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THERMAL AND ELECTRON-IMPACT INDUCED 1,4 ARYL MIGRATION FROM PHOSPHORUS TO CARBON

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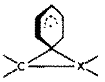
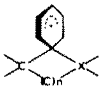
Abstract—1,4-Migration of a phenyl group has been observed when 9-phenyl-10-t-butyl-9,10-dihydro-9-phospha-anthracene **7** was subjected to pyrolysis at 500° or to electron-impact. The reaction is proposed to occur via 1-phosphabicyclo[2.2.1]heptyl-type species such as **10**.

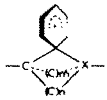
The vicinal migration of a phenyl group via radicals of type **I** is well known for X = C[1], less common for X = N[2] and X = O[3] and has not been found for X = Si[4]. Analogous rearrangements via **II** (n = 2 or 3) for X = C[5], O[6] and Si[7] have been reported occasionally. The migration of a phenyl group across the cyclohexane ring via bicyclo[2.2.1]heptyl species **III** has also been achieved.[8]



I



II

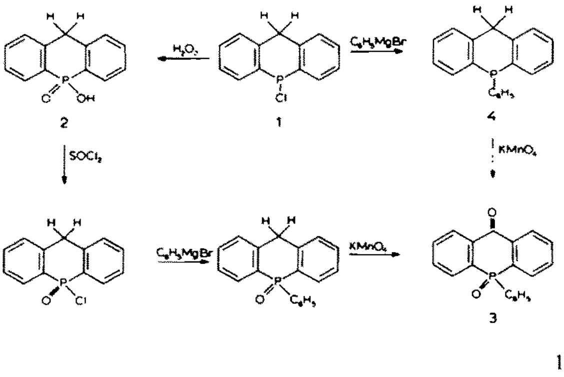


III

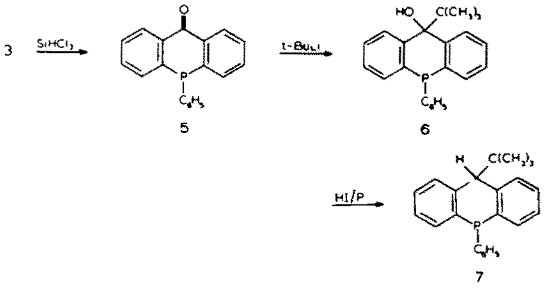
This radical rearrangement is interesting because the analogous cationic reaction is unknown.[9] Normally cationic rearrangements have a considerably stronger driving force[10,11] and may lead to extensive migrations in cases where the corresponding radical processes show none. Moreover migration of a phenyl group from phosphorus to carbon or vice versa has, to our knowledge, never been observed. We want to report the thermal and electron-impact induced migration of the phenyl group starting from 9-phenyl-10-t-butyl-9,10-dihydro-9-phospha-anthracene **7** from phosphorus to carbon-10, a 1,4 aryl migration.

Synthesis of 7

The synthesis of **7** started from 9-chloro-9,10-dihydro-9-phospha-anthracene **1** or from the corresponding phosphinic acid **2**.[12] **3** was obtained by treatment of **2** with thionyl chloride followed by reaction with phenylmagnesium bromide and oxidation with potassium permanganate or, in better yield, by reacting **1** with phenylmagnesium bromide yielding 9-phenyl-9,10-dihydro-9-phospha-anthracene **4** which was oxidized with potassium permanganate.



3 was selectively reduced by trichlorosilane to the ketophosphine **5**,[13] which was reacted with t-butyl-lithium to give the alcohol **6** in low yield. Reducing this alcohol with hydrogen iodide and red phosphorus we obtained 9-phenyl-10-t-butyl-9,10-dihydro-9-phospha-anthracene **7**.



Mass spectrum of 7

The molecular ion (*m/e* 330) has two important modes of cleavage. The first is the loss of isobutene by McLafferty rearrangement to the fragment ion at *m/e* 274. After scrambling of the hydrogen atoms the ion expels benzene and delivers ion **a** at *m/e* 196. Ion **a**, the radical cation of 9-phospha-anthracene **8**$^{+\cdot}$ undergoes a fragmentation analogous to that of 2-phosphanaphthalene,[14] namely the loss of C_2H_2, of P, or after migration of the phenyl group of HCP, resulting in fragment ions at *m/e* 170, 165 and 152, respectively.

