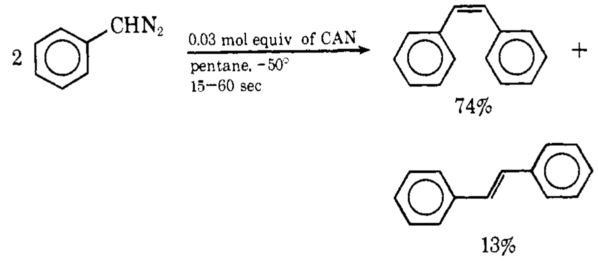
Oxidation of Organic Compounds with Cerium(IV). XIII. Cerium(IV)-Catalyzed Decomposition of Aryldiazomethanes to *cis*- and *trans*-Stilbenes[1]

Sir:

We have found that phenyldiazomethane in pentane at −5° rapidly decomposes to *cis*- and *trans*-stilbenes when treated with catalytic amounts of ceric ammonium nitrate (CAN). The high yield of the cis isomer is particularly noteworthy.



Phenyldiazomethane was prepared by treating the tosylhydrazone of benzaldehyde with sodium methoxide.[2] The reaction mixture was extracted with pentane, and analysis by nmr using 1,1,2,2-tetrachloroethane, δ 5.8 (s), as an internal standard showed that the pentane solution was 0.381 *M* in phenyldiazomethane, δ 5.1 (s, 1, $-CHN_2$) and 7.1 (m, 5, C_6H_5-). This solution (10 ml) was transferred to a flask that contained a magnetic stirring bar and was immersed in a bath at −10°. Approximately 1 ml of a 0.1 *M* CAN solution in acetonitrile was added over a period of a few seconds as the reaction mixture was being stirred. A gas was vigorously evolved and in a few seconds the pentane layer turned colorless. The reaction mixture was poured into a flask containing 50 ml of an aqueous saturated sodium bicarbonate solution covered with 50 ml of pentane. After extraction, the pentane layer was separated, dried ($MgSO_4$), and concentrated. A known amount of the standard, 1,1,2,2-tetrachloroethane, was added and the yields of *cis*- and *trans*-stilbenes were determined by nmr analysis. The nmr showed the presence of only the two stilbenes and the standard. The identities of the stilbenes were further confirmed by positive glpc peak enhancement with authentic samples. The high cis to trans ratio was confirmed by the glpc analysis.

Table I. Yields of Stilbenes from the Reaction of Aryldiazomethanes, $ArCHN_2$, with Ceric Ammonium Nitrate[a]

Ar–	$ArCHN_2$ used, mmol	CAN used, mmol[b]	ArCH=CHAr yield, %[c] Cis (rel)	Trans (rel)	Total (abs)
C_6H_5–	3.81[d]	0.1	84.5 ± 1.7[d]	15.4 ± 0.13[d]	87.5 ± 2.9[d]
p-$CH_3C_6H_4$–	0.52[e]	0.15	76.0 ± 2.9[f]	23.5 ± 2.0[f]	79.5 ± 2.3[f]
p-ClC_6H_4–	0.39[e]	0.15	70.0 ± 1.4[f]	30.0 ± 1.4[f]	98.3 ± 1.6[f]

[a] In 10 ml of pentane at −5°. [b] Added as a 0.1–0.15 *M* solution in acetonitrile. [c] Standard deviations based on at least three runs are given. [d] Determined by nmr analysis using 1,1,2,2-tetrachloroethane as a standard. [e] Determined by adding benzoic acid and titrating the unreacted acid; see W. R. Bamford and T. S. Stevens, *J. Chem. Soc.*, 4735 (1952). [f] Determined by glpc analysis using bibenzyl as a standard.

p-Methylphenyldiazomethane and *p*-chlorophenyldiazomethane were found to react in a similar way and the yields of stilbenes from these three diazo compounds are given in Table I.

The cerium(IV) is necessary for the reaction since no decomposition of phenyldiazomethane was noted when it was treated with a CAN solution that had been reduced with acetone. Also, benzalazine[3] was excluded as an intermediate since it could be quantitatively recovered from a 0.1 *M* CAN solution in acetonitrile.

Diazo compounds have usually been decomposed thermally, photochemically, or with a Lewis acid.[4] Only a few reports exist which describe the decomposition of diazoalkanes under oxidative conditions.[4,5] In no case has a large amount of a cis olefin been obtained from a diazoalkane and often olefin formation is not the main mode of reaction.[4,5] Jugelt and Pragst[5e] have reported that the electrochemical oxidation of diphenyldiazomethane leads to tetraphenylethylene by an oxidative chain reaction with the first step being the formation of the radical cation of diphenyldiazomethane. They have confirmed the presence of radical cations in the reaction and studied the oxidation of other diazo compounds, but not aryldiazomethanes.[6]

We propose an analogous oxidative chain reaction for the cerium(IV)-catalyzed decomposition of phenyldiazomethane. This mechanism accounts for the

$$\mathrm{PhCHN_2 + Ce^{IV} \longrightarrow PhCHN_2\cdot^+ + Ce^{III}}$$

$$\mathrm{PhCHN_2\cdot^+ + PhCHN_2 \longrightarrow PhCHCHPh\cdot^+ + 2N_2}$$

$$\mathrm{PhCHCHPh\cdot^+ + PhCHN_2 \longrightarrow PhCHN_2\cdot^+ + PhCH{=}CHPh}$$

$$\mathrm{cis/trans} = 6/1$$

formation of stilbene, but an unequivocal explanation for the formation of the high yield of the cis isomer is still lacking.

