The Reaction between Azo-compounds and Trialkylboranes

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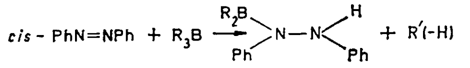
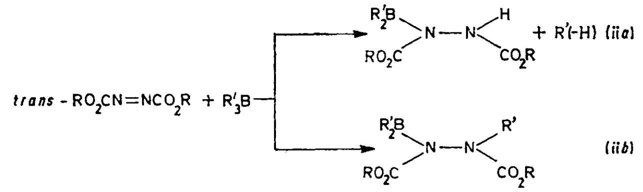
trans-Azobenzene does not react with organoboranes, but *cis*-azobenzene, prepared separately or *in situ* by irradiation, reacts essentially instantaneously, undergoing hydroboration according to equation (i).



(i)

The reaction involves *cis*-elimination of the olefin, and probably follows a cyclic six-centre mechanism. Dialkyl *trans*-azodicarboxylates react in the same way [equation (ii*a*)], but the *trans*-hydroboration is now accompanied by homolytic alkylboration of the unsaturated systems according to equation (ii*b*).



THE thermal reaction of aldehydes[1] and of olefins[2] with trialkylboranes is well established, and a similar reaction of 2-methyl-2-nitrosopropane[3] has recently been described [equation (1), X=Y = RHC=O, $R_2C{=}CR_2$, or Bu^{t}N=O respectively].

$$\mathrm{X{=}Y + HCCB{<} \longrightarrow HXYB{<} + C{=}C} \qquad (1)$$

An alternative photochemical process occurs when ketones are irradiated with u.v. light in the presence of organoboranes [equations (2) and (3), X=Y = $R_2'C{=}O$].[4]

$$\mathrm{X{=}Y \xrightarrow{h\nu} X{=}Y^*} \qquad (2)$$

$$\mathrm{X{=}Y^* + BR_3 \longrightarrow \dot{X}YBR_2 + R\cdot \longrightarrow coupling\ products} \qquad (3)$$

Neither type of process appears to be known for azo-compounds, and, in the gas phase, *trans*-azomethane does not react with triethylborane below 90°.[5] We report here a study of the thermal reaction of *cis*-azobenzene, and the photochemical reaction of *trans*-azobenzene (X=Y = PhN=NPh), which behave according to equation (1),[6] and of the thermal reaction of di-ethyl and di-t-butyl azodicarboxylates (X=Y = $RO_2CN{=}NCO_2R$), where reaction (1) is accompanied by a free-radical chain reaction.

EXPERIMENTAL

Reagents.—Trialkylboranes were prepared by standard methods from the appropriate Grignard reagents, and were stored and handled under oxygen-free nitrogen; n.m.r. spectroscopy showed that they contained less than 2% of the oxidation product, R_2BOR. Dibutylisopropoxyborane was prepared from the reaction between equimolar amounts of dibutylchloroborane and isopropyl alcohol; b.p. 71°/*ca.* 10 mm., τ 8·84 (*Me*$_2$CHO) and 5·60 (Me$_2$C*H*O) (*J* 6 Hz).

Commercial *trans*-azobenzene (B.D.H.) gave a strong red colour when an organoborane was added. The azo-compound was recrystallised three times from ethanol and dried under reduced pressure, after which it showed no change in u.v. and visible spectrum in the presence of the boranes; the impurity which gave rise to the colour was not identified. The ^{11}B chemical shift of tri-n-butylborane (−84·3 p.p.m. with respect to Et_2O,BF_3) and of tri-s-butylborane (−84·6 p.p.m.) did not change when *trans*-azobenzene was added at room temperature; if any complex is formed, it must therefore be present only in small concentration.

cis-Azobenzene was prepared by irradiation of *trans*-azobenzene by Hartley's procedure[7] modified by using a high pressure mercury arc (250 W), as shorter wavelengths increase the *cis*/*trans* photostationary ratio.[8]

Diethyl azodicarboxylate (Koch–Light) was dried by azeotropic distillation with benzene. Di-t-butyl azodicarboxylate and benzo[*c*]cinnoline (Emmanuel) were used without further purification.

