

Oxidation of Phenyl-substituted Allenes with Peracids

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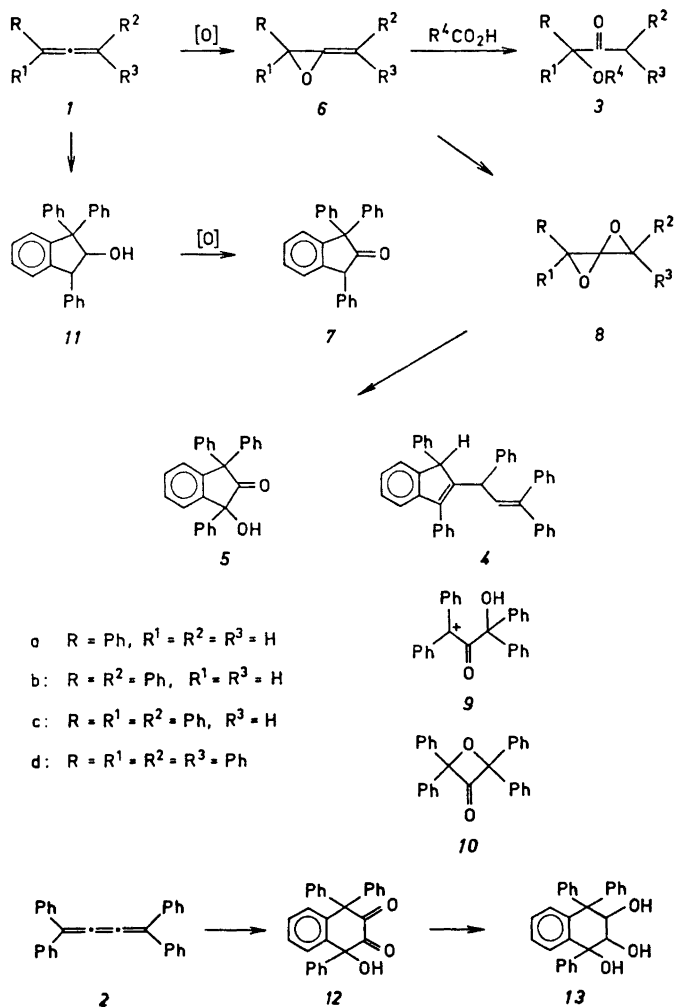
Oxidation of phenyl-substituted allenes with performic acid or *m*-chloroperbenzoic acid has been investigated. Phenylallene (*1a*) and 1,3-diphenylallene (*1b*) gave benzaldehyde and the respective acyloin ester **3** as products. Triphenylallene (*1c*) underwent acid-catalyzed dimerization to the indene **4** while tetraphenylallene (*1d*) oxidized to the indanone **5**. The respective allene oxide is clearly an intermediate in the oxidation reactions; moreover, the formation of **5** is best explained *via* the spiro dioxide **8**. Peracid oxidation of tetraphenylbutatriene (**2**) gave the tetralindione **12**.

Peracid oxidation of alkyl-substituted allenes has been reported.¹⁻⁵ The isolation of allene oxides was successfully achieved from reactions of both 1,3-di-*t*-butylallene³ and 1,1,3-tri-*t*-butylallene⁴ with *m*-chloroperbenzoic acid. Furthermore a buffered peracetic acid oxidation of *t*-butyl-1,1-dimethylallene resulted in the formation of a spirodioxide.⁵ On the other hand, from tetramethylallene no allene oxides were isolated, although some of the products could be rationalized as resulting from both allene oxide and spirodioxide intermediates.²

We want to report the peracid oxidation of some phenyl-substituted allenes, *viz.* phenylallene (*1a*), 1,3-diphenylallene (*1b*), 1,1,3-triphenylallene (*1c*), and tetraphenylallene (*1d*). * We have also oxidized the cumulene tetraphenylbutatriene (**2**) under similar conditions. As oxidizing agents we employed both performic acid (PFA) and *m*-chloroperbenzoic acid (MCPBA).

