Intermediates in the Decomposition of Aliphatic Diazo-compounds. Part XI.[1] Mechanistic Studies on the Reaction of Diphenylmethylene with Amines in Solution

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The kinetics and products of thermal decomposition of diphenyldiazomethane in acetonitrile containing n- and t-butylamines have been investigated. It is established that the principal product, *N*-(diphenylmethyl)butylamine is formed by reaction of the primary amine with diphenylmethylene. In the formation of the secondary amine, the absence of an intermolecular hydrogen isotope effect, determined from the ratio of yields from reactions with butylamine and *NN*-dideuteriobutylamine, and the substantial value of the intramolecular isotope effect, obtained from the radioactivity of the secondary amine produced from *N*-tritiated butylamine, are shown to be consistent with initial attack of the singlet carbene on the nitrogen atom of the amine followed by rearrangement of the resulting ylide rather than a hydrogen-abstraction–recombination mechanism. The latter mechanism for reaction of the triplet carbene has been detected by CIDNP studies, the intermediate radical pair giving rise to diphenylmethane as well as the secondary amine, but both in small amounts. The principal product arising from the triplet carbene is, however, tetraphenylethane, and comparison of the inter- and intra-molecular isotope effects on its formation suggest that conversion of the singlet state of diphenylmethylene into the triplet may be irreversible under these reaction conditions.

CARBENES attack amines in a variety of ways. Insertion into C–H bonds of organic groups can take place, insertion into the N–H bond of primary and secondary amines has been reported both as a discrete reaction and as one step of a more complex reaction sequence, and insertion into the C–N bond of tertiary amines has been described, the final product in this case arising by rearrangement of an initially formed nitrogen ylide.[2] Although plausible pathways from the carbene and amine to the observed reaction products have been put forward, no detailed mechanistic study appears to have been undertaken. The present paper describes kinetic and product studies, examination of isotope effects, and investigation of the occurrence of chemically induced dynamic nuclear spin polarization (CIDNP) in the reaction of diphenylmethylene, thermally generated from the diazoalkane, with aliphatic primary amines. The principal reaction involved is the insertion of diphenylmethylene into the N–H bond of the amine giving the secondary alkyl(diphenylmethyl)amine.

In previous papers we have described mechanistic investigations of analogous insertions of diarylmethylenes into the O–H bond of water[3] and of simple alcohols.[4,5] By comparing the isotope effects on insertion into deuterium oxide (D_2O) and tritiated water (HTO), we were able to demonstrate that initial attack by the carbene occurs at the oxygen atom resulting in the formation of an oxygen ylide rather than by hydrogen or proton abstraction.[6]

It seemed to us that a comparison of the intra- and inter-molecular isotope effects on the competing reactions of diphenylmethylene with amines would permit a clear distinction to be made between the ylide mechanism of N–H insertion and possible abstraction–recombination mechanisms just as had been possible in the reaction with water. Accordingly, we have investigated the kinetics of thermal decomposition of diphenyldiazomethane at 85° in solution in acetonitrile to which had been added n- or t-butylamine. By examination of the effect on the product proportions of using RND_2 in place of RNH_2, the intermolecular deuterium isotope effect on the reactions of the carbene could be evaluated and compared with that deduced from an examination of the radioactivity of the products of reaction of the carbene with RNHT. To assist in the delineation of reaction pathways, CIDNP was sought in analogous reactions under slightly different conditions[7] (using n-heptylamine in the higher boiling solvent heptyl cyanide at 120°).

By comparing the proportion of products derived from singlet diphenylmethylene and alcohols (alkyl ethers) with those from the triplet (diphenylmethane + benzophenone from reaction with oxygen) as the alcohol concentration varied, it had been shown previously[5] that the two electronic states of the carbene were able to equilibrate before reaction. This confirmed earlier suggestions[8,9] concerning diphenylmethylene and was in line with gas-phase work on methylene itself.[10] As well as throwing light on the mechanism of insertion of the carbene into the N–H bonds of amines, the present

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[1] Part X, D. Bethell and M. F. Eeles, *J.C.S. Perkin II*, 1974, 704.

[2] W. Kirmse 'Carbene Chemistry,' Academic Press, New York and London, 2nd edn., 1971, p. 409. For another recent review of carbene chemistry, see D. Bethell in 'Organic Reactive Intermediates,' ed. S. P. McManus, Academic Press, New York and London, 1973, ch. 2.