Quantum Yields.—Quantum yields were determined with a 'merry-go-round' apparatus immersed in water at 30 ± 2° to ensure that different samples received the same radiation dose.

Light from a Hanovia 125 W mercury arc contained in a quartz housing, was filtered through 3 mm of soda glass, and 2 mm thick OX-1 Chance filters, to isolate the 365/6

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[1] H. Meerwein, G. Hinz, H. Majert, and H. Sönke, *J. prakt. chem.*, 1963, **147**, 226; B. M. Mikhailov, Yu. N. Bubnov, and V. G. Kiselev, *Zhur. obshchei. Khim.*, 1966, **36**, 62; T. Okushi, O. Manabe, H. Hoyama, and Z. Yoshida, *Kogyo Kagaku Zasshi*, 1969, **72**, 1702, 1707.

[2] B. M. Mikhailov, M. E. Kuimova, and E. A. Shagova, *Doklady Akad. Nauk S.S.S.R.*, 1968, **179**, 1344.

[3] K. G. Foot and B. P. Roberts, *J. Chem. Soc.* (*C*), 1971, 3475.

[4] A. G. Davies, D. Griller, B. P. Roberts, and J. C. Scaiano, *Chem. Comm.*, 1971, 196; A. G. Davies, B. P. Roberts, and J. C. Scaiano, *J. Chem. Soc.* (*B*), 1971, 2171.

[5] J. Grotewold, E. A. Lissi, and J. C. Scaiano, *J. Chem. Soc.* (*B*), 1971, 1187.

[6] A preliminary account of some of the present work has been given by A. G. Davies, K. G. Foot, B. P. Roberts, and J. C. Scaiano, *J. Organometallic Chem.*, 1971, **31**, C1.

[7] G. S. Hartley, *J. Chem. Soc.*, 1938, 633.

[8] E. Fischer, M. Frankel, and R. Wolovsky, *J. Chem. Phys.*, 1955, **23**, 1367.

nm lines. From the spectrum of the filters and the spectral composition of the source,[9] it can be concluded that at least 98% of the incident beam was of the desired wavelength, the stray light having mainly the wavelength 334·1 nm. Cooling water was continuously circulated around the lamp house and filters.

The reaction cells were Pyrex tubes, i.d. 0·98 cm, o.d. 1·18 cm (±0·02 cm), and contained 3 ml of solution. The concentration of *trans*-azobenzene was determined by its absorption at 470 nm. Linear Beer plots were obtained over the range of concentrations used (up to 5 mg ml^{-1}); at this wavelength, absorption by the products was negligible.

Radiation doses incident upon the samples were determined using 0·007M-potassium ferrioxalate as actinometer;[10] doses were usually about $1{\cdot}2 \times 10^{15}$ quanta ml^{-1} s^{-1}.

Irradiation of trans-*Azobenzene and Tributylborane*.—A solution of tri-n-butylborane (0·01 mol) and *trans*-azobenzene (0·01 mol) in iso-octane (2,2,4-trimethylpentane; 5 ml) was irradiated in a quartz vessel for 2·5 h with light from a 250 W high-pressure mercury arc at a range of 10 cm. The sample tube was cooled in a current of air. The product was a slightly yellow solution.

The n.m.r. spectrum showed that, in the product, the signals of the aromatic rings had shifted upfield, suggesting that the N=N double bond had become saturated. When a small amount of hydrogen peroxide was added to an aliquot of the solution, the colour and n.m.r. spectrum of azobenzene was restored.

When water was added to a second aliquot of the solution, 1,2-diphenylhydrazine was formed, and was identified by its m.p. (125—126°) and n.m.r. spectrum. Another fraction was treated with gaseous hydrogen chloride for 15 min; the excess was then removed under reduced pressure, and isopropyl alcohol was added. Dibutylisopropoxyborane was isolated from the product, and characterised by comparison with the authentic material.

The yield of olefin was determined (g.l.c.) from similar experiments in which the reagents were at lower concentrations (*ca.* 0·2M) to minimise loss by evaporation. Within experimental error, the yield of olefin was quantitative.

Several experiments were carried out using different relative concentrations of organoborane and azobenzene, but the reaction always occurred with a 1 : 1 stoicheiometry, and a second B–C bond could not be caused to react. Reactions were also carried out using benzene, tetrahydrofuran, and cyclohexane as solvents, but the same results were obtained.

