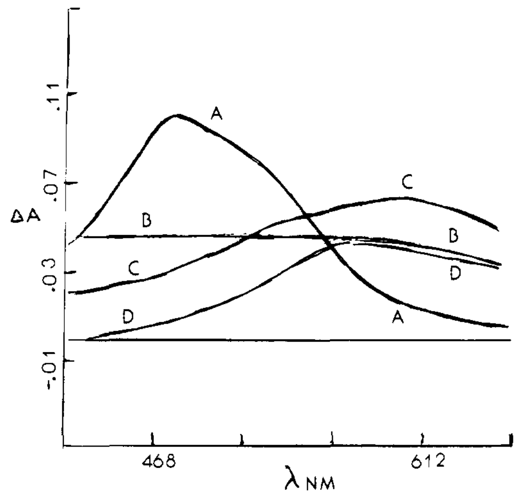

Figure 1. Curve A, the transient spectrum of *trans*-Co(en)(NO$_2$) at a pulse delay of 44 ps. Curves B, C, and D, transient spectra of *cis*-Co(en)NCSCl at 0-, 20-, and 50-ps probe pulse delays, respectively. Note that in the 420–550-nm region the transient appears with the pulse (0 delay) and decays monotonically. In contrast, the 0- and 50-ps curves are nearly coincident in the 550–650 region, but the intermediate-time 20-ps curve shows higher absorbance. Curves represent smoothed average of 10 records. Standard deviation is 0.01 A with a shape following the average curve.

Two possibilities susceptible of interpretation suggest themselves as assignments for the visible transients: (1) a transition from the halogen or pseudo-halogen formed by homolytic fission of the Co–X bond to the Co(II) species produced by the same fission event or (2) a transition from the lowest ligand field triplet ($^3T_{2g}$ in O_h symmetry and analogous to the nanosecond emitting state in Rh(III)) to a ligand based acceptor orbital (π^*).

The assignment based on homolytic fission offers no reason for the apparent requirement for a nitro or –NCS ligand with a low-lying acceptor orbital. Furthermore, the optical electronegativity of Co(III) is given[4] as 1.6–1.9, whereas the lower subshell of Co(II) is given as 1.9. There is no clear basis for predicting a large red shift of ligand to metal charge transfer on homolytic fission. The other assignment may be more attractive.

The assignment, ligand field triplet to ligand π^* is the one most consistent with discussions of Rh(III) and Co(CN)$_6^{3-}$ luminescence. It also provides a rationale for the apparent requirement for ligands like –NO$_2$ and –NCS. It can be evaluated energetically by using standard LF parameters[5] and vibronic relaxation estimates derived from Rh(III) Stokes shift data.[2] Using O_h symmetry labels, the $^3T_{2g}$ LF triplet states are estimated to lie, after relaxation, between 4.00 and 10 kK below the $^1T_{2g}$ absorption positions. Spectral assignments of Yamasaki et al.[6] place the first LF singlet at 23.4 kK for the dinitro complex and at 19.9 kK for the isothiocyanato. (This difference of 3.5 kK compares to the difference of 3.7 for the transients!) The relaxed triplet of the dinitro complex should lie between 13.5 and 19.5 kK. We take 16.5 as a "trial" value. On this basis, the 488-nm transient corresponds to excitation to a state at 37 kK above the ground state. In ground-state spectra,[6] a band that is unique to nitro, –NCS, and –N$_3$ complexes among Co(III) amines appears near 40 kK in the *trans*-Co(en)$_2$(NO$_2$)$_2^+$ case. This band may identify the ligand π^* level. If so, the LF triplet to ligand π^* assignment for the transient is possible.

Following the kinetic analysis developed by Ford for the Rh(III) amines,[2] we find that a lifetime that is 100 times shorter than the 10–40 ns characteristic of Rh(III) can account for the difference in substitution quantum yields between Rh(III) and Co(III) amines. If triplet formation yields and rate constants for the reactive pathway were chosen very close to values for the Rh(III) amines, the shorter triplet lifetime would account for the overall reduction in quantum yield.

Acknowledgment. We thank NSERC Canada and FCAC Quebec for support. A.Y.S.M. thanks the Government of Iraq for a scholarship.

