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Author(s)	Maruyama, Kazuhiro; Ogawa, Takuji; Kubo, Yasuo
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PATERNO-BÜCHI REACTION OF ACID ANHYDRIDE
OXETANES FROM GLUTARIC ANHYDRIDEKazuhiro MARUYAMA, Takuji OGAWA, and Yasuo KUBO
Department of Chemistry, Faculty of Science,
Kyoto University, Kyoto 606

Glutaric anhydride underwent the Paterno-Büchi reaction with olefins and gave oxetanes in good yields. The quantum yield was 0.16. Acetic anhydride didn't undergo this reaction contrarily.

It has been established that simple carbonyl compounds, ketones and aldehydes, undergo the Paterno-Büchi reaction with olefins. However, examples of the reaction involving carboxylic acid derivatives as the carbonyl component are not so common. Previously we reported that N-methyl-glutarimide underwent the Paterno-Büchi reaction with a series of olefins to give oxetanes.¹⁾ We extended the reaction to carboxylic anhydrides, which can be regarded as more principal acid derivatives. Carboxylic anhydrides similarly reacted with olefins to give oxetanes upon irradiation. As for the photochemical reaction of acid anhydride, only α -cleavage reactions have been reported.²⁾ This is the first report of the Paterno-Büchi reaction of acid anhydrides.

Typically an acetonitrile solution of glutaric anhydride (0.175M) 1a and excess isobutene (ca. 1.3M) 2a was placed in a quartz vessel and irradiated with 120W low pressure Hg-lamp. After irradiation for about 240h., when almost all glutaric anhydride was consumed, excess isobutene and solvent were removed. Distillation of the brown residue by a Kugelrohr gave colorless oil in a yield of 67%, which was determined to be a mixture of oxetane isomers 3a and 4a based on the spectral data. ¹H NMR (CCl₄) δ 1.27 (s, 3H, Me), 1.30 (s, 3H, Me), 1.6-3.0 (m, 6H, methylene), 3.97 and 4.31 (ABq, J=6Hz, 2H, OCH₂) ; IR (neat) 1744, 932 cm⁻¹ ; MS (20eV) m/e (rel. intensity) 170 (M⁺, 18), 140 (91), 98 (100), 97 (100) ; elemental analysis, required C 63.51%, H 8.29%, found C 63.76%, H 8.39%. Isomeric oxetanes 3 and 4 can be distinguished by their ¹H NMR spectra of the mixture and the ratio of them (3 / 4) is about 7 estimated from the ¹H NMR signal area of methyl groups on oxetane ring. Other examples are summarized in Table.

The quantum yield of oxetane formation was determined to be 0.16, using 1a 0.1M and 2b 1.2M. This reaction was suppressed in the presence of about 0.7M butadiene, and the isomer 3 produced via more stable biradical intermediate was major. Therefore, it seems reasonable to conclude that this reaction occurs from the n π * triplet state of acid anhydride.

Under similar conditions photochemical reactions of acetic anhydride and N-methyl-acetylimide with olefins were also examined, but none of them succeeded to react. Extinction coefficient of acetic anhydride (log ϵ ~1.3 at 254nm³⁾) is comparable to that of glutaric anhydride (log ϵ ~1.2 at 254nm⁴⁾). We think the difference of photochemical behavior between open chain compounds (acetic anhydride and N-methyl-acetylimide) and cyclic compounds (glutaric anhydride and N-methyl-glutarimide) may be due to the differences of their triplet life time. Open chain

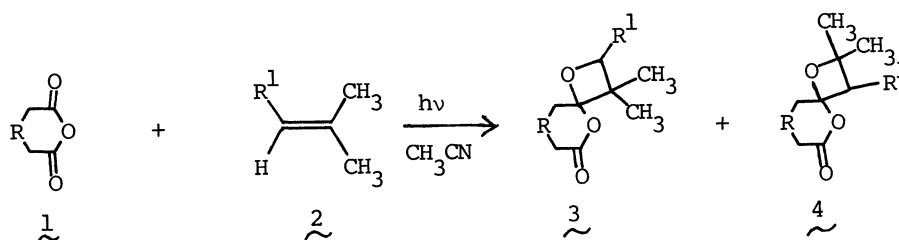


Table						
	R	R ¹	Products ⁷⁾	Yield(%) ^{a)}	b.p. (°C/torr) ^{b)}	
1a	CH ₂	2a	H	3a , 4a	67	90-95/0.03
1a	CH ₂	2b	Me	3b , 4b	54	93-96/0.03
1b	HCMc	2a	H	3c , 4c	59	80-85/0.01
1b	HCMc	2b	Me	3d , 4d	61	80-85/0.01
1c	CMe ₂	2a	H	3e , 4e	62	98-105/0.02
1c	CMe ₂	2b	Me	3f , 4f	70	102-110/0.02

a) Isolated yield b) Kugelrohr

compounds are apt to be more easily deactivated than cyclic compounds because of the larger freedom on molecular movement.⁵⁾

Succinic anhydride also undergo the Paterno-Büchi reaction, but the rate of the reaction was rather slower than glutaric anhydride and the anhydride cannot convert to the oxetane perfectly. Small extinction coefficient ($\log \epsilon \sim 0.1$ at 254nm⁶⁾) may reflect this slow conversion rate.

References and Notes

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