for II there are two bands with maxima at 547 and 398; and for III two bands exist with maxima at 605 mμ and two poorly resolved maxima at approximately 435 and 415 mμ. For IV a broad structureless band exists with a maximum at approximately 650 mμ and another with a maximum in the region 400–425 mμ. Finally, for V a strong structureless band exists with a maximum at 575 mμ and shoulders at 485 and 455 mμ. The colored intermediates are stable at 77°K but generally can be eradicated either by warming or by irradiating into a visible absorption band. Trozzolo, *et al.*,[3] while not eliminating a radical intermediate, favored an ionic intermediate formed initially or rapidly from a radical intermediate. Our results on the tetraphenyloxirane (III) and episulfide (IV) indicate that a biradical intermediate resulting from C–S or C–O cleavage is the preferred form. That is, it would be unlikely that the episulfide intermediate resulting from C–S bond cleavage would be of ionic nature. Further, since the spectrum of the oxirane intermediate is similar to that of the episulfide, except for an expected blue shift, a similar structure for this intermediate should prevail. Furthermore, other photoproducts can be formed (see below).

The second point of importance is the existence of two separate one-photon processes. These are the production of the colored intermediate and the subsequent formation of final photoproducts. Irradiation into the visible absorption bands of the intermediate of either the dinaphthyloxirane (V) or the tetraphenyloxirane (III) produces additional final photoproducts (as well as recyclization).

In all cases, final photoproducts were identified by comparison of emission spectra with independent authentic samples. Furthermore, selective excitation of the photoproduct mixture was used to clarify the nature of the components.

For diphenyloxirane (I), the final primary products are *trans*-stilbene, benzaldehyde, and phenylmethylene. In order to establish *trans*-stilbene as a primary product and not the result of phenylmethylene radical reaction, an additional photochemical study was made because 3MeP is a relatively soft glass at 77°K. Another hydrocarbon matrix (isononane–isooctane) with a viscosity some 10^7 times greater than 3MeP was used as a matrix. In this case, radical recombination certainly would not occur and *trans*-stilbene is still formed. Additional subsequent data from the study of triphenyloxirane (see below) indicate that, essentially, radical recombination does not occur in 3MeP at 77°K. Phenylmethylene is inferred from the existence of a highly resolved emission (0–0 band at 388 mμ) which disappears on warming with the consequent formation of additional *trans*-stilbene.

Benzophenone, diphenylmethylene, and tetraphenylethylene are primary products of tetraphenyloxirane (III). The tetraphenylethylene was not considered by Trozzolo, *et al.*[3] The emission of diphenylmethylene was similar to that previously given,[3] although better defined. This emission disappeared upon warming and recooling the solution.

In the case of triphenyloxirane (II), the primary products are diphenylmethylene, phenylmethylene, benzaldehyde, and benzophenone. There is indication of the formation of triphenylethylene. Diphenylmethylene was identified on the basis of its emission spectrum and its disappearance upon warming with consequent formation of tetraphenylethylene. Phenylmethylene was inferred primarily from the fact that photolysis in rigid medium gave no *trans*-stilbene; however, warming the solution resulted in the formation of *trans*-stilbene. This would occur because of phenylmethylene radical recombination in fluid solution but not in a rigid matrix. Previous workers[3] did not find either the benzophenone or the phenylmethylene. Solution photochemistry results in products derived from both diphenyl- and phenylmethylenes.[1]

The nature of the final photoproducts from all three of the phenyloxiranes is such that they arise from splitting of bonds in pairs and where all pair combinations are possible; that is, a C–C bond and one or the other of the C–O bonds split, as well as no C–C bond but both C–O bonds split.

Further details concerning the spectroscopy, the mechanism, the nature of the intermediates, and the relative reaction rates of the photochemistry of oxiranes will appear in the near future.