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(4) Jorgenson, C. K. *Experientia, Suppl.* **1964**, *No. 9*, 98.

(5) Sastri, V. S.; Langford, C. H. *Can. J. Chem.* **1969**, *47*, 4237.

(6) Yamasaki, K.; Hidaka, J.; Shimura, Y. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 2624.

Photohydration via Intramolecular Proton Transfer to Carbon in Electronically Excited States

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We wish to report that (*o*-hydroxyphenyl)acetylene (**1**) and *o*-hydroxystyrene (**2**) photohydrate cleanly and efficiently in both neutral aqueous and dilute acid solution, to give *o*-hydroxyacetophenone and 1-(*o*-hydroxphenyl)ethanol, respectively.[1] We believe these to be the first clear[2] examples of excited-state intramolecular proton transfer leading to irreversible[3] photochemical reaction. Quantum yield dependence[5] on pH has been measured for these two substrates, as well as for the corresponding *o*-methoxy derivatives, which also photohydrate but show quite different dependence on acidity.

The acid-catalyzed photohydrations of substituted phenylacetylenes,[6] styrenes,[6] and related compounds[7] opened up the possibility that such processes could be catalyzed by intramolecular proton transfer in the excited state. Although intramolecular proton transfer in electronically excited aromatic systems has been a well-studied phenomenon[4,8] since the classic work of Weller[9] on salicylic acid derivatives, this has dealt almost exclusively with proton transfers between heteroatoms, and emphasis has been on possible equilibria involved and the importance of proton transfer as a mechanism for electronic deactivation of excited states.[10]

The quantum yield dependence on pH is shown in Figure 1a for the reaction of **1** (irradiated at 300 nm), with that of several other substituted phenylacetylenes for comparison. The *o*-hydroxy derivative attains its maximum quantum yield[11] for product

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(1) Products were identified by comparison of their UV, IR, and NMR spectra with those of authentic samples.

(2) Ferris and Antonucci (Ferris, J. P.; Antonucci, F. R. *J. Am. Chem. Soc.* **1974**, *96*, 2010) have investigated the photochemical reactions of **1** in acetonitrile and in neutral and basic aqueous solution. The major product observed in all cases was 2,3-benzofuran, and only in 0.01 M OH$^-$ was any 2-hydroxyacetophenone found, as a minor product. However, they irradiated (Rayonet reactor) at 254 nm for up to 13 h, whereas in the present work irradiations (Rayonet reactor) were carried out at 300 nm for only 20–40 min. Only traces of 2,3-benzofuran were found under the latter conditions, and it may be that under Ferris and Antonucci's reaction conditions this is a secondary photochemical product. It is doubtful whether the formation of 2,3-benzofuran, even as a primary photochemical product, would meet Wubbels' (Wubbels, G. *Acc. Chem. Res.* **1983**, *16*, 285) definition of an acid-catalyzed photochemical reaction.

(3) Photochromism[4] caused by intramolecular proton transfer is excluded, since such color changes are easily reversible, thermally or photochemically.

(4) Klopffer, W. *Adv. Photochem.* **1977**, *10*, 311.

(5) Reactions of **1**–**4** were followed by changes in UV absorption, which showed sharp isosbestic points in every case, indicating that there are only two interconvertible absorbing species present, reactant and product. Reactions were followed to at least 50% completion, except for **1** and **2** above pH 7 where the photoreactions are inefficient.

(6) Wan, P.; Culshaw, S.; Yates, K. *J. Am. Chem. Soc.* **1982**, *104*, 2509. Wan, P.; Yates, K. *J. Org. Chem.* **1983**, *48*, 869.

(7) (a) Rafizadeh, K.; Yates, K. *J. Org. Chem.*, in press. (b) Wan, P.; Yates, K. *Rev. Chem. Intermed.*, in press.

(8) Martynov, I. Y.; Demyashkevich, A. B.; Uzhinov, B. M.; Kuzmin, M. G. *Russ. Chem. Rev.* (*Engl. Transl.*) **1977**, *46*, 1.

(9) Weller, A. *Z. Elektrochem.* **1956**, *60*, 1144. Weller, A. *Progr. React. Kinet.* **1961**, *1*, 187.

