Photochemistry of Ferrocenyl Ketones and Acids in Dimethyl Sulphoxide and Related Solvents

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Compounds of the type FcCOAr, FcCOR (R = Alkyl), and FcCHO undergo photoaquation ($\lambda > 280$ nm) in wet dimethyl sulphoxide, pyridine, dimethylformamide, and related solvents to give a cyclopentadienyliron salt of the acid $ArCO_2H$ or RCO_2H together with a molecule of free cyclopentadiene derived from the originally substituted ring. At shorter wavelengths in DMSO a secondary reaction gives rise to the intense purple colouration described previously. Ferrocenecarboxylic acid undergoes similar consecutive changes in these solvents yielding initially a carboxylate and free cyclopentadiene, but then CO_2 and a new carboxylate from which starting material could be recovered in 48% yield. With shorter wavelength light a purple colouration developed. The esters of this acid were also found to be photosensitive but subject to strong autoretardation.

NOT only is ferrocene itself apparently remarkably inert to photo-irradiation except in chlorocarbon solvents,[1] but the presence of a ferrocenyl group (Fc) in a molecule containing a photoactive functional group, such as that of an aromatic carbonyl compound, can impart a remarkable change in the level and direction of photoreactivity.[2] Bozak [2] has summarised the several attempts to photoreduce benzoylferrocene using such solvents as propan-2-ol which are well known to reduce benzophenone to benzpinacol *via* the triplet state of the solute in a quantum yield of almost one. Nesmeyanov has found ferrocene-1,1′-dicarboxylic [3] and -disulphonic acids [4] to undergo metal–ring cleavage on prolonged photolysis in aqueous or aqueous-alkaline solution to give derivatives of cyclopentadiene or its dimer. An interesting report of Tarr and Wiles [5] refers to a somewhat greater photoreactivity of 1,1′-dibenzoylferrocene towards propan-1-ol and methanol and brief reference is given to a relatively rapid colour change to deep purple in the solvents, pyridine, dimethyl sulphoxide (DMSO), and dimethylformamide (DMF) (but not acetonitrile), but no attempt was made to characterise these reactions further. One possible explanation for the colour change lies in the formation of a ferrocene ketyl radical-anion $FcCOPh^{\cdot -}$ which has been characterised by e.s.r. spectroscopy,[6,7] and we report here a detailed account of the relatively rapid photoreaction of benzoylferrocene in these particular solvents and observations on a number of related compounds of the general formula FcCOX where X = Ph, Ar, Me, H, OH, OR, and NH_2: our results indicate that the photoreaction does not involve radicals derived from ferrocene but is rather a photoaquation involving solvent impurity followed by both ring–metal and ring–carbonyl cleavage in the case of the ketones, and a ring–metal cleavage in the case of $FcCO_2H$ followed by a decarboxylation to give a second carboxylate from which starting material could be recovered. A preliminary account of this work has appeared.[8]

EXPERIMENTAL

Irradiations.—The source of light was a Hanovia high-pressure mercury arc model u.v.s. 250, fitted with a Hanovia power supply unit model 220/A. The irradiation vessel was a 15 × 1·5 cm Pyrex condenser sealed at one end and with a greaseless joint at the open end. All irradiations were carried out at ambient temperature, with water flowing through the condenser jacket. Alternatively a thin layer (0·01—0·02 cm) of a solution of the particular compound was directly irradiated in the i.r. cell (NaCl windows) fitted with a suitable filter. For unfiltered u.v. irradiations, solutions were placed in a quartz tube fitted with a greaseless joint, and exposed to the lamp at a distance of *ca.* 30 cm. The vessel was cooled with a continuous blast of cold air.

Solutions were deoxygenated either by nitrogen bubbling or by vacuum freeze–pump–thaw technique. They were handled in a nitrogen-flushed dry-box.

Actinometry.—The method of Hatchard and Parker [9] was utilised. The irradiation wavelength of 435 ± 20 nm was isolated with a Balzer filter.

Monitoring Equipment.—The spectroscopic measurements were carried out with the following instruments: u.v.–visible, Cary 14 and Unicam SP 800; i.r., Perkin-Elmer 457; n.m.r., Perkin-Elmer R12; mass spectrometry, A.E.I. MS902.

Materials.—2-Carbonylferrocenes and related compounds (except the t-butylferrocenes and acetonylferrocene) were either prepared by standard methods or obtained from:

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[1] E. Koerner von Gustorf and F. W. Grevels, *Fortschr. Chem. Forsch.*, 1969, **13**, 366.

[2] R. E. Bozak, *Adv. Photochem.*, 1971, **8**, 227.

[3] A. N. Nesmeyanov, V. A. Sazonova, and V. I. Romanenko, *Doklady Akad. Nauk S.S.S.R.*, 1963, **152**, 1358.

[4] A. N. Nesmeyanov, V. A. Sazonova, V. I. Romanenko, and G. P. Zohikova, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1965, 1964.

[5] A. M. Tarr and D. Wiles, *Canad. J. Chem.*, 1968, **46**, 2725.

[6] C. Elsenbroich and M. Cais, *J. Organometallic Chem.*, 1969, **18**, 135.

[7] J. M. Lister and T. J. Kemp, unpublished observations.

[8] L. H. Ali, A. Cox, and T. J. Kemp, *J.C.S. Chem. Comm.*, 1972, 265.

[9] C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc.*, 1956, **A235**, 518.

Koch–Light Laboratories Ltd., Research Organic Chemicals (ROC/RIC) Corp., or Alfa Chemicals.

All compounds were purified by chromatography on silica gel (eluting with benzene) and crystallised from hexane or hexane–benzene. Dry DMSO was obtained by distillation from powdered CaH_2, and dry pyridine by distillation from KOH pellets.

Preparation and Separation of t-Butylbenzoylferrocenes.—This was based on the acetylation procedure of Nagai *et al.*[10] To a solution of t-butylferrocene (6·3 g) in dry CH_2Cl_2 (100 ml) in a 250 ml three-necked flask connected to a reflux condenser was added dropwise 50 ml of a solution in CH_2Cl_2 of $AlCl_3$ (3·1 g) and benzoyl chloride (4·3 ml). Precautions were necessary to ensure dryness. After the addition of the benzoylating agent was completed (2 h), the solution was stirred further for 1 h at room temperature and then slowly poured onto ice (100 g) which had been previously acidified by addition of dilute HCl (10 ml). The organic layer was separated and the aqueous layer was extracted several times with CH_2Cl_2, the extracts being combined with the organic layer. The CH_2Cl_2 solution was washed twice with water and dried over $MgSO_4$. Removal of solvent resulted in a red viscous liquid which was chromatographed on silica gel with benzene eluant. These components were resolved:

(a) R_F 0·9 band was unreacted t-butylferrocene (0·1 g).