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The Preparation and Probable Structure of $(CH_3)_2As\overline{C{=}CAs(CH_3)_2CF_2C}F_2Fe_3(CO)_{10}$

Sir:

Ditertiary arsines are well known for their ability to form chelate complexes with metal carbonyls.[1] In addition, complexes have recently been obtained in which the ligand acts as a bridging group between two metal carbonyl moieties.[2] The recently discovered cyclobutene derivative $(CH_3)_2As\overline{C{=}CAs(CH_3)_2CF_2CF_2}$ (ffars) acts as both a chelating bidentate ligand and a tridentate ligand with the double bond acting as the third electron donor.[3]

We now wish to report the synthesis of a compound ffars$Fe_3(CO)_{10}$ which probably has structure I. In such a compound ffars is acting as a bridging ligand, but more interestingly it is bonded to a fragment of a polynuclear carbonyl, $Fe_3(CO)_{12}$. One similar compound, Fe_3-

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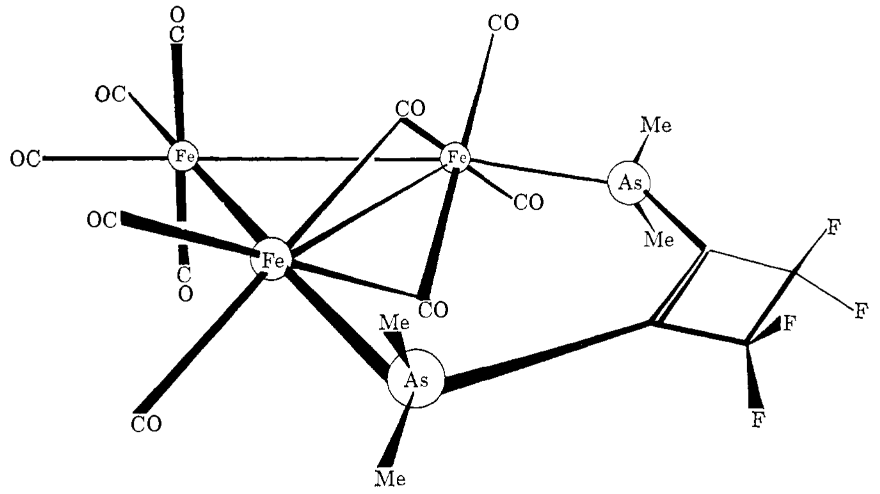
(1) T. A. Manuel, *Advan. Organometal. Chem.*, **3**, 181 (1965).

(2) R. J. Mawby, D. Morris, E. M. Thorsteinson, and F. Basolo, *Inorg. Chem.*, **5**, 27 (1966); T. A. Manuel, *ibid.*, **2**, 854 (1963); F. Zingales, E. Canziani, and R. Ugo, *Gazz. Chim. Ital.*, **92**, 343, 761 (1962); R. S. Nyholm, S. S. Sandu, and M. H. B. Stiddard, *J. Chem. Soc.*, 5916 (1963).

(3) W. R. Cullen, P. S. Dhaliwal, and C. J. Stewart, *Inorg. Chem.*, **6**, 2256 (1967); F. W. B. Einstein and J. Trotter, *J. Chem. Soc.*, *A*, 824 (1967).

$(CO)_{11}P(C_6H_5)_3$, is known.[4] The compounds $(C_6H_5)_3M$ ($M = P, As, Sb$) also react with $Co_4(CO)_{12}$ to give $Co_4(CO)_{11}M(C_6H_5)_3$.[5]



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The new complex I, a black crystalline solid, mp ~160° dec, was obtained in 7% yield by chromatographing the mixture obtained when ffars and $Fe_3(CO)_{12}$ are irradiated with ultraviolet light in a sealed tube.

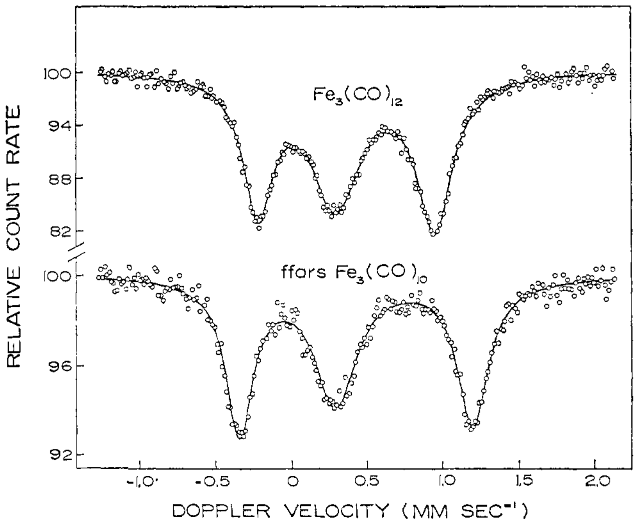

Figure 1. Mössbauer spectra of $Fe_3(CO)_{12}$ and ffars$Fe_3(CO)_{10}$ at 80°K.