(10) Many substances capable of intramolecular proton transfer in the first singlet excited state are used as photochemical stabilizers.[4]

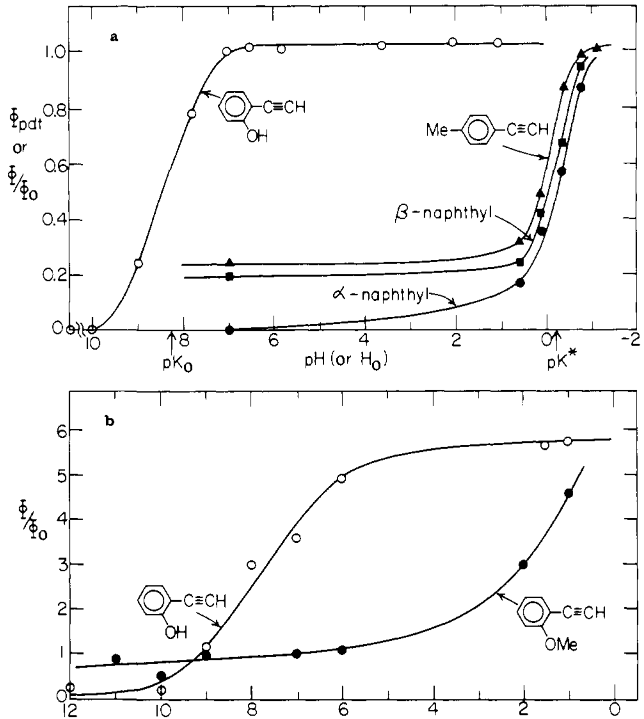
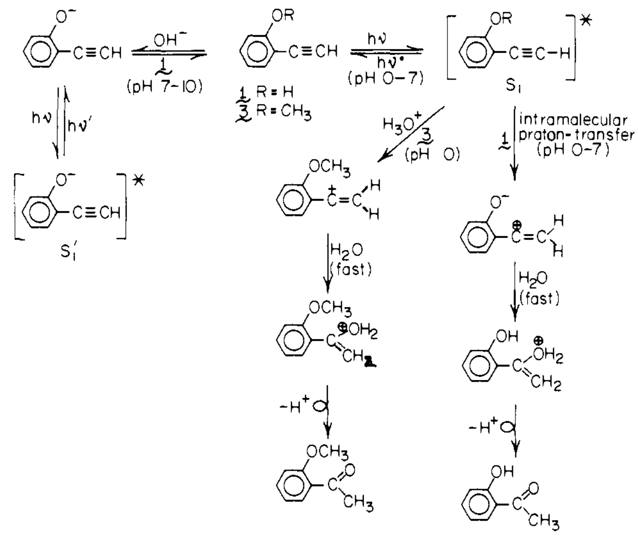


Figure 1. (a) Quantum yield dependence on pH for photohydration of substituted phenylacetylenes in aqueous solution. Open circles, relative quantum yields Φ/Φ_0, where Φ_0 is the quantum yield in neutral H_2O. Closed circles, squares, and triangles are absolute Φ_{pdt} values from ref 4. (b) Quantum yield dependence on "pH" for photohydration of **1** and **3** in aqueous acetonitrile. All points are relative Φ/Φ_0 values, where Φ_0 is the quantum yield for **3** in neutral solution.

formation at pH 7, and there is no further observable pH dependence down to pH 0 (in aqueous H_2SO_4). This is in contrast to the other phenylacetylenes studied,[6] which show strong sigmoid dependence of Φ_{pdt} on pH, with an inflection point near pH 0. The appearance of this sigmoid behavior, concurrent with sigmoid fluorescence quenching (decrease of Φ_f)[6] as a function of pH, has been taken to be due to external acid-catalysis by H_3O^+, and estimated[12] excited-state pK^* values for the S_1 states of phenylacetylenes are typically in the region of 0 to −2. The sigmoid Φ_{pdt} dependence observed for **1** at high pH is due to the deprotonation of the ground state is basic solution, since on excitation the phenoxide ion can neither transfer a proton intramolecularly nor accept a proton externally within its lifetime[13] due to the low concentration of H_3O^+ at such pH values. Potentiometric determination of the ground-state acidity of **1** gives pK_0 = 8.6, which coincides closely with the high-pH inflection point in the Φ/Φ_0 curve in Figure 1. The dominant processes occurring in different pH regions are shown in Scheme I.