[3] D. Bethell, A. R. Newall, G. Stevens, and D. Whittaker, *J. Chem. Soc.* (*B*), 1969, 749.

[4] D. Bethell, A. R. Newall, and D. Whittaker, *J. Chem. Soc.* (*B*), 1971, 23.

[5] D. Bethell, G. Stevens, and P. Tickle, *Chem. Comm.*, 1970, 792.

[6] W. Kirmse, *Annalen*, 1963, **666**, 9; a similar pattern of reactivity of alcohols towards thermally generated 4-bischlorophenylmethylene has been reported, D. Bethell and R. D. Howard, *J. Chem. Soc.* (*B*), 1969, 745.

[7] For reviews of mechanistic applications of CIDNP, see D. Bethell and M. R. Brinkman, *Adv. Phys. Org. Chem.*, 1973, **10**, 53; 'Chemically Induced Magnetic Polarization,' eds. A. R. Lepley and G. L. Closs, Wiley, New York, 1973.

[8] D. Bethell, D. Whittaker, and J. D. Callister, *J. Chem. Soc.*, 1965, 2466.

[9] G. L. Closs, *Topics Stereochem.*, 1968, **3**, 193.

[10] H. M. Frey and R. Walsh, *Chem. Comm.*, 1969, 158.

results also throw additional light on this interconversion of singlet and triplet states of diphenylmethylene.

RESULTS

Products and Kinetics of Reaction.—As in previous investigations, all reactions in the product and kinetic studies were conducted in acetonitrile solution in closed polytetrafluoroethylene vessels to minimise the effects of heterogeneous decomposition of the diazoalkane. Diazoalkane concentrations were usually *ca.* 0·1M and, in general, amines were present in at least ten-fold excess. All experiments were carried out at 85·0°.

The rate of disappearance of diphenyldiazomethane was followed spectrophotometrically at 526 nm. As for reactions in the presence of alcohols, the addition of amine to the acetonitrile solution of the diazoalkane led to a rate reduction compared with reactions in pure acetonitrile. Indeed, at a given additive concentration, the apparent first-order rate coefficient was almost the same, within experimental uncertainty, for n- and t-butylamine as it was for t-butyl alcohols (see Table 1). Clearly the amines do not provide a new and separate pathway for the consumption of diphenyldiazomethane, for example, by proton transfer from the amine to the diazo-carbon atom.

TABLE 1

Apparent first-order velocity constants for the consumption of diphenyldiazomethane at 85° in acetonitrile containing additives

$[Ph_2CN_2]_0$/M	0·0148	0·0104	0·0104	0·0614
Additive		Bu^nNH_2	Bu^tNH_2	Bu^tOH
Concentration (M)		1·00	1·00	1·06
$10k_{obs}$/min^{-1}	0·96 [a]	0·82 ± 0·02	0·80 ± 0·02	0·86 [a]

[a] Data from ref. 8.

The pattern of products from the decomposition of diphenyldiazomethane in acetonitrile containing amines is analogous to that from the reaction with alcohols. Benzophenone azine is the principal dimeric product, just as it is in the absence of additives, together with a little tetraphenylethylene. Reaction of the intermediate diphenylmethylene with the amine gives *N*-(diphenylmethyl)butylamine as the major product. The most revealing difference between reaction with amines and reaction with alcohols, however, is the appearance in substantial amounts of tetraphenylethane in place of diphenylmethane, showing a reversion to the situation in pure acetonitrile where tetraphenylethane is the major identifiable ' radical product.'

TABLE 2

Products (%) [a]from the thermal decomposition of diphenyldiazomethane in acetonitrile containing n- or t-butylamine at 85·0°

$[Ph_2CN_2]_0$/M	0·058	0·115	0·116	0·117	0·116
Additive	Bu^nNH_2	Bu^nNH_2	Bu^nND_2	Bu^tNH_2	Bu^tND_2
$[Amine]_0$/M	3·00	0·959	0·959	0·973	0·973
$Ph_2C{\cdot}N{\cdot}N{:}CPh_2$ [b]	3·3	17·1 ± 0·9	16·8 ± 0·4	34·1 ± 1·1	35·1 ± 1·1
$Ph_2C{:}CPh_2$	0·4	0·5	0·6	0·5	0·4
$Ph_2C{:}O$	0·3	0·3	0·01	0·1	1·0
Ph_2CH_2	0·0	0·2	0·01	0·1	0·1
$Ph_2CH{\cdot}CHPh_2$	9·5	9·96 ± 0·51	10·5 ± 0·1	17·4 ± 1·6	17·6 ± 1·9
$Ph_2CHNHBu$	86·3	70·0 ± 0·7	71·6 ± 0·3	43·4 ± 1·4	44·2 ± 0·4
Unknown [c]	0·0	0·4	0·4	2·2	0·7
Ph_2CHOH	0·4	1·5	0·07	2·0	1·0

