.8 (s, 3 H), 6.2 (s, 1 H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 129.86, 129.36, 128.52, 128.34, 128.30, 128.24, 127.27, 126.59, 114.03, 105.97, 55.34; mp 90–92 °C. Anal. ($C_{23}H_{18}O_4$) C, H.

3,3-Diphenyl-5-(4-*tert*-butylphenyl)-1,2,4-trioxolane: IR (KBr) 2980, 1610, 1490, 1450, 1419, 1385, 1365, 1320, 1255, 1217, 1190, 1125, 1110, 1060, 1020, 965, 955, 930, 837, 790, 755, 700 cm^{-1}; ^{1}H NMR (60 MHz, $CDCl_3$) δ 7.0–8.0 (m, 14 H), 1.5 (s, 9 H), 6.2 (s, 1 H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 129.33, 128.34, 128.23, 128.19, 128.06, 127.25, 126.61, 125.61, 31.22; mp 88–90 °C. Anal. ($C_{24}H_{24}O_3$) C, H.

3,3-Diphenyl-5-(4-methylphenyl)-1,2,4-trioxolane: ^{1}H NMR (60 MHz, $CDCl_3$) δ 7.0–8.0 (m, 14 H), 2.3 (s, 3 H), 6.3 (s, 1 H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 140.72, 129.35, 129.30, 128.98, 128.55, 128.35, 128.30, 128.22, 128.14, 127.28, 126.66, 105.98, 21.42; mp 78–80 °C. Anal. ($C_{21}H_{18}O_3$) C, H.

3,3-Diphenyl-5-(4-fluorophenyl)-1,2,4-trioxolane: IR (KBr) 1660, 1605, 1510, 1450, 1430, 1320, 1280, 1230, 1205, 1150, 1015, 920, 855, 835, 770, 700 cm^{-1}; ^{1}H NMR (60 MHz, $CDCl_3$) δ 7.0–8.0 (m, 14 H), 6.3 (s, 1 H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 140.17, 137.75, 136.57, 130.99, 129.54, 129.48, 128.91, 128.78, 128.42, 128.34, 127.26, 126.64, 111.15, 105.06; mp 90–92 °C. Anal. ($C_{20}H_{15}O_3F$) C, H, F.

3,3-Diphenyl-5-(4-chlorophenyl)-1,2,4-trioxolane: IR (KBr) 1685, 1595, 1495, 1450, 1430, 1320, 1280, 1200, 1178, 1130, 1110, 1090, 1062, 1018, 940, 855, 810, 760, 700 cm^{-1}; ^{1}H NMR (60 MHz, $CDCl_3$) δ 7.0–8.0 (m, 14 H), 6.3 (s, 1 H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 129.62, 128.92, 128.88, 127.57, 126.68, 105.65; mp 111 °C. Anal. ($C_{20}H_{15}O_3Cl$) C, H, Cl.

3,3-Diphenyl-5-(4-(trifluoromethyl)phenyl)-1,2,4-trioxolane: IR (KBr) 3030, 2915, 1620, 1495, 1462, 1430, 1325, 1250, 1215, 1170, 1135, 1065, 1030, 970, 940, 920, 855, 840, 790, 755, 700 cm^{-1}; ^{1}H NMR (60 MHz, $CDCl_3$) δ 7.0–8.0 (m, 14 H), 6.3 (s, 1 H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 139.90, 138.90, 138.40, 129.90, 128.60, 128.10, 127.60, 126.40, 125.70, 111.40, 104.60; mp 84 °C. Anal. ($C_{21}H_{15}O_3F_3$) C, H, F.

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