The second mode of cleavage of the molecular ion is the loss of a t-butyl radical to give the fragment ion at *m/e* 273 (base peak), which undergoes transannular aryl migration followed by expulsion of a hydrogen atom to fragment ion **b** at *m/e* 272. The formation of fragment ion **b** (an odd electron system) from *m/e* 273 (an even electron system) is probably due to the stability of fragment ion **b** = **9**$^{+\cdot}$, derived from the aromatic 10-phenyl-9-phospha-anthracene **9**. It is therefore conceivable that fragment ion **a** is also formed from the ion of *m/e* 273. Fragment ion **b** then expels either a phosphorus atom to give an ion of *m/e* 241 followed by loss of H_2 to give an ion of *m/e* 239, or H_2 to give an ion of *m/e* 270 followed by loss of phosphorus atom to give the ion of *m/e* 239, which is in qualitative accordance with the behaviour of **b**$^{+\cdot}$ formed on direct electron-impact from **9**.[15]

Pyrolysis of 7

The facile loss of a t-butyl radical from **7**$^{+\cdot}$ followed by a transannular aryl migration under electron-impact encour-

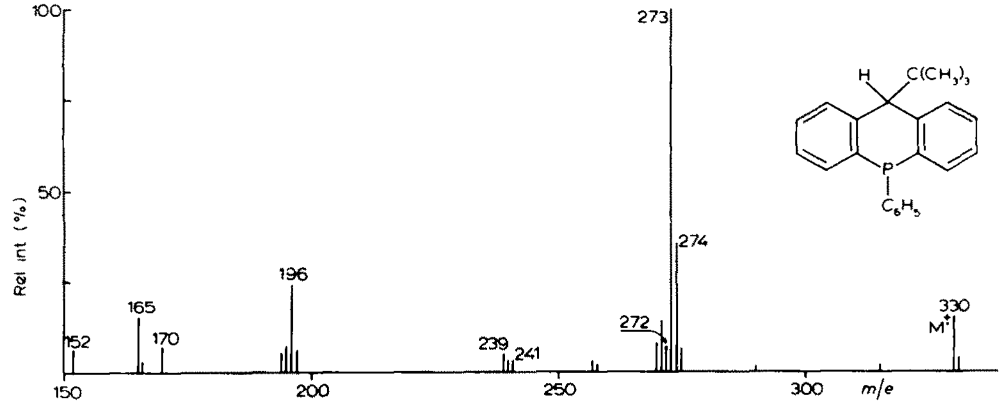
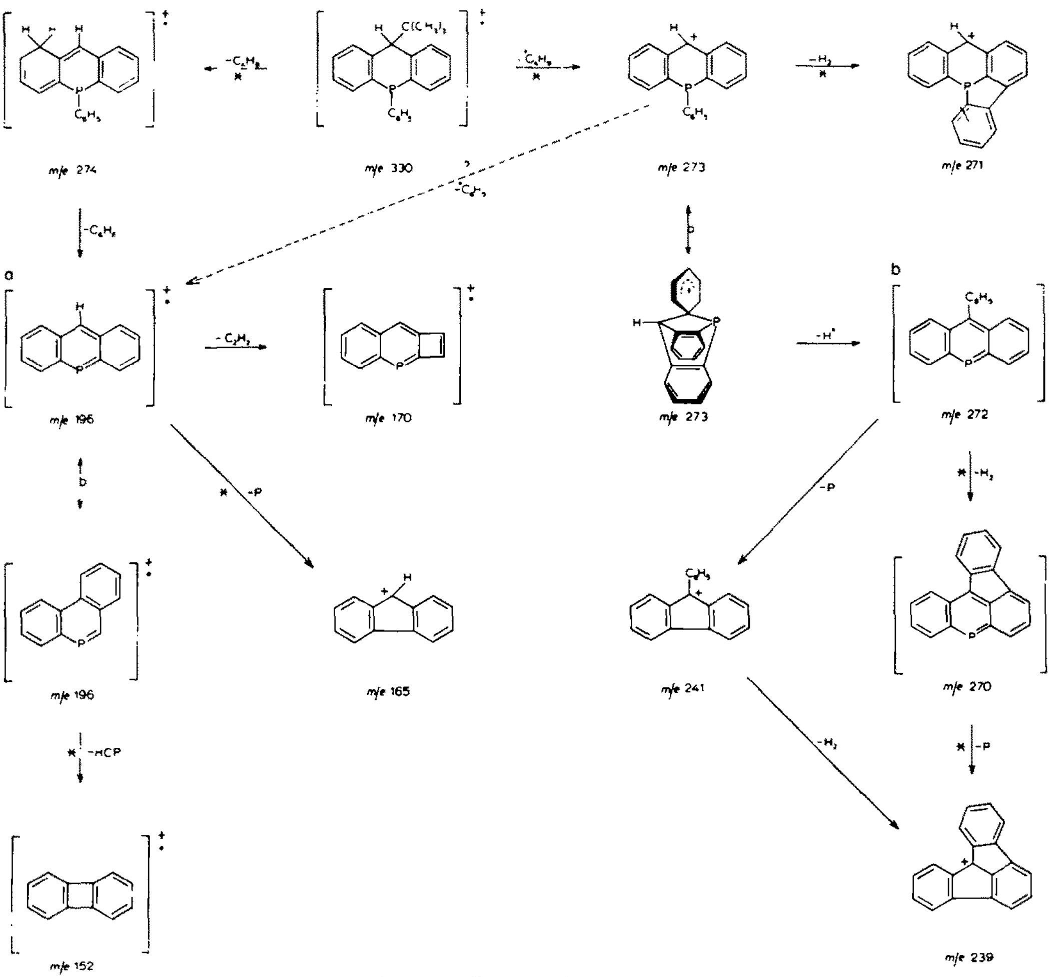