(b) R_F 0·8 band (red-purple, 0·4 g). This was a viscous liquid, ν(CO) absorption at 1638 cm^{-1} (DMSO), ' MC ' band at $\lambda_{max.}$ 460 nm (DMSO) and n.m.r. absorptions at τ 2·20 (m, 3H), 2·67 (m, 2H), 5·92 (s, 5H), 5·85—5·95 (m, 3H), and 8·95 (s, 9H), measured in $[^2H_6]$DMSO, proves it to be 1-benzoyl-2-t-butylferrocene (*A*). The mass spectrum exhibited the molecular ion at *m/e* 346 and the other major peaks, their assignments and intensities are as follows: 346, $C_{21}H_{22}FeO^+$ (molecular ion M^+), (100); 331, ($M^+ - CH_3$), (0·8); 316, ($M^+ - 2CH_3$), (0·7); 301, ($M^+ - 3CH_3$), (0·6); 289 ($M^+ - C_4H_9$), (0·9); 226, $[M^+ - (C_4H_9 + \pi\text{-}C_5H_3)]$, (40); 121, $C_5H_5Fe^+$, (12); 105, $C_6H_5CO^+$, (44); 77, $C_6H_5^+$, (20); 65, $C_5H_5^+$, (3); 63, $C_5H_3^+$, (2·4); 56, Fe^+, (8) 28, CO^+, (24) (Found: C, 73·3; H, 6·7; Fe, 15·4; O, 4·6. Calc. for $C_{21}H_{22}FeO$: C, 72·8; H, 6·35; O, 4·65; Fe, 16·2%).

(c) R_F 0·55 band (7·6 g). A viscous red liquid exhibiting n.m.r. absorptions at τ 9·1 and 9·2 in a ratio of 2 : 1 suggesting a mixture of two t-butylferrocenes. The assignment of these two compounds to 1-benzoyl-3-t-butylferrocene (*B*) and 1-benzoyl-1-t-butylferrocene (*C*) respectively, is compatible with the other n.m.r. absorption bands in the τ 2—3 (phenyl protons) and 4—5 regions ($\pi\text{-}C_5H_5$ protons), and the ν(CO) absorption at 1638 cm^{-1}. Additional,support for this assignment comes from the mass spectrum of the mixture which exhibited the following *m/e* ratio, ions, and % intensities: 346, $C_{21}H_{22}FeO^+$ (molecular ion M^+), (100); ($M^+ - CH_3$), (15); 316, ($M^+ - 2CH_3$), (1·5); 301, ($M^+ - 3CH_3$), (0·3); 289, ($M^+ - C_4H_9$), (0·5); 226, $[M^+ - (C_4H_9 + \pi\text{-}C_5H_3)]$, (43) {in B}; 197, $[M^+ - (C_3H_8 + C_6H_5CO)]$, (8); 186, $C_{10}H_{10}Fe^+$ (ferrocene), (3); 141, $[M^+ - (C_6H_5 + O + C_4H_9 + \pi\text{-}C_5H_5)]$, (16) {in B} $[M^+ - (C_6H_5CO + C_3H_4 + \pi\text{-}C_5H_4)]$ (29) {in C}; 63, $C_5H_3^+$, (2); 56, Fe^+, (30); 28, CO^+, (53).

Chromatographic separation of the two isomers, *B* and *C*, proved impossible and no resolution occurred with a range of eluants employing a 3 × 60 cm silica gel column.

Preparation of Acetonylferrocene.—Ferrocene (9 g, 0·048 mol) was dissolved in CH_2Cl_2 (80 ml) and chloroacetone (4·6 g, 0·05 mol) was added. BF_3 Was bubbled through the solution until white fumes were evolved (1—2 min) and the solution was stirred overnight, following which aqueous sodium acetate (100 ml) was added. The aqueous layer was separated, washed twice with CH_2Cl_2 (20 ml), and the washings were combined with the original organic layer. The combined organic layer was then washed twice with 30 ml portions of aqueous Na_2CO_3 and three times with 30 ml portions of H_2O and subsequently dried with $CaCl_2$. CH_2Cl_2 Was removed by evaporation on a water-bath and the orange residue was chromatographed on silica gel (activated, 1 h at 105 °C), eluting first with light petroleum (b.p. 40—60 °C) (which only removed unreacted ferrocene), then with 50%–50%, hexane–benzene mixture. Two components were resolved by using the latter combination of solvents, the fast eluting one (major component) is acetonylferrocene, and the other component is probably 1,1-diacetonylferrocene.

The acetonylferrocene (obtained in 15% yield) consists of yellowish orange crystals which decomposed at *ca.* 130 °C. It was characterised spectroscopically, *viz.* $\lambda_{max.}$ 445 nm, $\nu_{max.}$ 1725 cm^{-1} in DMSO, n.m.r. absorptions at τ 5·90(s) 9H, 6·00(m) 2H, 8·40(s) 3H (in $CHCl_3$); the τ 6·00 absorption is more accurately described as a slightly broadened singlet with a suggestion of additional coupling.

Isolation of Cyclopentadiene from the Photolysis Products of Benzoylferrocene.—Benzoylferrocene (1 g, 0·026 mol) was dissolved in dry DMSO (10 ml) and water (0·1 ml, 0·05 mol) was added by means of a microsyringe. The solution was photolysed for 16 h in a Pyrex vessel, which resulted in a 50% conversion as determined by i.r. spectroscopy. The irradiated solution (5 ml) was introduced in a 100 ml round-bottomed flask and about 1 ml of water was added and the solution was allowed to stand 5 min with occasional shaking. (The addition of water was carried out to decompose the carboxylate which results in releasing further free cyclopentadiene). Methyl ethyl ketone (MEK) (30 ml) was added and the solution was cooled to −60 °C in a dry ice–acetone bath, and kept 10 min at this temperature. This resulted in freezing out the DMSO and water, whilst maintaining the cyclopentadiene in the MEK (MEK: m.p., −86°). The solution was quickly filtered using packed glass wool in the neck of a pre-cooled glass funnel. To the filtrate, 0·1 g of maleic anhydride (MA) was added and the solution was refluxed for 24 h (using a $CaCl_2$ tube on the open end of the reflux condenser). MEK was removed by distillation (under vacuum in the later stages to remove residual DMSO) and the residue was chromatographed on silica gel. The column was eluted first with diethyl ether, which removed all unreacted MA, then with MEK which removed the adduct: 5-norbornene-*endo*-2,3-dicarboxylic anhydride, m.p. 155—160° (lit., 164°) which was authenticated by its i.r., n.m.r., and mass spectra.

