fluorides do contain substantial amounts of radical species.

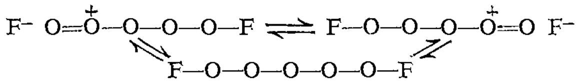
Properties. O_5F_2 is a reddish brown liquid at 90°K, similar to O_4F_2. Whereas O_4F_2 forms clusters of long needle-like crystals at 77°K,[3] O_5F_2 appears to be an oil at 77°K. It is thermally stable at 77°K; at least it decomposed to less than 0.1 mole% during 4 hr. At 90°K it decomposed readily, the final products being O_2 and F_2. At 77°K, it is practically insoluble in liquid N_2 and may be soluble to the extent of $\simeq$0.02 mole % in liquid oxygen. It is soluble at least to 0.1 wt % in CF_4 (+ $\simeq$3 wt % O_2) at 77°K. In liquid OF_2 at 65°K it is soluble in amounts of about 5 wt %. It has been characterized by its epr spectrum;[8] the spectrum is substantially different from that of O_4F_2.

O_6F_2 is dark brown in color and is a crystalline solid at 60°K; the crystal faces show a distinct *metallic* luster. At 60°K there is no noticeable thermal decomposition (*i.e.*, below 0.1 mole %) during 4.0 hr. On slow warming (*i.e.*, at a rate of $\simeq$10°K/hr) to 90°K, it decomposes quietly, forming lower oxygen fluorides and *ozone!* On fast warming to 90°K (for example, by changing the cooling bath), it explodes to O_2 and F_2. The compound is very sensitive. If quantities of over $\simeq$20 mg accumulate in the reaction vessel during preparation, it often explodes but does not *detonate* (*i.e.*, the reaction vessel is not shattered). (If similar quantities of O_3 are condensed with it they detonate, shattering the vessel as soon as the last traces of O_2 are pumped off!) O_6F_2 also explodes from the discharge of a Tesla high-frequency coil and in some cases when illuminated with a flashlight.

O_6F_2 is insoluble at 60°K in a liquid mixture of 95 vol % N_2–5 vol % O_2. In liquid oxygen at 60°K perhaps traces, *i.e.*, $\simeq$0.01 mole %, are soluble. In liquid OF_2 at 60°K it is soluble in amounts of about 5 wt %.

Attempts to produce *still higher* oxygen fluorides, under the same mild conditions (see Table I), but using a $5O_2 + F_2$ gas mixture, produced only the known oxygen fluorides and ozone; this would indicate that oxygen fluorides higher than O_6F_2 are not stable under the above conditions. This is not to say that they may not form and be sufficiently stable at 4°K.

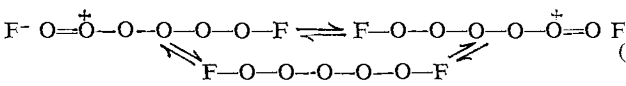
The recent infrared studies of Arkell[9] suggest that the valence bond notation for O_5F_2 and O_6F_2 be, respectively



$$F^-\ O{=}\overset{+}{O}{-}O{-}O{-}O{-}F \rightleftharpoons F{-}O{-}O{-}O{-}\overset{+}{O}{=}O\ F^- \qquad F{-}O{-}O{-}O{-}O{-}O{-}F$$

(a)

and

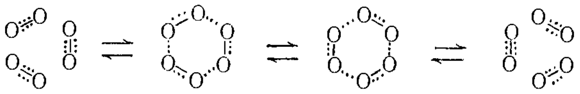


$$F^-\ O{=}\overset{+}{O}{-}O{-}O{-}O{-}O{-}F \rightleftharpoons F{-}O{-}O{-}O{-}O{-}\overset{+}{O}{=}O\ F^- \qquad F{-}O{-}O{-}O{-}O{-}O{-}O{-}F$$

(b)

We have suggested[3] that by abstracting the two F atoms (for example, with atomic hydrogen at low temperatures), the interesting cyclic O_5 and O_6 molecules, *i.e.*, new modifications of oxygen, may be produced.

According to Arkell[10] it is probable that O_6 might have a resonance, involving three electron bonds of the Pauling type, as shown below.



Jackson's[11] interatomic distances in oxygen fluorides and Arkell's force constants indicate that significant differences exist between the bond energies of the O–F and the O–O bonds. Thus, it would be of interest to determine the heats of formation of O_4F_2, O_5F_2, and O_6F_2.

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[8] A. G. Streng and A. V. Grosse, Second Quarterly Progress Report for the Office of Naval Research, Contract Nonr 3085(01), Research Institute of Temple University, Philadelphia, Pa., June 25, 1965. The measurements were made by Dr. P. H. Kasai and A. D. Kirshenbaum.

[9] A. Arkell, *J. Am. Chem. Soc.*, **87**, 4057 (1965).

[10] A. Arkell, private communication to A. G. Streng.

[11] R. H. Jackson, *J. Chem. Soc.*, 4585 (1962).

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A Memory Effect in the Generation of 2-Bicyclo[3.2.1]octyl Cation. On the Mechanism of Racemization of 2-Bicyclo[2.2.2]octyl Cation[1]

Sir:

The genetic memory effects previously observed in the ring expansions of *endo*- and *exo*-2-norbornylcarbinyl[2] and *syn*- and *anti*-2-norbornene-7-carbinyl[3] derivatives also occur in the ring expansion of 7-norbornylcarbinyl derivatives (**1**).