Fig. 1.



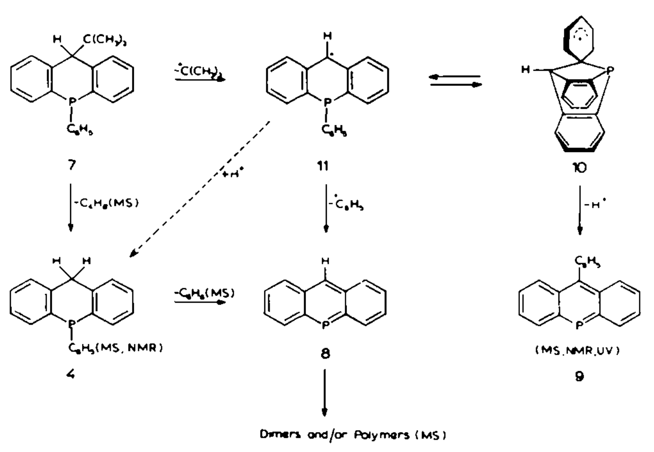
Scheme 1. Fragmentation pattern of 7

aged us to search for analogous products in the thermal reaction of **7**; compound **7** was sublimed in vacuum through a Pyrex tube at *ca.* 500°. A series of cold traps condensed the products, shown in Scheme 2 together with the proposed mechanism of their formation.

4 is probably formed by a 1,5 hydrogen shift (analogous to the McLafferty rearrangement under electron-impact) followed by a hydrogen transfer to recover the resonance energy of the benzene ring.

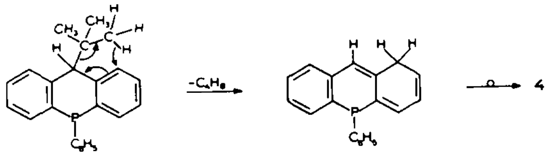
9-Phospha-anthracene **8** was not observed in most of the reactions; it is known to be thermally unstable[16] and forms a number of dimeric or disproportionated products[17-19] (Experimental). **8** could be formed in one of two ways which cannot be distinguished at present; either by cleavage of a t-butyl radical from **7** to give **11** followed by the expulsion of phenyl radical, or by further thermal elimination of benzene from **4**. Pyrolysis of **4** under the same conditions yielded **8**, which was detected by its characteristic UV spectrum.

