

Reactions of Unsaturated Compounds.IV
"Oxidation of Some Tetra-aryl Aliphatic Olefins by
Chromium Trioxide"

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(Received 24th March, 1986)

Summary: The oxidation of 1,1,3,3-tetraphenyl-2-methyl,1,1-di-*p*-tolyl-3,3-diphenyl-2-methyl,1,1-dibenzyl-3,3-diphenyl-2-methyl,1,1,3,3,-tetraphenyl and 1,1-di-*p*-tolyl-3,3-diphenyl propenes by chromium trioxide-acetic anhydride gives the corresponding epoxide with fission products. Chromic acid in aqueous sulphuric acid brings about oxidative fission of the double bond without any rearrangement. The isolation of terephthalic acid and *p*-toluic acid from oxidation of 1,1-di-*p*-tolyl-2-methyl-3,3-diphenyl and 1,1-di-*p*-tolyl-3,3-diphenyl propenes was discussed. The action of perbenzoic acid on these tetra-aryl olefins was also studied.

Introduction

Recently, it has been reported [1-3] that in the oxidation of a wide number of aryl substituted aliphatic mono-olefins by chromium trioxide in acetic anhydride, as anhydrous medium, normal fission products as well as abnormal fission products were obtained.

The chromium trioxide-acetic anhydride oxidation of 1,1-diaryl ethylenes having terminal CH₂ group has been reported [4] to yield no epoxide and instead an acid having the same number of carbon atoms as the original olefin, was isolated. A plausible explanation was given on the basis that 1,2-epoxy-1,1-diaryl ethane which would be formed undergoes rearrangement or break down, in the oxidation medium, into aldehyde or an acid and could not be isolated.

It seemed desirable to extend the work to other poly-aryl substituted mono-olefins which have not been fully investigated, namely, tetra-aryl olefins with the object of obtaining more

precise information on the course of the epoxidation of olefins by chromic acid.

In the present investigation, it was found that the oxidation of the title tetra-aryl olefins by chromium trioxide-acetic anhydride, yielded the corresponding epoxides, in crystalline form (except 1,2-epoxy-1,1-dibenzyl-2-methyl-3,3-diphenyl propane) which were identified by comparison with authentic specimens obtained by the action of perbenzoic acid on the olefins, and other fission products (cf. Table 1). Formation of a stable epoxy compound indicates that oxidation in anhydrous medium proceeds via the intermediate complex I[5] or II[6], i.e. active Cr species in Ac₂O, from which the epoxide would be obtained by splitting CrO₂:

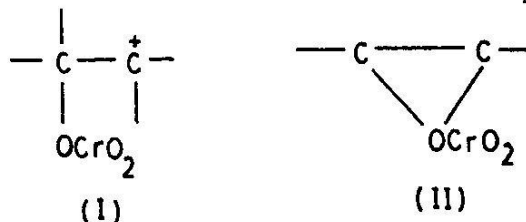


Table-1: Products of oxidation by chromium trioxide-acetic anhydride.

