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THE SYNTHESIS OF DIENE AND OF VINYL COPOLYMERS CONTAINING PREDETERMINED QUANTITIES OF POLYNUCLEAR HYDROCARBON OR HETEROCYCLIC ADDUCTS—III

COPOLYMERS FORMED FROM POLYNUCLEAR HYDROCARBONS AND ALKYLDIHALIDES

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Abstract—The reaction in tetrahydrofuran between the disodium salt of anthracene (A) and alkyl dihalides (RX_2) results in oligomeric products with a repeat unit —[A—R]—. The same reaction with the dilithium derivative is complicated by the high reactivity of this species toward solvent; oligomers with —$(CH_2)_4OH$ end groups are isolated. The xylylene dihalides undergo metallation and Wurtz coupling, and they produce low yields of oligomers rich in xylylene units.

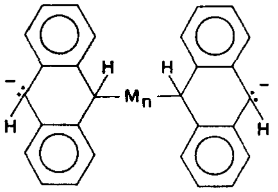
The reaction with dilithium acenaphthylene and alkyl dihalides gives a high yield of copolymer but there is evidence of crosslinking. Although addition occurs principally across the 1,2 position, some 1,5 addition is believed to cause this crosslinking.

With dilithium phenanthrene the reaction is mainly one of electron transfer; the oligomers produced in low yield are low in phenanthrene adducts.

INTRODUCTION

We have previously outlined a method of synthesizing diene and vinyl polymers containing predetermined amounts of polynuclear hydrocarbon adducts [1]. This contribution is the third in a series describing in detail the chemistry of the processes involved.

The technique involves reacting a suitable monomer (M) dissolved in tetrahydrofuran (THF) with alkali metal in the presence of a known quantity of polynuclear hydrocarbon. A dimeric dianion is initially formed and diffuses away from the alkali metal surface to homopropagate until an addition occurs with the hydrocarbon to form a stable anionic species. With anthracene, addition occurs across the 9,10 position to give an oligomeric dianion of structure (I).



(I)

These highly coloured solutions are then titrated with linking agents such as alkyldihalides to form polymeric species of general structure —A—M_n—A—R—, where A = adduct and R = ligand of dihalide.

It is clear that, if the ratio of monomer to polynuclear hydrocarbon in the oligomeric dianions formed initially is greater than the reagent ratio, then the monomer will be depleted more quickly than the polynuclear hydrocarbon. Thus a situation will be reached where the direct reaction of the latter with alkali metal will become increasingly important.

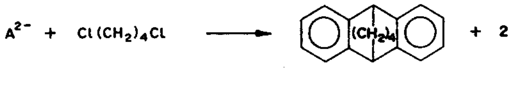
In Part I [2] the nature of this reaction with sodium and with lithium under our polymerization conditions was studied; the stabilities of the resulting electron transfer species toward THF were evaluated. Part II dealt with the reaction of these species with alkylmonohalides to form small molecules, the structure and yield of which gave some insight into the microstructure of some of the copolymers formed.

The present paper is concerned with the reaction of polynuclear hydrocarbon dianions with alkyl dihalides to give polymers by the route indicated in Eqn. (1). It is obvious that this reaction

$$A^{2-} + RBr_2 \rightarrow [—A—R—] + 2Br^- \qquad (1)$$

will be important in those polymerization systems where *n* is large in structure (I) and hence the monomer will be comparatively rapidly consumed.

Lipkin *et al.* [4] have used this reaction where the condensation is effected intramolecularly to prepare new cyclic derivatives. For example, with anthracene and dichlorobutane the compound (II) was synthesized by Eqn. (2). The experimental conditions used by these authors, aimed to maximize the yield of cyclics, differed significantly from ours. It will be shown, however, that under our conditions, although the intermolecular reaction is important in all cases, when dibromopropane and dibromobutane are used the cyclization becomes very prominent.