Similar results were obtained when *trans*-azobenzene was irradiated in the presence of tri-n-propyl-, tri-isobutyl-, tri-s-butyl-, and tri-n-hexyl-boranes. No reaction occurred with triphenylborane; no hydrocarbon was formed from trineopentylborane, but the azobenzene was slowly consumed on prolonged irradiation.

Reaction of cis-*Azobenzene with Trialkylboranes*.—Solutions of *cis*-azobenzene (*ca.* 0·2M) in benzene, iso-octane, or tetrahydrofuran were treated with various trialkylboranes [$Pr_3{}^nB$, $Bu_3{}^nB$, $Bu_3{}^iB$, $Bu_3{}^sB$, and $(n\text{-}C_6H_{13})_3B$] in the dark under nitrogen. In every case the reactions were essentially instantaneous, and the products (alkene and hydroborated hydrazobenzene) were the same as those obtained from the photochemical reaction of *trans*-azobenzene.

No change in the absorption spectrum of a solution of benzo[*c*]cinnoline in iso-octane could be observed during 100 h after tri-n-butylborane (0·3M) had been added.

The Reaction of 2-Methyl-2-nitrosopropane with the Tributylborane–Azobenzene Adduct.—A mixture of *trans*-azobenzene (20 mg) and tri-n-butylborane (0·04 ml) in benzene (3 ml) was irradiated until the reaction was complete. 2-Methyl-2-nitrosopropane in slight excess was then added in the dark; the solution, which was initially blue, turned green in *ca.* 3 h and, finally after *ca.* 7 h, orange. The u.v.–visible spectrum of the product corresponded to that of azobenzene, and was unchanged when tributylborane was added, showing that only the *trans*-isomer was present.

Reactions of Azodicarboxylic Esters.—(a) *With trialkylboranes*. Diethyl azodicarboxylate reacted rapidly and exothermically with boranes containing unbranched alkyl groups, and violently with tri-n-propylborane. Di-t-butyl azodicarboxylate reacted more slowly, and sometimes its reactions could be followed spectrophotometrically at 405 nm, but otherwise its behaviour was similar.

The reactions were carried out in the same way as those of *cis*-azobenzene. The rate of disappearance of the azodicarboxylates was markedly increased when air was injected into the reaction mixture.

In the reaction of diethyl azodicarboxylate, although efforts were made to exclude moisture, the precipitation of small amounts of diethyl hydrazodicarboxylate could not be avoided completely. The addition of water after the reaction caused the precipitation of a large amount of the hydrazo-compound, which was identified by its m.p. (134—135°) and elemental analysis [Found (from Pr_3B): C, 40·2; H, 6·7; N, 15·7. Found (from Hex_3B): C, 41·6; H, 6·8; N, 16·0. Calc. for $C_6H_{12}N_2O_4$: C, 40·9; H, 6·9; N, 15·9%].

(b) *With tribenzylborane*. The reaction of tribenzylborane with both diethyl and di-t-butyl azodicarboxylate was usually complete in a few minutes, and gave colourless products which showed a surprisingly large difference between the chemical shifts of the two alkoxy-groups. The product from the ethyl ester showed τ 5·90 and 6·22 (CH_2), and 8·91 and 9·30 (CH_3), whilst that from the t-butyl ester showed τ 8·48 and 9·03 (Me_3C); after the stoicheiometric amount of water had been added, this latter compound showed τ 8·58 and 8·66; the chemical shifts in the corresponding azo esters are τ 5·84 (CH_2) and 8·94 (CH_3), *J* 7 Hz, and 8·65 (Me_3C), respectively.

Although galvinoxyl reacts only very slowly with the reactants or products, it is immediately consumed if the reaction is carried out in its presence.

