Ring-opening of Diethyl 2-Vinylcyclopropane-1,1-dicarboxylate

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Summary The title compound is shown to undergo preponderant nucleophilic attack at the methine position but suffers ring-opening *via* free radicals by attack at the terminal methylene.

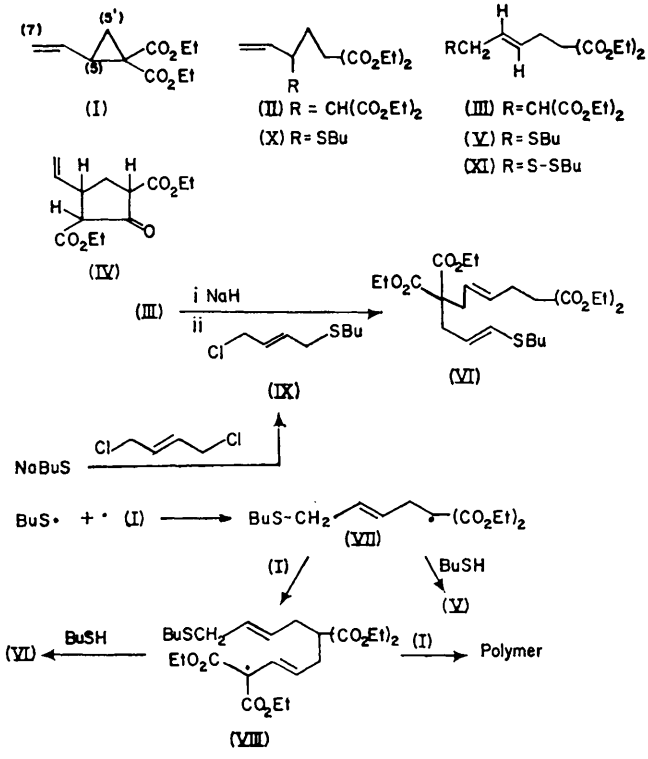
COMPOUND (I) is, in principle, susceptible to attack by nucleophiles in a 1,5-, 1,5′-, or 1,7-sense.[1]† When (I) is heated with diethyl sodiomalonate in ethanol under reflux,[2] a series of products‡ is produced which arises almost exclusively from the 1,5- (in this case indistinguishable from 1,5′) mode of opening. Stewart[3] and Rovnyak[4] reported that amines react with (I) exclusively *via* the 1,5-pathway. The report[3] that the uncatalysed reaction of butanethiol with (I) proceeds, exclusively, by the 1,7-pathway is thus surprising. Competitive (to an unspecified extent) 1,5- and 1,7-attack was reported when the thiol addition was catalysed by sodium ethoxide.[3] The thermal (190°) opening of (I) with enamines is reported to occur, exclusively by the 1,7-mode.[1] We present here and in the following communication related results.

In contrast to the Linstead conditions,‡[2] the reaction of (I) with diethyl sodiomalonate (generated *via* NaH) in dimethoxyethane (dme) leads, after rapid quenching, to a two-component mixture (5:1) of the primary products of homoconjugate addition (II) and (III).§ After prolonged heating of the dme solution under reflux, acidification gives a 5:1 mixture of (IV)[2] and (III). Reversibility between the anionic precursors of (II) and (III) appears unlikely since the 5:1 ratio of (II + IV) to (III) is maintained, after acidification, through the process.

Reinvestigation of the uncatalysed reaction of butanethiol showed that the only 1:1 adduct was (V)§ (17%). However, we also obtained a nearly equivalent yield of (VI)§ whose structure was confirmed by independent synthesis *via* alkylation of the sodium salt of (III) with the chlorosulphide (IX).

One scheme for the formation of (V) and (VI) entails attack by a butanethiol radical at the terminus of the olefinic linkage of (I) with concurrent ring opening to afford the malonyl radical (VII)[6] The latter could abstract hydrogen from the thiol to give (V) or cause another radical opening of (I) to give radical (VIII). Hydrogen abstraction by (VIII) would then produce (VI) or alternatively, reaction with (I) (*etc.*) would give polymer.

The reaction of butanethiol in ethanol with (I), in the presence of EtONa (0·1 equiv.) gave, cleanly, (X)‡¶ (79%). However, reactions in dme under reflux were less specific. After prior conversion of all the thiol into mercaptide (with NaH) reaction with (I) gave an 81:19 mixture [combined yield 60%with 4% recovered (I) and no detectable (VI)] of (X) and (V). The same reaction, after 50% prior conversion into sodium mercaptide, gave a 2:1 mixture [combined yield 59%, with 5% recovered (I) and 2% of (VI)] of (X) and (V). When only 10% of the thiol was used in the form of its sodium salt, a 1:1 mixture [51% combined yield, 24% recovered (I) 6% of (VI)] of (X) and (V) was



produced. When the same reaction was conducted in the presence of excess of elemental sulphur, traces of a 1:12 mixture of (X) and (V) were obtained. The major product (35%) was the disulphide (XI).§

These results are most readily interpreted in terms of competing 1,7-radical and 1,5-nucleophilic pathways. The former is reduced in importance relative to the latter with

† See footnote in ref. 1 for use of this numbering.

‡ The mixture produced under the Linstead[2] conditions is complex (g.l.c.–m.s.). Qualitatively, it consists primarily of (II), (IV) and monode-ethoxycarbonylated derivatives, and also a 1,5-adduct with ethanol. Compound (III) was not identified positively under these conditions. However, its presence (or a de-ethoxycarbonylated derivative) in small amount was inferred since traces of suberic acid were obtained after catalytic hydrogenation, hydrolysis, and decarboxylation of a partially purified portion of the reaction mixture.

§ The structures of all new compounds are in accord with their i.r., n.m.r., and mass spectra. The *trans*-geometry of the disubstituted double bonds was assigned on the basis of i.r. analysis.

¶ Although it was not obtained pure, its presence along with (V) was inferred by Stewart[3] by i.r. analysis. In this sense, our findings in ethanol differ sharply from those previously reported, but those in DME (mixtures) are comparable to those previously reported for ethanol. These mixtures were analysed by g.l.c. comparison with homogeneous samples of (V), (VI), and (X).

increasing amounts of mercapatide. In the presence of sulphur the reacting species is primarily the n-butyldithiyl radical which reacts, as above, in a 1,7-fashion. Whether the minor amount of (V) which is produced in dme from the 100% mercaptide reflects the competition of the 1,7-nucleophilic process (*cf.* malonate reaction in the same solvent) or arises from autoxidation,[7] as a preliminary to the radical pathway, is unclear. In any case, the enamine reaction is an exception to the proposition that 1,5-addition is the predominant pathway for nucleophilic attack upon compound (I).

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