

nals of **8** at 6.21 ppm, near 6.02 ppm and 3.78 ppm were disappeared. The formation of an aromatic system could be the driving force in this reaction.

The extension of the photoaddition reactions of *o*-quinones to conjugated systems, and the chemistry of these photoproducts, will be investigated.

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- Spectral data of **3**: IR (KBr), 3064, 3029, 2917, 1693, 1595, 1447, 1278, 969, 786, 758, 695 cm^{-1} ; UV (*n*-hexane), λ_{max} 330, 277, 263, 251, 222 nm; $^1\text{H-NMR}$ (CDCl_3), δ 8.12-7.02 (18H, aromatic), 6.21 (1H, d, $J=16.0$ Hz, $\text{PhCH}=\text{CH}$ -), 6.09-6.03 (2H, m, $\text{PhCH}=\text{CH}$ - and $\text{PhCH}(\text{O})$ -), 3.78 ppm (1H, dd, $\text{PhCH}(\text{O})\text{CH}$ -); $^{13}\text{C-NMR}$ (CDCl_3), δ 199.3 ppm ($\text{C}=\text{O}$), 134.7, 129.4, 128.8, 128.5 (2 C's), 128.2, 128.1, 127.8, 126.3, 126.2, 125.3, 123.9, 123.0 ppm (14 different aromatic CH's), 134.3 ($\text{PhCH}=\text{CH}$ -), 123.3 ($\text{PhCH}=\text{CH}$ -), 81.2 ($\text{PhCH}(\text{O})$ -), 62.8 ppm ($\text{PhCH}(\text{O})\text{CH}$ -), 140.5, 138.8, 136.9, 135.9, 130.0, 129.6, 89.7 ppm (7 quaternary C's); Mass (EI), m/e 414 (M), 206 (100%, DPBe), 77.
- The two overlapped ^1H signals of a vinyl proton ($\text{PhCH}=\text{CH}$ -) and a methine proton ($\text{PhCH}(\text{O})$ -) was well resolved into two distinct signals at 123.3 ppm and 81.2 ppm in the ^{13}C dimension.
- Spectral data of **8**: UV (*n*-hexane) λ_{max} 356, 338, 310, 302, 294, 270 nm; IR (KBr) 3029, 2917, 1560, 1426, 969, 786, 758, 695 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3), δ 7.39-7.23 (10H, m), 6.67 (1H, d, $J=16.0$ Hz, $\text{PhCH}=\text{CH}$ -), 5.96 (1H, dd, $J=16.0$ Hz and 5.92 Hz, $\text{PhCH}=\text{CH}$ -) 4.87 (1H, d, $J=7.65$ Hz, $\text{PhCH}=\text{CH}$ -), 4.70 ppm (1H, m, $\text{PhCH}=\text{CH}$ -); Mass (EI), m/e 394 (M).
- MMX calculation using PC Model (v. 3.2) showed different coupling constants for two isomers. The calculated values, $^3J(\text{cis})$ and $^3J(\text{trans})$, for the two adjacent CH bonds of $\text{Ph}-\text{CH}=\text{CH}$ - moiety were 4.77 Hz and 0.59 Hz, respectively, in which the calculated dihedral angles were 48° for *cis*-adduct **8** and 81° for *trans*-adduct.
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- Carbon peaks at 135.2, 121.3, 80.13, and 78.77 ppm were correlated with proton peaks at 6.67 ($\text{PhCH}=\text{CH}$ -), 5.96 ($\text{PhCH}=\text{CH}$ -), 4.87 ($\text{PhCH}=\text{CH}$ -), and 4.70 ppm ($\text{Ph}-\text{CH}=\text{CH}$ -), respectively. All aromatic carbons were observed between 129.4 ppm and 126.2 ppm.
- Spectral data of **9**: UV (*n*-hexane), λ_{max} 292, 285, 233, 223 nm; IR (KBr), 3064, 2959, 1595, 1461, 744, 702 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3), δ 7.72-7.68 (5H, m, aromatic) and 7.54-7.50 ppm (5H, m, aromatic); Mass (EI), m/e 390 (M).