Diethyl azodicarboxylate was added to a mixture of tribenzylborane (1·5 g) and benzene (1·5 ml) until the colour was no longer discharged. After 5 min, water (0·5 ml) was added and the mixture was stirred for 30 min. Ether (10 ml) and 4N-sulphuric acid (30 ml) were then added; the organic layer was separated, and was left in contact with air for several hours to oxidise B–C bonds. The solution was washed with 2·5N-sodium hydroxide, dried ($CaCl_2$), and volatile material removed at 70°/1 mm, leaving as a viscous liquid, diethyl benzylhydrazodicarboxylate, contaminated with a trace of benzyl alcohol τ *ca.* 2·8 (complex; Ph, 5·5 H), 5·42 (broad; CH_2Ph) 5·91 and 5·98 (2q, CH_2CH_3, 4·0H), 8·81 and 8·87 (2t, CH_2CH_3 6·0H) *J* 7—8 Hz (Found: C, 58·9; H, 6·4; N,

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[9] J. N. Pitts, *J. Chem. Educ.*, 1957, **34**, 112.

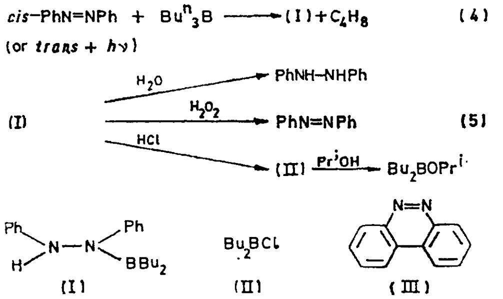
[10] C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc.* (*A*), 1956, **235**, 518.

8·9. Calc. for $C_{13}H_{18}N_2O_4$: C, 58·6; H, 6·8; N, 10·5%). The oil was treated with acetyl chloride, but acetylation was incomplete (n.m.r.) and no crystalline derivative could be isolated.

Stereochemical Experiments.—In order to examine the stereochemical course of the reactions, two isomeric boranes were prepared by the hydroboration of *cis*- and *trans*-3-methylpent-2-ene with a 1·2M-solution of diborane in tetrahydrofuran. The reaction mixtures were left for 48 h at room temperature, and then volatile material was removed under reduced pressure during 3 h. Samples of the organoboranes which were formed were then caused to react with the azo-compounds, and the products were analysed by g.l.c. (15 : 85 Apiezon L on Chromosorb P, 80—100 mesh). The results are given in Table 1.

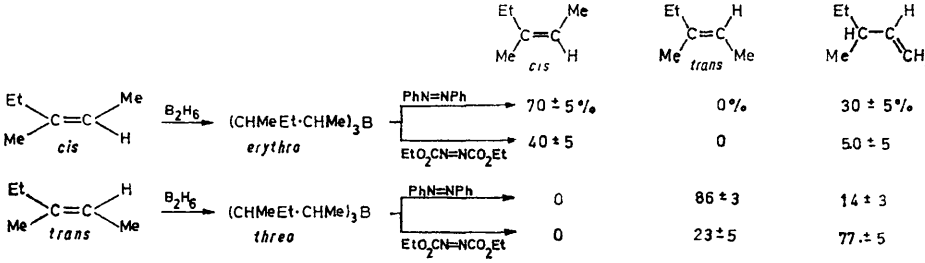
DISCUSSION

The Azobenzene System.—*cis*-Azobenzene reacts almost instantaneously with tri-n-propylborane, tri-n-, tri-iso-, and tri-s-butylboranes, and tri-n-hexylborane, to give the corresponding olefins in essentially quantitative yields. The same products are obtained when *trans*-azobenzene is irradiated with u.v. light in the presence of the organoboranes, but in the dark, no reaction occurred (with tri-n- and tri-s-butylborane) during 100 days at room temperature.



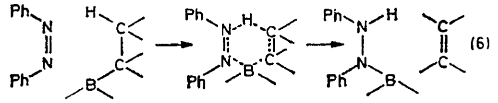
The boron-containing product (I) from the reaction of tri-n-butylborane was identified, by the reactions shown in equation (5), as the hydroborated azobenzene, whence the intermediate (II) is di-n-butylchloroborane. Benzo[*c*]cinnoline (III) did not react with organoboranes under the conditions where the reaction of *cis*-azobenzene was instantaneous.

