521. *The Copper-catalysed Decomposition of Aliphatic Diazo-compounds: The Formation of Paraffins of High Molecular Weight.*

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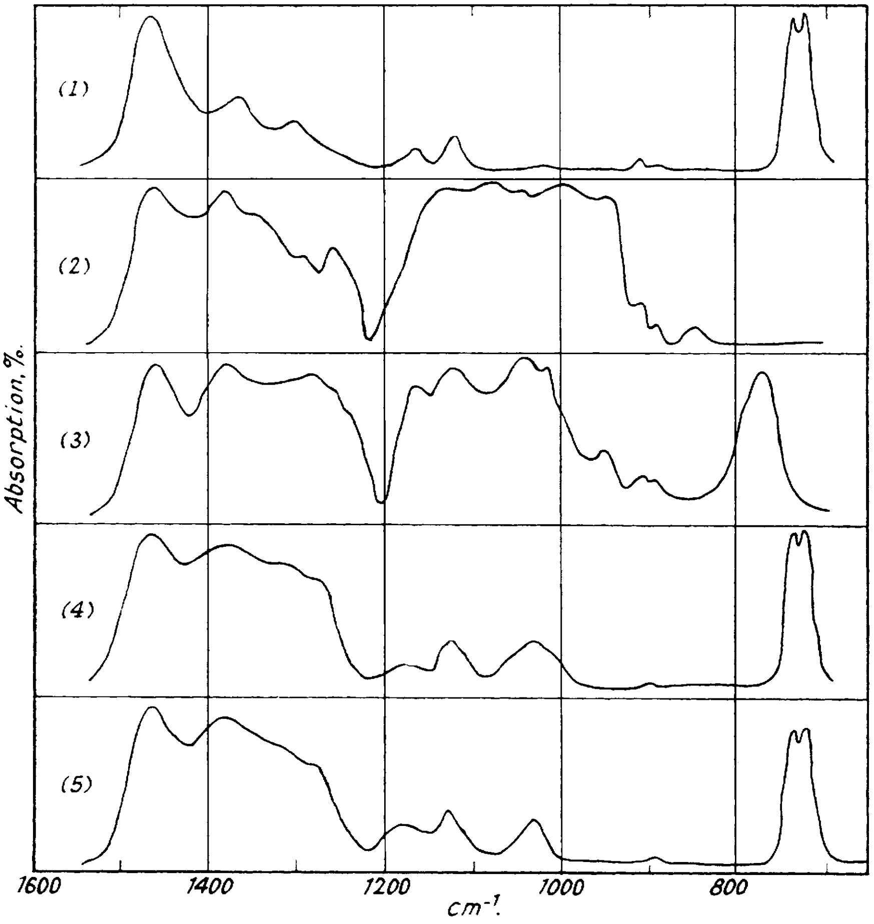
The copper-catalysed decomposition of a series of aliphatic diazo-compounds in ethereal solution has been studied. Diazomethane gives *ca.* 10% of polymethylene, a straight-chain, highly crystalline paraffin of high molecular weight. Diazoethane gives almost quantitative yields of polyethylidene, a hard brittle glass, and 1-diazopropane gives the very similar polypropylidene. 1-Diazobutane gives only but-1-ene, and secondary and higher primary diazo-compounds give only simple ketazines and aldazines.

Interpolymers have been prepared by the decomposition of mixtures of diazomethane and diazoethane. With small proportions of diazoethane the products are crystalline waxes, but higher proportions of diazoethane yield amorphous glasses.

Bamberger and Tchirner (*Ber.*, 1900, **33**, 956) observed that on long storage ethereal solutions of diazomethane deposit a white precipitate which has the composition $[CH_2]_x$ (cf. also Meerwein, Rathjen, and Werner, *Ber.*, 1942, **75**, 1610). Copper and its salts have been shown to catalyse the decomposition of certain aliphatic diazo-compounds with the production of olefins (Loose, *J. pr. Chem.*, 1909, **79**, 507; Lorey, *ibid.*, 1930, **124**, 185); thus diazoacetic ester gives fumaric ester, and ω-diazotoluene gives stilbene on treatment with copper or anhydrous copper sulphate. Leitch and Cambron (" National Research Council of Canada Review," 1948, p. 94) found that copper powder catalysed the decomposition of solutions of diazomethane and diazodideuteromethane to give much improved yields of polymethylene and polydeuteromethylene, respectively.