In support of this mechanism, the photohydration of (*o*-methoxyphenyl)acetylene (**3**) was also studied as a function of pH but in 40% aqueous acetonitrile (for solubility reasons).[14] Its quantum yield dependence on "pH"[15] is shown in Figure 1b and is quite similar to that previously reported[6] for typical meta- and para-substituted phenylacetylenes. The photobehavior of **1** was reinvestigated in this solvent mixture, for comparison purposes,[16] and again shows a maximum quantum yield in essentially neutral solution and no dependence on pH except in the high pH region due to anion formation, similar to that observed for **1** in purely aqueous solution.

Scheme I. Reaction Scheme for the Photohydration 1 and 3 in Different pH Regions



The photochemical behavior of **2** is similar to that of the phenylacetylene analogue **1**; its maximum quantum yield for photohydration is attained in neutral aqueous solution, with no observed increase at higher acidities (down to pH 3).[17] There is also a sigmoid decrease in Φ/Φ_0 for this substrate in basic solution (pH 7–11) due to phenoxide ion formation (pK_0 of **2** was determined potentiometrically to be 9.7). In contrast, *o*-methoxystyrene (**4**) behaves similarly to other substituted styrenes previously studied,[6] with very low quantum yields in neutral solution and a sharp increase near pH 0, and only attains its maximum Φ/Φ_0 value at $H_0 \cong -2$ (30% H_2SO_4).

It may at first seem surprising that intramolecular proton transfer can take place so readily in **1** (and **2**), since proton transfers to carbon are generally considered to be slow,[18] even in the excited state,[4,8] and the intrinsic ground-state pK difference between these typical donor (phenol) and acceptor (aceylene) groups is so large (Δp$K_0 \sim 20$).[19] However, on electronic excitation, it is well-known[20] that phenols become much stronger acids (Δp$K^* \cong -7$) and it is clear from their photochemical reactivity[6] that phenylacetylenes must have large pK shifts to higher basicity (Δp$K^* \approx 8$–10) in their S_1 states. In addition, the substituent effects of each group on the other in **1** are such as to reduce

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[11] Although the quantum yields (Φ) for **1** in Figure 1a are only relative to the value in pure water (Φ_0), it is clear from the similar irradiation times used and product yields obtained in the present work that the maximum values of Φ/Φ_0 shown are comparably in magnitude with those previously determined for other substituted phenylacetylenes and styrenes.[6] These have maximum values of the absolute quantum yield for product formation (Φ_{pdt}) in the 0.5–1.0 range.

[12] These pK^* values have been estimated by fluorescence titration of S_1 only, since the protonated species formed does not fluoresce.[7b] Therefore they are only approximate (see: Schulman, S. G.; Capomacchia, A. C. *J. Phys. Chem.* **1975**, *79*, 1337).

[13] The measured lifetimes (by pulsed fluorometry and single-photon counting) for several substituted phenylacetylenes and styrenes[6] are in the 5–50-ns region, and the maximum value of $k_H{}^+$ measured for any of these substrates is 5×10^7 M^{-1} s^{-1}. Therefore at H_3O^+ concentrations of 10^{-9} M or less, external proton could not compete effectively with other deactivational processes.

[14] The solvent composition used was 40% AN and 60% H_2O (w/w).

[15] The "pH" values are the pH values of the aqueous buffer solutions used previously, before dilution with acetonitrile. These should give reliable measures of *relative* acidities of aqueous acetonitrile solutions, sufficient for comparison purposes.

[16] The values of Φ/Φ_0 shown for both **1** and **3** in Figure 1b are more directly comparable with each other than the values in Figure 1a,[9] since they were all determined relative to the product yield for **3** in pure water.

[17] It is of course quite possible that at sufficiently high acidities external proton transfer can begin to compete effectively with the intramolecular process for both **1** and **2**. Whether this would significantly increase the quantum yield is presently under investigation.