Isolation of Benzoic Acid from the Photolysis Products of Benzoylferrocene.—Benzoylferrocene (0·15 g) dissolved in DMSO (8 ml) containing a two-fold molar excess of H_2O, was photolysed 5 h in a Pyrex vessel. 0·1M-HCl (1 ml) was added to the irradiated solution with shaking, after which dilute aqueous $NaHCO_3$ was added dropwise until the solution was alkaline. This was extracted with ether and the extracts rejected; to the water layer 0·1M-HCl was added dropwise to pH 5 and the solution was extracted with diethyl ether. The extracts were dried with $MgSO_4$, the

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[10] Y. Nagai, J. Hooz, and R. Benkeser, *Bull. Chem. Soc. Japan*, **1964**, **37**, 53.

solvent removed and the residue was crystallised from hot water. Benzoic acid was authenticated by m.p., i.r. spectrum, and mass spectrometric measurements.

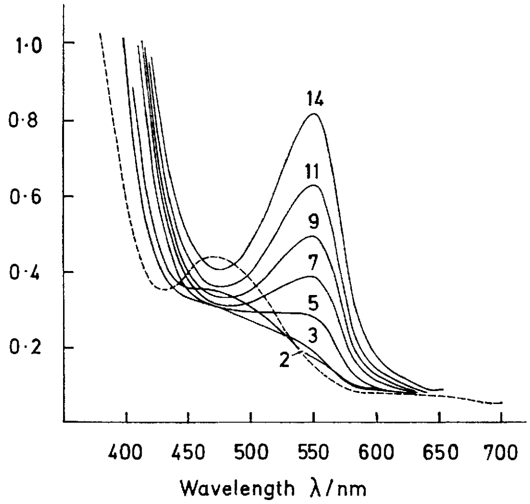

FIGURE 1 U.v. spectral profile for the (unfiltered) irradiation of 340 μM benzoylferrocene in moist DMSO, numbers refer to min of irradiation, the dashed line to the original solution

RESULTS

Benzoylferrocene.—Irradiation of a deoxygenated 300 μM solution in reagent grade DMSO in a quartz vessel (14 min) induced a colour change, light yellow-orange ($\lambda_{max.}$ 470 nm) to purple ($\lambda_{max.}$ 550 nm) (Figure 1) similar to that described by Tarr and Wiles [5] for dibenzoylferrocene in this solvent using light filtered through Pyrex. Irradiation for a short period (23 min) with a Pyrex filter gave very little purple colouration, but the 359 and 470 nm peaks characteristic of ferrocenes gradually disappeared (Figure 2), giving way to a new, intense absorption at 340 nm. (As indicated later, it was found that this transformation does not occur when freshly distilled, rigorously dried DMSO is employed and all photochemical changes described here refer to reagent grade solvents which have not been especially dried.) At 435 ± 20 nm ϕ (−benzoylferrocene) is 0·33.

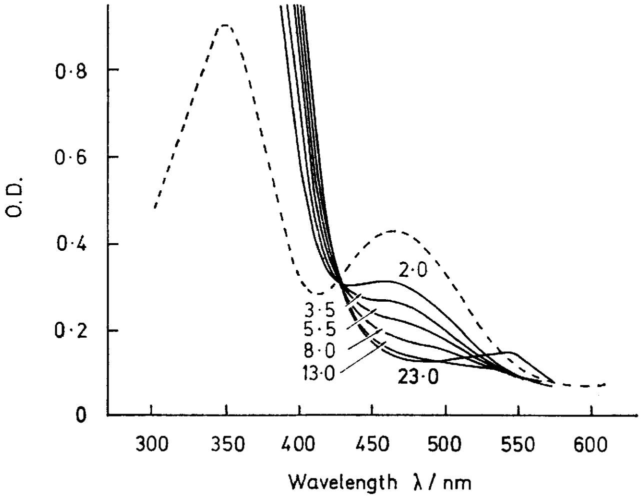

FIGURE 2 U.v. spectral profile for the filtered ($\lambda > 280$ nm) irradiation of 340 μM benzoylferrocene in moist DMSO (see caption to Figure 1)

I.r. examination of the photolysis of 90 mM benzoylferrocene in DMSO in bulk (irradiation time 100 min, Pyrex filter) showed that the carbonyl absorption of benzoylferrocene (1638 cm^{-1}) largely disappeared, giving new absorptions at 1538 and 1350 cm^{-1}. Both u.v. and i.r. measurements were carried out at intervals (after suitable dilution) on irradiated 55 mM benzoylferrocene in DMSO (Pyrex filter) and the point of extinction of the 1638 cm^{-1} peak of benzoylferrocene corresponded to that complete development of the absorptions at 1538 cm^{-1} and 340 nm (the latter overlapped with the 359 nm peak of benzoylferrocene throughout, giving the appearance of a gradual u.v. shift of the latter). Figure 3 illustrates these changes and also the photosensitivity of the intermediate compound (I) with $\nu_{max.}$ 1538 cm^{-1}. Removal of the Pyrex filter greatly accelerated the photodecomposition of (I), yielding the compound (II) with $\lambda_{max.}$ 550 nm.

