Photocyclic Addition of Carbonyl Compounds to Allenes

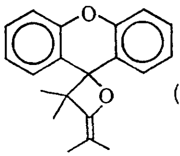
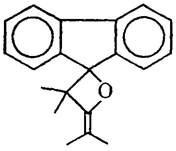
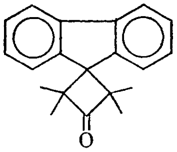
By HANS GOTTHARDT, REINHARD STEINMETZ, and GEORGE S. HAMMOND*
(*Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California* 91109)

THE recent report by Arnold and Glick[1] of some photochemical cycloaddition reactions between ketones and allenes prompts us to present the summary of related observations shown in the Table.

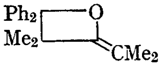
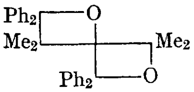
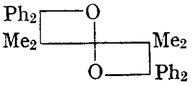
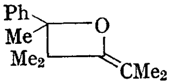
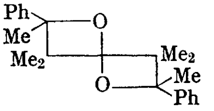
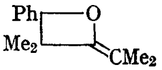
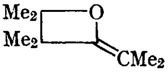
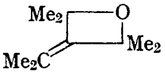
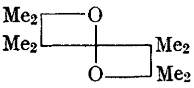
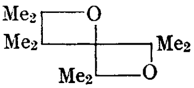
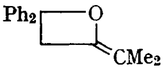
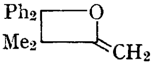
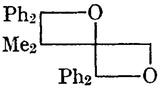
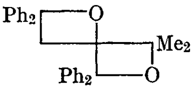
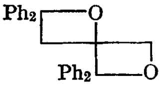
The results obtained in the two laboratories are very similar and our examples are largely complementary to those reported by the Carbide workers. Originally there was at least one puzzling inconsistency that has now been partially resolved. A solution of benzophenone in tetramethylallene was irradiated and worked up by distillation, column chromatography on Florisil, and recrystallization from methanol. After repeated recrystallization a bis-adduct melting at 87—89° was obtained. Arnold and Glick isolated two adducts melting at

TABLE

Photoaddition of ketones to allenes

Ketone	Substrate	Products	
Xanthone	$Me_2C:C:CMe_2$	 (I) m.p. 114–115°	
Fluorenone	$Me_2C:C:CMe_2$	 (II)[a]	 (III) m.p. 205–206°

TABLE—*continued*

Ketone	Substrate	Products
Ph_2CO	$Me_2C{:}C{:}CMe_2$	 (IV)[b]  (V)[c] m.p. 149–151°  (VI)[c] m.p. 150–152°
$PhCO{\cdot}Me$	$Me_2C{:}C{:}CMe_2$	 (VII)[b]  (VIII) m.p. 133–134·5°
$PhCHO$	$Me_2C{:}C{:}CMe_2$	 (IX)[b]
Me_2CO	$Me_2C{:}C{:}CMe_2$	 (X)[b]  (XI)[b]  (XII)[b]  (XIII) m.p. 81–82°
Ph_2CO	$Me_2C{:}C{:}CH_2$	 (XIV)[b]  (XV)[b]  (XVI)[b]  (XVII) m.p. 117–119°
Ph_2CO	$H_2C{:}C{:}CH_2$	 (XVIII) m.p. 127–127·5°

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[a] Not obtained free of contamination from (III).

[b] Liquid characterized by spectra, retention times in vapour chromatograms, and by chemical reactions.

[c] See text.

150·5—152·5° (their II) and 152—154° (their III). Direct comparison of infrared spectra indicated that our product was closely identical with their compound (II); similar comparison indicated that their (III) could be no more than a minor constituent of our sample. Thin-layer chromatography on benzene separated our product into three fractions. The principal fraction was recrystallized from aqueous ethanol giving a product melting at 147°, spectroscopically indistinguishable from Arnold and Glick's compound (II). The other products were obtained in only trace amounts and could not be crystallized; infrared spectra of carbon tetrachloride extracts showed that they were not Arnold and Glick's compound (III). We repeated the photoreaction by irradiation of a 0·1 M-solution of tetramethylallene and benzophenone in benzene. This led to formation of a mixture from which two bis-adducts were isolated. These products melted at 150—152° and 149—151° respectively and are apparently identical with the compounds isolated in the Carbide Laboratories, although exhaustion of the supply of their compound (III) prevents direct comparison. We conclude that there may be an interesting medium effect on the course of the cycloaddition reaction since somewhat different results are obtained from irradiations using neat tetramethylallene and those done in benzene solution.

There are two other interesting features in our results. The first is the formation of only one bis-adduct, spiroketal (VIII), from acetophenone and tetramethylallene. The second is the isolation of a small amount of a mono-adduct (XI), having what we should now consider to be abnormal orientation,[2] from acetone and tetramethylallene.

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[1] D. R. Arnold and A. H. Glick, *Chem. Comm.*, 1966, 813.