(II) (2)

EXPERIMENTAL

Materials

All materials were of the highest grade obtainable from BDH. Anthracene of blue fluorescence grade was used without further purification. Sodium was used as 2 mm dia wire and lithium was washed with 60–80 petroleum ether before slicing into sections about 3 mm thick.

Tetrahydrofuran was distilled under nitrogen after the addition of sufficient 0·7 M sodium naphthalene solution to destroy all reactive impurities and give a permanent green colour to the solvent.

A Jack-o-matic/Thermowatch combination manufactured by Instruments for Research and Industry was used to maintain the reaction at constant temperature.

Method

In a typical experiment, 0·1 moles of anthracene was dissolved in 200 ml THF and stirred under nitrogen with 0·3 moles of sodium for 5 hr at room temperature to give a blue solution of the dianion [2]. The excess metal was filtered off by transferring the solution through a plug of glass wool into a second flask, the operation being carried out under nitrogen. The stirred solution was brought to and maintained at 0° by the Jack-o-matic system and dibromobutane diluted with about 50 ml THF was added dropwise until the blue colour of the dianion was just quenched.

The solution was then added slowly to about 5 l. of methanol with constant stirring. The white precipitate was filtered, washed with methanol and dried in a vacuum oven. The methanol solution was evaporated and the residual organic material separated by ether–water extraction followed by removal of the ether on a rotary evaporator.

Analysis

The compounds resulting from the ether–water extraction were separated using gas–liquid chromatography. A Pye series 105 automatic preparative chromatograph was used with 6 mm bore 3 ft columns with Chromosorb G 80/100 mesh support coated with OV 101.

NMR spectra of these separated compounds and of the precipitated polymers were recorded as solutions in $CDCl_3$ at ambient temperature with TMS as internal reference. The spectra were recorded on a Perkin–Elmer R10 spectrometer operating at 60 MHz or on a Jeol PS100 spectrometer at 100 MHz.

RESULTS AND DISCUSSION

Experiments were mostly carried out using anthracene as the polynuclear hydrocarbon. Formation of the anthracene dianion, followed by reaction with dibromoalkane produces polymeric material which can be precipitated in methanol. The mean composition of the precipitated materials was estimated by NMR spectroscopy from the relative areas of the aliphatic and aromatic peaks, and the spectra confirmed that copolymers of anthracene and the alkyl ligands were produced.

The reaction of disodium anthracene with the aliphatic dihalides of general formula $(CH_2)_nBr_2$ gave polymeric materials with structure close to that predicted in Eqn. (1) i.e. NMR spectral analysis indicated a polynuclear hydrocarbon with alkyl/ligand ratio close to unity. These results and the remainder discussed in this section are given in Table 1. In practice, it was found that, in order to decolorize the solution of the sodium dianion, a slight excess of dibromide was sometimes required (although the end-point was not

Table 1. Copolymers of aromatic hydrocarbons and alkyl dihalides

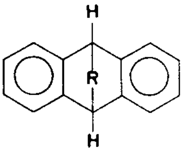
Aromatic hydrocarbon	Linking agent	Metal	Apparent composition by NMR: Aromatic hydro-carbon	Apparent composition by NMR: Linking agent	Viscosity (1% soln in THF)	Pptd yield (%)
Anthracene	$(CH_2)_3Br_2$	Na	1·00	1·02	0·07	24
	$(CH_2)_4Br_2$	Na	1·00	1·09	0·09	58
	$(CH_2)_{10}Br_2$	Na	1·00	1·07		98
	$(CH_2)_4Br_2$	Li	1·00	1·35	0·06	57
	$(CH_2)_4Br_2$*	Li	1·00	1·85	0·29	67
	p-Xylylene Cl_2	Na	1·00	2·1		55
	p-Xylylene Br_2	Na	1·00	3·2		42
	o-Xylylene Br_2	Na	1·00	4·0		34
Acenaphthylene	$(CH_2)_4Br_2$	Li	1·00	1·05		94
Phenanthrene	$(CH_2)_4Br_2$	Li	1·00	3·3		10

* Anthracene and dihalide both present throughout the reaction.