Reaction of phenylallene (*1a*) with one equivalent of MCPBA resulted in recovery of almost half the amount of starting material. Using two equivalents of peracid, most of the allene reacted, and benzaldehyde was obtained in 50 % yield as the main product. From the residue the benzoate **3a** ($R^4 = m\text{-ClC}_6\text{H}_4\text{CO-}$) was isolated in 9 % yield. Oxidation of *1a* with PFA gave a small yield of benzaldehyde besides almost equal amounts (30 %) of 1-hydroxy-1-phenyl-2-propanone (**3a**, $R^4 = \text{H}$) and its formate (**3a**, $R = \text{HCO-}$). Similar results were obtained from the oxidation of 1,3-diphenylallene (*1b*); in this case benzaldehyde and the benzoate (**3b**, $R = m\text{-ClC}_6\text{H}_4\text{CO-}$) were obtained in 20 and 40 % yields, respectively, using MCPBA as oxidizing

* Note added in proof. After this paper was submitted for publication the peracid oxidation of *1d* to the hydroxyindanone **5** was reported by Oku *et al.* [*Bull. Chem. Soc., Japan* **46** (1973) 275].



Scheme 1.

agent. With PFA the allene *1b* was oxidized to the formate *3b* ($\text{R}^4 = \text{HCO}-$) and a small amount of benzaldehyde.

The reaction of triphenylallene with PFA took another course; the allene is extremely sensitive to acids which cause dimerization to 1,3-diphenyl-2-[1,3,3-triphenylallyl]indene *4*.⁶ This compound was also one of the products using MCPBA together with a mixture of several compounds including acyloin esters which we could not separate.

So far neutral compounds have been described, but acidic compounds were also products from these reactions. They were removed with the alkaline washings and thus provide an explanation for the poor material balances.

However, attempts to obtain pure compounds from these mixtures were unsuccessful.

The oxidation of tetraphenylallene (*1d*) with either PFA or MCPBA proceeded slowly and was complete after the consumption of two equivalents of peracid. A single product was obtained in 83 % yield and identified as 1-hydroxy-1,3,3-triphenyl-2-indanone (*5*) on the basis of spectral data. The structure was subsequently proven by comparison with an independently synthesized authentic sample.⁷

There is ample evidence in the literature supporting the view that the formation of allene oxide *6* is the first step in the peracid oxidation of allenes. The fact that all our reactions followed approximately second order kinetics indicates that this must also be the rate-determining step. This oxide could rearrange to the corresponding cyclopropanone or react with the available carboxylic acid to the ring-opened product *3*. In our examples the latter reaction took place while no evidence for the presence of the cyclopropanone was obtained. If the ketone *3* is enolizable,* we have shown that it is further oxidized to benzaldehyde at a rate faster than that of the initial oxirane formation.⁸ However, the corresponding compound from tetraphenylallene would not be enolizable and rearrangement *via* the carbonium ion to the indanone *7* could take place; further oxidation could then possibly lead to the observed product *5*. Another possibility available would be further oxidation of the allene oxide to the spiro dioxide *8* which in analogy with compound *6* could form the ketone *9*. Acid-catalyzed rearrangements to an oxetanone *10* or to the observed hydroxyindanone *5* are also possible reactions of the spiro dioxide. In order to distinguish between these alternative routes to *5* we synthesized the indanone *7* starting from tetraphenylallene. Acid-catalyzed rearrangement gave the corresponding indene. Hydroboration lead to 1,1,3-triphenylindan-2-ol (*11*) which by oxidation with Jones reagent afforded the indanone *7*. Treatment of this with MCPBA under conditions similar to those employed with tetraphenylallene gave no reaction. Hence we must conclude that the spiro dioxide is formed as a transient intermediate in the oxidation of *1d* to *5*. All attempts to isolate or to obtain evidence for the presence of the spiro oxide in the reaction mixture were unsuccessful. This is perhaps not surprising considering the strained structure and the observations by Crandall *et al.*^{2,5} that compounds of this class are very sensitive to acids. The rearrangement of *8* to *5* would involve the carbonium ion *9* which also is the origin of tetraphenyl-oxetanone⁹ (*10*). The latter is stable under the reaction conditions but we could not detect its presence in the reaction mixture. In this connection it is interesting that the oxetane *10* is formed by autooxidation of tetraphenylallene.⁹

