709. *The Decomposition of Aliphatic Diazo-compounds by Trimethyl Borate: The Preparation of Branched-chain Paraffins of High Molecular Weight.*

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The decomposition of mixtures of diazomethane and higher aliphatic diazo-compounds by small amounts of trimethyl borate at 0° gives branched-chain paraffins of high molecular weight whose physical properties vary, with the number and length of the branches, from amorphous solids, through rubbers, to crystalline polymers resembling polythene but of very much higher melting point; their molecular weights are estimated to be of the order of 100,000. In contrast to the copper-catalysed decomposition of diazo-compounds, the presence of ether is not essential to the reaction, but the higher aliphatic diazo-compounds do not form polymers in the absence of diazomethane.

Meerwein (*Angew. Chem.*, 1948, **60**, *A*, 78) found that diazomethane was decomposed by catalytic amounts of a wide range of organic boron compounds, to give a polymer which he described as similar in appearance to filter-paper. Because it decomposed when heated, without melting, and was insoluble in all solvents tried, he concluded that it was a cross-linked polymer. This preparation has now been repeated, trimethyl borate being used as catalyst at 0°, and has been extended to a series of mixtures of higher aliphatic diazo-compounds with diazomethane; a wide variety of products has been obtained.

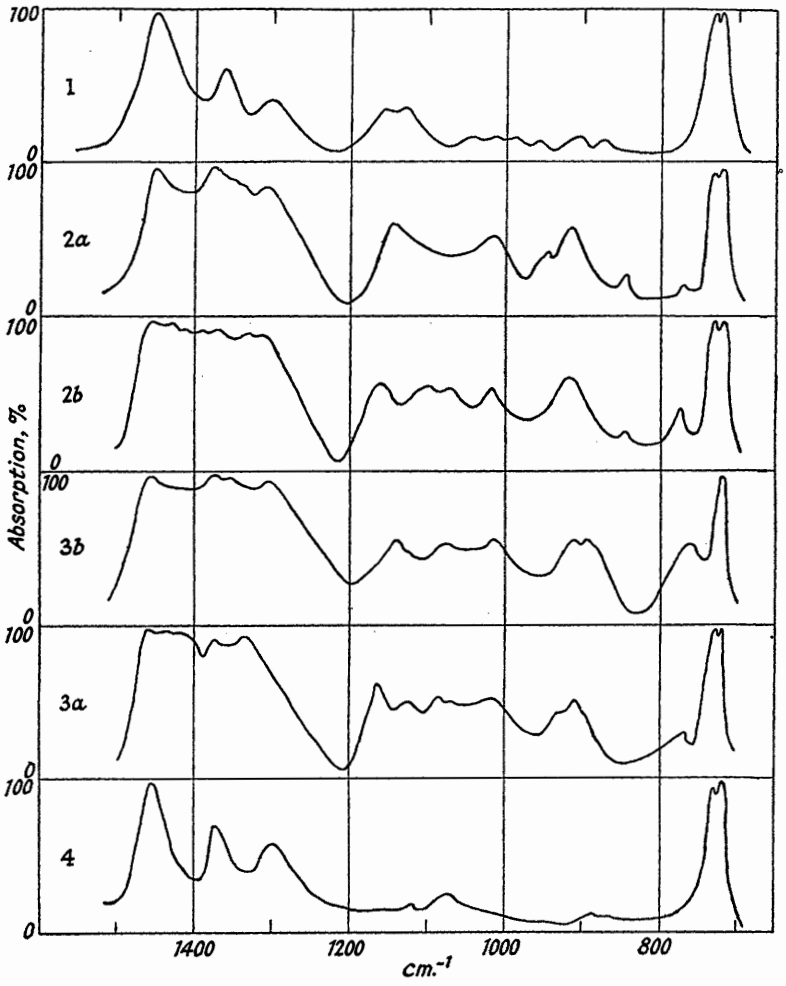
The product from the decomposition of diazomethane was a polymethylene of very high molecular weight; it did not melt without decomposition, but could be pressed into a film between rock-salt plates at *ca.* 180°. The infra-red absorption spectrum (Fig. 1) and the *X*-ray diffraction pattern were identical with those of a polymethylene prepared by the copper-catalysed decomposition of diazomethane (Buckley, Cross, and Ray, *J.*, 1950, 2714). The polymer dissolved in boiling tetralin, and from viscosity measurements its molecular weight was estimated at 200,000; on this evidence it was concluded that it was not cross-linked, and was essentially a straight-chain paraffin.