[18] See, for example: Bell, R. P. "The Proton in Chemistry"; Chapman and Hall London, 1973; p 131. Albery, W. J. *Progr. React. Kinet.* **1969**, *4*, 355.

[19] Phenol itself has pK_a = 9.9 (Bigs, A. I.; Robinson, R. A. *J. Chem. Soc.* **1961**, 388) and although the ground-state pK_{BH^+} for phenylacetylene cannot be determined directly, it is presumably less basic than the isoelectronic benzonitrile, with pK_{BH^+} = −10.3 (Liler, M.; Kosanovic, D. *J. Chem. Soc.* **1958**, 1084).

[20] Ireland, J. F.; Wyatt, P. A. H. *Adv. Phys. Org. Chem.* **1976**, *12*, 131.

the pK gap even further, so that ΔpK_0 in **1** would probably be much less than 20,[21] and ΔpK^* could easily become zero, since substituent electronic effects are generally more pronounced in excited states.[22] In addition, we have already shown that external proton transfers to carbon in S_1 can be quite fast ($k_{H^+} \sim 10^6-10^7$ M^{-1} s^{-1}).[6]

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[21] Using available ρ and σ values (Jones, R. A. Y. "Physical and Mechanistic Organic Chemistry"; Cambridge Univ Press: Cambridge, 1979. Hammett, L. P., "Physical Organic Chemistry"; McGraw-Hill: New York, 1970. Noyce, D. S.; Schiavelli, M. D., *J. Am. Chem. Soc.* **1968**, *90*, 1020) and assuming $\sigma_0 \simeq \sigma_p$, we can estimate that for **1**, the ground-state pK gap between pK_a (phenol) and p$K_{BH}{}^+$ (phenylacetylene) would be reduced by approximately 4 log units.

[22] Baldry, P. J. *J. Chem. Soc., Perkin Trans.* **1979**, *2* 951.

Selective Cyclobutane Adduct Formation in Competition with Diels-Alder Addition in Cation Radical Cycloadditions

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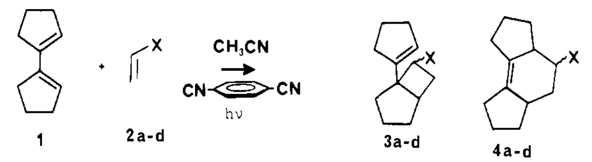
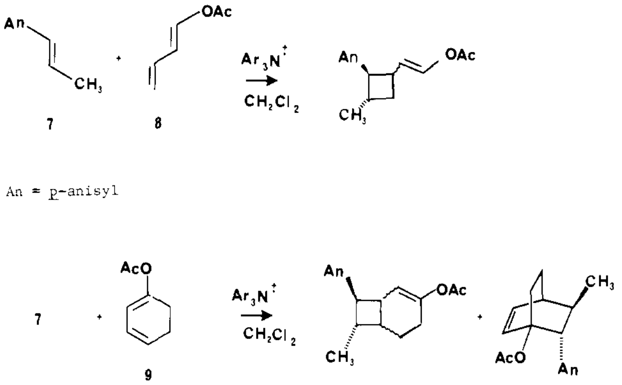
Although cyclodimerization of conjugated dienes could, a priori, yield adducts of three distinct types (vinylcyclohexenes, divinylcyclobutanes, and cyclooctadienes), in reality essentially only Diels-Alder adducts are obtained in the cation radical catalyzed cyclodimerizations of dienes,[1-3] in accord with formal selection rules.[4] More detailed theoretical considerations, however, suggest that irrespective of their formal symmetry status cation radical pericyclic reactions quite generally have extraordinarily low activation barriers.[4] Indeed, the symmetry-forbidden cation radical cyclodimerization of alkenes to give cyclobutanes has recently been shown to proceed efficiently under conditions identical with those of the (allowed) cation radical Diels-Alder.[5] Consequently, though the preference for the Diels-Alder mode in diene/diene cycloadditions is synthetically useful, it appears unlikely to be overwhelmingly large, so that competitive or even selective cyclobutane formation might be feasible in some cycloadditions. We wish to record the initial observations of selective cyclobutane formation in competition with the Diels-Alder mode in the cycloaddition of electron-rich alkenes and styrenes to certain conjugated dienes. In addition to the theoretical interest in this novel chemoselection mode and its basis, the reaction represents an attractive synthetic approach to selective construction of functionalized vinylcyclobutanes. Efficient transformation of the latter into cyclohexenes is found to provide the further option of convenient, indirect access to the formal Diels-Alder adducts.