Anal. Calcd for $C_{18}H_{12}As_2F_4Fe_3O_{10}$: C, 27.7; H, 1.54; F, 9.73; mol wt, 782. Found: C, 27.9; H, 1.85; F, 9.62; mol wt (mass spectrometry), 782 ± 2. Other products from the reaction are ffars$Fe(CO)_3$ (two isomers) (50% yield), ffars$Fe_2(CO)_6$ (20%), and a trace of a compound believed to be ffars$Fe_3(CO)_9$. The mass spectrum of I can be interpreted in terms of a stepwise loss of ten carbonyl groups. The infrared spectrum in the carbonyl region is very similar to that reported for $(C_6H_5)_3PFe_3(CO)_{11}$.[4a,6] The presence of only three bands at 2069 (s), 2002 (vs), and 1945 (w, br, sh) cm^{-1} (CCl_4 solution) indicates a symmetrical structure. Weak bridging carbonyl bands are present at 1793 and 1749 cm^{-1}. Their intensity is greater in a KBr disk. Both the ^1H and ^{19}F nmr spectra show only one absorption. Thus the ligand is bonded symmetrically to the rest of the molecule and is either planar or is flexing rapidly about the As···As axis. The ^1H nmr peak broadens only slightly on cooling the sample (−30°); hence the ligand is probably planar.

All these data are consistent with structure I, but the most convincing evidence comes from a comparison of its ^{57}Fe Mössbauer spectrum with that of $Fe_3(CO)_{12}$ which consists of three lines of nearly equal intensity (Figure 1). The central broad line arises from the single octahedrally coordinated iron atom, and the outer lines constitute a quadrupole doublet arising from the two equivalent iron atoms connected by bridging carbonyl groups in the triangular structure.[7-9] The Mössbauer parameters for $Fe_3(CO)_{12}$ at 80°K are in agreement with published values.[7] To our knowledge, the room-temperature spectrum has not been reported previously. Replacement of two carbonyl groups by the ffars ligand leaves the central line virtually unaltered both in width and position, but markedly increases the splitting of the outer lines and shifts their center of gravity to higher velocity (Table I). It is thus clear that the ligand is attached symmetrically to the two equivalent iron atoms (so that they remain equivalent), rather than bonding to the third, nonequivalent iron atom.

Table I. Isomer shifts, δ, quadrupole splittings, Δ, and linewidths, Γ (FWHM), for $Fe_3(CO)_{12}$ and ffars$Fe_3(CO)_{10}$

Compound	Temp, °K	$\delta^{a,b}$	Δ^a	Γ^a
$Fe_3(CO)_{12}$	80	0.303	0	0.38
		0.373	1.136	0.26
	295	0.219	0	0.52
		0.295	0.982	0.25
ffars$Fe_3(CO)_{10}$	80	0.283	0	0.38
		0.420	1.523	0.23
	295	0.218	0	0.36
		0.338	1.416	0.21

[a] In mm sec^{-1}, ±0.01 mm sec^{-1}. [b] Relative to sodium nitroprusside.

The increase in isomer shift for the outer lines indicates a lower total s-electron density at these iron

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(4) (a) R. J. Angelici and E. E. Siefert, *Inorg. Chem.*, 5, 1457 (1966); (b) D. J. Dahm and R. A. Jacobson, *Chem. Commun.*, 496 (1966).

(5) G. Cetini, O. Gambino, R. Rossetti, and P. L. Stangellini, *Inorg. Chem.*, 7, 609 (1968)

(6) This compound, however, is a mixture of two isomers in the solid state, both of which contain bridging carbonyl groups.[4b]

(7) R. H. Herber, W. R. Kingston, and G. K. Wertheim, *Inorg. Chem.*, 2, 153 (1963).

(8) L. F. Dahl and J. F. Blount, *ibid.*, 4, 1373 (1965).

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nuclei in the ffars compound. This could be caused by a decrease in 4s population, or by an increase in 3d density which would shield the nucleus from the 4s electrons. The former would imply that a CO group is a slightly more efficient σ donor than the $AsMe_2$ group.

The alternative explanation, an augmented 3d electron density, could arise from three possible effects: (1) an increase in σ donation of $As(CH_3)_2$ relative to CO which would then increase the 3d character; (2) an increase in ligand-to-metal π donation; (3) a decrease in metal-to-ligand back π donation. It seems likely that the direct 4s term is greater than the direct 3d term, in which case an increase in σ donation would cause a negative rather than positive change in the isomer shift. Both the other possible explanations would yield positive shifts.