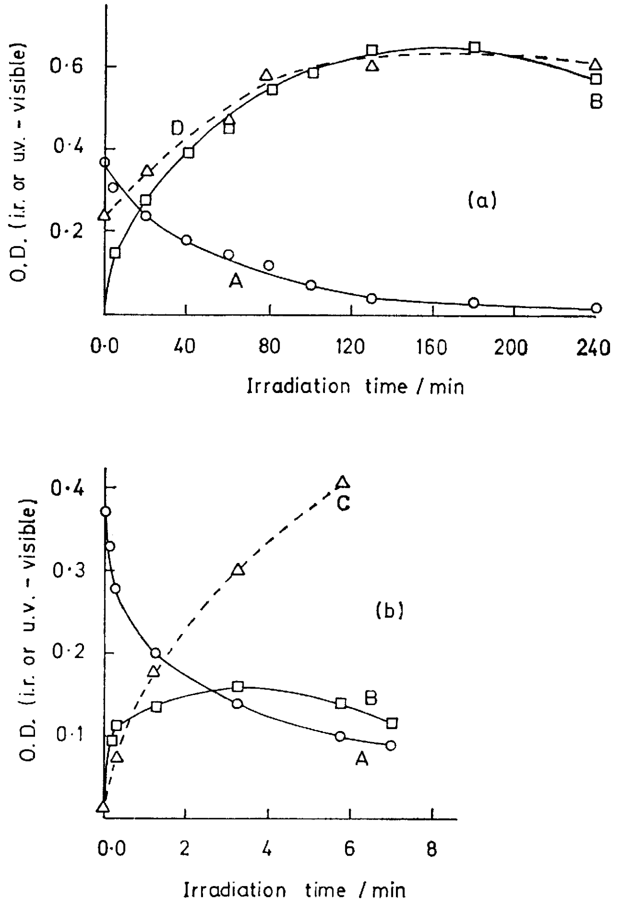

FIGURE 3 Spectral profiles at peak maxima for the irradiation of 55 mM benzoylferrocene in DMSO; A, 1638; B, 1538 cm^{-1}; C, 550; D, 359—340 nm; (a), $\lambda > 280$ nm; (b) unfiltered light

Attempted isolation of (I) was frustrated by its sensitivity to heat, oxygen, water, and light. Irradiation of benzoylferrocene for 15 h in pyridine [which gave the same transformation of benzoylferrocene to (I)] followed by removal of solvent by pumping and dissolution in [$^2H_6$]DMSO gave the i.r. spectrum of (I) (Figure 4) which we assign to a carboxylate on the basis of the peaks at 1538 and 1350 cm^{-1}.

The transformations described for solutions of benzoylferrocene in DMSO and pyridine were reproduced in the following solvents; dimethylformamide (DMF), hexamethylphosphoric triamide (HMPT), and tetrahydrothiophen oxide (THTO), but not in acetonitrile, triethylamine, tetrahydrofuran, diethyl ether, dioxan, methyl ethyl ketone, methanol, dichloromethane, or sulpholan. No effects on the rate or course of photoreaction were apparent on the addition to a 70 mM solution of benzoylferrocene of naphthalene, potassium t-butoxide, hydroquinone, or galvinoxyl.

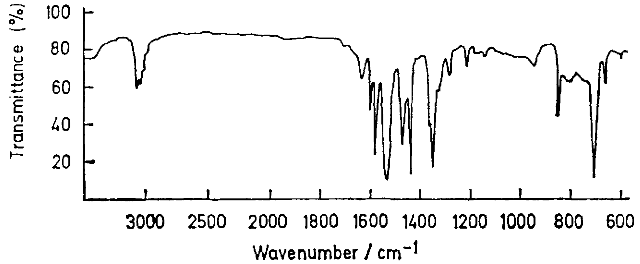

FIGURE 4 I.r. spectrum of product obtained by irradiation ($\lambda > 280$ nm) of benzoylferrocene in pyridine (15 h) followed by removal of solvent and dissolution in [$^2H_6$]DMSO

When the solvents promoting photoreaction of benzoylferrocene were rigorously dried, no decomposition of the latter occurred, but systematic addition of H_2O (or D_2O) to 160 mM benzoylferrocene in pyridine induced reaction [determined by the appearance of (I) at 1538 cm^{-1}] until a 1 : 1 molar ratio of solute : H_2O was achieved when further addition of water produced only a marginal increase in the rate of photodecomposition of benzoylferrocene. When lower molar ratios of water were introduced, reaction terminated when the appropriate fraction of (I) had appeared.

The transformation of (I) to (II) took place in DMSO under conditions of deoxygenation with unfiltered light but it was barely perceptible when a Pyrex filter was introduced. In the case of pyridine and DMF, the formation of (II) did not proceed even with unfiltered light, but when air was admitted (II) was produced even with the filter present. Clearly a source of oxygen is necessary to effect the change (I)—(II), which is the solvent only in the case of DMSO.

When a large molar excess (>5-fold) of water over benzoylferrocene was utilised, the i.r. profile of reaction altered, the 1538 cm^{-1} absorption of (I) being supplanted by a new peak at 1700 cm^{-1}. At even higher H_2O : substrate ratios (*ca.* 10) the 1538 cm^{-1} absorption almost vanished. The same i.r. change could be effected by adding a trace of aqueous HCl to an irradiated solution of benzoylferrocene in DMSO.

^{1}H N.m.r. measurements on irradiated solutions of benzoylferrocene in deuteriated solvents were informative, although care was needed to avoid excessive photodecomposition which led to line broadening, presumably as a result of paramagnetic products. The n.m.r. spectra of 120 and 80 mM benzoylferrocene after 2 and 15 h irradiation respectively in [$^2H_6$]DMSO and [$^2H_5$]pyridine respectively (the latter experiment corresponds to complete removal of solute) exhibit absorptions at τ 3·5—3·6 and 7·1—7·3 in a ratio of 2 : 1 in conformity with the presence of free cyclopentadiene. Other (broadened) absorptions correspond to the presence of π-C_5H_5 and Ph protons. An n.m.r. profile of the photoreaction indicated that gradual removal of the absorption of the substituted π-C_5H_5 ring [τ 5·2(t), 5·5(t)] takes place simultaneously with the formation of free cyclopentadiene. At the final stages, the integrated absorption of the five aromatic protons practically matched that of the five equivalent protons in the unsubstituted π-C_5H_5 ring.