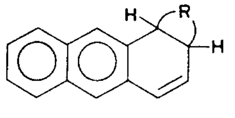
very sharp) and this is reflected in the fact that the proportion of linking agent is generally greater than unity.

In the NMR spectra of the anthracene copolymers, the aromatic protons occur principally as a singlet at 3·0 τ so that these, and the characteristic peak at 6·2 τ due to the bridge protons, indicate that the anthracene is linked predominantly across the 9,10 positions. However, there are also significant aromatic peaks in the region 2·4–2·8 τ, and olefinic protons in the region 3·5–4·2 τ indicating the presence of 1,2 and 1,4 linked structures. Estimates of the area of the olefinic resonances indicate approximately 20 per cent 1,2 and 1,4 structures overall, in good agreement with previous values for monohalides [3].

Table 1 shows that the precipitated polymer yield, which is virtually quantitative when dibromodecane is used, reduces sharply to 58 per cent with dibromobutane and to 28 per cent with dibromopropane. It is reasonable to assume that this drop is associated with the formation of cyclic compounds as found in somewhat similar circumstances by Lipkin *et al.* [4]. Accordingly the methanol-soluble fractions were examined by GLC and subsequent NMR analysis and shown to contain as major products the cyclic species (II) and (III) and regenerated anthracene (proton terminated samples of these solutions indicated complete conversion to A^{2-}). The percentage anthracene converted into these products were 15, 10 and 10 per cent, respectively, for dibromobutane, and 22, 14 and 34 per cent for dibromopropane.* Thus the cyclization reactions observed, and indeed expected, with these dihalides are accompanied by a prominent electron transfer reaction which regenerates anthracene. As the structure of the precipitated material in these cases remains close to the initial equimolar ratio of reactants, the "missing" alkane ligands cannot have been incorporated into the polymer. It is therefore suggested that intramolecular reaction has occurred to form cyclopropane or cyclobutane, although these were not looked for in the methanol-soluble product. This explanation has the advantage that both reactions would be expected to proceed via a similarly structured transition state so that a parallelism in yield should occur, as is observed.



(II) (a) $(CH_2)_3$
(b) $(CH_2)_4$

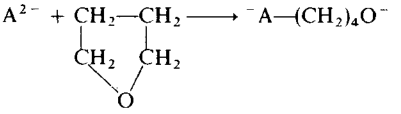


(III) (a) $(CH_2)_3$
(b) $(CH_2)_4$

When lithium metal replaces sodium, the reaction mechanism is more complicated. It is clear from Table 1 that the linking reaction between dilithium anthracene and dibromobutane results in a product containing more aliphatic groups than expected from Eqn. (1). NMR spectra of these materials again show the principal aromatic absorption at 3·0 τ with bridge protons absorbing at 6·2 τ. Thus, as with sodium, addition occurs predominantly across the 9,10 position and the total amount of 1,2 and 1,4 addition, estimated from the small peaks appearing in the 2·4–2·8 τ and the 3·5–4·2 τ regions, is about 20 per cent.

The spectra, however, also show a peak at 6·4 τ which, by analogy with the similar reactions with monohalides [3], arises from CH_2O groups derived from attack of the dilithium anthracene complex on the THF solvent. This infers, therefore, that the proportions of linking agent in the copolymers given in Table 1, and calculated with the assumption that all the aliphatic protons other than those derived from anthracene are due to the linking agent, are too high. Estimates based on the relative intensity of the 6·4 τ peak indicate that the products contain about 20 per cent, relative to dibromobutane, of units derived from THF.

