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PHOTOCYCLOADDITION OF O-ALKYL THIOBENZOATES TO OLEFINS. A CONVENIENT METHOD TO TRANSFORM OLEFINS TO KETONES (1)

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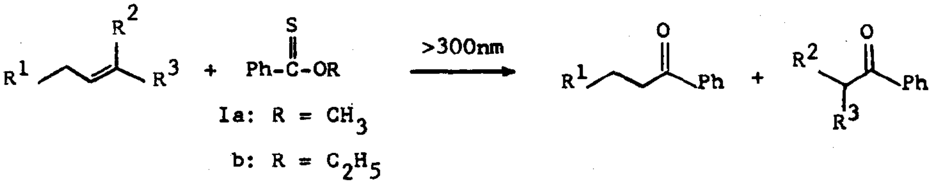
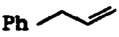
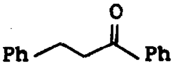
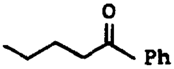
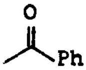
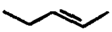
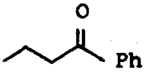
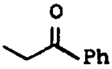
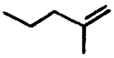
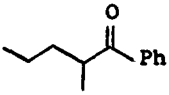
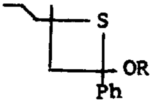
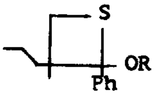
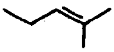
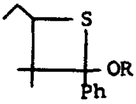
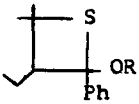
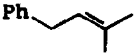
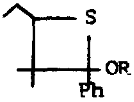
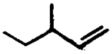
Thiocarboxylic acids and their esters have scarecely been subjected to photochemical studies (2). As an extension of our studies on photocycloadditions of thiocarbonyl compounds to olefins (3), we have employed O-alkyl thiobenzoates as substrates and found that the reaction has versatile synthetic applicability.



In a typical run, 0.5g of Ia and 2.6g of allylbenzene was sealed in a Pyrex reaction vessel (4) under atmosphere of carbon dioxide. The mixture was irradiated with light from 400 W high-pressure mercury lamp (Toshiba HP-400) for 10 days. The mixture was cooled with running water during the reaction. After the reaction, the low-boiling materials were evapolated under reduced pressure and the residue was chromatographed on a column of silica-gel with n-hexane as an eluent. Colorless oil thus obtained (0.69g, 100% yield) was identified as phenethyl phenyl ketone(II) by confirming the identity of spectral data with those of the authentic sample. The same reaction with O-methyl p-chlorothiobenzoate gave phenethyl p-chlorophenyl ketone, which implies that no bond-fission takes place, during the reaction, between thiocarbonyl-carbon and the aromatic ring. As summarized in

TABLE I. Photochemical Reactions of Olefins with O-Alkyl Thiobenzoates.

Olefin	Products (Yield, %)[a]							
	With Ia				With Ib			
	 II	100 (—)			II	100 (9.0)		
	 III	24.7 (7.1)	 IV	— (trace)	III	62.0 (19.0)	IV	— (3.9)
	 V	13.5 (8.3)	 VI	18.0 (5.0)	V	28.4 (10.9)	VI	27.8 (11.4)
	 VII	40.0 (7.9)	IV	— (trace)	VII	80.0 (4.5)	IV	— (trace)
	 VIIIa	4.7	 VIIIb	11.8	VIIIa	3.9	VIIIb	7.8
	 IXa	36.8	 IXb	26.2	IXa	52.9	IXb	33.1
	II	20.0			II	24.9		
	 X	48.0			X	65.0		
	No Reaction				No Reaction			