As indicated previously, (I) was too unstable to be isolated in a pure form. However, it was possible to treat a solution of (I) in DMSO (following irradiation of benzoylferrocene) with dilute HCl [a treatment which converts the 1538 cm^{-1} absorption of (I) to one of 1700 cm^{-1}] and, following work-up and extraction, to isolate a yield of impure benzoic acid of 50% (based on the original PhCO-group in benzoylferrocene). This was purified by column chromatography and characterised by m.p., i.r., and mass spectrometry. Refluxing a similar irradiated solution with maleic anhydride produced a 70% yield of the Diels–Alder adduct of free cyclopentadiene, *i.e.* 5-norbornene-*endo*-2,3-dicarboxylic anhydride (yield based on two π-C_5H_5 rings in the starting material, see Discussion section), which was identified by n.m.r. and mass spectrometry.

It had been suspected in the early stages of this work that free ferrocene was one product, and this compound was isolated from irradiated benzoylferrocene in DMSO solution after quenching the reaction with water and also by sublimation from the residue of irradiated benzoylferrocene in pyridine following removal of solvent. The yield was 4% (based on starting material) and ferrocene was identified by m.p. (171 °C), i.r., n.m.r., and mass spectrometry. Quenching of the DMSO solution with D_2O gave no [^2H]ferrocene.

t-Butylmonobenzoylferrocenes.—Our preparation yielded one pure compound, 1-benzoyl-2-t-butylferrocene (*A*), and a chromatographically unresolvable 66 : 33% mixture (*B* : *C*) of 1-benzoyl-3-t-butylferrocene (*B*) and 1-benzoyl-1′-t-butylferrocene (*C*). Whilst all the π-C_5H_5 protons of *A* absorb in the same n.m.r. region, those of both *B* and *C* are reasonably well differentiated. The pattern of changes in the n.m.r. spectra of both *A* and the *B* : *C* mixture can be summarised (the numbers refer to integration of spectra in arbitrary units).

	A			*B* : *C*				
				C_5H_5 protons				
	C_5H_5 protons (total)	Ph protons (total)	Bu^t protons	(Total in substituted rings)	Unsubstituted ring (of *B*)	Ph protons	Bu^t protons	
	τ	τ	τ	τ	τ	τ	(*B*)	(*C*)
	5·9	2·3, 2·7	8·9	5·3, 5·8	6·1	2·1, 2·6	9·2	9·3
Before photolysis [a]	8·1	5·9	9·0	4·7	4·7	7·0	9·0	3·3
After photolysis [a]	5·7	5·8	9·0	3·3	4·6	9·3	9·0	10·9
		also {3·7; 1·0 units 7·3; 0·6 units			also {3·7; 4·0 units 7·3; 2·8 units			

[a] The numbers in these rows refer to relative absorption intensities.

The approximate ratio 2 : 1 for τ 3·7 : 7·3 protons in the cyclopentadiene liberated from *A* accords equally well with an assignment to C_5H_6 or C_5H_5-Bu^t, for the latter would exist as a mixture of the isomers obtained when C_5H_4-Bu^t is protonated either at the free or t-butylated ring positions (in a statistical ratio of 4 : 1) to give isomers with methine : methylene proton ratios of 3 : 2 and 4 : 1 respectively. However, the unsubstituted ring of *B* absorbs at τ 6·1, being clearly differentiated from the substituted rings in *B* and *C*, and its t-butyl group appears at τ 9·2 (that of *C* appears at τ 9·3). After photolysis, the ratio of the absorptions τ 6·1/(τ 5·3 + 5·8) rose from one to 2·1, indicating selective retention of the unsubstituted π-C_5H_5 ring in *B*, *i.e.* loss of the ring carrying t-butyl and benzoyl substituents. Again, the ratio of the absorptions at τ 6·1 (unsubstituted ring in *B*) and aromatic protons (from *B* and *C*) was barely altered by irradiation.

Carbonyl stretching frequency changes in the photoreaction of ferrocenyl ketones (FcCOR) with water in selected solvents $\nu_{max.}$ (in cm^{-1})

Compound R	DMSO		THTO		HMPT		Pyridine	
	Initial	Final	Initial	Final	Initial	Final	Initial	Final
Ph	1638	1538	1638	1538	1639	1548	1639	1535
H	1663	1593	1665	1599	1668	1599, 1575		
CH_3	1666	1562	1666	1562	1668	*ca.* 1570 [a]	1670	? [a]
C_6H_4–OCH_3-*p*	1630	1530	1631	1531	1632	? [a]		
1,1′-Dibenzoylferrocene	1641	1538						
FcCH=CHCOMe	1660	1553	1659	1555	1660	1556		
1-Benzoyl-2-t-butylferrocene	1638	1537						

[a] Inaccurate or unobtainable through solvent interference.

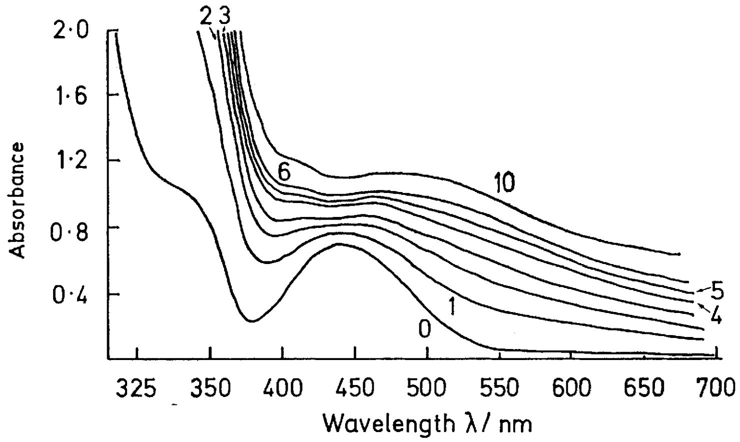

FIGURE 5 U.v. spectral profile for irradiated (λ > 280 nm) 2·7 mM $FcCO_2H$ in DMSO, numbers give time of irradiation in min

Other Ferrocenyl Ketones.—Compounds FcCOR (R = H, Me, and –C_6H_4–OMe-*p*), FcCH=CHCOMe, and dibenzoylferrocene all underwent a photochemical change in the group of solvents effective in the photoreaction of benzoylferrocene. The i.r. measurements giving the characteristic change of the ketonic carbonyl frequency to that of carboxylate species are given in the Table. Those compounds investigated in detail also displayed u.v. changes analogous to those described for benzoylferrocene, for example, formylferrocene in pyridine solution ($\lambda_{max.}$ 452 and 334 nm) photoreacted to give a new band at 318 nm and acetylferrocene in DMSO ($\lambda_{max.}$ 450 and 330 nm) behaved similarly. Anisoylferrocene photodecomposed about 20% faster than benzoylferrocene when 90 mM solutions of each in DMSO were irradiated. From the latter reaction, anisic acid was removed (identified by i.r. and n.m.r. spectra). Acetonylferrocene, $FcCH_2COMe$, was unreactive under our conditions of reaction. Quantum yields for destruction of solutes were: FcCHO 0·22, FcCOMe 0·18, FcCH=CHCOMe 0·056.