The decomposition of a series of aliphatic diazo-compounds has now been studied. Polymethylene, prepared from diazomethane by Leitch and Cambron's method (*loc. cit.*), was a brittle crystalline wax, m. p. 135°, of molecular weight *ca.* 20,000, insoluble in ether and cold hydrocarbons, though soluble in boiling benzene and toluene. Its infra-red absorption spectrum (see figure) shows bands at 721 $cm.^{-1}$ and 732 $cm.^{-1}$, characteristic of a polymethylene chain (Thompson and Torkington, *Proc. Roy. Soc.*, 1945, **184**, *A*, 3). The weak absorption at 1365 $cm.^{-1}$ is not due to the methyl but to the methylene group (R. B. Richards, private communication).

Copper and certain of its salts catalysed the decomposition of diazoethane and 1-diazopropane in ethereal solution with the production of paraffins of high molecular weight in 90—95% yield. Although a variety of substances, such as silver powder, iron powder, zinc dust, and powdered glass were found to catalyse the decomposition of an ethereal solution of diazoethane, only copper powder, anhydrous cupric sulphate, cupric oxide, and cuprous cyanide induced the formation of paraffins of high molecular weight in good yield. Other copper compounds gave traces of these polymers. The presence of ethyl ether was also essential, since solutions of diazoethane in toluene, hexane, or tetrahydrofuran were decomposed only very slowly by copper powder, and did not give polymers. However, on addition of ether to such a reaction mixture a more vigorous decomposition occurred and a polymer was formed. The polymers from diazoethane and diazopropane remained dissolved in the ether, in contrast to polymethylene, which was precipitated gradually as the decomposition proceeded. The products were brittle amorphous glasses, m. p. 80—100°, soluble in ether and cold hydrocarbons, but insoluble in alcohol. Analysis showed that they were hydrocarbons of empirical formula $[CH_2]_x$, and their infra-red absorption spectra (see figure) were consistent with the structures of polyethylidene and polypropylidene.



(1) *Polymethylene from diazomethane.*
(2) *Polyethylidene from diazoethane.*
(3) *Polypropylidene from diazopropane.*
(4) *Ether-insoluble interpolymer No.* 1 *containing* 3·0 *moles* % *of diazoethane.*
(5) ,, ,, ,, ,, 2 ,, 6·7 ,, ,, ,,

The spectrum of the product from diazoethane showed no bands in the 720- and 730-cm.$^{-1}$ regions, indicating absence of a polymethylene chain, and strong absorption at about 1380 cm.$^{-1}$, indicating a high concentration of methyl groups (Thompson and Torkington, *loc. cit.*). There was a series of very strong bands in the region 940—1125 cm.$^{-1}$; the 1125-cm.$^{-1}$ band is commonly found in paraffins containing adjacent methyl groups (Thompson, *J.*, 1948, 328), and the spectrum of 2 : 3 : 4-trimethylpentane, for example, shows several absorptions in this region (" Amer. Petr. Inst. Research Project 44, Nat. Bur. Standards, Catalogue of infra-red spectral data," serial No. 666) though of much lower intensity.

The spectrum of the product from 1-diazopropane was superficially similar except for an intense band at 785 cm.$^{-1}$, indicating the presence of ethyl groups (Thompson, *J.*, 1948, 328) and suggesting that this hydrocarbon is a homologue of polyethylidene. The molecular weights of these hydrocarbons were determined, where possible, by the cryoscopic method, benzene being used as solvent. This was unsatisfactory, however, for molecular weights above 3000, and for such cases the intrinsic viscosity was measured in di*iso*butene at 20°. The relation $[\eta] = 1{\cdot}08M^{0{\cdot}7} \times 10^{-3}$ (Oakes and Richards, *J.*, 1949, **2929**) which is used for polythene and polymethylene was clearly not applicable to polyethylidene and polypropylidene; instead the relation $[\eta] = 3{\cdot}60M^{0{\cdot}64} \times 10^{-4}$ (Flory, *J. Amer. Chem. Soc.*, 1943, **65**, 372) which holds for poly*iso*butene, was used as being the best available approximation. The combination of these two methods showed that the polymers ranged in molecular weight from 2,000 to 14,000.