[a] Product yields are expressed as the percentage of diazoalkane initially present which is converted into that product. Unless otherwise indicated, product compositions were determined by g.l.c. [b] Determined spectrophotometrically. [c] Possibly $(Ph_2CH)_2$-NBu; yield estimated assuming product has formula $C_{30}H_{31}N$.

The quantitative analyses of the products of reactions of diphenyldiazomethane with n- and t-butylamines in acetonitrile solution are in Table 2. Results for reactions under analogous conditions with *N*-deuteriated amines are also given. Azine yields were determined spectrophotometrically on individual samples from several different reaction vessels; other compounds were determined by g.l.c. on samples from the combined reaction mixtures.

The results in Table 2 show a consistent pattern. High yields of N–H insertion product are obtained at high initial concentrations of primary amine and the insertion apparently occurs more readily in the n- than the t-alkylamine. A quantitative estimate of the relative reactivities of the amines was obtained by direct competition using a reaction mixture containing initially 0·116M-diphenyldiazomethane, 0·407M-n-butylamine, and 1·142M-t-butylamine. The ratio of n- to t-butyl-diphenylmethylamines was 1·95 ± 0·02 and, using the average ratio of amine concentrations during the reaction, 0·307, the relative reactivity of n- to t-butylamine is 6·35 ± 0·05.

Decreased N–H insertion leads to greater yields of benzophenone azine as expected on the basis of partitioning of diphenylmethylene between attack on the amine and on the unchanged diazoalkane. The variation in the yield of benzophenone is probably without significance, the values merely reflecting the varying degrees of success in eliminating oxygen from the reaction vessel. Diphenylmethanol can only arise from reaction of diphenylmethylene with water, but the origin of the water has not been established. In any case, the occurrence of both these reactions has little bearing on the mechanistic discussion in hand. The origin of the diphenylmethane in the reactions with t-butylamine is not clear: it may not be a primary reaction product but could arise by attack of the carbene on the methine hydrogen of *N*-(diphenylmethyl)-t-butylamine.

The most notable feature of the results is the absence of a significant observable intermolecular isotope effect. In the two comparable sets of experiments for n- and t-butylamine, over 95% of the initial diazoalkane is accounted for in three products, the azine, tetraphenylethane, and (diphenylmethyl)butylamine, and yet the proportions of these are insignificantly different when the NH_2 group is replaced by ND_2. Assuming that there is no deuterium isotope effect on azine formation and on singlet–triplet interconversion (which is further assumed to be irreversible; see Discussion section) the intermolecular isotope effects are given by the ratios of yields of the secondary amine. For both amines, $k_H/k_D = 0.98$. The conclusion that diphenylmethylene attacks both amines initially on their nitrogen atoms rather than by abstraction of hydrogen or a proton from their nitrogen or by direct insertion seems inescapable. It should be noted, however, that there is also no isotope effect on the formation of tetraphenylethane which is plausibly derived from triplet diphenylmethylene, unlike the other two major products which come from the singlet. On the basis of the yields of tetraphenylethane in the presence of deuteriated and undeuteriated amines, the intermolecular isotope effect here is 0·99.

Tritium Isotope Effects.—In order unequivocally to distinguish the ylide mechanism from abstraction–recombination and direct (three-centre) mechanisms of insertion, it is necessary to compare the intermolecular (deuterium) isotope effect on the products with the intramolecular isotope effect determined in a system in which two isotopic atoms compete within the same molecular species. Intramolecular isotope effects are most conveniently measured using tritium and, accordingly, diphenyldiazomethane was allowed to decompose in acetonitrile containing n- and t-butylamines labelled on nitrogen with tritium. Because of equilibriation of the radioactive label among all hydrogen atoms bound to nitrogen, only tritium bound to carbon was sought. The secondary amine resulting from insertion of diphenylmethylene was isolated by column chromatography, and, by repeated exchange with methanol, nitrogen-bound tritium was removed. Comparison of the specific activity of the product with that of the starting amine then gave the observed tritium isotope effect, k_H/k_T. The results are in Table 3.