In order to explain the formation of 10 - phenyl - 9 - phospha-anthracene **9**[20] we propose a 1,4 aryl migration via the 1-phosphabicyclo[2.2.1]heptyl species **10**, leaving

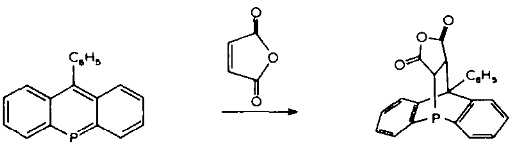


$(CH_3)_3CC(CH_3)_3\,(MS) + C_6H_5C(CH_3)_3\,(MS) + C_4H_{10}(MS)$

Scheme 2. Prolysis of 7 and detection method of the products



open the question whether **10** is an intermediate or a transition state. The yield of **9** was 15–20% according to UV measurements; 15% Diels-Alder adduct **12** was isolated after reaction with maleic anhydride.



9 12

The other products, 2,2,3,3-tetramethylbutane, t-butylbenzene, benzene, isobutane and isobutene were detected and identified by standard mass spectroscopic procedures; they are presumably formed from phenyl and t-butyl radicals, thus confirming the proposed reaction pathways.

The relatively high yield of 20% of **9**, compared to 2% in the transannular 1,4 aryl migration in the 1,1-diphenylcyclohexyl radical,[8] is presumably caused mainly by two factors. In the first place, as pointed out by Wilt,[8] the 1,1-diphenylcyclohexyl radical is effectively scavenged by tributyltin hydride under the reaction conditions; **11** is not consumed in similarly efficient competing reactions. Secondly, the geometric situation in **11** may be more favourable than in the cyclohexyl case; in particular the cyclohexyl radical has to assume the less favourable boat conformation before the rearrangement can occur, whereas **11** is fixed in a rigid boat conformation.

EXPERIMENTAL

M.ps are uncorrected. Mass spectra were recorded on a Varian MAT CH-5 single focussing mass spectrometer with electron impact at 70 eV. Samples were introduced via the direct insertion probe under nitrogen (solids) or vacuum (liquids). ^1H NMR spectra were recorded with a Varian A-60 spectrometer. Chemical shifts are given in δ (ppm) from internal TMS. The IR spectra were recorded with a Perkin-Elmer 237 and the UV spectra with a Perkin-Elmer spectrophotometer, model 137. Elemental analysis were performed under supervision of Mr. W. J. Buis at the Micro-analytical Department of the Institute for Organic Chemistry TNO, Utrecht, The Netherlands.

9 - *Phenyl* - 9,10 - *dihydro* - 9 - *phospha-anthracene* - 10 - *one* - 9 - *oxide* 3

(a) A suspension of 9 - hydroxy - 9,10 - dihydro - 9 - phospha-anthracene - 9 - oxide **2**[12] (8·3 mmol), thionyl chloride (45 mmol) and 7·5 ml of dry $CHCl_3$ was refluxed under N_2 for 1 hr. The solution was evaporated *in vacuo* and the residue was dissolved in 50 ml of dry ether. Phenylmagnesium bromide (10 mmol) in 100 ml of dry ether was added at −15° to this solution and after refluxing for 1 hr. 2N HCl (25 ml) was added. The ethereal layer was separated, dried and evaporated to dryness. A stirred suspension of this residue (1·4 g) in water (50 ml) was kept at 70–80° and powdered potassium permanganate (1·5 g) was added in *ca.* 0·25 g portions in 5 min.[21] The mixture was boiled for 2 min, cooled and extracted with $CHCl_3$ (50 ml). Removal of the solvent gave a residue which on recrystallization (EtOH) afforded **3**[13] (560 mg, 22%), m.p. 220–222°.[13] (Found: C, 74·95; H, 4·46; P, 10·28; $C_{19}H_{13}PO_2$ (M = 304·26), requires: C, 75·00; H, 4·31; P. 10·18%). IR (KBr) ν_{max} in cm^{-1}: 1670 (s) C=O, 1200 (s) P=O. NMR (D_6-DMSO): 8·55–8·13 (m, 2, aryl protons), 8·13–7·67 (m, 6, aryl protons), 7·67–7·27 (m, 5, aryl protons). Mass spectrum *m/e* (%): 304 (100), 303 (80), 275 (12), 229 (84), 228 (35), 227 (49), 211 (37), 183 (14), 180 (26), 152 (39).

(b) A stirred suspension of **4** (19·7 mmol) in water (200 ml) was kept at 70–80° and powdered potassium permanganate (6·0 g) was added in portions in about 15 min. The mixture was worked up in the same way yielding after crystallization **3** (4·35 g, 73%).