Olefin	Amount oxidized (g.)	Neutral products	Acidic products
1,1,3,3-tetraphenyl-2-methyl propene ^{10*} (Ph) ₂ CHC(CH ₃)C=C(Ph) ₂	(8)	1,1-Diphenylpropanone (0.32 g), benzophenone (1.14 g), 1,2-epoxy-1,1,3,3-tetraphenyl-2-methyl propane (2.78 g).	--
1,1-Di- <i>p</i> -tolyl-2-methyl-3,3-diphenyl propene (<i>p</i> -CH ₃ C ₆ H ₄) ₂ C=C(CH ₃)CH(Ph) ₂	(8)	1,1-Diphenylpropanone (0.32 g), <i>p-p'</i> -ditolyl ketone (1.74 g), 1,2-Epoxy-1,1-di- <i>p</i> -tolyl-2-methyl-3,3-diphenylpropane (1.6 g).	<i>p</i> -Toluic acid (0.12 g), terephthalic acid (0.2 g).
1,1-Dibenzyl-2-methyl-3,3-diphenyl propene (PhCH ₂) ₂ C=C(CH ₃)CH(Ph) ₂	(4)	1,1-Diphenylpropanone (1.2 g), dibenzyl ketone (0.9 g), 1,2-epoxy-1,1-dibenzyl-2-methyl-3,3-diphenyl propane (1.6 g).	Benzoic acid (0.7 g).
1,1,3,3-Tetraphenyl propene (Ph) ₂ C=CHCH(Ph) ₂ ¹¹	(9.8)	Benzophenone (6.6 g), 1,2-epoxy-1,1,3,3-tetraphenyl propane (2.9 g).	Diphenylacetic acid (0.2 g).
1,1-Di- <i>p</i> -tolyl-3,3-diphenyl propene (<i>p</i> -CH ₃ C ₆ H ₄) ₂ C=CHCH(Ph) ₂	(8)	<i>p-p'</i> -Ditolyl ketone (3.77 g), 1,2-epoxy-1,1-di- <i>p</i> -tolyl-3,3-diphenylpropane (2.05 g).	Diphenylacetic acid (0.45 g), terephthalic acid (1.5 g).

* No m.p. is recorded for the carbinol.

The aqueous chromic acid-sulphuric acid oxidation of the tetra-aryl olefins brought about oxidative fission of the double bond without any rearrangement (cf. Table 2). However, in the case of 1,1-di-*p*-tolyl-2-methyl-3,3-diphenyl propene or 1,1-di-*p*-tolyl-3,3-di-phenyl propene, terephthalic and *p*-toluic acids were obtained.

In these and previous [1,7-9] oxidations with aqueous chromic acid an epoxide can not be considered as

the precursor for rearrangement or fission products and instead the addition complex of the olefin and the oxidising agent (I or II) is more likely to be the true intermediate. The complex can give rise to glycols with subsequent fission of these hydrated products by the oxidising agent to give the normal fission products.

The normal fission products in most cases are the precursors for the abnormal fission products as can be seen from the following explanation.

Table-2: Products of oxidation by chromic acid-aqueous sulphuric acid.

Olefin	Amount oxidized (g.)	Neutral products	Acidic products
1,1,3,3-Tetraphenyl-2-methyl propene	(8)	1,1-Diphenylpropanone (2.41 g), benzophenone (4.61 g).	--
1,1-Di- <i>p</i> -tolyl-2-methyl-3,3-diphenyl propene.	(12)	1,1-Diphenylpropanone (3.71 g) <i>p,p'</i> -ditolyl ketone (4.0 g).	<i>p</i> -Toluic acid (0.5 g), terephthalic acid (1 g).
1,1-Dibenzyl-2-methyl-3,3-diphenyl propene	(4)	1,1-Diphenylpropanone (1.66 g), dibenzyl ketone (1.05 g).	Benzoic acid (1.86 g).
1,1,3,3-Tetraphenyl propene.	(10)	Benzophenone (8.1 g).	Diphenylacetic acid (0.75 g).
1,1-Di- <i>p</i> -tolyl-3,3-diphenyl propene	(8)	<i>p,p'</i> -Ditolyl ketone (5.37 g).	Diphenylacetic acid (0.55 g), terephthalic acid (0.27 g).

Table-3: Physical and analytical data of III-VI.

Compound	M.p. °C	Formula	Analysis (Found/Calcd %)	
			C	H
III	95-97	$C_{28}H_{26}O$	88.90	6.90
			88.85	6.94
IV	87-88	$C_{30}H_{30}O$	88.10	7.50
			88.65	7.20
V	133-35	$C_{30}H_{30}O$	89.00	7.10
			88.63	7.20
VI	78-79	$C_{29}H_{28}O$	88.50	7.36
			88.73	7.19