TABLE 3

Specific radioactivities (S) of tritiated butylamines and the products of their reactions with diphenylmethylene in acetonitrile at 85°

$[Ph_2CN_2]_0/\text{M}$	0·115	0·058	0·117
$[\text{Amine}]_0/\text{M}$	0·959- Bu^nNH_2	3·00- Bu^nNH_2	0·973 Bu^tNH_2
10^{-3} S (disint. s^{-1} mmol^{-1})	112 ± 3	112 ± 3	126 ± 1
$Ph_2CHNHBu$			
10^{-3} S (disint. s^{-1} mmol^{-1})	28·7 ± 0·1	26·9 ± 0·9	31·8 ± 0·9
k_H/k_T	$3{\cdot}9_2 \pm 0{\cdot}09$	$4{\cdot}1_8 \pm 0{\cdot}17$	$3{\cdot}9_7 \pm 0{\cdot}12$
$Ph_2CH{\cdot}CHPh_2$			
10^{-3} S (disint. s^{-1} mmol^{-1})	19·7 ± 0·1		20·7 ± 0·1
k_H/k_T	$5{\cdot}7_0 \pm 0{\cdot}13$		$6{\cdot}1_0 \pm 0{\cdot}07$

Tetraphenylethane was also isolated chromatographically from the reaction mixtures and this too proved to be radioactive. Clearly the compound must have arisen by abstraction by the carbene of a hydrogen atom from the amino-group of the amine, followed by dimerisation of the resultant diphenylmethyl radicals [reaction (1)]. This

$$Ph_2C\colon + RNH_2 \longrightarrow RNH{\cdot} + Ph_2CH{\cdot} \longrightarrow Ph_2CH{\cdot}CHPh_2 \quad (1)$$

then raises two questions. First, how can this conclusion be reconciled with the absence of a deuterium isotope effect, and, secondly, which if any of the other reaction products may have arisen from diphenylmethyl radicals formed in this way?

CIDNP.—This phenomenon, the observation of emission and/or enhanced absorption signals in the n.m.r. spectrum of reaction products when reactions involving intermediate radicals are carried out in the spectrometer probe, is very valuable mechanistically.[7] The observation of polarised signals indicates the involvement of radicals, and the phase of the polarisation, A or E net polarisation or A/E or E/A multiplet polarisation, can indicate the pathway, by which the product arose and in particular the electronic multiplicity of the precursor of the intermediate radical pairs.

In the present instance, possible products of radical reactions are tetraphenylethane, benzophenone, diphenylmethane, and the secondary amine. Of these the first two will be expected to show no detectable polarisation. Tetraphenylethane arising from dimerisation of identical radicals could, according to radical pair theory, show only multiplet polarisation of its aliphatic protons, but, since the aliphatic protons are chemically and magnetically equivalent and therefore appear as a singlet, no polarisation is expected. Benzophenone has no aliphatic protons and polarisation of the aromatic ones is, at best, likely to be obscured by unpolarised signals of the reactant and products. Thus polarisation was sought in the n.m.r. spectra of the methine proton of the secondary amine and in the methylene protons of diphenylmethane by repetitive scanning of the appropriate region of the proton spectrum. For thermal reactions, optimum polarisation is achieved with radical reactions having half-lives in the range of a few minutes; consequently the conditions of the previously described kinetic and product studies ($t_{\frac{1}{2}}$ *ca.* 100 min) were unsuitable. Previous CIDNP studies [11] had shown that diphenyldiazomethane decomposes at a satisfactory rate at *ca.* 120°, and to permit such a temperature to be used in a system analogous to the butylamine–acetonitrile solvent, n-heptylamine (25% by volume) in n-heptyl cyanide was used. Monitoring of the peak due to the aromatic protons of diphenyldiazomethane showed that at 120° $t_{\frac{1}{2}}$ was *ca.* 80 s.

The methylene protons of diphenylmethane showed very clear enhanced absorption during the course of the reaction. Indeed, because the yield of this product is so low (Table 2), the signal was detectable only while the reaction was taking place. This is indicated in the Figure in which the time variation of the signal intensity is shown together with that for the aromatic protons of diphenyldiazomethane.

For the methine proton of the secondary amine the situation is much less clear. Because this is the major product, any polarisation is necessarily superimposed on the normal signal of the unpolarised product. The curve of intensity *versus* time shows, however, a small but distinct hump before the signal reaches its final maximum value. There is no comparable disturbance in the steady fall of the intensity of the signal due to the aromatic protons of the diazoalkane. The additional intensity of the methine proton of the secondary amine is maximal at about the same time as the diphenylmethane signal is at its peak.