The molecular weight of polyethylidene was found to depend inversely on the concentration of the diazoethane solution in ether. Dilution of an ethereal solution of diazoethane with benzene, however, had no significant effect upon the molecular weight of the polymer produced.

When mixtures of diazomethane and diazoethane in various proportions in ether were treated with copper, the polymers obtained could be divided into two groups: those insoluble in ether, which were precipitated and required to be extracted from the copper with hot toluene, and those soluble in ether, which were isolated on evaporation of the solution. When the mixture contained 10% or less of diazoethane the polymers resembled polythene; they were of higher melting-point than polyethylidene, crystalline, and insoluble in ether. Although ether-soluble fractions were also obtained in these cases, they were not polymeric hydrocarbons, but oily impurities containing large amounts of nitrogen; small amounts of similar bodies were occasionally found in polyethylidene preparations and could be removed by extraction with alcohol. With 40% or more diazoethane in the mixture the products were entirely ether-soluble; they were brittle amorphous glasses, resembling unmodified polyethylidene. The infra-red absorption spectra of the ether-insoluble polymers (see figure) showed small absorptions in the 950—1200-cm.$^{-1}$ region, at different frequencies from those given by polyethylidene, indicating that they were true interpolymers and not simple mixtures. There were new absorptions at 721 cm.$^{-1}$ and 732 cm.$^{-1}$, indicating a polymethylene chain, and their intensities diminished as the proportion of diazomethane in the reaction mixture was reduced.

Higher aliphatic diazo-compounds did not give polymers when decomposed by copper. 1-Diazobutane lost nitrogen to give mainly but-1-ene, and 1-diazopentane and 1-diazoheptane gave valeraldazine and heptaldazine, respectively, losing only half of their nitrogen:

$$2\mathrm{RCHN_2} \longrightarrow \mathrm{RCH{:}N{\cdot}N{:}CHR} + \mathrm{N_2}$$

2-Diazopropane gave dimethylketazine when decomposed by copper, but ω-diazotoluene gave stilbene and ethyl diazoacetate gave ethyl fumarate, as has been observed previously (Loose, *loc. cit.*).

3-Diazoprop-1-ene was not decomposed by copper; the only product isolated from it was pyrazole, the formation of which involves no loss of nitrogen (Adamson and Kenner, *J.*, 1935, 286).

Part of this work is the subject of B.P.Appln. 26313/49.

EXPERIMENTAL.

(Microanalyses are by Dr. A. F. Colson. All m. p.s are corrected.)

Preparation of Diazo-compounds.—Diazomethane, diazoethane, and 1-diazopropane were prepared from the methyl *N*-nitroso-2-alkylamino*iso*butyl ketones as described by Jones and Kenner (*J.*, 1933, 363) and Adamson and Kenner (*loc. cit.*). It was found advisable to use the nitroso-ketones shortly after they had been made, otherwise poor yields of diazo-compounds were obtained. 1-Diazobutane, 1-diazopentane, and 1-diazoheptane were prepared from the corresponding nitrosoureas, and 2-diazopropane by oxidation of acetone hydrazone with mercuric oxide (Staudinger and Gaule, *Ber.*, 1916, **49**, 1905).

Molecular-weight Determinations.—The molecular weights of polymethylene and of the ether-insoluble interpolymers from diazomethane and diazoethane were calculated from their intrinsic viscosities measured in tetralin at 75°, the equation $[\eta] = 1{\cdot}08M^{0{\cdot}7} \times 10^{-3}$ (Oakes and Richards, *loc. cit.*) being used. See also above.

Infra-red Absorption Spectra.—The instrument used was a Grubb Parsons, model S.3, single-beam infra-red recording spectrometer; 0·15 mm. thick films between rock-salt plates were used throughout, and the cell compartment was kept at 28° ± 2°. The effective slit widths were 11 cm.$^{-1}$ at 6μ., 6 cm.$^{-1}$ at 10μ., and 3 cm.$^{-1}$ at 14μ.