9 - *Phenyl* - 9,10 - *dihydro* - 9 - *phospha-anthracene* 4

A solution of phenylmagnesium bromide (50 mmol) in 300 ml of dry ether, was added under nitrogen at −70° in 2 hr to a solution of 9 - chloro - 9,10 - dihydro - 9 - phospha-anthracene **1** (18 mmol). After stirring overnight at room temp a few drops of dry MeOH were added to the red solution, which decolourized immediately; the solution was evaporated *in vacuo*. Distillation of the residue (140°/0·01 mm) yielded **4** (3·7 g, 75%), a colourless liquid. (Found: C, 83·16; H, 5·66; P, 10·78. $C_{19}H_{15}P$ (M = 274·28), requires: C, 83·19; H, 5·51; P, 11·29%). NMR ($CDCl_3$): 7·76–7·02 (m, 13, aryl protons), 3·93 (d, 1, methine proton H_A, J_{AB} = 17 Hz), 3·70 (d, 1, methine proton H_B, J_{AB} = 17 Hz). Mass spectrum *m/e* (%): 274 (100), 273 (15), 230 (15), 196 (70), 165 (40), 154 (75).

9 - *Phenyl* - 9,10 - *dihydro* - 9 - *phospha-anthracene* - 10 - *one* 5

A mixture of **3** (14·8 mmol), $SiHCl_3$ (25 mmol) and 200 ml of dry benzene was refluxed under N_2 for 18 hr, cooled and stirred with 50 ml oxygen-free 1N NaOH and water (20 ml). The benzene layer was separated under N_2, dried and evaporated *in vacuo*. The residue was crystallized under N_2 from ethanol yielding **5** (3·1 g, 73%), m.p. 141–142°.[13] (Found: C, 79·09; H, 4·61; P, 10·63. $C_{19}H_{13}PO$ (M = 288·28), requires: C, 79·16; H, 4·54; P, 10·74%). IR (KBr) ν_{max} in cm^{-1}: 1645 (s) C=O. NMR ($CDCl_3$): 8·70–8·37 (m, 2, aryl protons), 7·63–7·20 (m, 11, aryl protons). Mass spectrum *m/e* (%): 288 (100), 259 (14), 228 (28), 211 (25), 183 (27).

9 - *Phenyl* - 10 - *t* - *butyl* - 10 - *hydroxy* - 9,10 - *dihydro* - 9 - *phospha-anthracene* **6**

A solution of **5** (3·6 mmol) in 50 ml of dry benzene was added under N_2 to a mixture of 30 ml of dry benzene and t-BuLi (7 mmol) in 5 ml of n-pentane at 5°. After 3 days, oxygen-free H_2O (17 ml) was added. The benzene layer was separated, dried and evaporated *in vacuo*. The residue was purified by TLC (toluene) and crystallization (ether) yielding **6** (210 mg, 17%), m.p. 179–183°. NMR ($CDCl_3$): 8·07–7·80 (m, 2, aryl protons), 7·56–6·83 (m, 11, aryl protons), 2·22 (s, 1, –OH), 0·90 (s, 9, t-butyl protons). Mass spectrum *m/e* (%): 346 (5), 289 (100), 288 (34), 242 (12), 241 (21), 228 (12), 211 (22), 183 (26).

9 - *Phenyl* - 10 - *t* - *butyl* - 9,10 - *dihydro* - 9 - *phospha-anthracene* **7**

A mixture of **6** (0·65 mmol), red phosphorus (3 g) and hydrogen iodide (10 ml, 57%) was heated at 140° for 2 days under N_2, cooled extracted with toluene (50 ml) and $CHCl_3$ (25 ml). The combined extracts were evaporated to dryness. The residue was crystallized from ethanol yielding **7** (51 mg, 24%), m.p. 200–201°. (Found: C, 82·74; H, 7·17; P, 9·49. $C_{23}H_{23}P$ (M = 330·38), requires: C, 83·63; H, 6·97; P, 9·39%). NMR ($CDCl_3$): 7·63–6·76 (m, 13, aryl protons), 4·00 (s, 1, methine proton), 0·91 (s, 9, t-butyl protons).