It was of interest to see whether the cumulene tetraphenylbutatriene would behave in a similar way. The reaction with MCPBA gave besides a number of unidentified products a 40 % yield of a yellow compound, C₂₃H₂₀O₃. The NMR spectrum exhibited aromatic absorption and a broad singlet which disappeared on treatment with deuterium oxide. The presence

* At least one non-enolizable compound of structure *3* has been shown to react with peracid, while others have been resistant.²

of carbonyl and hydroxyl groups was evident from the infrared spectrum. As expected, the carbonyl absorption disappeared on reduction of the compound with sodium borohydride. The mass spectrum showed the molecular ion M (m/e 404) and the $M - CO$ as well as $M - 2 CO$ fragments corresponding to aryl-substituted α -diketones. The data are in agreement with the structure 1-hydroxy-1,4,4-triphenyltetralindione (12). The formation of this dione is quite analogous to the formation of 5 from 1*d*. Several routes leading to 12 can be depicted including one *via* a spirotrioxide; however, without more information, further speculation is unwarranted.

Some simple kinetic measurements were carried out by following the consumption of peracid. For the first 50 % reaction, fairly good second order plots were obtained for compounds 1*a*, 1*b*, and 1*d*; the rate constants were 0.7×10^{-3} , 0.7×10^{-3} , and $0.2 \times 10^{-3} \text{ l mol}^{-1} \text{ sec}^{-1}$, respectively. For comparison, the rate of oxidation of 3-methyl-1,2-butadiene was measured to $4.5 \times 10^{-3} \text{ l mol}^{-1} \text{ sec}^{-1}$ which shows that phenyl-substitution does result in a significant rate decrease, as expected.

EXPERIMENTAL

General. NMR spectra were recorded on Varian Associates A60A and HA 100-15D spectrometers. Mass spectral data were obtained using an A.E.I. MS 902 mass spectrometer, and a Perkin Elmer model 457 spectrophotometer was used for obtaining infrared spectra. Elemental analyses were carried out by Ilse Beetz Microanalytical Laboratory, 8640 Kronach, Germany.

Oxidation of phenylallene (1a). (a) *With m-chloroperbenzoic acid.* To a solution of the allene 1*a*¹⁰ (3.5 g, 30 mmol) in 100 ml dichloromethane was added 2.9 g of 70 % MCPBA (60 mmol) and the reaction mixture left with stirring at 0° overnight. The solution was washed with aqueous Na_2CO_3 and dried (Na_2CO_3). Evaporation gave 3.6 g of a liquid which by distillation gave 1.5 g (50 %) of benzaldehyde. The residue was chromatographed on silica gel and 0.75 g (9 %) of the viscous liquid 3*a* ($\text{R}^4 = \text{C}_6\text{H}_4\text{COO}-$) was isolated. (Found: C 66.27; H 4.48. Calc. for $\text{C}_{16}\text{H}_{13}\text{O}_3\text{Cl}$: C 66.50; H 4.51.) NMR (CDCl_3) CH_2 δ 2.2 (s), CH δ 6.3 (s), arom. H δ 7.2–8.1 in a ratio of 3:1:9. IR (CCl_4) 1720 and 1730 cm^{-1} . The mass spectrum exhibited a small molecular ion, but fragments corresponding to α -fission to carbonyl groups were all present.

(b) *With performic acid.* Phenylallene (3.5 g, 0.03 mol) was added to a solution of 30 % H_2O_2 (0.03 mol) in 90 % formic acid (30 ml) at room temperature. The mixture was stirred overnight, concentrated at reduced pressure and the residue dissolved in ether. The ether solution was washed with aqueous Na_2CO_3 and the ether evaporated. The NMR spectrum of the residue (3.0 g) revealed a mixture of 5 % yield of benzaldehyde, 30 % of 1-hydroxy-1-phenyl-2-propanone (3*a*, $\text{R}^4 = \text{H}$), and 30 % of its formate (3*a*, $\text{R}^4 = \text{HCO}-$). Further treatment with aqueous Na_2CO_3 solution, followed by distillation, gave 1.6 g (36 %) of 3*a* ($\text{R}^4 = \text{H}$), b.p. 70° (0.05 mm),¹¹ the *semicarbazone* was formed, m.p. 193–194° (lit.¹² m.p. 194°).