Experiments in which *cis*-azobenzene was caused to react with *erythro*- and *threo*-tris-(1,2-dimethylbutyl)-borane obtained by (*cis*) hydroboration of *cis*- and *trans*-3-methylpent-2-ene respectively, showed that the dehydroboration was stereoselectively *cis*. These results are summarised in the Scheme; the results of similar experiments with 2-methyl-2-nitrosopropane are given in reference 3.



SCHEME

This suggests strongly that the reaction proceeds through the six-centre cyclic transition state (IV).



(IV)

Two alternative mechanisms [equations (7)—(11)] can be proposed for the photochemical reaction of *trans*-azobenzene, in which the reacting species is either an excited state of azobenzene [equation (10)], presumably the triplet,† or *cis*-azobenzene in its ground state [equation (11)] as discussed above. No cyclic reactions of the excited state appear to have been reported, but reactions involving the abstraction of hydrogen from isopropyl alcohol[12] or from cumene,[13] are known.

$$trans\text{-A} \xrightarrow{h\nu} \text{A}^* \quad (\text{A} = \text{azobenzene}) \qquad (7)$$

$$\text{A}^* \longrightarrow trans\text{-A} \qquad (8)$$

$$\text{A}^* \longrightarrow cis\text{-A} \qquad (9)$$

$$\text{A}^* + \text{R}_3\text{B} \longrightarrow \text{products} \qquad (10)$$

$$cis\text{-A} + \text{R}_3\text{B} \longrightarrow \text{products} \qquad (11)$$

As the rate of reaction of *cis*-azobenzene with trialkylboranes is very much faster than the rate of its reversion to *trans*-azobenzene under our conditions, the quantum yield for the consumption of azobenzene (Φ_{-A}) is given by equation (12), where Φ_7 is the quantum yield for the generation of the excited species A*.

$$\Phi_{-A} = \Phi_7 \frac{k_9 + k_{10}[R_3B]}{k_8 + k_9 + k_{10}[R_3B]} \qquad (12)$$

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† This is known to be excited species which is involved in the photoisomerisation of aliphatic azo-compounds.[11]

[11] I. I. Abram, G. S. Milne, B. S. Solomon, and C. Steel, *J. Amer. Chem. Soc.*, 1969, **91**, 1221.

[12] B. E. Blaisdell, *J. Soc. Dyers Colourists*, 1949, **65**, 618.

[13] J. K. S. Wan, L. D. Hess, and J. N. Pitts, *J. Amer. Chem. Soc.*, 1967, **86**, 2069.

If reaction (10) does not participate in the mechanism Φ_{-A} will be independent of the concentration of the borane, and will be given by equation (13).

$$\Phi_{-A} = \Phi_7 \frac{k_9}{k_8 + k_9} = \Phi_{trans \rightarrow cis} \qquad (13)$$

If reaction (10) is significant, the value of Φ_{-A} for equation (12) will be greater than Φ_{-A} for equation (13), such that:

$$\lim_{[R_3B] \rightarrow 0} (\Phi_{-A}{}^{12}) = \Phi_{trans \rightarrow cis} \qquad (14)$$

A series of measurements of Φ_{-A} were carried out for the reaction of *trans*-azobenzene with tri-n-, tri-s-, and tri-isobutylborane using a conventional 'merry-go-round' apparatus, and irradiation with the mercury 365/6 nm lines. The results are summarised in Table 1. No trend in the value of Φ_{-A} with borane concentration could be observed (within a fifteen-fold variation of concentration of tri-n-butylborane). Moreover, Φ_{-A} was always slightly less than the reported value of $\Phi_{trans \rightarrow cis}$ (0·12) for this wavelength;[14] this slight difference might be due to the different experimental conditions, or the use of a different chemical actinometer, or some source of systematic error.