A qualitative estimate suggests that when polarisation of the secondary amine signal is maximal, the intensity is about double what it would be in the absence of polarisation. This represents a very low enhancement of the signal and suggests that only a few percent at most of the secondary amine rises from the combination of $Ph_2CH{\cdot}$ and $RNH{\cdot}$ radicals. The phase (A) of the polarisation is consistent with recombination of a radical pair derived from a triplet (carbene) precursor, since for the diphenylmethyl

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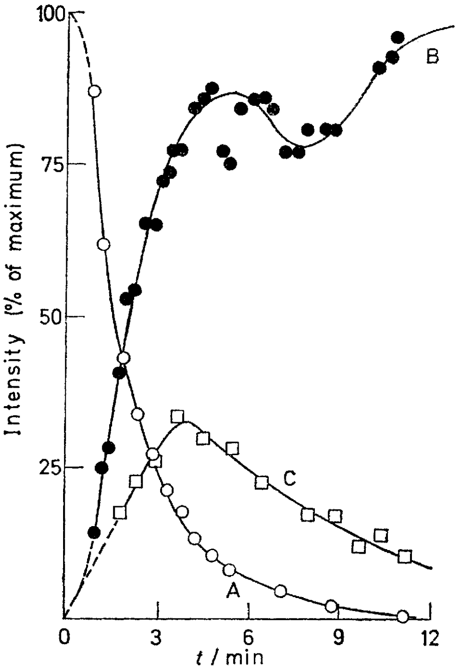
[11] D. Bethell, M. R. Brinkman, and J. Hayes, *J.C.S. Chem. Comm.*, 1972, 475, 1323, 1324.

radical a_H is negative and the g factor will be smaller than that of RNH·;[12] from Kaptein's rules,[13] $\Gamma_N = \mu\varepsilon\Delta g a_H = + + - - = + \equiv A$.

It may be noted that the enhanced absorption observed for diphenylmethane indicates that this product is not obtained by trapping of escaping diphenylmethyl radicals. A more likely interpretation is that it is derived by disproportionation either of the pair $\overline{Ph_2CH\cdot \ \cdot NHR}^T$ responsible for the polarised secondary amine or a pair formed by hydrogen abstraction from the α-C–H bond. No polarised signals attributable to the other disproportionation product were detected, however.



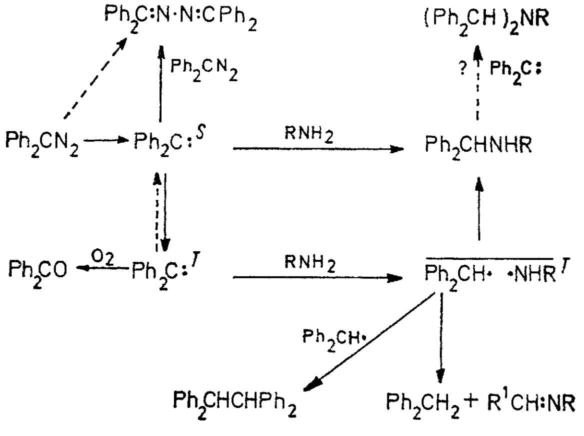
Intensities of n.m.r. signals (60 MHz) during thermal decomposition of diphenyldiazomethane (1·0M) in n-heptylamine–heptyl cyanide (1 : 3 v/v) at 120°. Curve A, phenyl protons of the diazoalkane; curve B, methine proton of $Ph_2CHNHC_7H_{15}$; curve C, methylene protons of Ph_2CH_2 (for clarity, the time scale of curve C is half that marked for curves A and B, and the intensities in curve C are shown as a percentage of the maximum signal intensity used for curve B)

DISCUSSION

We interpret our kinetic findings as indicating that the principal reactions under study are indeed reactions of diphenylmethylene produced in a rate-limiting thermolysis of diphenyldiazomethane. Direct formation of benzophenone azine without the intermediacy of the carbene undoubtedly also occurs,[3] and, for this reason, no attempt has been made to interpret quantitatively the results of Table 2 in terms of the relative reactivities of n- and t-butylamines towards diphenylmethylene. The results of the competitive experiment are in line with expectation in that the primary is much more reactive than the tertiary alkylamine; considerable steric hindrance to co-ordination of the divalent carbon to the nitrogen atom in t-butylamine might be anticipated.

