[5] *G.Schetty*, Chimia *18*, 244 (1964).
[6] *E.J.Haselbach*, Dissertation Nr. 3969, ETH Zürich, 1967.
[7] *G.Schetty & W.Kuster*, Helv. *44*, 2193 (1961); *G.Schetty*, Helv. *45*, 1026 (1962); *45*, 1095 (1962); *46*, 1132 (1963); *47*, 921 (1964).
[8] *H.C.Mez*, Z. El.-Chem. *72*, 389 (1968).
[9] *C.J.Brown*, Acta cryst. *21*, 146 (1966).
[10] *C.J.Brown*, Acta cryst. *21*, 153 (1966).
[11] *H.Hope*, Acta cryst. *25*, 1849 (1969).
[12] *E.L.Eichhom*, Acta cryst. *12*, 746 (1959).
[13] *A.G.Amit & H.Hope*, Acta chem. scand. *20*, 835 (1966).
[14] *C.T.Grainger & J.F.McConell*, Acta cryst. *25*, 1962 (1969).
[15] *Sun'Ichiro Ooi, D.Carter & Q.Fernando*, Chem. Commun. *1967*, 1301.
[16] *J.A.J.Jarvis*, Acta cryst. *14*, 961 (1961).
[17] *A.Burawoy, A.G.Salem & A.R.Thompson*, J. chem. Soc. *1952*, 4793; *1953*, 1443.
[18] *A.H.Berrie, P.Hampson, S.W.Longworth & A.Mathias*, J. chem. Soc. *1968*, 1308.
[19] *M. V. Sidgwick*, Ann. Reports *31*, 40 (1934).
[20] *H.Zollinger*, «Azo and Diazo Chemistry», S.322, Interscience Publisher Inc., New York; Interscience Publisher Ltd., London 1961.
[21] *Heinosuke Yasuda & Hiroshi Midorikava*, J. org. Chemistry *31*, 1722 (1966); *V.N.Drozd, V.J.Sějcěnko & V.N.Postnov*, Izvest. Akad. Nauk SSSR, Ser. khim. *1965*, 1888; *F.A.Snavely & C.H.Yoder*, J. org. Chemistry *33*, 513 (1968).
[22] *V.Bekárek, K.Rothschein, P.Vetěsnik & M.Večeřa*, Tetrahedron Letters *1968*, 3711; *W.R.Brode, I.L.Seldin, P.E.Spoerri & G.M.Wyman*, J. Amer. chem. Soc. *77*, 2762 (1955); *J.N.Ospenson*, Acta chem. scand. *4*, 1351 (1950); *5*, 491 (1951).
[23] *G.Schetty*, Helv. *50*, 1039 (1967).
[24] *V.Prelog & P.Wieland*, Helv. *27*, 1127 (1944).
[25] *D.Felix & A.Eschenmoser*, Angew. Chem. *80*, 197 (1968).
[26] *M.Raban, F.B.Jones & G.W.J.Kenney, jr.*, Tetrahedron Letters *1968*, Nr.49, 5055.
[27] *J.C.Speakman*, Acta cryst. *6*, 784 (1953).
[28] *J.D.Bell, H.C.Freeman & Ailsa M.Wood*, Chem. Commun. *1969*, 1441.
[29] *A.H.Clark & A.Haaland*, Chem. Commun. *1969*, 912.
[30] *H.C.Freeman, J.C.Schoone & J.G.Sime*, Acta cryst. *18*, 831 (1965).
[31] *G.Schetty*, Helv. *51*, 505 (1968); *G.Schetty & M.Eder*, Helv. *51*, 1882 (1968).
[32] *G.Schetty*, Helv. *52*, 1016 (1969).
[33] *P.Weselsky & R.Benedikt*, Liebigs Ann. Chem. *196*, 339 (1878).