Ferrocenecarboxylic Acid.—The u.v. changes following irradiation of 2·7 × 10^{-3} ferrocenecarboxylic acid in DMSO are illustrated in Figure 5 (Pyrex filter). Identical changes took place when unfiltered light was employed but in addition a subsequent rapid formation of a red-purple colouration ($\lambda_{max.}$ 525 nm) was evident. ϕ(–$FcCO_2H$) was 0·52 at irradiation wavelength of 435 ± 20 nm.

The i.r. profile of the first stage of the photoreaction was measured in pyridine and [$^2H_6$]DMSO. In pyridine, the carbonyl stretching of –CO_2H (1695 cm^{-1}) gradually disappeared, giving way to a broad absorption at 1560—1600 cm^{-1} (m) which overlapped with solvent bands. During the course of this transformation a new very sharp peak developed at 2323 cm^{-1} attributable to CO_2 whilst the formation of the 1580 cm^{-1} band slowed perceptibly. When the starting material was exhausted, CO_2 evolution continued at the expense of the 1580 cm^{-1} absorption but finally ceased at which point no further decrease in the 1580 cm^{-1} was apparent. No CO_2 was observed until a substantial quantity of ferrocenoic acid had been removed. In [$^2H_6$]DMSO the essentially identical changes were more sharply differentiated as solvent interference of the 1580 cm^{-1} band was negligible (Figure 6). Rigorous drying of solvents did not prevent the photoreaction in contradistinction to the observations with benzoylferrocene.

An n.m.r. profile of the photoreaction of $FcCO_2H$ in [$^2H_6$]DMSO revealed several effects (τ values were measured relative to the sharp singlet at τ 7·5 of ^1H impurity in

$[^2H_6]$DMSO). $FcCO_2H$ absorbs at τ 5·78 (*s*, 5H, unsubstituted π-C_5H_5 ring), 5·55 (t, 2H, 3,4-protons in substituted π-C_5H_5 ring), 5·30 (t, 2H, 2,5-protons in substituted π-C_5H_5 ring). Even after 60 s irradiation the singlet was appreciably broadened and shifted to τ 5·7 and the two triplets broadened to singlets and shifted to τ 5·3 (from 5·55) and 5·15 (from 5·30): after 120 s the singlet had moved to τ 5·66 and the triplets had almost coalesced at 5·05—5·10, meanwhile tiny peaks were appearing at 3·5 and 7·1 in a ratio of *ca.* 2 : 1. This behaviour continued until at 9 min the singlet was positioned (and diminished in intensity) at τ 5·62 and the 'coalesced triplet' as a broad singlet at 4·85. Further shifts and broadening of the $FcCO_2H$ spectrum took place after 15 and 30 min, and at 60 min only the vestiges of the singlet remained, although the singlets at τ 3·5 and 7·1 were now strong and a new relatively sharp singlet appeared at 5·8. A generally similar pattern of behaviour (after long and short irradiations) was given by solutions of $FcCO_2H$ in $[^2H_5]$pyridine.

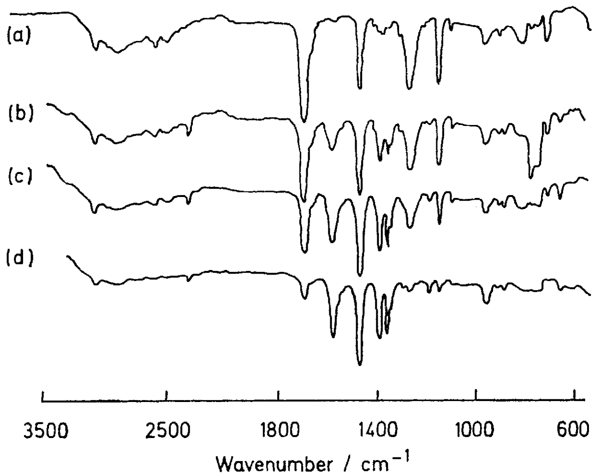

FIGURE 6 I.r. spectral profile for irradiated ($\lambda > 280$ nm) 6·7 mM $FcCO_2H$ in $[^2H_6]$DMSO

The broadening of lines suggest a paramagnetically induced relaxation, but addition of acetone to an irradiated 100 mM solution of $FcCO_2H$ in $[^2H_5]$pyridine which exhibited broadening of the lines in the τ 5—6 region, left the singlet of acetone τ 8·1 quite unaffected, suggesting an intramolecular effect.

Attempts to characterise the 1580 cm^{-1} intermediate were made as follows: (*i*) a 100 mM solution of $FcCO_2H$ in pyridine was irradiated for 60 min (Pyrex filter) at which time $>90\%$ of $FcCO_2H$ was decomposed. The solvent was pumped off and the i.r. spectrum of the residue in Nujol showed the characteristic broad absorption of the intermediate at 1580 cm^{-1} and others at 3070—3090, 1104, 1000, and 698 cm^{-1}. However, in $[^2H_6]$DMSO the residue showed a spectrum varying in the 1580—1600 cm^{-1} region with time; (*ii*) complete photodecomposition of 120 mM $FcCO_2H$ in DMSO followed by acidification (dilute aq. HCl) regenerated a fresh sharp absorption at 1695 cm^{-1}, *i.e.* $\nu_{max.}$ of the starting material. $FcCO_2H$ Was recovered from this solution in 48% yield and authenticated by m.p. (220 °C, lit.,[11] 225 °C), u.v., i.r., and n.m.r. spectra.