A similar product was obtained from a solution of diazomethane in benzene, showing that ether was not essential in this reaction, in contrast to the copper-catalysed decomposition. Similar products were also obtained when boron trifluoride, triphenyl borate, and tri*cyclo*hexyl borate were used as catalysts; as there did not appear to be any advantage in using another catalyst, trimethyl borate was used in all subsequent experiments on account of its ready availability.

Diazoethane did not give a high polymer by itself on treatment with trimethyl borate; the product was a tar, which was not investigated. In admixture with diazomethane, however, a paraffin of high molecular weight was obtained, which differed from the polymethylene formed from diazomethane alone in having greater solubility and lower melting point; its infra-red spectrum (Fig. 2, *a* and *b*) showed an absorption band at 1378 cm.$^{-1}$, indicative of methyl groups, and the intensity of this absorption was correlated with the proportion of diazoethane in the reaction mixture. The yield of the mixed polymers increased at first with increasing proportions of diazoethane, to a maximum at about 10 moles %, then decreased rapidly, approaching zero with more than 50 moles % of diazoethane in the mixture. From viscosity measurements, their molecular weights were estimated to lie between 100,000 and 200,000.

Similar mixed polymers were produced from mixtures of diazomethane and higher aliphatic diazo-compounds, up to 1-diazododecane, and the physical properties of these

materials depended on both the number and length of the branches introduced into the molecule. Crystallinity was decreased, and solubility increased, either by increasing the proportion of second component or by increasing its chain length: for example, a polymer from diazomethane and diazoethane containing 15 or more methyl groups per 100 carbon atoms was a rubber and soluble in cold chloroform; with diazohexane as second component these properties were apparent in a polymer containing 5 or more branches per 100 carbon atoms, and with diazododecane, only 3 branches per 100 carbon atoms were necessary to produce them.



1, *Polymethylene.*
2*a*, *b*, *Polymethylenes with methyl side chains.*
3*a*, *b*, *Polymethylenes with* n-*amyl side chains.*
4, *Polymethylene with* n-*undecyl side chains.*

The addition of a small proportion of 1 : 6-bisdiazohexane as second component to diazomethane resulted in the formation of a completely insoluble polymer; it was swollen by hot tetralin and, although it softened at 200°, it did not melt without decomposition.

Experimental

Preparation of Diazo-compounds.—Diazomethane, diazoethane, 1-diazohexane, and 1 : 6-bis-diazohexane were prepared from the corresponding nitrosoureas.

1-*Diazododecane.*—Dodecylurea (160 g.) and glacial acetic acid (640 c.c.) were warmed on a steam-bath until a clear solution was obtained, then cooled to 0° with vigorous stirring. A solution of sodium nitrite (200 g.) in water (340 c.c.) was added during 15 minutes, and stirring

continued for a further 15 minutes. An equal volume (*ca.* 1 l.) of ice-water was added, and the nitrosododecylurea collected at 0°.

