Some Reactions of Trismethylenemethyl from the Photolysis of Tricarbonyltrismethylenemethyliron

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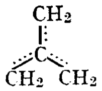
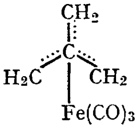
Trismethylenemethyl (2-methylenetrimethylene) (I) has received much theoretical attention;[1] and recently Dowd has demonstrated the existence of the species as a ground-state triplet by e.s.r. spectroscopy[2] (*cf.* also ref. 3). The molecule (I) is possibly an intermediate in the reaction between 3-iodo-2-iodomethylpropene and Na–K vapour, which gives 1,4-bismethylenecyclohexane (V) and its dehydrogenation product, *p*-xylene.[4] Species of this kind have been postulated in several other experimental studies.[5] We have studied the photolysis of the known[6] metal complex, trismethylenemethyliron tricarbonyl (II), as a possible method of generating trismethylenemethyl (*cf.* the photolysis of tricarbonylcyclobutadieneiron[7]), and report here the formation of trismethylenemethyl dimers and cycloadducts.



(I)



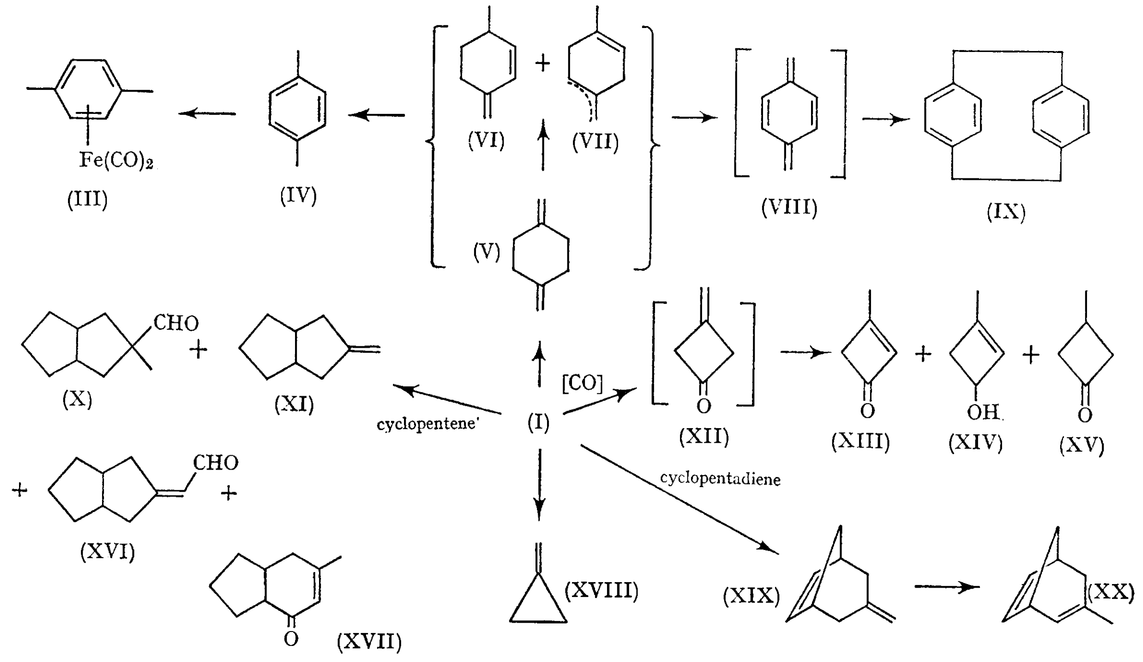
(II)

The complex (II) was photolysed (medium-pressure mercury lamp; nitrogen atmosphere; room temperature) in n-pentane, as inert solvent, and in cyclopentene and cyclopentadiene, as potential trapping agents for the species (I). The cyclopentadiene reaction was carried out in Pyrex to minimise photodimerisation of the diene; quartz apparatus was used with the other solvents. All three photolyses gave many products, and for analysis the combined gas chromatography–mass spectrometry technique was necessary. We note here only those products of most interest within the present context. Quoted yields are based on g.l.c. peak areas (flame detector), and are thus only a very rough guide to product composition.