The mode of attack on THF is as indicated in Eqn. (3) [2, 3], so that the anthracene adduct becomes monofunctional with respect to the linking agent and the tetramethylene alcohol ligands appear at the ends of the polymer chains. Assuming this reaction to be the only chain stopping process, the observation that these end groups account for 20 per cent of the aliphatic content implies that these oligomers have a number average molecular weight of about 2200. This degree of reaction with solvent is consistent with the reactivity of the dilithium anthracene toward THF observed in previous work [2, 3].



$$A^{2-} + \underset{\underset{\displaystyle O}{\displaystyle CH_2\quad CH_2}}{CH_2\text{—}CH_2} \longrightarrow {}^{-}A\text{—}(CH_2)_4O^{-} \qquad (3)$$

Undoubtedly, however, the situation is more complicated than that represented by Eqns. (1) and (3). Previous work with alkyl monohalides [3] has shown that appreciable amounts of tri alkyl adducts (5–10 per cent) were formed, balanced by roughly equal amounts of mono alkyl adducts. Thus, in the present system where alkyl dihalides are used, a degree of chain branching is to be expected, and also some chain termination by anthracene adducts.

Again, as the sodium, about 25 per cent of the cyclic molecules (II) and (III) were observed in the methanol-soluble fraction.

Because of the reaction of dilithium anthracene with solvent, a variation of the normal method was employed and an equimolar mixture of anthracene and dibromobutane was stirred with metallic lithium. In this way, any anthracene dianions generated could react immediately with the alkyl dihalide present and

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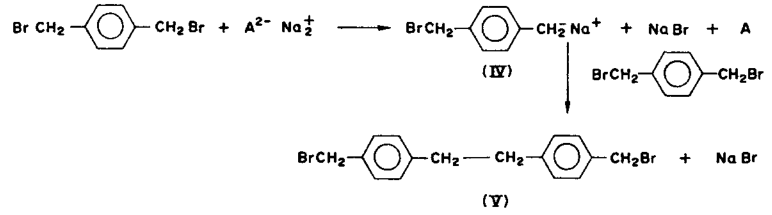
* In a previous communication [1], we incorrectly stated that the yield of cyclic materials was less than 5 per cent. This was due to an analytical error.

thus minimize reaction with THF. This system is similar to that used previously to prepare copolymers of a vinyl or diene monomer and an alkyl dihalide [5].

Clearly if the anthracene reacted with lithium uniquely to form the dianion, then a regular copolymer as described by Eqn. (1) would be produced but the results given in Table 1 indicate that this does not occur. Although there was no evidence of reaction of anthracene dianion with the solvent, a number of side reactions now become feasible in this new system. For example, the alkyl halide can react directly with the alkali metal to form alkyl lithium which can result in Wurtz condensations to form chain extended dibromides amongst other products. Also the possibility exists of reaction with the anthracene radical anion before its further reduction to the dianion. Nevertheless, despite these possibilities, the molecular weight of the product as indicated by its viscosity is significantly higher than materials produced by the two-step synthesis. NMR studies on the product also indicated that there was a rather higher proportion of 1,2 and 1,4 addition (about 30 per cent) than previously.

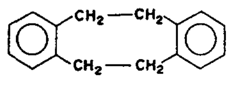
THF solutions of the disodium anthracene salt were also titrated with *ortho*- or *para*-xylylene dihalides. The yields of the precipitated polymeric materials were generally lower than those obtained with aliphatic dihalides. Moreover, NMR analysis (Table 1) showed that these polymers contained very much higher proportions of the xylylene ligand than expected from Eqn. (1). GLC analysis of the reaction mixture indicated that large percentages of the anthracene were recovered unchanged (76, 61 and 76 per cent for *p*-xylylene dibromide, *p*-xylylene dichloride and *o*-xylylene dibromide, respectively). It is clear that significant electron transfer from the anthracene dianion to the xylylene dihalide has occurred to produce coupling reactions as illustrated in Eqn. (4) for *p*-xylylene dibromide.



