actions in nitromethane were accompanied by considerable decomposition of VII to undetermined, nonvolatile products, but yields were high (80–95%) in the other solvents. The decomposition reaction was assumed to be first order in VII. The results are summarized in Table I.

Both of the products VIII and IX were reasonably stable to heating to 200° for 8–12 hr.

The data of Table I show only a threefold effect on the reaction rate over the series of solvents studied, well within the range of solvent effects observed in other Diels–Alder reactions.[2] Moreover, the relative rates do not vary appreciably over the temperature range (65°), nor is there a large effect of either solvent or temperature on the isomer ratios.

The above data may, of course, be interpreted as pertaining to two separate (one-step) reactions possessing different transition states[8] but having extraordinarily similar influences of solvents on their activation parameters. However, we would like to suggest the alternate explanation that the reaction is proceeding through a single transition state such as I to an intermediate (cf. II).[11] This intermediate may then continue through either of two subsequent, lower energy transitions similar to III and IV to the two observed products.

Additional support for the two-step intermediate II may be found in the structure of the vinylcyclobutanes (IX): only the 2-vinyl isomers were detected under conditions (g.l.p.c.) which should have shown the presence of >1% yield of either of the 3-vinyl isomers (assuming no unusual instability of the latter). The products (IX) are those which would be predicted by the accepted[12–14] two-step mechanism for a (cyclobutane-forming) thermal cycloaddition reaction.

Examination of the activation parameters for this reaction may disclose more subtle, but possibly more meaningful differences in the two reaction paths. The question of whether such differences would support the contention that dual, one-step mechanisms[8] are involved in the formation of VIII and IX, or merely reflect variations in the second, product-determining step of the two-step mechanism, which we favor, would appear to be subject to debate. Unfortunately, the present data are not suitable for comparison, but more complete studies of this aspect are in progress. Stereochemical examinations suggested by previous observations with other systems[4,5,13] are also under consideration.

In summary, it seems possible that study of this simple and yet versatile system may offer a fresh approach to the intricacies of the Diels–Alder and related reactions.

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The Photodecomposition of Pivaloyl Azide

Sir:

In the Curtius rearrangement[1] carbonyl azides of the type R–CO–N$_3$ (R = alkyl or aryl) are converted to isocyanates (R–NCO) when decomposed by heat[1] or light.[2] Alkoxycarbonyl azides (RO–CO–N$_3$) when decomposed by light[3] or heat[4,5] give carbalkoxynitrenes (RO–CO–N) which insert into C–H bonds and add to double bonds in intermolecular reactions.

Carbonyl nitrenes (R–CO–N) have often been postulated as intermediates in the Curtius rearrangement,[6–8] and the lack of unrearranged intermolecular reaction products has been explained by assuming a very high rate of rearrangement to isocyanate.[9] This seemed to be in accord with the observation, first made by ApSimon and Edwards,[10] of the formation of intramolecular C–H insertion products in photolyses of carbonyl azides containing a C–H function in positions sterically favorable for cyclization. Furthermore, photolysis of benzazide in dimethyl sulfoxide[11] gave an addition product of C$_6$H$_5$–CO–N to the solvent in a reaction interpreted as the capture of the nitrene intermediate of the Curtius rearrangement. Also, ethyl azidoformate, shown to be a source of carbethoxy nitrene,[3] was observed to undergo some Curtius rearrangement in methanol solution.[12] The hypothesis of a common nitrene intermediate for rearrangement as well as for C–H insertion leaves unexplained the absence of intramolecular C–H insertion products in the thermal decomposition of ApSimon's compounds.[10,13]

In this communication we wish to show: (1) that in the photolysis (but not in the thermolysis) of pivaloyl azide (t-Bu–CO–N$_3$, I) an intermediate capable of selective intermolecular reactions is formed; (2) that this intermediate possesses properties similar to those of carbethoxy nitrene, and (3) that the intermediate is not involved in the (thermal) Curtius rearrangement of pivaloyl azide.

We have studied the decomposition of pivaloyl azide (I) in hydrocarbon solvents. Thermolysis in cyclohexene and 2-methylbutane is rapid above room temperature and gives a virtually quantitative yield of

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(13) Prof. Huisgen kindly informed us in Oct. 1964 of positive trapping experiments. The photolyses of acetyl azide in benzonitrile and phenylacetylene gave 2-methyl-5-phenyl-1,3,4-oxadiazole or -oxazole, respectively. In thermolysis experiments with acyl azides no evidence for nitrene intermediates was obtained.

t-butyl isocyanate (*t*-Bu–NCO). With our analytical methods we would have detected a 1% yield of insertion or addition products. However, photolysis of solutions of I in cyclohexene, cyclohexane, or 2-methylbutane with a medium pressure mercury lamp at −15 to +5° gave, in addition to *t*-butyl isocyanate, a spectrum of products best explained as arising from the insertion of pivaloyl nitrene into C–H bonds or its addition to double bonds. Chart I shows these inter-