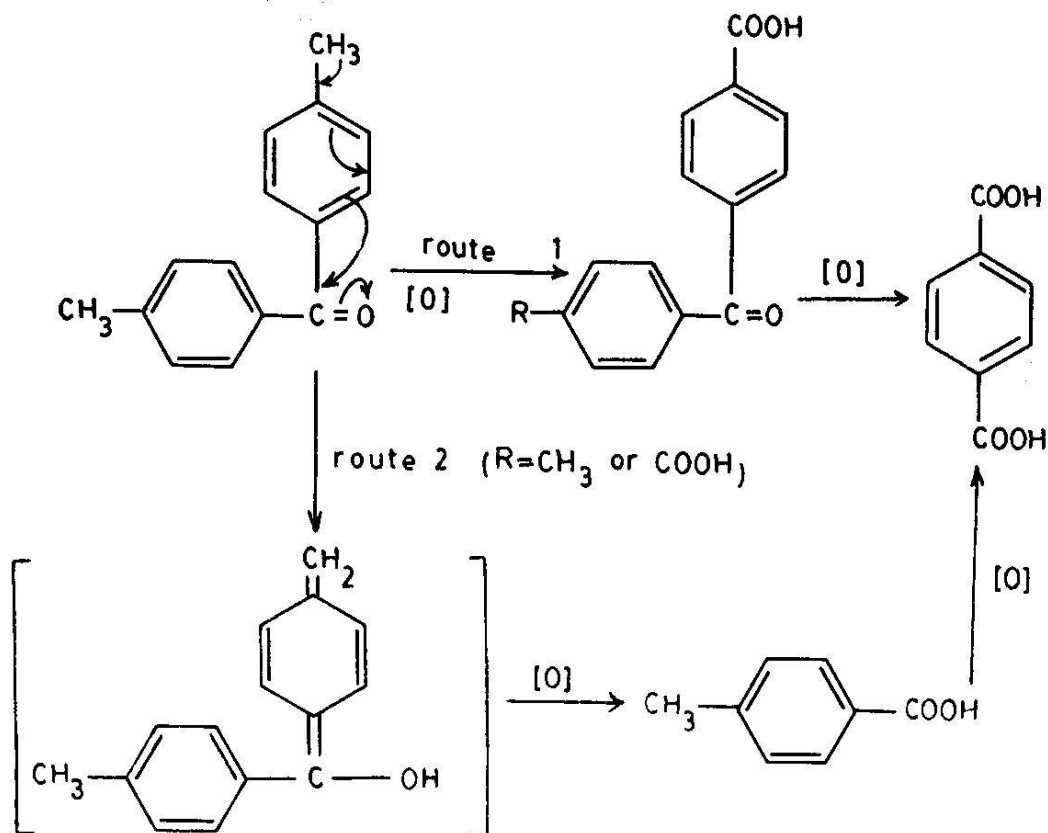
All recrystallized from light pet. (60-80°) as colourless crystals, yield 60-75%.

Formation of p-toluic and terephthalic acids in the oxidation of 1,1-di-p-tolyl-2-methyl-3,3-diphenyl, 1,1-di-p-tolyl-3,3-diphenyl propenes:

This can result from *p,p'*-dimethyl ketone which is firstly formed

as an oxidative fission product. Its formation may be explained by one of the following routes (1) or (2):

The driving force for route (2) is the hyperconjugation effect of the methyl group to give species (a).



This result finds analogy with those obtained by Moussa *et al.* [2,4] who isolated the same acid during chromic acid oxidation of 1,1-*p*-tolyl ethylene, 1-phenyl-1-tolyl ethylene and 1,1,3,3-tetra-*p*-tolyl but-1-ene. The authors tested this view experimentally by subjecting *p,p'*-dimethylbenzophenone to chromic acid-aqueous sulphuric acid

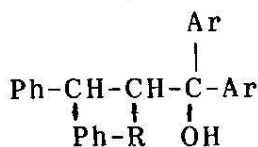
Experimental

All melting points are uncorrected. The carbonyl fission products were identified as their 2,4-dinitrophenylhydrazone derivatives (m.p. and m.m.p. with an authentic specimens showed no depression).