Oxidation of 1,3-diphenylallene (1b). (a) *With m-chloroperbenzoic acid.* A solution of 1,3-diphenylallene¹³ (1.92 g, 10 mmol) in dichloromethane was treated with MCPBA as described for 1*a*. Reaction time was 3 days at 0°. The product was worked up in the usual way and analyzed by NMR. This revealed that benzaldehyde was formed in 20 % yield and the benzoate ester 3*b* ($\text{R}^4 = \text{C}_6\text{H}_4\text{COO}-$) in 40 % yield. A pure sample of the latter was obtained as a viscous liquid by chromatography on silica gel. (Found: C 73.25; H 4.87. Calc. for $\text{C}_{22}\text{H}_{17}\text{O}_3\text{Cl}$: C 72.45; H 4.67.) IR (CCl_4) 1720 and 1730 cm^{-1} . NMR (CDCl_3) CH_2 3.8 δ (s), CH 6.3 δ (s), arom. H 7.1–8.1 δ . The expected α -fission fragment of the carbonyl group was observed in the mass spectrum.

(b) *With performic acid.* 1,3-Diphenylallene (1.92 g, 10 mmol) was treated with performic acid as described under 1*a*. After 24 h at room temperature and the usual work-up a liquid, 1.5 g (68 %), was obtained which consisted of a small amount of benzaldehyde

and the formate ester of *3b* ($R^4 = \text{HCO}-$). Hydrolysis of this with aqueous Na_2CO_3 gave pure 1,3-diphenyl-1-hydroxy-2-propanone (*3b*, $R^4 = \text{H}$), m.p. 115–116°, undepressed on admixture with an authentic sample.¹⁴

Oxidation of triphenylallene (1c). (a) *With m-chloroperbenzoic acid.* Triphenylallene⁸ (2.68 g, 10 mmol) was treated with MCPBA as described under *1a*. After 3 days at 0° and the usual work-up, 0.7 g of a mixture of compounds was obtained.

Chromatography on neutral alumina (activity II) gave starting material (0.15 g), mixture of acyloin esters (0.25 g) and 1,3-diphenyl-2-[1,3,3-triphenylallyl]indene (*4*, 0.1 g), m.p. 211–213° from cyclohexane-hexane, undepressed on admixture with an authentic sample,¹⁵ m.p. 214–215°.

(b) *With performic acid.* Reaction of triphenylallene (2.68 g, 10 mmol) with performic acid as described under *1a* gave as the only isolable product the indene *4* in 56% yield.

1-Hydroxy-1,3,3-triphenyl-2-indanone (5). A cold (0°C) solution of 70% *m*-chloroperbenzoic acid (3.65 g, 15 mmol) in dichloromethane (50 ml) was added to a solution of triphenylallene (1.72 g, 5 mmol) in dichloromethane (50 ml) at 0°. After 5 days at 0°, the reaction mixture was washed with aqueous sodium carbonate solution and dried (Na_2CO_3). The filtrate was evaporated giving 1.55 g (83%) of *5* which was recrystallized from cyclohexane, m.p. 156–157°. (Found: C 85.92; H 5.45. Calc. for $\text{C}_{27}\text{H}_{20}\text{O}_2$: C 86.14; H 5.36.)

The product (*II*) was in all respects identical with authentic material which was synthesized according to literature;⁷ m.p. 157–159°.

1,3,3-Triphenyl-indan-2-ol (11). To a solution of 1,3,3-triphenylindene¹⁶ (1.72 g, 5 mmol) in dry tetrahydrofuran (30 ml) NaBH_4 (0.38 g, 10 mmol) was added under nitrogen. A solution of BF_3OEt_2 (1.42 g, 0.1 mol) in THF (10 ml) was added to the cooled (0°) reaction mixture during 3 h. The mixture was stirred at room temperature overnight and treated with sodium hydroxide/hydrogen peroxide in the usual way. The ether extract was washed with water and dried. The solvent was evaporated and the residue purified by chromatography on neutral alumina (activity III).