Chart I. Products from Cyclohexene and Cyclohexane

stucture assigned on basis
of infrared and n.m.r. spectra
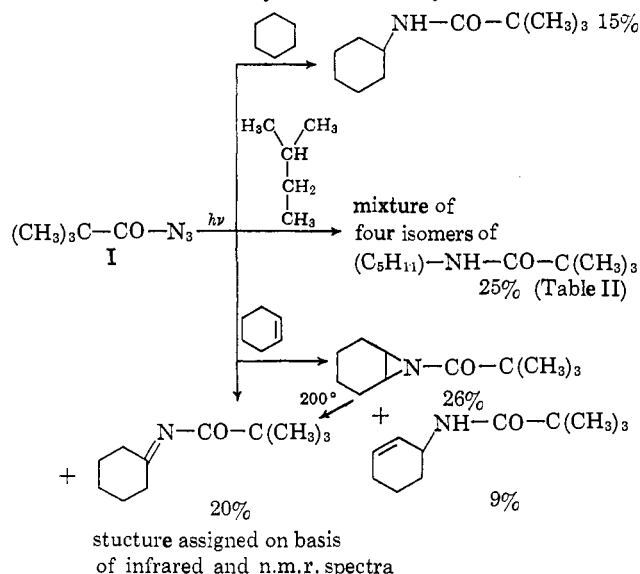
molecular products, Table I the relative reactivities of the intermediate with the three kinds of C–H bonds in 2-methylbutane. In this solvent, insertion into the tertiary, secondary, and the two types of primary C–H bonds took place. The four isomeric isopentylpivalamides were synthesized from the corresponding amines and the synthetic compounds used for identification (by v.p.p.c. retention time and infrared and n.m.r. spectra) and for calibration of the vapor phase partition chromatograph.[14] In the photolysis of I, the isopentyl pivalamides were formed in a total yield of 25%, indicating that at least that much of the azide I is converted to the selective intermediate.

Table I. Reactivities of the C–H Groups in 2-Methylbutane toward Pivaloyl Nitrene (corrected for the number of hydrogens)

	Tertiary	Secondary	Primary
		Type of C–H bond	
Rel. reactivity	160	8.6	1
Rel. error	±25%	±12%	..

Photolysis in cyclohexane gave N-cyclohexylpivalamide, photolysis in cyclohexene the allylic C–H insertion product plus products from addition to the double bond, as shown in Chart I. The products were identified by comparison of their v.p.p.c. retention times and infrared and n.m.r. spectra with those of samples prepared by independent, unequivocal syntheses.[14]

The qualitative similarity of the reactions observed here to those of carbethoxy nitrene[3] make us inclined to

(14) All new compounds gave satisfactory elemental analyses. The small v.p.p.c. peaks of the primary and secondary insertion products were rather broad, causing the large relative errors noted in Table II.

think that pivaloyl nitrene, *t*-Bu–CO–N, is the reactive intermediate in the intermolecular reactions. Since thermal decomposition of I did not give unrearranged intermolecular products, the same intermediate cannot be involved in the thermal rearrangement, which might proceed in a concerted fashion or perhaps through a different intermediate. This question is currently being studied in our laboratory.

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The Synthesis of Spinochromes A, C, D, and E

Sir:

Investigation of the pigments derived from the spines of sea urchins began in 1885[1] and for many years the literature in the field abounded in unsubstantiated structural proposals of at least twelve presumably distinct compounds. As a result of recent researches this number has been reduced to six pigments of unquestioned identity. They are echinochrome A (**1**) and spinochromes A (**2**), B (**3**), C (**4**), D (**5**), and E (**6**). The structure of echinochrome A
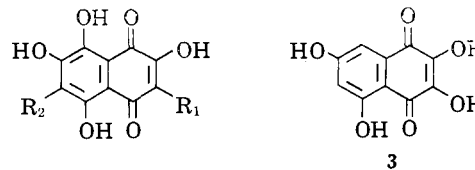
1, $R_1 = C_2H_5$; $R_2 = OH$
2, $R_1 = COCH_3$; $R_2 = H$
4, $R_1 = COCH_3$; $R_2 = OH$
5, $R_1 = OH$; $R_2 = H$
6, $R_1 = OH$; $R_2 = OH$

was unambiguously demonstrated by synthesis more than 20 years ago.[2] The nature of the spinochromes had remained obscure until Thomson established the structures of D[3] and E[4]; Sutherland unraveled the structural tangle of B[5]; and work in this laboratory resulted in structural elucidation of A and C.[6,7] Failure to achieve clean separation of the pigments on calcium carbonate columns coupled with heavy reliance on combustion data often led to serious misinterpretation. Structural proof by synthesis is therefore needed to remove any remaining elements of doubt. This was achieved for spinochromes B (then

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