---

172. Thermal Interconversion of Phenylcarbene and Tropylidene

Preliminary communication[1])

by **C. Wentrup** and **K. Wilczek**

Institut de Chimie Organique, Université de Lausanne

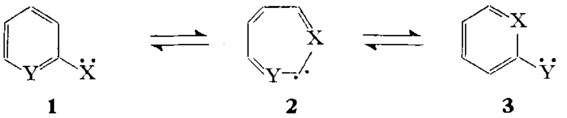
(22. VII. 70)

Summary. Phenylcarbene and tropylidene interconvert in the gas-phase, as evidenced by the formation of stilbene and heptafulvalene (**5**) from both at 300°. Heptafulvalene itself rearranges to stilbene and anthracene above 500°. Phenylcarbene, but not tropylidene, undergoes ring contraction to fulvenallene (**9**) at 900°. Formation of fluorene from diphenylcarbene involves a complete ring expansion to 2-phenyltropylidene (**14**), and subsequent ring contraction to 2-biphenylylcarbene (**15**).

---

[1]) A detailed paper will probably be published in Helv.

The gas-phase reactions of aromatic nitrenes and carbenes led us to conclude that phenylnitrene (**1a**) [1] [2], 2-pyridylcarbene (**1b**) [1] and 2-pyridylnitrene (**1c**) [3] undergo reversible ring expansion to azatropylidenes (**2a–c**).

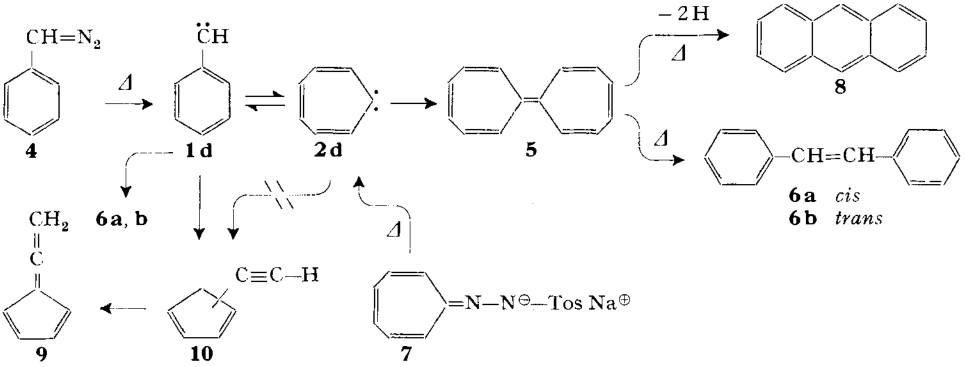


a: X = N, Y = CH
b: X = CH, Y = N
c: X = N, Y = N
d: X = CH, Y = CH

The phenylnitrene-2-pyridylcarbene equilibrium [1] [2] was strongly in favour of phenylnitrene, and this led us to predict [3] that phenylcarbene (**1d**) and tropylidene (**2d**) should form a similar pair in which phenylcarbene is favoured. Allowing for a sufficient number of interconversions of **1d** and **2d**, carbon scrambling in phenylcarbene should result.

Phenyl diazomethane (**4**) was generated by pyrolysis of the dry sodium salt of benzaldehyde tosylhydrazone [4] at 90°; the vapour was led directly into the pyrolysis tube[2]). At 300° a 45% yield of a mixture of heptafulvalene (**5**), *cis*-stilbene (**6a**) and *trans*-stilbene (**6b**) (5:4:6) was obtained[3]). Pyrolysis of the dry sodium salt of tropene tosylhydrazone (**7**) [8] under the same conditions also gave a mixture of **5**, **6a** and **6b** (10:1:4; total yield ~4%). The yields were lower in this case due to extensive decomposition with tar-formation before entrance into the pyrolysis tube. In addition, a 2% yield of benzene was obtained[4]).

Pyrolysis of either **4** or **7** above 500° gave *cis*- and *trans*-stilbene and anthracene (**8**); at 900° in the ratio 1:3:1 (total yield 40% from **4**, and 8% from **7**). The gas chromatograms of the products from **4** and **7**, including minor, unidentified peaks, were very similar. Pure heptafulvalene (**5**) [8] at 900° gave the same products in the ratio 1:4:5. It did not give any stilbene or anthracene at 300°; instead it gave other, unidentified products which were also formed by gas chromatography at an injection port temperature of 200°. The resulting peaks serve to identify heptafulvalene by



---

[2]) All pyrolyses were carried out in a 30 cm quartz or pyrex tube at ⩽ 10^{-3} Torr.