Aqueous potassium hydroxide (250 c.c.; 40%), ethanol (500 c.c.), and ligroin (500 c.c.; b. p. 80—100°) were mixed and cooled to 0°, and the crude nitrosododecylurea (200 g.) was then added during 30 minutes with vigorous agitation. After a further 15 minutes' stirring at 0°, the upper layer (900 c.c.) was removed and filtered. This solution of 1-diazododecane was used without further purification in the experiments described below; for estimation and characterisation, one portion (30 c.c.) was added to benzoic acid (0·5 g.); nitrogen was evolved and the colour was discharged. The excess of acid was titrated with 0·1N-sodium hydroxide (15·0 c.c. required; whence concentration of diazododecane solution = 5·2 g./l.), and the solution extracted with ether. The ethereal extract was dried and evaporated, leaving an oily residue which was presumed to be impure *n*-dodecyl benzoate (0·3 g.) (Found: C, 67·5; H, 9·4. Calc. for $C_{19}H_{30}O_2$: C, 65·5; H, 9·66%).

Intrinsic Viscosities.—These were measured in tetralin solution at 75°, except where stated otherwise, by use of an Ubbelohde suspended level viscometer, modified by the addition of a large reservoir bulb to enable a series of dilutions to be made.

Branching and Crystallinity.—Infra-red absorption spectra were measured in the same instrument as was used in previous work (Buckley, Cross, and Ray, *loc. cit.*) and the amount of branching was determined by the method described by Cross, Richards, and Willis (*Discuss. Faraday Soc.*, 1950, **9**, 235). The intensity of the absorption band at 1304 cm.$^{-1}$ was used as a measure of the amorphous content; it was correlated with the amorphous : crystalline ratio as determined by *X*-ray diffraction.

General Procedure for Preparation of Polymers.—In a typical experiment, trimethyl borate (0·7 g.) was added to a solution of diazomethane (15 g.) and diazoethane (2 g.) in ether (710 c.c.) kept at 0°. Nitrogen was evolved slowly and a precipitate started to form in the solution. After 24 hours the solution was colourless; the precipitate was collected, washed with ether, and triturated with alcoholic approx. 2N-potassium hydroxide to remove boric acid and trimethyl borate. Finally it was washed with water, alcohol, and ether and dried. The product (5·3 g.) was a white, rubbery, fibrous mass, softening at 235° (in nitrogen), soluble in chloroform, benzene, and tetralin; it had d_4^{20} 0·899 and $[\eta]$ 3·3 (Found: C, 85·7; H, 14·3; B, nil. Calc. for $[CH_2]_x$: C, 85·7; H, 14·3%).

Infra-red absorption measurements gave 10·5 methyl groups per 100 carbon atoms and 22% crystallinity (Fig. 2*b*).

Polymethylene.—Diazomethane (13·7 g.) was decomposed by trimethyl borate (0·3 g.) in the manner described. The product (3·6 g.) was unchanged when heated in nitrogen up to 300°, above which it became progressively softer and darker, finally decomposing, as described by Meerwein (*loc. cit.*) to a brittle wax, m. p. about 110°. However, by heating it to 180° under pressure between rock-salt plates it was possible to obtain a thin, flexible, transparent film; its infra-red spectrum (Fig. 1) showed bands at 721 and 732 cm.$^{-1}$ characteristic of polymethylene, almost complete absence of methyl, and an amorphous content of 18%. Its *X*-ray diffraction pattern showed it to be a highly crystalline substance, and the interplanar spacings of the (110) and (200) reflections were identical with those of a polymethylene sample prepared by the copper-catalysed decomposition of diazomethane (Buckley, Cross, and Ray, *loc. cit.*). It dissolved slowly in tetralin at 160° and remained in solution at 100°; it had $[\eta]$ (at 100°) 5·4.