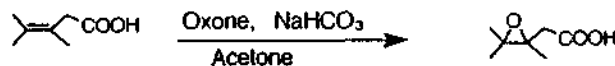
Epoxidation of β,γ -Unsaturated Carboxylic Acids by Dimethyldioxirane

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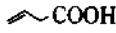
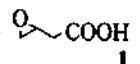
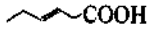
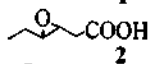
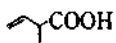
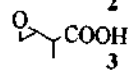

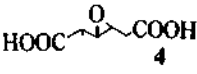
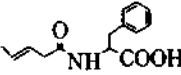
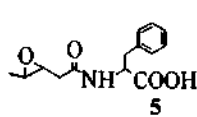

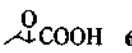
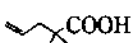
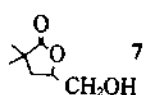
Peroxy acids, one of the most commonly used electrophilic epoxidizing agents, are not effective in the epoxidation of olefins containing carboxyl groups because of electron withdrawing property of the carboxyl group¹. Moreover the acid generated from the peroxyacid is difficult to separate from the desired product, epoxy acid. Nucleophilic epoxidizing agents, hydrogen peroxide together with various catalysts (base, tungsten, etc.), are effective only to α,β -unsaturated acids². Recently dimethyldioxirane³ has been employed for epoxidation of α,β -unsaturated ketones⁴, acids⁵ and esters. Not only electron rich alkenes such as enol ethers⁶ and lactones⁷ but also electron poor alkenes such as vinyltetrazoles⁸, flavons⁹ are also epoxidized by dimethyldioxirane in high yield. But not many unsaturated carboxylic acids have been epoxidized by dimethyldioxirane. Here we report this powerful agent, which can be generated *in situ* from potassium peroxomonosulfate (oxone) and acetone¹⁰, is effective in the epoxidation of β,γ -unsaturated acids.



Most β,γ -unsaturated acids tested in this study were rapidly reacted with dimethyldioxirane to give the corresponding epoxy acids in good yield (Table 1). The product yield decreased when there were two carboxyl groups or an amide group in the molecule. We confirmed that the epoxidation of α,β -unsaturated carboxylic acids are smoothly carried out by dimethyldioxirane, as reported previously⁴. But under the same reaction condition, a γ,δ -unsaturated carboxylic acid was transformed to the lactone instead of the epoxide. This is probably due to the spontaneous opening of epoxide.

The procedure⁸ for epoxidation of β,γ -unsaturated acids was very simple and convenient: Unsaturated acid (0.001

Table 1. Epoxidation of unsaturated carboxylic acids by dimethyldioxirane

Unsaturated acids	Epoxy acids	Time (h)	% yield
	 1	0.5	74
	 2	0.5	96
	 3	0.5	82
	 4	0.5	59
	 5	2.5	71
	 6	0.5	55
	 7	0.5	51

mol) was dissolved in 5 ml of acetone and 3 ml of water. With vigorous stirring, sodium bicarbonate (0.014 mol) and oxone (0.004 mol) were added to this solution. The stirring was continued for two hours at room temperature. The reaction mixture was acidified to pH 1-2 with conc. hydrochloric acid, then 50 ml of ethyl acetate was added. After filtration, two layers were separated and the water layer was extracted with ethyl acetate. The combined organic layer was dried and the solvent was removed *in vacuo*, yielding the epoxides. The products were reasonably pure judging from their NMR spectra¹¹. Only epoxy acid **5** required chromatographic separation.

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11. Spectral Data for epoxy acids
 Epoxy acid **1**: IR (neat): 3680-2400, 1730, 1050 cm^{-1} ; ¹H-NMR (100 MHz, CDCl_3): δ 2.4-2.6 (m, 2H), 3.4-3.6 (m, 2H), 4.1-4.2 (m, 1H); Epoxy acid **2**: ¹H-NMR (100 MHz, CDCl_3): δ 1.1 (t, 3H), 1.6-1.8 (m, 2H), 2.7 (t, 2H), 3.9-4.0 (m, 1H), 4.1-4.2 (m, 1H); Epoxy acid **3**: ¹H-NMR (100 MHz, CDCl_3): δ 1.2 (d, 3H), 2.6-2.8 (m, 1H), 3.5-3.6 (m, 2H), 4.0-4.2 (m, 1H); Epoxy acid **4**: ¹H-NMR (100 MHz, acetone-*d*₆): δ 2.4-2.7 (m, 4H), 4.0-4.3 (m, 2H); Epoxy acid **5**: ¹H-NMR (100 MHz, CDCl_3): δ 1.5 (dd, 3H), 2.6 (d, 2H), 3.1-3.2 (m, 2H), 3.9-4.2 (m, 2H), 4.8 (s, 1H), 7.3 (s, 5H), 7.8 (s, 1H); Epoxy acid **6**: ¹H-NMR (100 MHz, acetone-*d*₆): δ 3.0 (m, 3H), 3.3-3.5 (m, 1H), 4.0-4.2 (m, 1H); Lactone **7**: IR (neat): 3400, 2950, 1760, 1040 cm^{-1} ; ¹H-NMR (100 MHz, CDCl_3): δ 1.2 (s, 6H), 1.9-2.1 (m, 2H), 3.5-3.8 (m, 2H), 4.0 (1H), 4.5-5.6 (m, 1H).