Reaction Pathways.—Scheme 1 summarises our views on the pathways by which the observed products are formed. The pathways shown are adaptations of those available to diphenyldiazomethane in the presence of alcohols.[4,5] Thus we envisage the principal route to the secondary amine being attack by the singlet carbene on the primary amine, since the presence of amines inhibits the formation of certain unidentified oily products which are believed[14] to have free radicals and therefore triplet carbenes as precursors.

Competing with the reactions of singlet diphenylmethylene with amines and residual diphenyldiazomethane is the intersystem crossing to triplet diphenylmethylene. The triplet carbene can react with traces of oxygen giving ultimately benzophenone or with the amine. Unlike its reaction with alcohols where, if possible, a hydrogen atom is abstracted from the α-carbon atom, triplet diphenylmethylene abstracts hydrogen from the N–H bond. This follows from the observation of radioactivity in the tetraphenylethane produced during reactions with tritiated amines and also from the identity of the product derived from the diphenylmethyl radicals so formed. In reactions with primary and secondary alcohols, the diphenylmethyl radical is generated simultaneously with an α-hydroxyalkyl radical, $R^1R^2\dot{C}OH$. Disproportionation within this geminal radical pair is clearly favoured resulting in the production of diphenylmethane. In the case of amine reactions, the radical pair $\overline{Ph_2CH\cdot \ \cdot NHR}^T$ appears to be much less disposed to combine or disproportionate, even though this is detectable in the CIDNP experiments. Instead, the radical-pair components separate and the diphenylmethyl radicals dimerise.



SCHEME 1

It is worth noting that in gas-phase reactions of

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[12] See, for example, R. O. C. Norman and B. C. Gilbert, *Adv. Phys. Org. Chem.*, 1967, **5**, 53.

[13] R. Kaptein, *Chem. Comm.*, **1971**, 732; Thesis, Leiden, 1971; *J. Amer. Chem. Soc.*, 1972, **94**, 6251.

[14] L. S. Singer and I. C. Lewis, *J. Amer. Chem. Soc.*, 1968, **90**, 4212; D. R. Dalton, S. A. Liebman, H. Waldman, and R. S. Sheinson, *Tetrahedron Letters*, 1968, 145; D. R. Dalton and S. A. Liebman, *Tetrahedron*, 1969, **25**, 3321.

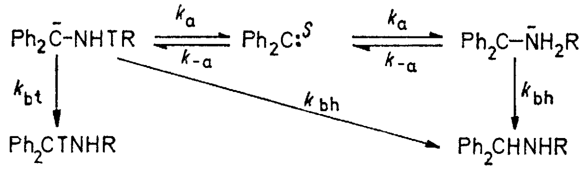
methyl radicals with methylamine, the N–H bond is more than twice as reactive as the C–H bond.[15a] The relative reactivity of the N–H and α-C–H bond in ethylamine, however, is almost exactly the inverse owing to an increased rate of hydrogen abstraction from carbon.[15b]

Isotope Effects.—The treatment of isotope effects in the abstraction of hydrogen (atoms or ions) from primary amines is exactly analogous to that for the reaction of diphenylmethylene with water.[3] The observed isotope effects, k_H/k_D and k_H/k_T, are for statistical reasons related to the isotope effects on the actual abstraction step, k_h/k_d and k_h/k_t, by the expressions, $k_h/k_d = k_H/k_D$ and $2k_h/k_t = k_H/k_T$.

Since there can be no doubt that tetraphenylethane is the product of hydrogen atom abstraction by triplet diphenylmethylene we can derive the value of k_h/k_t as 2·9 for n-butylamine and 3·1 for t-butylamine. We discuss the absence of an observable deuterium isotope effect on this process below, but note that a value of k_h/k_d of 3·3 (150°) has been reported[15b] for gas-phase abstraction of hydrogen from the amino-group of ethylamine by methyl radicals.

If we assume the reaction pathways in Scheme 1 and neglect the formation of secondary amine by way of the triplet carbene, then, for an abstraction–recombination mechanism of reaction of singlet diphenylmethylene with either amine, $k_h/k_t = 2$. Swain's equation[16] would thus yield a value of k_h/k_d of 1·6. Such an isotope effect would be readily detectable in the analysis of the products of reactions of diphenylmethylene with *NN*-dideuteriated amines. The absence of an isotope effect is, we believe, unequivocal evidence against the abstraction–recombination mechanism for the formation of the secondary amines.