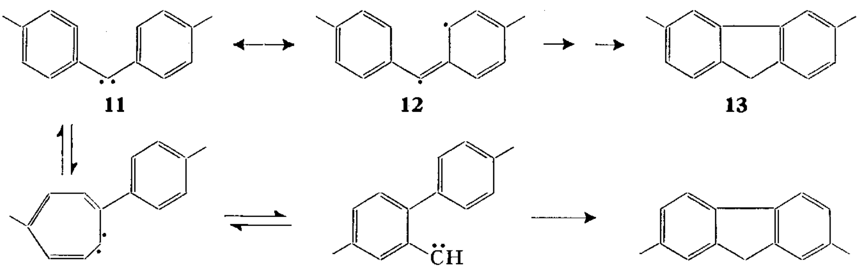
[3]) This reaction was recently reported by two other groups of workers [5] [6], but evidence for the reversibility of the ring expansion **1d** → **2d** was lacking [5], and it was assumed that tropylidene would be stable relative to phenylcarbene [5]. It is not evident that this should be so; for instance, dibenzo[*b,f*]tropylidene is known to be much more reactive than diphenylcarbene, apparently adding instantaneously to olefins at 77 K [7].

vapour phase chromatography. However, at 600° **5** gave a 70% yield of **6a**, **6b** and **8** (1:5:22). Stilbene was stable to pyrolysis at 900°. These results indicate that heptafulvalene is the source of anthracene and some of the stilbene obtained from **4** or **7** above ca. 500°, but heptafulvalene cannot be the source of the stilbene obtained from **7** at 300°. Accordingly, the results are best explained in terms of thermal interconversion of phenylcarbene (**1d**) and tropylidene (**2d**). The apparatus used by *Jones et al.* [5] (pyrolysis at 250° in a stream of N_2 over glass beads (cf. ref. [6], footnote [12])) apparently favoured dimerisation of **2d** before it could rearrange to **1d**.

The rearrangement of heptafulvalene to stilbene may be rationalised in terms of a double cycloheptatriene-norcaradiene valence tautomerisation, with subsequent opening of the three-membered ring and hydrogen migration.

Pyrolysis of **4** at 900° also gave a liquid product (7–20%) which after distillation was analysed by NMR., IR. and vapour phase chromatography, and found to consist of benzene, toluene and fulvenallene (**9**) (1:1:2) together with a trace of the primary ring contraction product, **10**[5]). Benzene and toluene were also formed by pyrolysis of **7** at 900°, but only a trace of fulvenallene (**9**) was present. Thus, as in the isosteric phenylnitrene [1] [9], ring contraction does not proceed *via* the ring-expanded carbene **2d**, but rather *via* 'hot' phenylcarbene (**1d**). Formation of benzene and toluene is analogous to the reactions of phenyl azide [9].

We have previously used the formation of carbazole from 2-biphenylylnitrene as an intramolecular trap for the phenylnitrenes formed by isomerisation of 2-pyridylcarbenes [1]. In order to gain more evidence for the carbene interconversion **1d** $\rightleftarrows$ **2d**, we have now used the formation of fluorene in the gas-phase pyrolysis of diphenyl diazomethane [10] as a trap for 2-biphenylylcarbene, supposedly formed by rearrangement of phenyltropylidene. Fluorene could be formed from diphenylcarbene (**11**) by either of two mechanisms which may be distinguished by methyl-labelling: (*a*) *via* the mesomer **12**, in which case the fluorene **13** would be formed; or (*b*) by phenylcarbene-tropylidene interconversion *via* **14** and **15**. In the latter case skeletal rearrangement to **16** would be observed.



Pyrolysis of *p,p'*-ditolyl diazomethane (precursor of **11**) at 500–800° gave a 75% yield of 2,7-dimethylfluorene (**16**) which was identified and distinguished from 3,6-

---

[4] Products were identified by NMR., mass spectrometry, and vapour phase chromatography (5% silicone oil 550 on Chromosorb G; N_2 carrier gas).