Decomposition of Diazomethane.—Copper powder (1 g.) was added to a solution of diazomethane (4·6 g.) in ether (200 c.c.). Nitrogen was evolved slowly and after 24 hours the solution was colourless and contained a white flocculent precipitate. The precipitate, together with the copper, was collected and, after being dried *in vacuo* at 60°, was extracted with boiling xylene. The cooled extract was diluted with twice its volume of methanol, giving polymethylene (0·15 g.), m. p. 132°, *M ca.* 20,000, d_4^{20} 0·965 (Found: C, 85·6; H, 14·1. Calc. for $[\mathrm{CH_2}]_x$: C, 85·7; H, 14·3%).

Decomposition of Diazoethane.—Copper powder (1 g.) was added to a solution of diazoethane (3·4 g.) in dry ether (500 c.c.). Nitrogen was slowly evolved and the solution was colourless after 21 hours; it was filtered and evaporated to dryness, and the residue was washed with ethanol and dried at 100°/3 mm. The product (1·5 g.) was a pale yellow, brittle glass, m. p. 90—100°, d_4^{20} 0·909, [η] 0·088, *M*, 5800 (Found : C, 85·7; H, 14·3. $[C_2H_4]_x$ requires C, 85·7; H, 14·3%). The infra-red absorption spectrum showed it to be a *polyethyliened* (see figure). The experiment was repeated, various catalysts being used, with the following results:

Catalyst.*	Reaction time.	Yield of polymer, g.	*M*.	Remarks.
Silver powder	24 hours	nil	—	—
Iron powder	2 days	nil	—	—
Zinc dust	3 days	nil	—	—
Cupric sulphate	5 mins.	1·5	7200	Very vigorous reaction
Cupric nitrate	<1 min.	trace	—	Violent reaction
Cupric acetate	<1 min.	trace	—	Violent reaction
Cuprous cyanide ...	5 mins.	1·5	2500	Vigorous reaction
Cupric oxide	2 days	0·7	500	Liquid product
Cuprous oxide	1 hour	trace	—	—
Powdered glass	3 days	nil	—	Very slow and incomplete reaction

* All salts were anhydrous.

Effect of Concentration.—Diazoethane solutions of various concentrations (each containing 1·04 g. of diazoethane) were treated with copper powder (1 g.) and the products isolated as described above. The effect of concentration on molecular weight is :

Concentration, g./l.	3·4	6·2	10·4
[η]	0·163	0·087	0·051
M	14,000	5,400	2,300

Effect of Other Solvents.—Solutions of diazoethane in toluene, hexane, and tetrahydrofuran were prepared by decomposing methyl *N*-nitroso-2-ethylamino*iso*butyl ketone in anisole with sodium *cyclo*hexyloxide (Adamson and Kenner, *J.*, 1937, 1551) and collecting the diazoethane in a wash-bottle containing the selected solvent cooled in "Drikold." Addition of copper powder to these solutions produced a slow evolution of nitrogen and the colour was discharged in 24 hours. After filtering off the copper and evaporating to dryness there was in each case only a trace of oily residue. To a solution of diazoethane (1 g.) in toluene (200 c.c.) was added ether (10 c.c.) and copper powder (0·5 g.). A more vigorous evolution of gas took place, the colour was discharged in 10 hours and polyethylidene (0·3 g.) was isolated as described above.

A number of ethereal diazoethane solutions were diluted with varying amounts of dry benzene, and treated with copper powder (2 g.). The results were :

				Product,	
Diazoethane, g.	Ether, c.c.	Benzene, c.c.	Diazoethane concentration, g./l.	[η].	*M*.
5·2	200	nil	26	0·070	3900
5·2	200	100	17·3	0·089	5600
5·2	200	200	13	0·073	4000
5·2	200	400	8·7	0·072	4000
5·2	200	800	5·2	0·090	5600

Decomposition of 1-*Diazopropane.*—Copper powder (1 g.) was added to a solution of 1-diazopropane (2·4 g.) in ether (260 c.c.). Nitrogen was evolved rapidly, and after 50 minutes the solution was colourless. The copper was removed by filtration and the solution evaporated to dryness, leaving *polypropylidene* (1·4 g.) as a pale yellow, brittle glass, m. p. 80—96°, [η] 0·105, *M* 7,000 (Found : C, 85·7; H, 14·3%). Its infra-red absorption spectrum is shown in the figure.