Ferrocenylacetic Acid.—This compound was much less photoreactive than $FcCO_2H$ but 40 h irradiation (Pyrex filter) of a 2·9 mM solution in DMSO removed the 434 nm band, and the other band at 321 nm became more intense. Irradiation ($\lambda > 280$ nm) of 200 mM $FcCH_2CO_2H$ for 2·5 h in an i.r. cell resulted in a gradual decrease of the carboxyl C=O peak at 1714 cm^{-1} to give new absorptions at 1600 (broad) and 2323 cm^{-1} (sharp), the latter due to CO_2. A 40 h irradiation of 200 mM $FcCH_2CO_2H$ in $[^2H_6]$DMSO gave the following proton n.m.r. changes: original solution, τ 5·9(s) (unsubstituted ring) superimposed upon 5·8—6·0(m) (substituted ring) and 6·75(s) (methylene); irradiated solution, methylene protons greatly broadened and shifted to τ 6·60, new sharp peak at 7·92. $\phi(-FcCH_2CO_2H)$ was 0·019 at irradiation wavelengths of 435 $\pm$ 20 nm.

Ferrocene-1,1'-*dicarboxylic Acid.*—This behaved essentially as the monoacid; irradiation of 150 mM substrate in DMSO removed the carbonyl absorption at 1700 cm^{-1} to give a new, strong, broad absorption at 1580 and the CO_2 peak at 2323 cm^{-1}. When a 320 mM solution in DMSO was irradiated to exhaustion of the substrate, its absorption bands (1700s, 1264s, 1155s, and 718m cm^{-1}) were replaced by bands at 2323s, 1650br, w, 1580br, s, and 795sharp, m cm^{-1}.

Methyl and Ethyl Esters of Ferrocenecarboxylic Acid.—Irradiation (30 s) of 560 μM $FcCO_2Me$ in DMSO (Pyrex filter) induced the following changes in the u.v. absorption spectrum of the substrate ($\lambda_{max.}$ 440, 350sh, and 305 nm): (*i*) the 440 nm band decreased in intensity and shifted to 421 nm, (*ii*) the 305 nm band intensified greatly (the 350 nm absorption was unchanged). After 1 min irradiation the trend continued and a new absorption at 522 nm began to emerge, and after a further 5 min the visible band of the starting material had vanished and the 522 nm absorption was stronger, imparting a purple-red colour to the solution.

The i.r. reaction profile for 300 mM $FcCO_2Me$ in DMSO ($\lambda_{irr} > 280$ nm) showed a fast removal of the substrate carbonyl frequency (1713 cm^{-1}) and appearance of a new strong band at 1637 cm^{-1}; however, this transformation appeared to be subject to autoretardation, ceasing after 60 min irradiation. In the later stages a new band at 1548 cm^{-1} also appeared very slowly. $FcCO_2Et$ behaved very similarly, the 1705 cm^{-1} band of substrate giving way to a new band at 1631 cm^{-1} and, much more slowly, a band at 1535 cm^{-1}. One significant new feature about the esters is that they are unreactive in pyridine, even in the presence of O_2.

Attempts to investigate further the photodecomposition of the esters in DMSO were largely frustrated by the autoretardation, which appeared to be totally effective, probably by virtue of an inner filter effect. Isolation of a yellow-orange residue from the reaction of $FcCO_2Me$ (Pyrex) was accomplished, however, and chromatography (5% ether–95% benzene) yielded bands with R_F values of 0, 0·11, 0·25, 0·40, 0·50, 0·68, and 0·96. The bands with R_F 0 and 0·68 were inorganic matter and starting material respectively; that with R_F 0·25 was the most abundant product (7% based on starting material) being identified by m.p. (114 °C), i.r., n.m.r., and mass spectra as the methyl ester of ferrocene-1,1'-dicarboxylic acid with i.r. absorptions in $[^2H_6]$DMSO at 3078w, 2944w, 1713s, 1468m, 1284s, 1192m, 1145s, and 960m cm^{-1}, n.m.r. peaks at τ 5·20 (t, 2H), 5·45 (t, 2H), and 6·26 (s, 6H), and *m/e* (parent ion) 302.

The R_F 0·96 band corresponded to a yellow solid ($\lambda_{max.}$ 440 nm), but its tiny yield afforded only i.r. identification with 2850—2980s, 1460m, br, 1380m, sharp, 1350m, sharp, and 1068m, sharp cm^{-1}. The R_F 0·11 band was the only

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[11] R. L. Shaaf, *J. Org. Chem.*, 1962, **27**, 107.

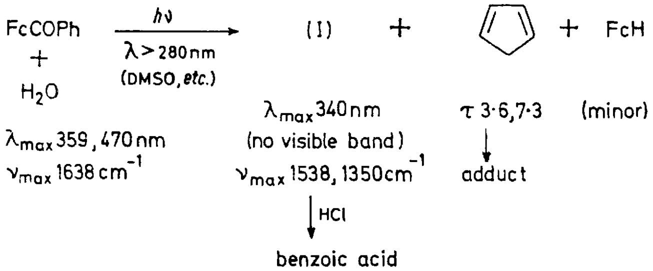
other one yielding sufficient material even for i.r. study with 2985s, 2858s, 1742s, 1716s, 1118s, and 1068m cm^{-1}.

Ferrocenecarboxamide $FcCONH_2$.—80 mM Substrate in DMSO underwent photolysis ($\lambda_{irr} > 280$ nm) to yield a new i.r. band at 1527 cm^{-1} which replaced that of the amide at 1664 cm^{-1}.

DISCUSSION

The systematic pattern of i.r. and u.v. changes following irradiation of a series of ferrocenyl ketones and acids in solvents including pyridine, DMSO, DMF, HMPT, and THTO indicates that a single general type of photochemical reaction (or sequence of reactions) is operative, differing only in detail from compound to compound. In all cases, the reaction is confined to members of this group of solvents and is characterised by transformation of the carbonyl-containing moiety ($>$C=O, $-CO_2H$, $-CO_2R$, $-CONH_2$) into what appears to be a carboxylate group judging by the i.r. spectra of the products and confirmed in the cases of two of the ketones and of the products from $FcCO_2H$ by isolation of the free acid. Again, disappearance of the visible band characteristic of ferrocenes (λ *ca.* 420—440 nm) occurs, indicating loss of the bis π-cyclopentadienyl structure which is confirmed by the appearance of free cyclopentadiene in the n.m.r. spectra of several of the compounds examined.