Polymethylenes with Side-chain Methyl Groups.—Mixtures of diazomethane and diazoethane in various proportions were decomposed at 0° as described, 0·01 mole of trimethyl borate being used per mole of total diazo-compound in each case. The following results were obtained:

Diazoethane, moles, %	Yield of polymer, % of theory	d_4^{20}	$[\eta]$	No. of Me groups per 100 C.	Crystallinity, %	Remarks
3	66	0·925	3·62	2·5	64	Polythene-like, soluble in boiling toluene
6	71	0·931	2·85	2·8	57	
9	88	0·899	3·3	10·5	22	Flexible, soluble in hot benzene
10	99	0·888	3·5	11·5	26	
10	67	0·890	4·6	8·5	22	
12·5	47	0·906	—	7	33	
14·3	43	0·905	—	13	18	Rubbery
16·7	44	0·891	—	15	11	Soluble in cold $CHCl_3$
20	40	0·878	—	16	6	
25	58	0·870	5·0	more	6	
33·3	73	0·889	2·95	than	—	
50	9	0·910	2·87	20	—	

Polymethylenes with n-*Amyl Side Chains.*—Mixtures of diazomethane and 1-diazohexane in various proportions were decomposed at 0° with 0·01 mole of trimethyl borate per mole of total diazo-compound. The following results were obtained :

Diazohexane, moles, %	Yield of polymer, % of theory	d_4^{20}	$[\eta]$	No. of Me groups per 100 C.	Crystallinity, %	Remarks
6·25	50	0·911	1·9	3	38	Similar to polythene, soluble only in hot solvents
10·0	30	0·907	2·4	3	32	
12·5	60	0·905	7·4	5	38	Very rubber-like, soluble in cold $CHCl_3$
25	49	0·871	—	12	4	

The infra-red absorption spectra of the polymers made from 6·25 moles % and 25 moles % of diazohexane are shown in Figs. 3*a* and *b*.

Polymethylene with n-*Undecyl Side Chains.*—Trimethyl borate (0·5 g.) was added to a solution of diazomethane (6 g.) and 1-diazododecane (2·2 g.) in ether (700 c.c.). After 24 hours the precipitate was collected, washed, and dried. The product (2·0 g.) was a translucent rubbery solid, soluble in chloroform, benzene, and tetralin; it softened at 250°, and melted at 370° (in nitrogen), and had d_4^{20} 0·891, $[\eta]$ 6·95; its infra-red absorption spectrum showed 2·9 methyl groups per 100 carbon atoms and 22% crystallinity (Fig. 4).

Cross-linked Polymethylene.—Triphenyl borate (0·2 g.) was added to a solution of diazomethane (9·2 g.) and 1 : 6-bisdiazohexane (0·15 g.) in ether (1 l.). The solution was kept at 20° for 96 hours, after which a precipitate had formed. This was collected, washed, and dried; the product (2·4 g.) was a tough, flexible substance, d_4^{20} 0·921, which softened (without melting) at *ca.* 200° and decomposed at *ca.* 240°. Its infra-red absorption spectrum showed no methyl bands and about 50% crystallinity. It was insoluble in all solvents tried, though swollen by hot tetralin.

Decomposition of Diazomethane in Benzene.—Trimethyl borate (0·7 g.) was added to a solution of diazomethane (16·5 g.) in benzene (300 c.c.) at 20°. Nitrogen was evolved slowly, and a precipitate was formed in the solution. After 24 hours the solution was colourless, and the precipitate was collected, washed, and dried. The product (1·5 g.) was identical in properties and infra-red absorption spectrum with the polymethylene prepared in ether solution.

Attempted Decomposition of Diazoethane with Trimethyl Borate.—Trimethyl borate (1·0 g.) was added to a solution of diazoethane (19 g.) in ether (1 l.) at 0°. A very slow evolution of nitrogen occurred at first but did not continue. The solution was allowed to warm to 20° in 24 hours, after which it was still deep orange. More trimethyl borate (2·0 g.) was added; after 56 hours the solution was colourless but contained no precipitate; it was evaporated almost to dryness at 50° and finally heated at 100°/1 mm. until free from ether. The residue was washed with alkali to remove boric acid, dried, and distilled, giving a syrup, b. p. 60—120°/3 mm. (0·8 g.), and a tarry residue (1·3 g.).

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