Again, by analogy with the treatment of the reaction of diphenylmethylene and water, we can see that the widely different inter- and intra-molecular isotope effects are consistent with the ylide mechanism of reaction of the carbene and amine. If the slow step of the reaction is the attack of the carbene on nitrogen (rate constant k_a, Scheme 2), then only a small secondary deuterium isotope effect would be anticipated, and the partitioning of the singlet carbene between reaction with amine, reaction with diazoalkane, and singlet–triplet interconversion should be virtually unaffected. The tritium incorporation in the product, however, would still be affected by the isotope effect on the prototropic shift in the ylide, whatever its mechanism.



SCHEME 2

Using the symbolism of Scheme 2, which neglects secondary isotope effects on all steps, the observed tritium isotope effect is given by equations (2) and (3).

$$k_H/k_T = [\mathrm{RNHT}][\mathrm{PH_2CHNHR}]/[\mathrm{RNH_2}][\mathrm{Ph_2CTNHR}] \quad (2)$$

$$= \frac{k_{-a} + k_{bh} + k_{bt}}{k_{bt}k_a}\left\{\frac{2k_{bh}k_a}{k_{-a} + 2k_{bh}} + \frac{k_{bh}k_a[\mathrm{RNHT}]}{(k_{-a} + k_{bh} + k_{bt})[\mathrm{RNH_2}]}\right\} \quad (3)$$

If $k_{bh} > k_{bt} \gg k_{-a}$, then, bearing in mind that $[\mathrm{RNHT}]/[\mathrm{RNH_2}]$ is very small, this reduces to $k_H/k_T = k_{bh}/k_{bt} + 1$. Thus the observed isotope effects refer essentially to the ylide rearrangement step and the isotope effects are $2{\cdot}9_2$ for n-butylamine and $3{\cdot}1_8$ for t-butylamine at 85°. These values may be compared with the value of *ca.* 7 for water under similar conditions and the almost identical values for hydrogen abstraction by triplet diphenylmethylene. The relative magnitudes of the isotope effects on the ylide rearrangements are in line with what is known about the relative pK_a values of the amines and water in acetonitrile as solvent.[17] Thus for example, in acetonitrile as in water, n- and t-butylamine have closely similar pK_a values and so their corresponding ammonium ions might be expected to protonate the anionic centre of $\mathrm{Ph_2\overset{-}{C}N\overset{+}{H}_2R}$, or more probably[4] $\mathrm{Ph_2\overset{-}{C}NHR}$, with isotope effects of similar magnitude.[18]

There remains to be explained the apparent paradox that the formation of tetraphenylethane shows an isotope effect in reactions with the tritiated amine but not when reactions with deuteriated and normal amines are compared. Now a prerequisite for the observation of an isotope effect when the kinetics of reactions are not being observed directly but are deduced from the proportions of products is that a reaction competing with that involving the isotope be available for comparison. Clearly, in the present study, such a competing reaction is available in those experiments in which the tritiated amine is used since both isotopes are available within the one reactant molecule. Using deuteriated amine, the triplet carbene for example must have another pathway available for reaction if deuterium atom abstraction is to be seen to be slower than abstraction of protium. It follows, therefore, from the observed tritium isotope effect and the lack of effect of deuteriation of the amine on the product proportions that under the reaction conditions triplet diphenylmethylene has no alternative reaction to abstraction of hydrogen from the amine. (The reaction with oxygen competes, of course, but it is an unreliable standard because of the variability in oxygen concentration from run to run.)

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[15] (*a*) P. Gray and J. C. J. Tynne, *Trans. Faraday Soc.*, 1963, **59**, 2275; (*b*) P. Gray and A. Jones, *ibid.*, 1966, **62**, 112.

[16] C. G. Swain, E. C. Stivers, J. F. Reuwer, and L. J. Schaad, *J. Amer. Chem. Soc.*, 1958, **80**, 5885.

[17] J. F. Coetzee, *Progr. Phys. Org. Chem.*, 1967, **4**, 45.

[18] R. P. Bell and D. M. Goodall, *Proc. Roy. Soc.* 1966, *A*, **294**, 273; but see also F. G. Bordwell and W. J. Boyle, *J. Amer. Chem. Soc.*, 1971, **93**, 512.

Consequently, we infer that, in the presence of primary amines, triplet diphenylmethylene does not revert appreciably to the singlet state as is the case in the presence of alcohols. Thus, in the reaction with deuteriated amines, the isotope effect on the abstraction of a deuterium atom does not lead to the formation of an increased yield of the secondary amine and the azine.