In the case of the ketones (but not acids), exemplified by the particularly detailed examination of benzoylferrocene, it is clear that the colour change reported by Tarr and Wiles [5] refers not to a reaction with solvent, but with water in the solvent and, since they used light filtered through Pyrex, this secondary reaction was occasioned by the presence of dissolved oxygen. Under conditions of deoxygenation and a Pyrex filter, the primary reaction is virtually isolated, *viz.* (I) is assigned to a carboxylate species on the basis of its i.r. maximum, and recovery of benzoic acid following hydrolysis suggests it is a benzoate. Retention of one π-bonded C_5H_5 ring is evident from the n.m.r. spectrum, as is the loss of one ring as free cyclopentadiene, and (I) is formulated as a solvated monocyclopentadienyliron benzoate, $(\pi\text{-}C_5H_5)Fe(solv)^+{}_nPhCO_2^-$, which accords with the u.v., i.r., and n.m.r. spectra of its solution.



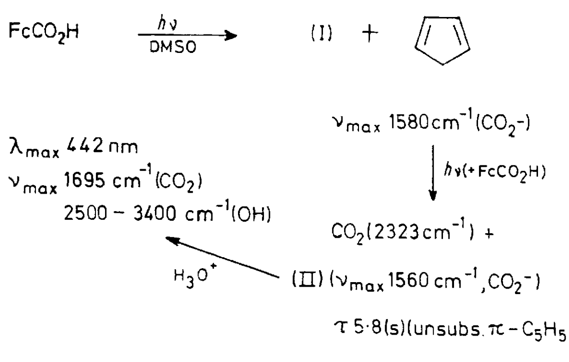
The possibility that (I) is a mixture of ferrocene and iron(II) or iron(III) benzoates seems improbable in view of the following points: (*i*) i.r. data, $\nu_{max.}$ of (I) is 1538 cm^{-1} in DMSO, yet $\nu_{max.}$ of sodium and ferric benzoates are 1565 and 1570 cm^{-1} in the same solvent; (*ii*) u.v. data, $\lambda_{max.}$ of (I) in DMSO is 340 nm: ferrocene has $\lambda_{max.}$ 325, 440 nm; no trace of the visible absorption of ferrocene is apparent in solutions of (I); (*iii*) n.m.r. data, the n.m.r. spectra of photolysed solutions of (I) in [$^2H_6$]-DMSO indicate that when (I) is fully formed (loss of π-C_5H_5 protons in substituted π-C_5H_5 ring), π-C_5H_5 protons in the unsubstituted ring remain in equivalent quantity to the five aromatic protons in the benzoate group; (*iv*) product isolation, ferrocene could be isolated from the reaction mixture in 4% yield.

That the ring lost in the photoreaction is that originally substituted is evident from the experiments with the t-butyl-substituted benzoylferrocenes. The role of water as the source of oxygen in the carboxylate is apparent from the experiments performed with absolutely dry pyridine and with mixtures of this with controlled amounts of water. The ' polar ' character of the reaction is suggested by the solvent selectivity and the absence of any effect of added free radical scavengers. Aquation of the carbonyl moiety followed by Fe–(π-C_5H_5) cleavage is the likely mechanism.

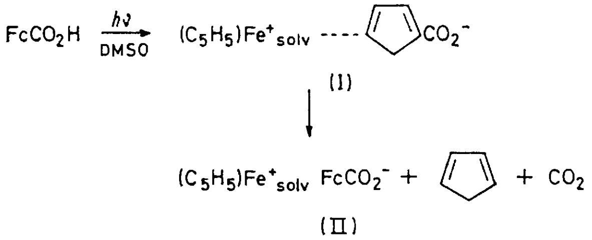
The quite general character of this primary reaction is clear from the data for anisoylferrocene, formylferrocene, acetylferrocene, and ferrocene-1,1′-dicarboxylic acid which undergo entirely analogous i.r. changes.

The nature of the secondary reaction is less well characterised. It depends on the presence of oxygen in all cases except when unfiltered light is applied to DMSO solutions. The dissolution of ferric salts of certain carboxylic acids in DMSO imparts a very similar intense red-purple colour to the solution and it seems possible that the secondary stage in the photolysis consists of photo-oxidation of $(C_5H_5)Fe^+$ to Fe^{III} species which form carboxylato-complexes of the type suggested.

The other compound examined in detail, ferrocenecarboxylic acid, photoreacts in dry solvents in two stages: the second stage, principally characterised by appearance of the very sharp band of CO_2 at 2323 cm^{-1}, commences before $FcCO_2H$ is exhausted, but continues beyond this point. Hydrolysis of the product at the point of disappearance of $FcCO_2H$ regenerates the latter in 48% yield, implying that this compound is present in anionic form in the product, indeed $\nu(CO_2^-)$ in $Na^+FcCO_2^-$ is at 1565 cm^{-1} (broad) in DMSO solution. The n.m.r. spectral profile demonstrates the formation of free cyclopentadiene (τ 3·5, 4H, 7·1, 2H) and, in late stages,



species exhibiting an (unbroadened) singlet at τ 5·8, typical of a π-bonded C_5H_5 ring. These various spectroscopic data suggest that (II) may be a ferrocenecarboxylate: one possible sequence involves an intermediate akin to that found in the reaction of benzoylferrocene, *viz.*



The role of the solvent would again be dual, *i.e.*, to promote the separation of charge in the formation of (I) and to solvate the $(C_5H_5)Fe^+$ species. The purple species is probably a complex of an Fe^{III} carboxylate with DMSO.

Attempts to characterise the photoreaction of the esters were frustrated by the build up of an intensely absorbing product which terminated reaction presumably by means of an inner filter effect. The most striking spectroscopic change is that of $\nu_{max.}$ from **1713** and **1705** cm^{-1} (methyl and ethylferrocenecarboxylate respectively) to **1637** and **1631** cm^{-1}. None of the products isolated absorb in this region, which is not associated with any of the simple functional groups to be expected: however, diferrocenyl ketone[12] absorbs at **1628** cm^{-1} (*i.e.* much lower than benzoylferrocene, $\nu_{max.}$ 1650 cm^{-1}) and a substituted derivative of this molecule such as methoxycarbonyldiferrocenyl ketone would display an appropriate $\nu_{max.}$.

[2/2308 *Received, 9th October,* 1972]

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[12] G. G. Dvoryantseva and Yu. N. Sheinker, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk,* 1963, 924.