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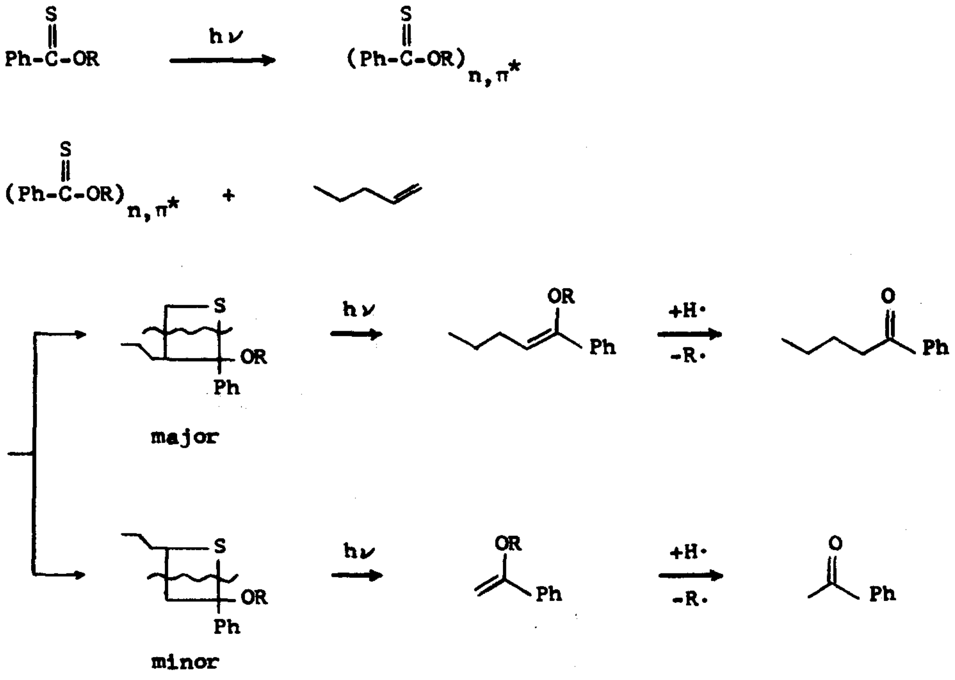
[a] Numbers in parentheses are the yields determined by vpc.

Table I, some olefins afforded 2-alkoxy-2-phenylthietanes (5).

On the other hand, when the reaction mixture was subjected to vpc analysis (XF-1150, 140°C), the yields of ketones were surprisingly low. For example, the yield of II from the reaction of allylbenzene with Ib was only 9.0% in contrast to quantitative yield by isolation. Thus, it is evident that a compound, which converts to a ketone on silica-gel quantitatively, is formed by the reaction. This compound was isolated and identified as 1-ethoxy-1,3-diphenylprop-1-ene. It is also confirmed that this olefinic ether affords II on standing with silica-gel. Similar results were obtained with other olefins.

We believe that the most prausible scheme for the reaction is as follows (exemplified by pent-1-ene):



Since the light of wavelength longer than 390nm is effective to the reaction (6, 7), there remains no doubt that the reaction is initiated by the n,π* state of I. The formation of methane and ethylene from the reactions of Ia and Ib, respectively, was confirmed by mass spectrometric analyses of gaseous products.

The intermediacy of a thietane derivative has been prooved by the fact that photo-irradiation to VIIIb transforms it to VII quantitatively. In contrast to the reactivity of VIIIb, decompositions of VIIIa, IX, and X do not take place so easily. Namely, a mixture of IXa and IXb gave isopropyl phenyl ketone in only 9% yield after photo-irradiation of 2 weeks. This fact suggests that substituents on a thietane ring play an important role for the photo-stability of these compounds (9).

It is noteworthy that an allylic methylene group is necessary for the reaction. In addition to 3-methylpent-1-ene listed in Table I, olefins that are quite reactive in photocycloadditions with thiobenzophenone but have no allylic methylene group, such as styrene, α- and β-methylstyrene, and ethyl vinyl ether (3), are also unreactive toward O-alkyl thiobenzoates.

Further studies on the scope, limitation, and mechanism of the reaction are in progress.

REFERENCES AND FOOTNOTES

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3. A. Ohno, Y. Ohnishi, and G. Tsuchihashi, J. Amer. Chem. Soc., **91**, 5038 (1969) and references cited therein.
4. A. Ohno, Y. Ohnishi, M. Fukuyama, and G. Tsuchihashi, ibid., **90**, 7038 (1968).
5. All new compounds gave satisfactory results of elemental analyses.
6. Toshiba UV-39 filter was used for this purpose.
7. O-Alkyl thiobenzoates have absorption maxima at around 290nm ($\varepsilon \approx 12{,}000$) and 420nm ($\varepsilon \approx 120$) due to π,π^* and n,π^* transitions, respectively (8).
8. A. Ohno, T. Koizumi, Y. Ohnishi, and G. Tsuchihashi, Bull. Chem. Soc. Jap., **42**, 3556 (1969).
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