The carbinol *II* was eluted with benzene; 0.8 g (56%), m.p. 60–65°. (Found: C 89.32; H 6.30. Calc. for $\text{C}_{22}\text{H}_{22}\text{O}$: C 89.50; H 6.08.) NMR (CDCl_3) OH δ 1.7 (s), CH δ 3.8 (d), CH δ 5.1 (d) ($J = 10$ cps) and arom. H δ 6.8–7.4 in a ratio of 1:1:1:19. MS: M (m/e 362), M–OH, M– H_2O , M–CHOH, M– CH_2OH .

1,3,3-Triphenyl-indan-2-one (7). To a solution of carbinol *II* (0.36 g, 1 mmol) in acetone (20 ml) was added Jones reagent (0.4 ml, 0.001 mol) and the mixture stirred for 2 h at room temperature. Water (25 ml) was then added, the solution extracted with ether, the organic phase washed with water and dried (MgSO_4). Evaporation gave 0.35 g (97%) of the pure compound. Recrystallisation from benzene/hexane gave a final m.p. at 85–90° after rearrangements in the crystalline phase at about 50°. (Found: C 89.75; H 5.40. Calc. for $\text{C}_{27}\text{H}_{20}\text{O}$: C 90.00; H 5.56.)

NMR (CDCl_3) CH δ 4.3 (s) and arom. H δ 6.9–7.4 in a ratio of 1:19. MS: M–CO (m/e 332), M–CHO, M–(CO)–Ph, M–CHO–Ph.

Attempted oxidation of *7*: To a solution of *7* in dichloromethane (20 ml) was added 2 equiv. of 70% MCPBA. No peracid was consumed, even after 6 days at 0°.

Oxidation of tetraphenylbutatriene (2). A cold solution of 70% *m*-chloroperbenzoic acid (4.80 g, 0.02 mol) in dichloromethane (100 ml) was added to a suspension of tetraphenylbutatriene *2*¹⁷ (1.78 g, 0.005 mol) in dichloromethane (100 ml) at 0°. After one week at 0°, the reaction mixture was washed with aqueous sodium carbonate solution, dried and evaporated. The residue was chromatographed on neutral alumina (activity III). Elution with benzene/ethylacetate (4:1) gave 0.8 g (40%) coloured *12*, m.p. 60–65° from cyclohexane. (Found: C 82.80; H 5.12. Calc. for $\text{C}_{28}\text{H}_{20}\text{O}_3$: C 83.20; H 4.96.)

NMR (CDCl_3) OH δ 4.7 (s) and arom. H δ 7–8 in a ratio of 1:19. IR (CCl_4) 3500 cm^{-1} OH and 1760 cm^{-1} CO.

Compound *12* (0.2 g) was treated with NaBH_4 (0.1 g) in ethanol (10 ml) overnight. The strong yellow colour had disappeared. The solution was worked up in the usual way with ether to give semicrystalline *13*. (Found: C 82.21; H 5.77. Calc. for $\text{C}_{28}\text{H}_{22}\text{O}_3$: C 82.75; H 5.42.) NMR (CDCl_3) CH δ 5.3 (m), OH δ 4.0–4.5 (m) and arom. H δ 6.8–7.5 in a ratio of 2:3:19. IR (CCl_4) 3600 cm^{-1} . MS: M (m/e 408), M–H, M– H_2O , M– $2\text{H}_2\text{O}$, M– H_2O –HCHO, M–Ph, M–Ph– H_2O –HCHO.

Kinetics. 0.005 mol of the allene was added to a solution of 70% *m*-chloroperbenzoic acid (0.01 mol) in methylene chloride (75 ml) at 0°C. The solution was stirred at 0°,

aliquots were withdrawn and the amount of peracid was determined by iodometrical titration. Rate constants were calculated from a second order plot.

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