STUDIES ON CARBENE AND KETENE REACTIONS

OBJECTIVES

The primary object of this work is to relate in a loose fashion the reactivity of car~~y~~benes and their starting molecules, the diazo compounds and α-diazo compounds with the ketenes. The work would then by itself indicate varied utility and procedures. The ketenes themselves may arise from the α-diazo ketones. [Hides Tomioka, Hiroshi Okuno, Yasuji Izawa, J.Org. Chem. 45 5278, 1980; Straesz, Gunning J.A.C.S. 91 1261, 1969]. In these cycloadditions a wide variety of changes may be effected and thereby the nature of products synthesized may be modified. For example studies recording cyclopropanation vs carbon-hydrogen or carbon-carbon insertion could be made. [Mignel E.Alonso, Patricia Janos, Maria I.Hernandez, J.Org. Chem. 45 5299, 1980; also J.C.S. Perkin I 2240, 1974, J.C.S. Chem. Commun. 142, 1975, R. Pellicciari, B.Nataline J.Chem.Soc. Perkin I 1822, 1977; E.W.Colvin B.J.Hamill J.Chem.Soc.Perkin I 869, 1977]. Then studies for the pathway for Thermal vs Photochemical reaction of the reactive intermediates may be made or isolation of the 1,3 addition products of the diazo compound and their subsequent changes studied. At present, work in this area has become more accessible for example it is possible to prepare α-diazoketones by a variety of methods. [L. Lombardo, L.N.Mander Synthesis 368, 1980].

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In the outstanding works in connection with the synthesis of Insect Juvenile Hormones [M.Julia, J.Julia R. Guegan Bull. Soc. Chim Fr. 1072, 1960; K.H.Dahm, B. Trost, H.Roeller J.A.C.S. 89 5292, 1967; M.Julia S.Julia, S.Y. Tchen, Bull. Soc. Chim. Fr. 1849, 1961; S.F.Brady, M.A. Ilton, W.S.Johnson JACS 90 2882, 6225, 1968; B.M. Trost Accounts Chem. Res. 3 120, 1970], We have one type of model for ring opening of cyclopropyl carbinyl alcohols to homoallylic halides. One thing that emerges is that the geometry of the resulting olefin should be determined mainly by the eclipsing interactions developing in the transition state for ring cleavage. The cyclopropane systems themselves could be prepared in a variety of ways apart from the methods used in this work [Cf. Tetrahedron 31 2785, 1975; Organic Syntheses 54 11 (1974); 55 12 (1976)]. The methods themselves can be varied [T.Hiyama, M.Shinada, M.Tsukanaka, H.Nozaki Bull Chem. Soc. Jpn. 53 1010, 1980; G.Backe, Klaus Buckl, D.Martens, D.R.Schneider H.Ulrich-Wagner Ber. 112 2961, 1979; J.P.McCormick, D.L.Barton J. Org. Chem. 45 2566-2570, 1980; Chem. Lett. 1025, 1976] as also the final objective for ring opening or ring enlargement and subsequent treatment of products. [C. Georgonlis, W.Smadja, J.M.Valery Synthesis 572, 1981] can be suitably modified.

The employment of pure cis or trans isomer of the olefinic substrate could in theory result in a particular favoured product isomer. Sometimes formation of isomeric product may be absent [Cf. M.P.Doyle, D.Van Lensen, W. Tamblyn Synthesis 787, 1981].

The character of the olefin can be changed from simple olefins like cyclohexene to strained system like norbornadienes etc. or from simple terminal systems like styrene to more heavily substituted carbon-carbon double bonded systems and their reactivity and product differences compared under various reaction conditions.

In recent years great use is being made of inorganic compounds in organic syntheses. In this field also various workers have tried Palladium II Acetate, Rhodium II, Moser catalyst, Copper acetylacetonate [Minoru Suda Synthesis 714, 1981; S.Kulkowit, M.A.McKervey J.Chem.Soc. Chem. Commun. 1069, 1978; M.P.Doyle, W.E.Buhro, J.F.Dellaria, Tetrahedron Lett 4429, 1979; Synthesis 629, 1975. Tetrahedron Lett. 629, 1975, N.Petiniot, A.J.Anciauk, A.F. Noels, A.J.Hubert, P. Teyssie, Tetrahedron Lett. 1239, 1978]. Thus use of various catalysts is another parameter that could be altered affecting reactivity and product yield.

In base catalysed reactions the use of quaternary ammonium salts in a two phase system or of crown ethers, is often immensely advantageous. Several workers have shown that even the use of these expensive chemicals can be avoided by the use of strong alkali and dioxane [F. Fedorynskii Synthesis 783, 1977, T.Fujita, S.Watanabe, K.Suga, K.Sugahara, Synthesis 1004, 1981; A.Jonczyk, J. Wlostowska Synth. Commun. **8** 567, 1978; Newman-Beal modification of Arndt-Eistert Organic Synthesis **50** 77, 1970].

The work detailed in this dissertation is to be viewed according to the above perspectives.