Reaction of Anthracene with Ethoxycarbonylnitrene: Concentration Dependence of Product Composition

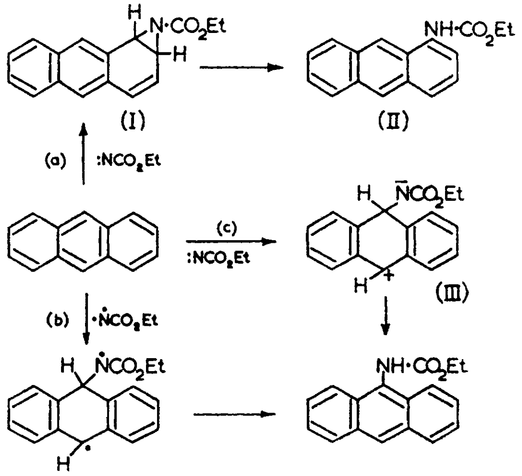
By A. J. L. BECKWITH and J. W. REDMOND

(*Organic Chemistry Department, University of Adelaide, Adelaide, South Australia*)

RECENTLY[1] we have argued that the nature and yields of products obtained by treatment of anthracene, phenanthrene, or pyrene with ethoxycarbonylnitrene are most easily rationalised in terms of a dichotomy of mechanism involving both direct substitution and intermediate aziridine formation. Also, we suggested that triplet ethoxycarbonylnitrene might undertake one mode of reaction and the singlet form the other. A study of the concentration dependence of the reaction of anthracene with ethoxycarbonylnitrene supports these hypotheses.

Anthracene, in excess, was treated with ethyl azidoformate in chlorobenzene solution at 132°, and the yields of anthrylurethanes were estimated by quantitative thin-layer chromatography. It is apparent (Table) that product composition is dependent on reactant concentration, the 9 : 1-isomer ratio at the lowest concentration of anthracene being similar to that observed in free-radical substitution.[2] These results accord with the view that ethoxycarbonylnitrene is generated in the singlet state and crosses over with the elapse of time to the triplet form.[3]

From these results and those previously reported[2] we conclude that singlet ethoxycarbonylnitrene behaves as a double-bond reagent and reacts preferentially at the bond of highest bond-order forming the aziridine (I) which rearranges to 1-anthrylurethane (II). Possibly singlet nitrene also undertakes direct substitution, predominantly at the 9-position, proceeding *via* a zwitterionic intermediate (III) formally analogous to the intermediate complex in electrophilic substitution. Triplet ethoxycarbonylnitrene, however, behaves as a biradical and the exclusive substitution pathway (b) is similar to that envisaged for homolytic attack on anthracene. We suggest that at relatively high concentration both the singlet and triplet forms are present and the reaction proceeds *via* pathways (a), and (b), and possibly (c). At the lowest concentration when the mean lifetime of the nitrene



TABLE

Yields of urethanes from reaction of anthracene with ethoxycarbonylnitrene at 132°

Solvent	Nitrene Source[a]	Anthracene conc. (mole %)[b]	Urethane (%) 1-Anthryl	Urethane (%) 9-Anthryl	9 : 1-isomer ratio
PhCl	A	0·95	2·6	25·3	9·7
PhCl	A	1·85	7·3	27·8	3·8
PhCl	A	2·80	14·2	26·4	1·86
PhCl	A	8·7	30	47	1·57
Cumene	A	8·7	15	17·1	1·13
PhCl/pyridine[c]	A	8·7	6·3	17·1	2·7
PhCl/R_2N[d]	A	0·95	1·8	3·8	2·1
PhCl	B	0·95	4·8	16·9	3·5
PhCl	B	2·80	8·9	17·7	2·0

[a] A, thermolysis of ethyl azidoformate; B, reaction of *N*-*p*-nitrobenzenesulphonoxyurethane with *NN*-diethylcyclohexylamine.

[b] In each experiment, concentration of nitrene precursor = [anthracene] × 0·17.

[c] Concentration of pyridine = 8·7 mole %.

[d] Concentration of *NN*-diethylcyclohexylamine = 0·95 mole %.

is high and the probability of cross-over into the triplet state is proportionately great, pathway (b) predominates. As expected there is an approximately linear dependence of the 1 : 9-isomer ratio on anthracene concentration.

When anthracene was treated with ethoxycarbonylnitrene generated by reaction of *N*-*p*-nitrobenzenesulphonoxyurethane with *NN*-diethylcyclohexylamine[4] a similar but smaller variation in isomer ratio with change in reactant concentration was observed. Apparently, at low concentration the amine acts as a radical trap. Thus the presence of *NN*-diethylcyclohexylamine during the reaction of anthracene with ethyl azidoformate caused a considerable lowering of the 9 : 1-isomer ratio.

The 9 : 1-isomer ratio was similarly affected by the presence of other reagents. Cumene, which yields some bicumyl when treated with ethoxycarbonylnitrene and hence may compete with anthracene for the triplet form decreases the 9 : 1-isomer ratio. Conversely, pyridine,[5] which undergoes irreversible betaine formation and thus might be expected successfully to intercept singlet nitrene, causes significant increase in the 9 : 1-isomer ratio.

(*Received, November 14th*, 1966; *Com.* 884.)

---

[1] A. L. J. Beckwith and J. W. Redmond, *Austral. J. Chem.*, 1966, **19**, 1859.

[2] S.C. Dickerman and G. B. Bermont, *J. Amer. Chem. Soc.*, 1962, **84**, 4150.

[3] W. Lwowski and J. S. McConaghy, *J. Amer. Chem. Soc.*, 1965, **87**, 5490; W. Lwowski and F. P. Woerner, *ibid.*, p. 5491.

[4] W. Lwowski and T. J. Maricich, *J. Amer. Chem. Soc.*, 1964, **86**, 3164; 1965, **87**, 3630.

[5] K. Hafner, D. Zinser, and K. Moritz, *Tetrahedron Letters*, 1964, 1733.