Several other diazo compounds when treated with CAN were not rapidly converted to high yields of the corresponding olefins. Both *p*-nitrophenyldiazomethane and α-trifluoromethylphenyldiazomethane did not react rapidly with cerium(IV), which is consistent with the strongly electron-withdrawing substituents making the formation of the initial radical cation difficult. *p*-Methoxyphenyldiazomethane reacted rapidly with

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[3] D. Bethell and D. Whittaker, *J. Chem. Soc. B*, 778 (1966).

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[6] (a) W. Jugelt and F. Pragst, *Tetrahedron*, **24**, 5123 (1968); (b) F. Pragst and W. Jugelt, *Electrochim. Acta*, **15**, 1543 (1970).

cerium(IV), but gave a complex mixture of products. When treated with CAN, α-methyl- and α-*tert*-butylphenyldiazomethanes were converted to the corresponding ketones, the diazo groups of azabenzil, $PhC(N_2)COPh$, and ethyl diazoacetate were converted to the corresponding alkyl nitrates, and diphenyldiazomethane was converted to a mixture of benzophenone, benzhydrol, and benzhydryl nitrate. Some of the expected olefins were obtained from α- and β-naphthyldiazomethanes, but additional products were also formed in both cases. Ortho substituents, such as a methyl group or chlorine atom, also caused new products to appear in addition to the expected stilbenes.

Thus, the olefin-formation reaction seems to be very sensitive to substituents, a fact which can be easily rationalized by the above mechanism.

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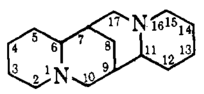
Biosynthesis of Lupin Alkaloids from $^{14}CO_2$. Evidence for the Independent Formation of Lupanine and Sparteine

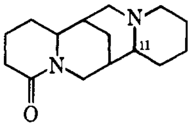
Sir:

The plant *Lupinus arboreus* is reported to contain the bases sparteine (I) and lupanine (IIa)[1] while another species, *L. angustifolius*, is reported to contain lupanine, α-isolupanine (IIb), angustifoline (III), 13-hydroxylupanine (IV) (plus several of its esters), but not sparteine.[2,3] Sparteine is widely viewed[4,5] to play a primary role in the formation of this group of compounds by a series of successive oxidation reactions in the order

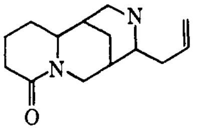
$$\mathrm{I} \longrightarrow \mathrm{IIa} \longrightarrow \mathrm{III} \longrightarrow \mathrm{IV} \qquad (1)$$



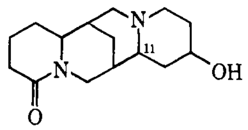
I



IIa (II*R*)
IIb (II*S*)



III



IV

A differing view, with the esters of hydroxylupanine playing a primary role, has been put forward on the basis of ontogenetic studies.[2] We now present kinetic evidence from exposure of plants of the above species and *L. polyphyllus* to $^{14}CO_2$ which indicate that sparteine and lupanine may be synthesized independently of one another.

It was anticipated that, following short periods of photosynthesis in an atmosphere of $^{14}CO_2$, early members of such a sequence of oxidations would be labeled more rapidly than latter ones and that their relative specific activities would lend further support to the preceding precursor–product relationships. Though data from this type of experiment cannot offer definite proof for such a sequence, it affords a unique opportunity in the case of CO_2 autotrophs to obtain information about *in vivo* rates of *de novo* synthesis, necessary for conferring on a compound the status of *intermediate* as opposed to that of *presursor*.[6,7] In addition, its potential for revealing kinetically interesting "secondary metabolites" has only begun to be exploited.[7,8]

Twenty-two *L. arboreus* and eight *L. angustifolius* plants, all 6 weeks old, were exposed separately to 3 and 1.2 mCi, respectively, of $^{14}CO_2$, in a flexible polyethylene chamber[7] for 2 hr at which time half of each group was immediately extracted for alkaloids as described previously.[6] The remaining plants were returned to normal air for 8 hr before being so extracted. Recovery of the above alkaloids was >90% by this procedure. The alkaloid extracts were analyzed by glpc-continuous combustion-flow counting[9] with all of the above compounds resolved on a 10% QF-1 column,[8] permitting their simultaneous specific activity determination. Tlc on three systems[8] followed by autoradiography confirmed the glpc labeling patterns. The identities of the sparteine and lupanine peaks eluted from glpc were confirmed by their mass spectra after collection from glpc.[8]

L. arboreus. In addition to the two major alkaloids, sparteine and lupanine, a third minor component eluting prior to lupanine from glpc was noted. Sparteine was the only labeled compound eluted from glpc in either time sample. Tlc–autoradiography confirmed sparteine as the only known alkaloid to be labeled, lupanine being completely inactive. About 25% of the total alkaloid ^{14}C was in several unidentified compounds (tlc–autoradiography) which were not eluted from glpc. By 8 hr, the specific activity of sparteine had nearly doubled yet lupanine was still inactive. Glpc data and specific activities for these two bases are given in Table I.

L. angustifolius. Lupanine, angustifoline, and hydroxylupanine were present in the ratio 5:7:2 as the major components on glpc, together with moderate amounts of two others, tentatively identified as hydroxylupanine ester(s) and α-isolupanine. Lupanine was the only labeled alkaloid detected by glpc of either time sample. Again about 25% of the ^{14}C was not eluted and was accounted for in several unidentified com-

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