Synthesis of an Enol-ether of a Cyclopropanone from a Diazoalkenylether: a Novel Class of Compound

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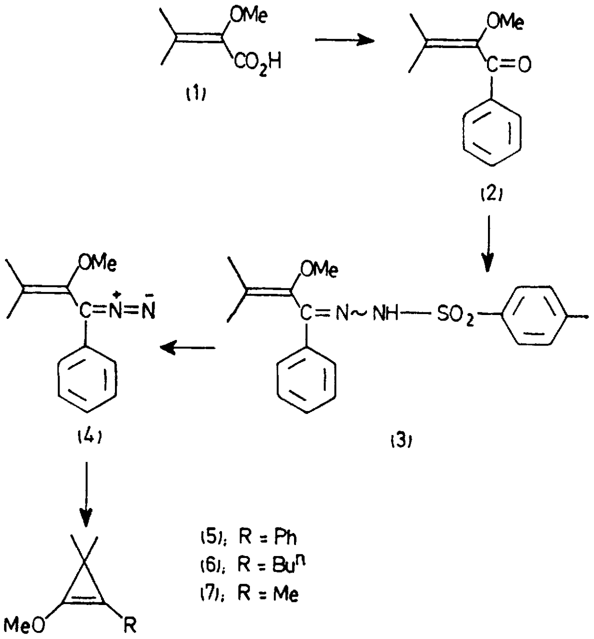
Summary Irradiation of 1-diazo-2-methoxy-3-methyl-1-phenylbut-2-ene (**4**), prepared from the *p*-toluenesulphonylhydrazones (**3**) of 2-methoxy-3-methyl-1-phenylbut-2-en-1-one (**2**), yields 1-methoxy-3,3-dimethyl-2-phenylcyclopropene (**5**).

Enol derivatives of cyclopropanones are potential intermediates of enolate anions of cyclopropanones[1] and of bicyclobutanes[2] with angular oxygen functions.[3] The synthesis of 1-methoxy-3,3-dimethyl-2-phenylcyclopropene (**5**), the first example of such compounds, has been reported[4] but it was prepared in disappointingly low yield. We now describe a more convenient synthesis of this compound.

Closs *et al.*[5] have reported a convenient synthesis of alkylcyclopropenes from diazoalkenes. We now report the synthesis of a diazoalkenylether which on irradiation undergoes smooth transformation to 1-methoxy-3,3-dimethyl-2-phenylcyclopropene (**5**). This route is also potentially a more general pathway† to these compounds than that described earlier.[4]

Stirring the lithium salt[6] of the acid[7] (**1**) with phenyllithium in ether at room temperature for 48 h gave 2-methoxy-3-methyl-1-phenylbut-2-en-1-one (**2**) b.p. 76°, 1·0 mmHg (73%). On treatment with *p*-toluenesulphonylhydrazine in methanol at 40° for 14 days the ketone (**2**) gave a mixture of the geometrically isomeric *p*-toluene sulphonylhydrazones (**3**) in virtually quantitative yield. Stirring an acid solution of (**3**) for several days at room temperature caused conversion to only one isomer, m.p. 145—146° (decomp.). Pyrolysis[8] of the dry lithium salts of (**3**) (170°, 0·7 mmHg) gave 1-diazo-2-methoxy-3-methyl-1-phenylbut-2-ene (**4**) as a liquid (70%) [i.r. (film) ν 2050, 1650 cm^{-1}; n.m.r. (CCl_4) δ 6·87—7·33 (5H, m), 3·40 (3H, s), 1·83 (3H, s), 1·63 (3H, s)]. Irradiation (Philips 125 W) of a 3% solution (CCl_4) of compound (**4**) in a pyrex vessel at room temperature for 40 min gave a solution containing only 1-methoxy-3,3-dimethyl-2-phenylcyclopropane (**5**) as shown by its n.m.r. spectrum[4] (CCl_4), δ 6·93—7·33 (5H, m), 3·97 (3H, s), 1·37 (6H, s). Complete evaporation of the solvent left an oil, the i.r. spectrum of which was identical to that obtained previously.[4] Of note is the strong absorption[9] at 1840 cm^{-1}. The neat liquid appeared to polymerise readily but solutions could be stored at low temperature for extended periods.



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† Preliminary work shows that compounds (**6**) and (**7**) can be synthesised by an analogous sequence.

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[9] 1840 cm^{-1} is the expected region for absorption of a fully substituted cyclopropene: G. L. Closs, *Adv. Alicyclic Chem.*, **1966**, **1**, 70.