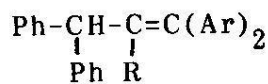
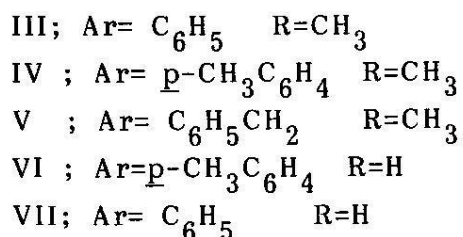
oxidation under similar conditions for oxidation the olefin and were able to isolate terephthalic acid in 12.5% yield together with unchanged ketone.

Formation of 1,1-diphenyl (III), 1,1-di-p-tolyl (IV) and 1,1-dibenzyl (V)-3,3-diphenyl-2-methyl propanols:

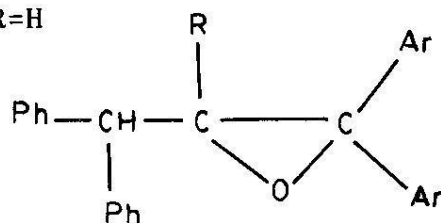
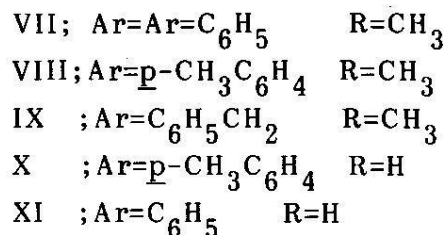
These carbinols were prepared by addition of methyl β,β -diphenyl- α -methyl propionate (0.01 mole) in dry ether (100 ml) in portion-wise to a solution of phenyl, *p*-tolylmagnesium bromide or benzylmagnesium chloride, respectively, (prepared from 0.2 mole bromobenzene, *p*-bromotoluene or benzyl chloride and 0.2 mole magnesium). The reaction mixture was refluxed for 3 hr. then decomposed on ice-cooled ammonium chloride-aqueous hydrochloric acid solution. The product was extracted with ether and the ethereal extracts were dried over anhydrous Na₂SO₄. Removal the ether by distillation under reduced



(III-VII)



(VII-XI)



(XII-XVI)

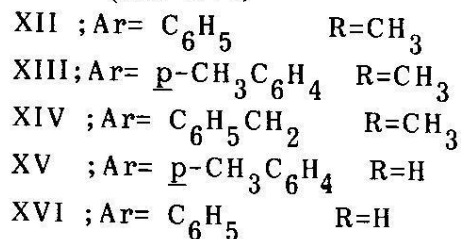


Table-4: Physical and analytical data of VII-X.

Compound	M.p. °C	Formula	Analysis (Found/Calcd. %)	
			C	H
VII [*]	132-33	C ₂₈ H ₂₄	93.50 93.33	6.54 6.67
VIII [*]	121-22	C ₃₀ H ₂₈	93.00 92.74	7.33 7.28
IX ⁺	49-51	C ₃₀ H ₂₈	92.50 92.74	7.51 7.28
X§	100-102	C ₂₉ H ₂₆	92.82 93.04	7.13 6.75

* Recrystallized from glacial acetic acid, as colourless crystals, yield 65-80%.

+ Recrystallized from light pet. (40-60°), as colourless crystals, yield 65-75%.

§ Recrystallized from light pet. (60-80°), as colourless crystals, yield 65-75%.

pressure afforded the title carbinols which were recrystallized from a suitable solvent (cf. Table 3).

1,1-Di-*p*-tolyl (VI), 1,1-diphenyl [11] (VII)-3,3-diphenyl carbinols were prepared as in previous procedure using methyl β, β -diphenyl propionate and *p*-tolylmagnesium bromide or phenylmagnesium bromide respectively, (cf. Table 3).

Dehydration of III-VI; Formation of 1,1-diphenyl (VII), 1,1-di-p-tolyl (VIII), 1,1-dibenzyl(IX)-3,3-diphenyl-2-methyl propenes and 1,1-di-p-tolyl-3,3-diphenyl propene(X):

The carbinols III-VI (0.032 mole) were dehydrated by refluxing with a mixture of glacial acetic acid (150 ml) and concentrated sulphuric acid (8 ml) for 3 hr. The reaction mixture was cooled whereby a solid product separated. Recrystallization the solid product from suitable solvent afforded VII-X, (cf. Table 4).