Photolysis in n-pentane (*ca.* 20 products) gave moderate amounts of the expected trismethylenemethyl dimer [(V); 6%], the dienes [(VI); 6%] and [(VII); 3%], and *p*-xylene [(IV); 20%]. The dienes (VI) and (VII) were probably formed from 1,4-bismethylenecyclohexane (V) by Fe(0)-catalysed[8] isomerisation, *p*-xylene by dehydrogenation of the C_8H_{12} isomers. (The presence of molecular oxygen was not essential for the formation of *p*-xylene; though exposure of the photolysate to air led to an increased yield of *p*-xylene at the expense of the dienes.) A particularly intriguing product was [2,2]paracyclophane [(IX); 3%], readily isolable because of its insolubility and identical in all respects with an authentic sample. This probably arose *via* *p*-xylylene (VIII), the dimerisation of which to [2,2]paracyclophane is well-known.[9]

In cyclopentene (*ca.* 16 products), the formation of the trismethylenemethyl dimers (V)—(VII) and *p*-xylene was completely suppressed. A product (5%) of molecular formula C_9H_{14} had a mass spectrometric fragmentation pattern consistent with the bicyclic structure (XI), and thus constitutes the first example of the cycloaddition of trismethylenemethyl to an isolated double bond. Skell and Doerr reported that trismethylenemethyl undergoes cycloaddition to cyclobutadienes[4a] but not to ethylene.[4b]

The three cyclobutane derivatives [(XIII); 29%],



[(XIV); 11%], and [(XV); 3%] were isolated from the cyclopentene reaction by preparative g.l.c. and fully characterised. They were probably formed by carbonylation of trismethylenemethyl, the primary product of which would be 3-methylenecyclobutanone (XII), and subsequent isomerisation and/or hydrogenation. Likewise, the products [(X); 4%; *exo–endo* isomers], [(XVI)?; 18%], and [(XVII); 1%] presumably derive from cyclopentene–trismethylenemethyl adducts by insertion of carbon monoxide. The cyclobutanes (XIII)—(XV) were also detected in the n-pentane photolyses, but in rather low yield (*ca.* 1%). Such carbonylated products provide no evidence for the intermediacy of free trismethylenemethyl in the reactions, since they must all be formed within the ligand sphere of a metal atom.

In cyclopentadiene (*ca.* 16 products), as in cyclopentene, none of the C_8-compounds (IV)—(VII) was formed. A substantial product was the 1,4-cycloadduct [(XIX); 23%] of trismethylenemethyl and cyclopentadiene. This underwent slow non-photochemical conversion to the endocyclic isomer (XX) when the crude photolysate was allowed to stand at 0°. Compounds (XIX) and (XX) were identified mass spectrometrically and, after isolation, by n.m.r. comparison with authentic samples prepared as recently described.[10] A bicyclic hydrocarbon C_9H_{16} (11%) formed in the photolysis is, on the basis of its mass spectrum, tentatively formulated as a tetrahydro-derivative of the methylenebicyclo-octene (XIX).

Intramolecular cyclisation of trismethylenemethyl was indicated by the detection of methylenecyclopropane (XVIII) and methylcyclopropane in the cyclopentadiene reaction. The yields (1—2%) are minimum estimates, since no precautions were taken to prevent loss of these highly volatile hydrocarbons. Attempts are currently under way to determine the yields of these compounds in all three photolyses.

In the photolyses in cyclopentene and cyclopentadiene, solvent dimers were produced. In pentane and cyclopentadiene, several metal complexes were formed: *inter alia*, hydrodicarbonylcyclopentadienyliron (32%) and ferrocene (10%) in cyclopentadiene; dicarbonyl-*p*-xyleneiron (III; 6%) and a complex $C_8H_{12}Fe(CO)_3$ (8%) in n-pentane. Some of the other complexes of secure structure, *e.g.* tricarbonylisopreneiron (5% in pentane), offer fascinating mechanistic problems which will be discussed later.

Such products as methylenecyclopropane (XVIII), 1,4-bismethylenecyclohexane (V), and *p*-xylene strongly suggest that free trismethylenemethyl is involved in the above reactions, particularly since the formation of dimers and *p*-xylene is suppressed by cyclopentene and cyclopentadiene.

Furthermore these compounds [(XVIII) in extremely low yields] were obtained by Skell in his entirely different approach to trismethylenemethyl.[4] Also, the formation of the cycloadducts (XI) and (XIX) can readily be rationalised on the basis of symmetry-allowed reactions of trismethylenemethyl. However, the role played by metal complexes in these reactions cannot yet be assessed.

(*Received, July 26th*, 1968; *Com.* 1013.)

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