Photochemical Preparation of Thiophen 1,1-Dioxide–Tricarbonyliron Complexes

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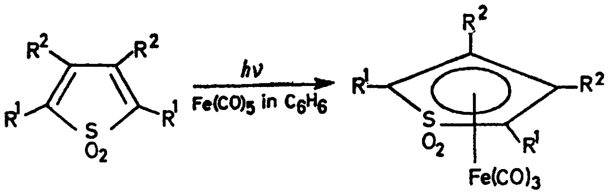
Summary The photochemical synthesis of the thiophen 1,1-dioxide–tricarbonyliron complex and two other related complexes substituted in the thiophen ring is described.

IT is well known that certain reactive dienes, such as cyclobutadiene, can be stabilized when complexed with a metal carbonyl moiety.[1,2] Syntheses of diene–metal complexes by heating are, however, not generally practicable due to the thermal instability of the reactive dienes. We now report that a stable tricarbonyliron complex of the hitherto unisolated thiophen 1,1-dioxide (**1**) can be synthesized by a photochemical method.

The feasibility of the photochemical synthesis was first shown using thermally stable 2,5-dimethylthiophen 1,1-dioxide[3] (**2**) and tetraphenylthiophen 1,1-dioxide[4] (**3**). Irradiation of a benzene solution of (**2**) (0·01M) and $Fe(CO)_5$ (ϵ *ca.* 1500 at 300 nm, 0·02M) in a Pyrex apparatus for 50 min gave 2,5-dimethylthiophen 1,1-dioxide–tricarbonyliron (**5**, m.p. 146—148°) in 90% yield after chromatography. Photolysis over a longer period led to the formation of an amorphous precipitate which was subsequently shown to be a photolysis product of (**5**). The structure of (**5**) was deduced from spectral data [λ_{max} 275 nm (ϵ 3100); n.m.r. δ 5·38 (s) and 1·75 (s)]. Similar irradiation in the presence of dioxide (**3**) was complicated by precipitation of the products thus decreasing the efficiency of the photoreaction. However, the corresponding

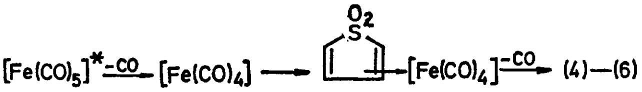


(**1**) $R^1 = R^2 = H$ (**4**)
(**2**) $R^1 = Me$ $R^2 = H$ (**5**)
(**3**) $R^1 = R^2 = Ph$ (**6**)

$Fe(CO)_3$ complex (**6**) (m.p. 232°, lit.[5] 232°) was isolated in 50% yield.

(**1**) has been previously prepared in solution and identified by its u.v. absorption and the decomposition products.[6,7] After some experimentation, a benzene solution of (**1**) was prepared by heterogeneous dehydrobromination, at ice-temperature, of 3,4-dibromotetrahydrothiophen 1,1-dioxide (m.p. 139—141°), which was, in turn, prepared by bromination of 2,5-dihydrothiophen 1,1-dioxide.† The benzene solution of (**1**) (0·02M) was irradiated in the presence of an excess of $Fe(CO)_5$ (2—5 fold excess) at room temperature for 1—2 h; (**4**) [m.p. 189—190°; λ_{max} 265 nm (ϵ 3200); n.m.r. δ 5·97 (m) and 4·48 (m)] was isolated in 60% yield after direct recrystallization from benzene. Among the most intense m.s. peaks are the 228, 200, 172, and 108 that correspond to the successive removal of three CO and SO_2 groups. This indicates that the iron π electron bonding system is very stable and that a cyclobutadienyl derivative may be formed as a transient species after the electron impact. While this fragmentation pattern is common to compounds (**4**), (**5**), and (**6**), that of tetraphenylcyclopentadienone–tricarbonyliron exhibits no tendency to extrude the ring CO before the iron atom is eliminated.

It has been suggested[8,9] that photolysis of $Fe(CO)_5$ gives a transient $Fe(CO)_4$ species which is expected to be a strong π-electron acceptor. This transient species is probably derived from an excited $Fe(CO)_5$ species and co-ordinates with one of the π-bonds of the dioxide to give intermediate (**7**). Collapse of the intermediate (**7**) to give the final product (**4**—**6**) is probably aided by an intramolecular displacement of a CO group.[8] This photochemical synthesis is very efficient and may be generally applicable to the preparation of other types of metal carbonyl complexes.



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We thank the National Research Council of Canada for financial support. J.F. is a fellow of the Coopération Culturelle au Canada, 1970—1971.

(*Received*, 1*st February* 1972; *Com.* 151.)

† The formation of dioxide (**1**) is followed by the u.v. absorption at 290 nm (ϵ is taken as 1000) and is found to be complete in *ca.* 1 h. Although in this heterogeneous system an excess of sodium hydroxide does not cause an appreciable decomposition of (**1**), in a homogeneous system (such as MeO^-–MeOH) the peak height decreases rapidly in the presence of an excess of the base.

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