Oxidation of VII-XI by chromium trioxide-acetic acid:

Chromium trioxide (0.04 mole) in acetic anhydride (25 ml) was added over 1 hr. to a stirred solution of the olefin (0.02 mole) in acetic anhydride (20 ml). Stirring was continued for 14 hr. at room temperature followed by 12 hr. gentle reflux. The reaction mixture was then poured into ice-water (200 ml) and extracted with ether. The ether extracts were neutralized with aqueous sodium carbonate, washed with water and dried over anhydrous Na_2SO_4 .

Distillation of the ether solution gave the neutral products. Acidification and ether extraction of the alkaline aqueous layer gave the acidic products.

The results are included in Table-1 (terephthalic acid is separated from *p*-toluic acid by its insolubility in cold acetic acid, while *p*-toluic acid dissolves in cold acetic acid).

Table-5: Physical and analytical data of XII-XVI.

Compound	M.p. °C	Formula	Analysis (Found/Calcd. %)	
			C	H
XII [*]	113-14	$\text{C}_{28}\text{H}_{24}\text{O}$	89.58 89.32	6.61 6.43
XIII ⁺	95-97	$\text{C}_{30}\text{H}_{28}\text{O}$	88.70 89.07	7.20 6.98
XIV ⁺	b.p. 155-156/7 mm	$\text{C}_{30}\text{H}_{28}\text{O}$	88.84 89.07	6.90 6.98
XV ⁺	87-88	$\text{C}_{29}\text{H}_{26}\text{O}$	89.48 89.19	6.94 6.71
XVI ⁺	130-31	$\text{C}_{27}\text{H}_{22}\text{O}$	89.18 89.47	5.90 6.17

* Recrystallized from light pet.(60-80°), yield 55%.

+ Recrystallized from absolute methanol, yield 55-60%.

Oxidation of VII-XI with perbenzoic acid : Formation of 1,2-epoxy propane derivatives (XII-XVI):

The olefin was added in portion-wise to a 20% excess perbenzoic acid in ice-cold chloroform and the reaction mixture was kept at 0°C for 6 days. The chloroform solution was then washed with saturated aqueous sodium carbonate solution, water and dried. Distillation the chloroform under reduced pressure gave the title compounds. The results are included in Table-5.

Attempted hydration or isomerisation of the epoxides (XII-XVI):

Shaking the epoxide (1 g) in suspension with aqueous sulphuric acid (30 ml; 45%) for ca.90 hr. at room temperature (or 1 hr. reflux) gave unchanged epoxide.

References

1. G.E.M. Moussa, S.O. Abdalla, *J. App. Chem.*, **20**, 256 (1970).
2. G.E.M. Moussa, N.F. Ewiss, *J. App. Chem.*, **20**, 281 (1970).
3. G.E.M. Moussa, N.F. Ewiss, *J. App. Chem.*, **21**, 93 (1971).
4. G.E.M. Moussa, M.N. Basyouni, M.E. Shaban and A.M. Youssef, *J. App. Chem. Biotechnol.*, **28**, 875 (1978).
5. W.J. Hickinbottom, D.J. Peters, *J. Chem. Soc.*, 1360 (1955).
6. H.H. Zeiss, F.R. Zwanzig, *Chem. Ind.*, 545 (1956); *J. Am. Chem. Soc.*, **79**, 1733 (1957).
7. G.E.M. Moussa, N.F. Ewiss, *J. App. Chem.*, **19**, 313 (1969).
8. W.J. Hickinbottom, M.A. Davis, *J. Chem. Soc.*, 1998 (1957).
9. G.E.M. Moussa, *J. App. Chem.*, **12**, 385 (1962).
10. C.F. Koelsch and R.V. White, *J. Am. Chem. Soc.*, **65**, 1639 (1943).
11. R.C. Fuson, T. San and J. Dickmann, *J. Org. Chem.*, **19**, 313 (1969); D. Vorlander and Siebert, *Ber.*, **39**, 1024 (1906).