TABLE 1

Quantum yields for the disappearance of azobenzene (Φ_{-A}) in the irradiation of mixtures of *trans*-azobenzene and organoboranes in iso-octane at 30 ± 2° and 366 nm

$[R_3B]$ (M)	[PhN=NPh] (M)	Φ_{-A}
	Tri-n-butylborane	
0·027	0·0125	0·095
0·041	0·0125	0·084
0·069	0·0125	0·094
0·096	0·0125	0·083
0·137	0·0125	0·088
0·206	0·0125	0·080
0·275	0·0125	0·088
0·410	0·0125	0·087
	Average	0·087 ± 0·006
	Tri-isobutylborane	
0·041	0·0105	0·078
0·069	0·0105	0·079
0·096	0·0105	0·071
0·137	0·0105	0·081
0·275	0·0105	0·086
0·410	0·0105	0·077
	Average	0·079 ± 0·007
	Tri-s-butylborane	
0·130	0·0105	0·068
0·390	0·0105	0·078
	Average	0·073 ± 0·010

We conclude that, under our experimental conditions, the only significant reaction is between *cis*-azobenzene and trialkylborane [equation (11)], and that the reaction between azobenzene in its excited state [equation (10)] and borane should be excluded from the mechanism, *i.e.* $k_{10}[R_3B] \ll 1/(\text{lifetime of A}^*)$. The reaction of *cis*-azobenzene and tributylborane by equation (6) can be calculated to be exothermic by *ca.* 30 kcal mol^{-1}; the corresponding reaction of *trans*-azobenzene would be *ca.* 10 kcal mol^{-1} less exothermic.

This clean, rapid, and selective reaction between *cis*-azobenzene and organoboranes may be useful as a further synthetic variant based on the hydroboration reaction, and could also provide the basis of a spectrophotometric method in the analysis of organoboranes, or in studies of the isomerization of azobenzene.

As both 2-methyl-2-nitrosopropane and azobenzene will displace olefins from trialkylboranes, it was of interest to see whether 2-methyl-2-nitrosopropane would displace azobenzene from 1,2-diphenyl-1-dibutylborylhydrazine. The reaction occurred to completion in *ca.* 7 h, hence the acceptor power toward the BH bond appears to follow the sequence Bu^{t}N=O > Ph-N=NPh > olefin. The azobenzene was entirely in the more stable *trans*-form, and the boron-containing product was not identified; this is permissive but not exclusive evidence for the six-centre process.

Azodicarboxylic Esters.—*trans*-Di-ethyl and *trans*-di-t-butyl azodicarboxylate[15] react with organoboranes in a stoicheiometry of 1 : 1. The rates of the reactions are roughly first order in each reagent, and some typical half-lives are given in Table 2; these figures are only approximate because the consumption of the azodicarboxylate is accelerated by traces of oxygen (indicating the presence of a homolytic component in the reaction), but it is clear that bulky alkyl groups in either the borane or the ester reduce the rate of the reaction.

TABLE 2

Half-life periods for the reaction between $RO_2CN{:}NCO_2R$ and $R_3'B$ in benzene at room temperature

R	R′	$[RO_2CN{:}NCO_2R]$[a] (M)	$[R_3B]$[a] (M)	$t_{\frac{1}{2}}$ (s)
Et	Pr^n	0·3—0·1	1·0—0·1	<1[b]
Et	Bu^n	0·3—0·1	1·0—0·1	<5
Et	Hex^n	0·3—0·1	1·0—0·1	<5
Bu^t	Hex^n	0·015	0·06	23
Bu^t	Hex^n	0·0076	0·18	9
Bu^t	Hex^n	0·0076	0·072	19·5
Bu^t	Bu^i	0·015	0·16	1100
Bu^t	Bu^i	0·015	0·32	640
Bu^t	Bu^i	0·015	0·08	2350

[a] Initial concentrations. [b] Very violent exothermic reaction, with evolution of propene.

All the reactions led to the formation of alkenes derived from the alkyl groups of the boranes, but the yields were lower than in the reactions of *cis*-azobenzene; typical values are given in Table 3.

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[14] G. Zimmerman, L.-Y. Chow, and U.-J. Paik, *J. Amer. Chem. Soc.*, 1958, **80**, 3528.

[15] G. O. Schenck, H.-R. Kopp, B. Kim, and E. Koerner von Gustorf, *Zeitschrift für Naturforschung*, 1965, **20***B*, 637; E. Koerner von Gustorf, D. V. White, B. Kim, D. Hess, and J. Leitich, *J. Org. Chem.*, 1970, **35**, 1155.

Hydrolysis of the boron-containing product from the reaction of ethyl azodicarboxylate with tripropyl- or trihexyl-borane gave diethyl hydrazodicarboxylate.