[5] *Hedaya et al.* [6] reported this ring contraction recently, and characterised the products **9** and **10**.

dimethylfluorene (**13**) by the m.p. (114–115°; lit. [11] for **16**: 114–115°; lit. [12] for **13**: 131°) and the NMR. spectrum[6][7]) (60 MHz (CCl_4)): δ 7.50 (*d*, $J = 7.65 \pm 0.10$ Hz; H–C4), 7.20 (*s*, H–C1), 7.04 (*d*, $J = 7.65$; H–C3), 3.68 (*s*, CH_2), 2.36 (*s*, CH_3). In addition, 11% *p*-tolunitrile (presumably formed by pyrolysis [14] of the tetramethylbenzophenone azine [15] corresponding to **11**) and a trace of tetratolylethylene (formed by dimerisation of **11** or pyrolysis [14] of the azine) were obtained.

The result demonstrates that phenylcarbene-tropylidene interconversion does take place, and that the equilibrium can be displaced in favour of phenylcarbene when this is intramolecularly trapped. Of the two carbenes **11** and **15**, **11** must be the more stable due to better orbital overlap [16].

The bombardment of benzene with high-energy carbon atoms leads to toluene and cycloheptatriene, presumably formed from phenylcarbene and tropylidene, respectively [17]. The distribution of radioactivity in the toluene obtained from benzene and ^{14}C-atoms decreases in the order $CH_3 \gg$ C-1 > C-2 > C-3 > C-4 [18]. This order is now explicable if it is assumed that a series of phenylcarbene-tropylidene interconversions takes place under conditions of high energy.

The tropylium ion is the commonly accepted structure for the $C_7H_7^+$ ions formed by mass spectrometry of benzylic compounds [19], but in some cases evidence for benzyl ions has been advanced [20]. The mass spectrum of doubly labelled toluene indicates the formation of a tropylium ion in which all carbon atoms have been randomised [21]. It may be that a series of benzyl-norcaradienyl-tropylium ion interconversions similar to the above mechanism is involved in this randomisation.

We thank the *Fonds National Suisse de la Recherche Scientifique* for financial assistance to Professor *H. Dahn*, whose support of this work is highly appreciated.

BIBLIOGRAPHY

[1] *W. D. Crow & C. Wentrup*, Tetrahedron Letters *1968*, 6149.
[2] *C. Wentrup*, Chem. Commun. *1969*, 1386.
[3] *W. D. Crow & C. Wentrup*, Chem. Commun. *1969*, 1387.
[4] *G. M. Kaufman, J. A. Smith, G. G. Vander Stouw & H. Schechter*, J. Amer. chem. Soc. *87*, 935 (1965).
[5] *R. C. Joines, A. B. Turner & W. M. Jones*, J. Amer. chem. Soc. *91*, 7754 (1969).
[6] *P. Schissel, M. E. Kent, D. J. McAdoo & E. Hedaya*, J. Amer. chem. Soc. *92*, 2147 (1970).
[7] *Y. Yamamoto, I. Moritani, Y. Maeda & S. Murahashi*, Tetrahedron *26*, 251 (1970).
[8] *W. M. Jones & C. L. Ennis*, J. Amer. chem. Soc. *91*, 6391 (1969).
[9] *W. D. Crow & C. Wentrup*, Tetrahedron Letters *1967*, 4379; *Ibid. 1968*, 5569.
[10] *F. O. Rice & J. D. Michaelsen*, J. physic. Chemistry *66*, 1535 (1962).
[11] *L. Mascarelli & B. Longo*, Gazz. chim. ital. *71*, 289 (1941).
[12] *L. Chardonnens & A. Würmli*, Helv. *29*, 922 (1946).
[13] *K. D. Bartle & D. W. Jones*, J. molec. Structure *1*, 131 (1967–1968).
[14] *N. P. Buu-Hoi & G. Saint-Ruf*, Bull. Soc. chim. France *1970*, 343.
[15] *D. Bethell, A. R. Newall, G. Stevens & D. Whittaker*, J. chem. Soc. (B) *1969*, 749.

---

[6]) We are indebted to Professor *L. Chardonnens*, Université de Fribourg, for providing reference spectra of **13** and **16**.

[7]) The NMR. spectrum of **16** is in excellent agreement with calculated values based on the analysis of the NMR. spectrum of fluorene [13], and therefore confirms the assignment of chemical shifts in fluorene chosen by *Bartle & Jones* [13].