Pyrolysis of 7

7 (0·13 mmol) was brought into vacuum vessel A (Fig. 2) and sublimed through a Pyrex tube at *ca.* 500°C. The solid products condensed in tube B, the gaseous products in vessel C which was cooled to −196°. Tube B was sealed off at a and b and vessel C at c.

In one run tube B was connected with a quartz cell, dry THF was added and the UV spectrum of the yellow solution was recorded and indicated the formation of **9** (15–20% from extinction coefficient[20]). Adding maleic anhydride (0·3 mmol) in dry THF (5 ml) decolourized the solution and after one day the vessel was opened and the solvent was evaporated at 60°/0·1 mm leaving a residue (38 mg) which after purification (TLC) yielded **12** (8·3 mg, 15%), m.p. 252–256 (dec). The NMR and IR spectrum were identical with the product obtained in the direct Diels-Alder reaction between pure **9** and maleic anhydride.

In a second run the disconnected tube B was joined to the high vacuum line and the residue sublimed at 160°/0·01 mm. The residue of the sublimation was sealed off at d and was introduced under N_2 into the direct inlet system of the mass spectrometer. It consisted of dimers of the type $[\mathbf{8}]_2$ and $[\mathbf{8} + H]_2$ as shown by the mass spectrum *m/e* (%): 394 (0·2), 392 (0·3), 390 (0·2), 197 (16), 196 (100), 195 (8), 194 (16), 170 (11), 166 (7), 165 (38), 163 (5), 152 (12), 151 (5); presumably, other polymers of **8** were also present.

NMR ($CDCl_3$) showed that the sublimate consisted of **9** (two protons at 8·7–8·4 ppm) and **4** (AB system of methine protons at 3·93 and 3·70).

Vessel C was connected to the direct inlet system of the mass spectrometer. Mass spectrum *m/e* (%): 134 (0·3), 120 (0·1), 119 (1·4), 99 (0·6), 91 (2), 79 (3), 78 (36), 77 (9), 58 (1·7), 57 (15), 56 (70), 55 (27), 52 (9), 51 (13), 50 (13), 44 (1·5), 43 (28), 42 (14), 41 (100), 39 (58). This indicates a mixture of isobutene (75·9%), isobutane (9·1%), benzene (13·1%), 2,2,3,3-tetramethylbutane (1·6%) and t-butylbenzene (0·3%).[22]

10 - *Phenyl* - 9,10 - *dihydro* - 9,10 - *ethano* - 9 - *phospha-anthracene* - 11,12 - *dicarboxylic anhydride* **12**

A solution of 10 - phenyl - 9 - phospha-anthracene **9** (1·27 mmol) in 23 ml of dry toluene was added to a solution ofmaleic anhydride (2·3 mmol) in 5 ml of dry THF in a vacuum-sealed vessel. The yellow colour disappeared within 2 min. After opening the vessel and removal of the solvent the crude product was crystallized from $CHCl_3$ yielding **12** (400 mg, 85%), m.p. 259–262° (dec). (Found: C, 74·66; H, 4·24; P, 8·17: $C_{23}H_{15}PO_3$ (M = 370·32), requires: C, 74·59; H, 4·08; P, 8·36%). IR (KBr) ν_{max} in cm^{-1}: 1770 (s), 1845 (s), anhydride. NMR ($CDCl_3$): 8·00–7·10 (m, 12, aryl protons), 6·58–6·31 (m, 1, aryl proton), 4·35 (dd, 1, H_A, J_{AB} = 10 Hz, $^3J_{P-H}$ = 1·5 Hz), 3·49 (dd, 1, H_B, J_{AB} = 10 Hz, $^2J_{P-H}$ = 2·5 Hz). Mass spectrum *m/e* (%): 370 (0·3), 272 (100), 271 (29), 270 (20), 239 (10), 135 (11).

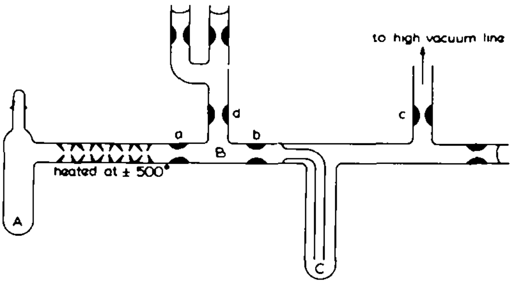


Fig. 2.

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