This inference does not seem readily capable of rationalisation in terms of a lower bond dissociation energy for the N–H bond in primary amines compared with the α-C–H bond in isopropyl alcohol, for example. In the gas phase, values obtained by kinetic methods [19] are about the same, 92 kcal mol^{-1}. On the other hand, it seems reasonable to suppose that the α-C–H bond in alcohols and the corresponding primary amines should be about the same. Yet we observe almost exclusive attack by diphenylmethylene on the amino-group of n-butylamine rather than on carbon-bound hydrogen. Clearly the gas-phase values of dissociation energies are modified in solution; assuming that all the observed diphenylmethane arises from initial attack of the carbene on the α-C–H bond, the N–H bond energy must be some 3 kcal mol^{-1} less than that for the α-C–H bond in the amine. Since this change in bond dissociation energy is sufficient to change a situation of equilibriation of singlet and triplet states of diphenylmethylene to one where the triplet–singlet transformation cannot effectively compete with hydrogen abstraction, then it follows that the energy separation of singlet and triplet states must be similar in magnitude. Clearly, in view of the current interest in the energy separation of the singlet and triplet states of carbenes [2,18] this aspect of our work needs more detailed study.

EXPERIMENTAL

Materials.—Acetonitrile was purified as described previously.[20] Diphenyldiazomethane was prepared by the oxidation of benzophenone hydrazone and purified as in our previous studies.[3,4]

Commercial samples of n- and t-butylamine were fractionated twice from potassium. Deuteriated n-butylamine was prepared by shaking the solution of the amine (20 ml) in dry ether (300 ml) successively with one 5 ml portion and four 3·6 ml portions of a saturated solution of sodium chloride (AnalaR grade) in deuterium oxide. Fractionation to remove the ether, followed by drying by distillation first from sodium and then from potassium gave the amine deuteriated to >95% (by n.m.r.). Deuteriated t-butylamine was prepared similarly except that di-n-butyl ether was used as solvent. Tritiated amines were prepared by shaking the amine with a small quantity of tritiated water in dioxan, followed by successive fractionations from sodium and potassium.

Products.—*N*-(Diphenylmethyl)-n-butylamine was prepared from diphenylmethyl chloride and n-butylamine by the method of Swain and Dittmer.[21] It had b.p. 112° at 0·25 mmHg (lit.,[21] 151—155 at 3 mmHg). N-(*Diphenylmethyl*)-*t-butylamine* was prepared analogously by heating diphenylmethyl chloride (2 g) in t-butylamine (80 ml) in a sealed tube at 85° for ten days. Treatment with alkali, followed by removal of the excess amine left a solid which, after recrystallisation from methanol, had m.p. 53·5—54° (Found: C, 85·3; H, 8·9; N, 6·0. $C_{17}H_{21}N$ requires C, 85·3; H, 8·8; N, 5·9%).

Procedures.—*Kinetics.* Rates of reaction were determined by following the disappearance of diphenyldiazomethane spectrophotometrically. Reaction vessels and their manipulation were as in previous investigations.[3,8,22]

Product analysis. Azine yields were determined by u.v. spectrophotometry on suitably diluted portions of reaction mixtures. Determinations were made on reaction mixtures from 7—11 different vessels in which the decomposition had taken place simultaneously.

For the other reaction products g.l.c. analysis was used. The column was 6 ft × 1/8 in stainless steel having 5% silicone oil SE30 on G-Cel (60—80 mesh) and was operated at 250°. Relative compositions were obtained from peak height × retention time, using response factors obtained from standard mixtures. At least four separate injections of the product mixture, obtained by combining the reaction solutions from the 7—11 vessels, were carried out, and the average yield determined.

Radioactive counting. This was carried out as described previously for the reaction of diphenylmethylene with water.[3] Tritium bound to nitrogen in the secondary amine was removed by exchange with methanol and the amine was then distilled or crystallised to constant activity.

CIDNP. Reactions were carried out in the probe of a Varian A56/60 n.m.r. spectrometer at 120°. The reaction mixture (0·5 ml) containing diphenyldiazomethane (1M) in a 5 mm tube was inserted into the pre-heated probe. A Varian C1024 CAT accessory was used automatically to trigger repeated scans of the spectral region of interest and the signals were recorded as a function of time on an auxiliary Servoscribe recorder.

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