Scheme I



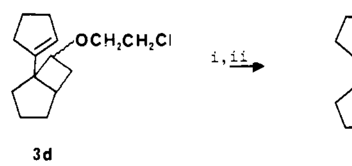
Cpd	X	%	%
a	OEt	98.1	1.9
b	OPh	82.5	17.5
c	SPh	68.7	31.3
d	OCH_2CH_2Cl	96.9	3.1

Scheme II



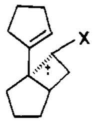
An = p-anisyl

Scheme III



i = n-BuLi,Et_2O,HMPA

ii = KH,THF,Δ



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Reaction of 1,1′-dicyclopentenyl (**1**) with ethyl vinyl ether (**2a**) under photosensitized electron-transfer (ET) conditions[3] was observed to yield the cyclobutane adduct **3a** (Scheme I) in 71% yield with high chemoselection (98.1%) relative to **4a** (1.9%). The latter, synthesized independently, proved to be stable under the ET reaction conditions. Cycloadducts **3a** and **4a** were not formed in control irradiations in the absence of the ET sensitizer. Owing to the instability of **3a** toward tris(*p*-bromophenyl)aminium hexachlorostibnate (**5**, $Ar_3N^{+}\cdot$) in methylene chloride, this reaction could not be effected by aminium salt catalysis, but all of the remainder of the reactions discussed herein except that of **2d** were carried out by both types of cation radical procedures (ET and $Ar_3N^{+}\cdot$), similar results being obtained from each method. Reaction of **1** with two other electron-rich alkenes (**2b,c**) also yielded primarily the cyclobutane adducts (**3b,c**) along with minor amounts of **4b,c** (Scheme I). Reaction of **2a** with 1,1′-dicyclohexeneyl proceeded likewise, giving only 2.4% of the Diels-Alder adduct. These results contrast sharply with the cation radical diene/diene cycloadditions and more directly with the additions of **2b,c** to 1,3-cyclohexadiene (**6**),[3] all of which show high Diels-Alder chemoselection (**2a** failed to add to **6**). The disparate behavior of **1** and **6** cannot derive solely from the relative s-cis populations of these dienes, since dienes like **1** are known to be relatively cis rich, whereas the additions to **1** are capable of very high cyclobutane chemoselection.

The ability of electron-rich styrenes to give similarly high cyclobutane chemoselection is illustrated (Scheme II) in the cation radical addition of *trans*-anethole (**7**) to 1-acetoxybutadiene (**8**) and 1-acetoxy-1,3-cyclohexadienbe (**9**). The former reaction was carried out under both ET (40% yield) and aminium salt (23%) conditions. In both cases only the cyclobutane adduct was obtained (3.8:1 t:c isomer ratio). The reaction with **9** was carried out by aminium catalysis only (28%) and gave the cyclobutane and

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[1] Bellville, D. J.; Wirth, D. W.; Bauld, N. L. *J. Am. Chem. Soc.* **1981**, *103*, 718.

[2] Bellville, D. J.; Bauld, N. L. *J. Am. Chem. Soc.* **1982**, *104*, 2665.

[3] Bauld, N. L.; Bellville, D. J.; Pabon, R. A. *J. Am. Chem. Soc.* **1983**, *105*, 5158.

[4] Bauld, N. L.; Bellville, D. J.; Pabon, R. A. *J. Am. Chem. Soc.* **1983**, *105*, 2378.

[5] Bauld, N. L.; Pabon, R. A. *J. Am. Chem. Soc.* **1983**, *105*, 633. For the photosensitized electron-transfer dimerization of olefins, see: Neunteufel, R. A.; Arnold, D. R. *Ibid.* **1973**, *95*, 4080. Farid, S.; Shealer, S. E. *J. Chem. Soc., Chem. Commun.* **1973**, 677.

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