The larger electric field gradient at the equivalent iron nuclei in the ffars compound may arise both from π delocalization in the cyclobutene ring and from the fact that the ligand lies in the plane of the iron atoms. The splittings for $Fe_3(CO)_{12}$ and $ffarsFe_3(CO)_{10}$ show a stronger temperature dependence than most d^{10} iron complexes. This may be due to the bridging carbonyls and merits further study as it implies the existence of a fairly low-lying electronic excited state in these compounds.

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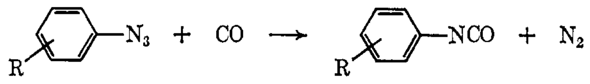
The Reaction of Organic Azides with Carbon Monoxide. A New Route to Isocyanates

Sir:

In the course of our work on new routes to isocyanates[1] we became interested in the reactions of nitrene intermediates. Investigations of nitrene intermediates have generated numerous publications in recent years.[2] In view of the similarity of nitrene reactions to those of carbenes, it was decided to investigate whether organic azides react with carbon monoxide to produce isocyanates.



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It is known[3] that methylene formed from the photochemical decomposition of ketene will react with CO to re-form ketone. Also, diazomethane has been decomposed in CO to produce ketene.[4] In addition, isocyanic acid has previously been found[5] as a product of the thermal decomposition of chloramine in CO. Chambers[6] and coworkers have reported that hexafluoroazomethane reacted with CO at 325° and 650 atm to give an 88% conversion to trifluoromethyl isocyanate. These authors postulated a nitrene intermediate which reacts with the CO. Most recently Collman and coworkers[7] have treated phenyl azide and acid azides with *trans*-chlorocarbonylbis(triphenylphosphine)iridium to form isocyanate products. Collman states,[8] however: "In the absence of a metal complex, CO and organic azides do not react at a measurable rate." We now report the first direct synthesis of free isocyanates from aromatic azides and uncomplexed CO in an uncatalyzed reaction.

Attempts to pyrolyze phenyl azide in a CO stream at atmospheric or reduced pressure resulted in only azobenzene and tar. However, when phenyl azide was thermally decomposed in an autoclave under sufficient CO pressure, phenyl isocyanate was obtained as the only product of the reaction. Benzene and 1,1,2-trichloro-1,2,2-trifluoroethane have been used as solvents. A pressure dependence has been noted for the reaction: at 37 atm equal amounts of phenyl isocyanate and azobenzene were obtained, at 136 atm the product was phenyl isocyanate with only a trace of azobenzene, and above this pressure only phenyl isocyanate was detected.

Examples of other azides which have been successfully converted to the corresponding isocyanates include **1** where R = o-CH_3, o-C_6H_5, p-CH_3, p-NO_2, p-OCH_3, and p-Cl. Ethyl azidoformate in benzene or cyclohexane appeared to yield products of reaction with the solvents. In trichlorotrifluoroethane, however, carbethoxy isocyanate was isolated [bp 25° (10 mm); 32% yield; ν_{NCO} 2230 cm^{-1}; N-carbethoxyurethan, mp 48–49° (lit.[9] mp 49–50°)].

The reactions have been run in stainless-steel, tantalum-lined and glass-lined autoclaves. Reaction times have varied from 15 to 90 min at 160–180°. To ensure complete conversion to isocyanate we have generally worked at pressures between 200 and 300 atm. A sample procedure is as follows. To a 250-ml, glass-lined autoclave was added 11.9 g (0.1 mol) of phenyl azide and 100 ml of 1,1,2-trichloro-1,2,2-trifluoroethane. The autoclave was flushed once with CO and then pressurized with CO (Air Products and Chemicals, Inc., CP grade) to 300 atm. The reaction mixture was heated with rocking at 180° for 1.5 hr. After cooling, the autoclave was discharged under N_2. The presence of phenyl isocyanate was shown by ir and vpc examination (100% conversion) with no indication of any other products. Vacuum fractional distillation yielded pure phenyl isocyanate, bp 50° (10 mm) (5.6 g, 47% yield). An additional 3.6 g of diphenylurea (presumably from moisture) was also obtained for a material balance of 80%.

This procedure gives a general method for making isocyanates from readily available azides. The reaction can be carried out in reactive solvents to yield iso-

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