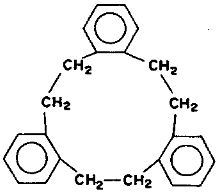
(4)

This electron transfer reaction is enhanced because of the resonance stabilization in the benzylic anion in (IV).

The central pair of methylene units in (V) is clearly in evidence in these copolymer materials as their NMR spectra all gave a characteristic singlet absorption at $7{\cdot}2\,\tau$ for the *p*-xylylene dimer or at $7{\cdot}1\,\tau$ for the *o*-xylylene dimer. The methanol-soluble fraction of the product from the *o*-xylylene dihalide reaction also contained about 10 per cent of the cyclic dimer (VI) and about 10 per cent of the cyclic trimer (VII). These were separated by vacuum distillation and identified by their NMR spectra ($2{\cdot}9\,\tau$, 8H, singlet; $7{\cdot}1\,\tau$, 8H, singlet). This is in accord with the results of Müller and Röscheisen [6] who obtained yields of 40 per cent (VI) and 35 per cent (VII) from the reaction of *o*-xylylene dihalide with the electron transfer reagent disodium tetraphenylethylene in THF.



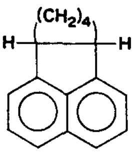
(VI)



(VII)

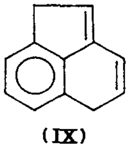
No cyclic products analogous to (VI) and (VII) were observed with the *p*-xylylene dihalides.

Similar reactions were carried out using acenaphthylene instead of anthracene. On addition of the aliphatic dihalide, the solution became very viscous and a considerable amount of gel was formed. A high yield of precipitate was obtained from methanol, but after separation and drying only a small fraction remained soluble which gave the NMR analysis reported in Table 1. The methanol-soluble material consisted mainly of acenaphthene together with a small quantity of the intramolecularly condensed product (VIII).



(VIII)

In a previous paper [2] we have shown that acenaphthylene forms the dianon with alkali metal in these systems and that on protonation, although reaction occurs principally at the 1,2 position, a significant amount of the 1,5 dihydroproduct (IX) is also formed.

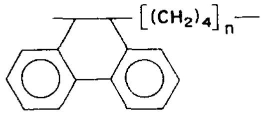


(IX)

Thus, assuming a similar circumstance in the reaction with alkyl dihalides, the formation of a 1,5 linked species during the reaction could result in an electron transfer to it from an acenaphthylene dianion [(IX) can be regarded as a butadiene derivative] and hence it could react with more dihalide to lead to the observed crosslinking and gelation. The further crosslinking observed with the separated material is presumably due to aerial oxidation at these diene units.

A third type of behaviour was observed with phenanthrene. Reaction of phenanthrene with lithium under these conditions yields predominantly the dianion [2]. On titration with monobromodecane, however, 67 per cent of the original phenanthrene was regenerated, 40 per cent of the monobromodecane was converted into a C_{20} hydrocarbon and 25 per cent into a mixture of decane and decene (0·36 moles of monobromodecane were required to decolorize the anions produced from 0·2 moles of phenanthrene).

Thus electron transfer clearly predominates in the reaction of the phenanthrene dianion with alkyl halides, and this was equally pronounced in the reaction with dihalides. When dibromobutane was used, 77 per cent of the phenanthrene was regenerated and only about 10 per cent of the product precipitated from methanol. This precipitated material contained 3·3 tetramethylene units per phenanthrene unit. The NMR spectrum also showed that the phenanthrene was bonded across the 9,10 positions so that the reaction produces oligomers of repeat units (X) with n having an average value of 3·3.