Decomposition of 2-*Diazopropane.*—Anhydrous copper sulphate (0·2 g.) was added to a solution of 2-diazopropane (0·44 g.) in ether (100 c.c.). The colour was discharged in 5 minutes, and the solution was filtered and evaporated; the residue was distilled giving dimethyl ketazine (0·3 g.), b. p. 130—131° (Found: C, 64·0; H, 10·5; N, 24·9%; *M*, 114. Calc. for $C_6H_{12}N_2$: C, 64·3; H, 10·7; N, 25·0%; *M*, 112).

Decomposition of 1-*Diazobutane.*—Copper powder (2 g.) was added to a solution of 1-diazobutane (3·5 g.) in ether (200 c.c.) in a flask connected to a liquid-air trap. A rapid evolution of gas took place and the reaction was complete in 10 minutes. The trap contained but-1-ene, b. p. −6°, and ether. The solution left in the flask was filtered and evaporated to dryness, leaving only a trace of oily residue.

Decomposition of 1-*Diazopentane.*—Copper powder (0·5 g.) was added to a solution of 1-diazopentane (1 g.) in ether (40 c.c.); there was an immediate reaction. The solution was filtered and evaporated, and the residue was distilled under reduced pressure to give *valeraldazine* (0·3 g.), b. p. 100°/2·5 mm (Found : C, 71·4; H, 11·7; N, 16·5. $C_{10}H_{20}N_2$ requires C, 71·4; H, 11·9; N, 16·7%). On treatment with Brady's reagent, valeraldehyde 2 : 4-dinitrophenylhydrazone, m. p. 98°, was obtained (Found : C, 50·0; H, 5·1; N, 20·8. Calc. for $C_{11}H_{14}O_4N_4$: C, 49·6; H, 5·3; N, 21·0%).

Decomposition of 1-*Diazoheptane.*—Anhydrous copper sulphate (0·1 g.) was added to a solution of 1-diazopheptane (5 g.) in ether (350 c.c.) (Chao-Lun Tseng and Teh-Sen Ho, *J. Chinese Chem. Soc.*, 1936, **4**, 335). There was an immediate and violent effervescence, and the solution became black. It was treated with charcoal and filtered, and the filtrate evaporated. The residue (4·8 g.) was distilled, giving heptan-1-ol (0·5 g.), b. p. 175—180° (Found : C, 72·5; H, 13·2. Calc. for $C_7H_{16}O$: C, 72·4; H, 13·8%), and heptaldazine (3·5 g.), b. p. 158—164°/21 mm. (Found : C, 74·5; H, 12·2; N, 12·3. Calc. for $C_{14}H_{28}N_2$: C· 75·0; H, 12·5; N, 12·5%), which on treatment with Brady's reagent gave heptaldehyde 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 107·5°. In addition a small fraction boiled at 180—185°/10 mm. and deposited crystals on storage; after recrystallisation from ether these had m. p. 90° but could not be identified (Found : C, 68·7; H, 10·7; N, 11·1%).

Interpolymers from Diazomethane and Diazoethane.—Ethereal solutions containing varying proportions of diazomethane and diazoethane were treated with copper powder (2 g.) and left until colourless. The solutions were filtered; the copper residues were extracted with boiling toluene, and the extract evaporated to dryness to isolate the ether-insoluble polymer fractions; the filtered ethereal solutions were also evaporated, giving the ether-soluble fractions. The following results were obtained :

					Products,					
					ether-soluble,			ether-insoluble,		
No.	Diazo-methane, g.	Diazo-ethane, g.	Ether, c.c.	Diazo-ethane, moles %.	yield, g.	m. p.	*M.*	yield, g.	m. p.	*M.*
1	7·3	0·3	700	3·0	0·5	viscous liquids	—	0·5	115°	3800
2	6·2	0·6	635	6·7	0·5		—	0·3	108	3900
3	3·1	2·9	638	41·2	1·3	70°	4000	nil	—	—
4	0·7	5·8	640	86·3	1·7	85	5000	nil	—	—

The ether-soluble fractions from Nos. 1 and 2 were also soluble in alcohol and contained large quantities of nitrogen; they were not investigated further. The two ether-insoluble fractions were white brittle waxes, insoluble in cold hydrocarbons, and showed *X*-ray diffraction patterns typical of crystalline compounds; their infra-red absorption spectra are shown in the figure. The ether-soluble fractions Nos. 3 and 4 were amorphous glasses, very similar to unmodified polyethylidene, soluble in cold hydrocarbons but not in alcohol.

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