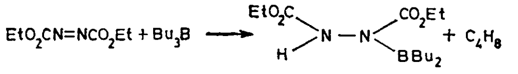
TABLE 3

Yields of alkenes (R′[—H]) from the reaction between $RO_2CN{:}NCO_2R$ and $R_3'B$ in benzene at room temperature

R	R′	$[R_3B]$ [a] (M)	$[RO_2CNO_2R]$ [a] (M)	Alkene [a] yield (%)
Et	Hex^n	1·1	1·0	53
Et	Bu^s	0·7	0·5	74 [b]
Et	Hex	0·8	0·7	87 [b]
Bu^t	Hex	0·072	0·0075	74 [c]
Bu^t	Bu^i	0·20	0·01	60 [d]

[a] Based on $RO_2CN{:}NCO_2R$. [b] After 18 h. [c] With different concentrations of reagents, yields between 46 and 83% were obtained. [d] After 2 h.

The principal reaction therefore is again a transhydroboration, *e.g.*:

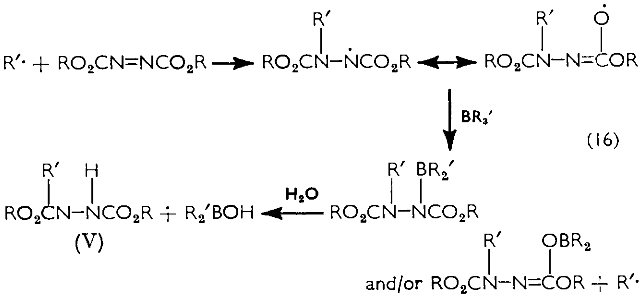


$$EtO_2CN{=}NCO_2Et + Bu_3B \longrightarrow (EtO_2C)(H)N{-}N(CO_2Et)(BBu_2) + C_4H_8 \qquad (15)$$

The rate of disappearance of the azodicarboxylate in some reactions (*e.g.* $Bu^i_3B + Bu^tO_2CN{:}NCO_2Bu^t$) could be reduced by the addition of a trace of galvinoxyl, while in others, an increase in the yield of alkene was observed although the reactions were still too fast to measure.

The results of stereochemical experiments, which are included in the Scheme, show that again the alkenes are formed by a process involving *cis*-elimination; again, a cyclic six-centre process is probably involved [*cf.* equation (6) for azobenzene], but now on the ***trans***- rather than the *cis*-azo-compound.

The facts that the yield of olefin is low, but is increased in the presence of galvinoxyl, and that the rate of consumption of azodicarboxylate can be accelerated by oxygen and reduced by galvinoxyl, all suggest that the cyclic reaction leading to olefin is accompanied by a homolytic chain component giving other products. In view of the propensity of azodicarboxylates to undergo homolytic addition,[16] * and of trialkylboranes to undergo homolytic substitution at boron,[17] it seemed likely that this reaction was the alkylboration of the unsaturated system by equation (15).



This was confirmed by carrying out the reaction between diethyl azodicarboxylate and tribenzylborane, which cannot undergo the elimination reaction; after hydrolysis the 1,2-dicarboxylate (V; R = Et, R′ = $PhCH_2$) was isolated and characterised. The reaction [equation (16)] is therefore similar to the homolytic alkylboration of the C=C–C=O system, which has recently been established,[18] but under the usual experimental conditions, these latter reactions do not appear to be accompanied by any polar, olefin-forming, component.

We are grateful to Mr. A. F. Frye for constructing the ' merry-go-round ' apparatus, to Mr. K. G. Foot for preparing trineopentylborane, and to Dr. R. G. Rees of the Polytechnic of North London for ^{11}B n.m.r. facilities. Support is acknowledged from the S.R.C. and the Royal Society (J. C. S.), and from the Turner and Newall Research Fellowships Committee (B. P. R.).

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* Isopropyl radicals were generated in the presence of ethyl azodicarboxylate by photolysing di-isopropyl ketone in an e.s.r. cavity at −20° in iso-octane.[4] The spectrum of a long-lived radical was observed, showing a_N 9·1 and a_N' 1·7 G; presumably this is the 1,2-bis(ethoxycarbonyl)-1-isopropylhydrazyl radical.

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