(X)

REFERENCES

1. F. J. Burgess, A. V. Cunliffe, D. H. Richards and P. Shadbolt, *Europ. Polym. J.* **10**, 193 (1974).
2. F. J. Burgess, A. V. Cunliffe and D. H. Richards, *Europ. Polym. J. Europ. Polym. J.* **10**, 645 (1974).
3. F. J. Burgess, A. V. Cunliffe and D. H. Richards, *Europ. Polym. J. Europ. Polym. J.* **10**, 657 (1974).
4. D. Lipkin, G. V. Divis and R. W. Jordan, *Preprints, Div. Petrol. Chem.* **13**, D60 (1968).
5. D. H. Richards, N. F. Scilly and F. J. Williams, *Polymer* **10**, 603 (1969).
6. E. Müller and G. Röscheisen, *Ber.* **90**, 543 (1957).

Résumé—La réaction du sel disodique de l'anthracène (A) avec les dihalogénures d'alcoyle (RX_2) dans le tetrahydrofuranne donne des oligomères comportant des unités —(A—R)—. La même réaction avec des dérivés di-lithiques est grandement facilitée par la grande réactivité de ces espèces envers le solvant; on a isolé des ologomères comportment des bouts de chaîne —$(CH_2)_4OH$. Avec les dihalogénures de xylylène ont lieu des réactions de métallation et de couplage de Wurtz, produisant de faibles quantités d'oligomères riches en unités xylène. La réaction entre l'acénaphtylène dilithium et les di-halogénures d'alcoyles produit des copolymères avec un rendement élévé mais on obtient également des produits réticulés. Bien que l'addition se produise principalement en position 1,2, on pense qu'elle se produit également en position 1,6 provoquant la réticulation.

Avec le phénanthrène dilithium, la réaction est essentiellement une réaction de transfert d'électrons; les oligomères obtenus avec un faible rendement, contiennent également peu d'unités phénanthrène.

Sommario—La reazione in tetraidrofurano tra il sale bisodico di antracene (A) e il bialogenuro alchilico (RX_2) conduce a prodotti oligomerici con il gruppo ripetitivo —[A—R]—. La stessa reazione con il derivato del dilitio viene completata dall'elevata reattività di questa specie nei confronti del solvente. Si sono isolati oligomeri con gruppo terminale —$(CH_2)_4OH$. I bialogenuri di xililene subiscono matallazione e accoppiamento di Wurtz, e producono una bassa resa di oligomeri ricchi di gruppi xililene.

La reazione con acenaftilene e bialogenuri alchilici danno un'elevata resa di copolimeri però vi è traccia di reticolamento. Sebbene l'addizione avvenga principalmente in corrispondenza della posizione 1,2, si pensa che siano alcune addizioni 1,6 che causano tale reticolamento.

Con il fenantrene di dilitio la reazione è principalmente di tipo con trasferimento di elettroni; gli oligomeri prodotti con basso rendimento sono poveri di prodotti aggiuntivi di fenantrene.

Zusammenfassung—Bei der Reaktion des Dinatriumsalzes von Anthracen (A) in Tetrahydrofuran mit Alkyldihalogeniden (RX_2) entstehen oligomere Produkte mit der wiederkehrenden Einheit —(A—R)—. Die gleiche Reaktion erfolgt von Seiten der Dilithiumderivate mit ihrer hohen Reaktivität gegenüber dem Lösungsmittel: Dabei entstehen und wurden isoliert Oligomere mit —$(CH_2)_4OH$-Endgruppen. Xyloldihalogenide unterliegen dabei entweder Metallierung oder einer Wurtz-Reaktion, wobei geringe Mengen an Oligomeren anfallen, die große Anteile an Xyloleinheiten enthalten.

Dilithiumacenaphthlen und Alkyldihalogenide liefern in hoher Ausbeute Copolymer, wobei auch Vernetzung beobachtet wird. Obwohl Wachstum prinzipiell über die 1,2-Position erfolgt ist wahrscheinlich eine Reaktion in 1,6-Stellung für die Vernetzung verantwortlich.

Mit Dilithiumphenanthren erfolgt vorwiegend Elektronenübertragung. Die dabei in nur geringer Ausbeute entstehenden Oligomeren enthalten nur geringe Mengen an Phenanthren.