[16] Cf. *R.W.Murray, A.M.Trozzolo, E.Wasserman & W.A.Yager,* J. Amer. chem. Soc. *84,* 3213 (1962); *A.M.Trozzolo, R.W.Murray & E.Wasserman, ibid. 84,* 4990 (1962); *R.Hoffmann, G.D.Zeiss & G.W.Van Dine, ibid. 90,* 1485 (1968).

[17] *R.L.Williams & A.F.Voigt,* J. physic. Chemistry *73,* 2538 (1969); *H.M.Pohlit, Tz-Hong Lin, W.Erwin & R.M.Lemmon,* J. Amer. chem. Soc. *91,* 5425 (1969).

[18] *R.Visser, C.R.Redvanly, F.L.J.Sixma & A.P.Wolf,* Rec. Trav. chim. Pays-Bas *80,* 533 (1961).

[19] *S.Meyerson, H.Hart & L.C.Leitch,* J. Amer. chem. Soc. *90,* 3419 (1968).

[20] *S.Majeti & D.A.Lightner,* Tetrahedron Letters *1970,* 1683.

[21] *K.L.Rinehart, Jr., A.C.Buchholz, G.E.Van Lear & H.L.Canthrill,* J. Amer. chem. Soc. *90,* 2983 (1968).

---

173. Utilisation d'ylides du phosphore non stabilisés en chimie des sucres

VI. Sucres ramifiés dérivés des di-O-isopropylidène-1,2:5,6-α-D-*ribo*-et -α-D-*xylo*-hexofurannosul-3-oses

par **J. M. J. Tronchet** et **J. M. Bourgeois**

Institut de chimie pharmaceutique de l'Université, 10, boulevard d'Yvoy, 1205 Genève

(26 VI 70)

Summary. The *cis* and *trans* isomers of 3-deoxy-1,2:5,6-di-O-isopropylidene-3-C-methylthiomethylene-α-D-*xylo*- and -α-D-*ribo*-hexofuranoses have been prepared by treatment of 1,2:5,6-di-O-isopropylidene-α-D-*xylo*- and -α-D-*ribo*-hexofuran-3-uloses with methylthiomethylene-triphenylphosphorane. Configurations are assigned by NMR. A new type of ^4J is described. Hydrogenation-desulfurization of the methylthiovinylic sugars affords 3-deoxy-3-methyl sugars of the D-*allo*, D-*gulo*, and D-*galacto* series. Derivatives of 3-deoxy-3-methyl-D-lyxose and 3-deoxy-3-methyl-D-ribose are prepared by chain-shortening of derivatives of the corresponding 3-deoxy-3-methylhexoses.

La première synthèse d'un sucre ramifié insaturé, par application d'une réaction de *Wittig* à un sucre cétonique, a été réalisée par *Rosenthal & Nguyen* [1] qui ont utilisé un réactif de *Wittig* modifié, stabilisé par résonance, amenant la fixation sur le sucre d'une chaîne latérale à deux carbones.

La plupart des sucres ramifiés naturels portant une chaîne latérale monocarbonée, nous avons exploré [2] [3] l'intérêt potentiel en chimie des sucres de trois ylides du phosphore non stabilisés permettant l'introduction d'une telle chaîne: le méthylène-triphénylphosphorane, le méthoxyméthylène-triphénylphosphorane et le méthylthiométhylène-triphénylphosphorane. C'est ce dernier ylide que nous avons finalement retenu en raison de sa facilité d'emploi et des rendements généralement très élevés en sucres insaturés qu'il nous a permis d'obtenir. Nous l'avons utilisé à l'extension de la chaîne carbonée d'aldéhydo-sucres [3] [4] et à la synthèse de sucres ramifiés [5] [6]. Quelques mois après notre première communication [2], *Lance & Szarek* [7] décrivaient quelques autres exemples de réaction du méthylène-triphénylphosphorane avec des sucres carbonylés.

Les résultats que nous décrivons ci-dessous et qui ont fait l'objet d'une communication préliminaire [5] sont relatifs à l'action du méthylthiométhylène-triphénylphos-