Rearrangements in the acetolysis of 7-norbornylcarbinyl *p*-bromobenzenesulfonate at 120° (10 mole % excess sodium acetate as buffer) produce 18.0% 2-*exo*-bicyclo[3.2.1]octyl acetate (**2**), 25.8% 2-bicyclo[2.2.2]octyl acetate (**3**), 0.84% 2-*endo*-bicyclo[3.2.1]octyl acetate (**4**) (all with Z = OAc), and 5.2% 7-methyl-7-norbornyl acetate (**7**). Also, 49.8% of unrearranged acetate is formed. The proportions of products **2**, **3**, and **4** (40.3:57.7:1.9) are very similar to if not identical with those observed in solvolyses (at lower temperatures) of either of the Wagner–Meerwein related pair of 2-bicyclooctyl *p*-bromobenzenesulfonates[4] or of 3-cyclohexenylethyl *p*-bromobenzenesulfonate.[5] Nitrosation of 7-norbornylcarbinylamine (aqueous acetic acid, room temperature) gives virtually the same ratio of products **2** and **3** as alcohols, Z = OH (40.9:59.1). These constitute 79% of the product mixture, the remainder being 2% acetates, 10% unrearranged alcohol, and 9% an unidentified component.

Specifically labeled *syn*- and *anti*-2,3-dideuterio-7-norbornylcarbinyl *p*-bromobenzenesulfonates (**1a** and **1b**, X = OBs) and the corresponding amines (**1a** and **1b**, X = NH_2) are prepared from the alcohols (**1a** and **1b**, X = OH), which are obtained by the action of

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[1] The support of this work by grants from the National Science Foundation (GP-1608) and from the National Institute of Arthritis and Metabolic Diseases (AM07505) is gratefully acknowledged.

[2] (a) J. A. Berson and P. Reynolds-Warnhoff, *J. Am. Chem. Soc.*, **84**, 682 (1962); **86**, 595 (1964); (b) J. A. Berson and D. Willner, *ibid.*, **84**, 675 (1962); **86**, 609 (1964).

[3] J. A. Berson and J. J. Gajewski, *ibid.*, **86**, 5020 (1964); J. J. Gajewski, Dissertation, University of Wisconsin, 1965.

[4] (a) H. M. Walborsky, J. Webb, and C. G. Pitt, *J. Org. Chem.*, **28**, 3215 (1963); (b) *cf.* H. L. Goering and M. F. Sloan, *J. Am. Chem. Soc.*, **83**, 1397 (1961); (c) H. L. Goering and G. Fickes, unpublished observations; G. Fickes, Ph.D. Dissertation, University of Wisconsin, 1964.

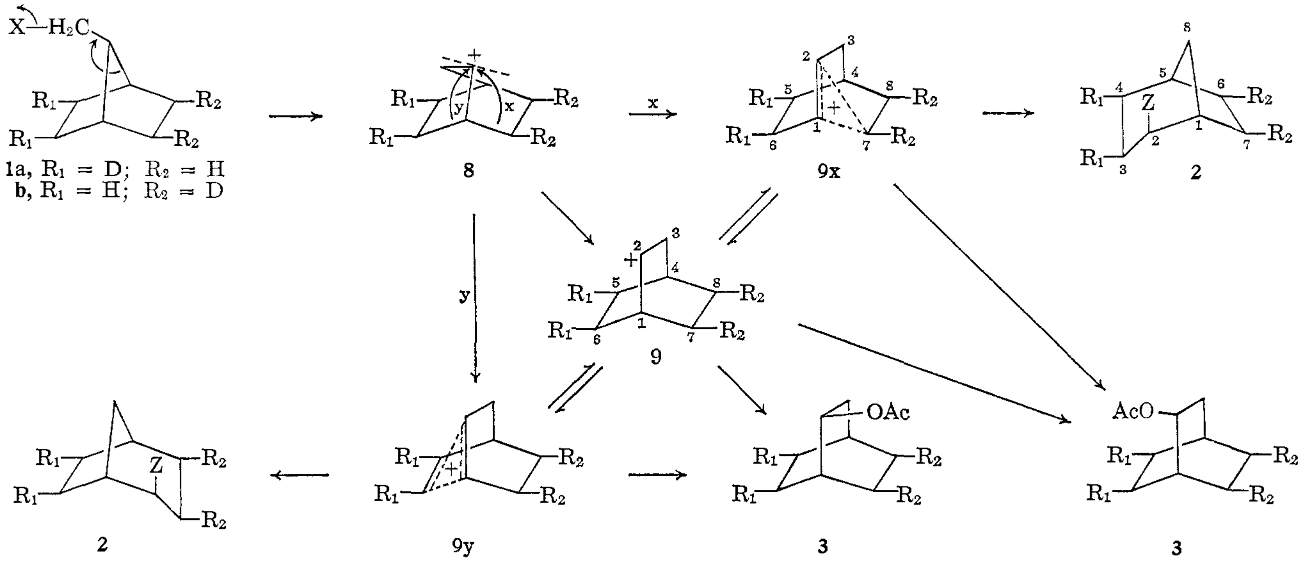
[5] S. Winstein and P. Carter, *J. Am. Chem. Soc.*, **83**, 4485 (1961).

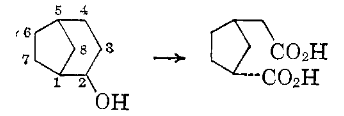
Table I. Deuterium Distributions in Products from Ring Expansions of **1a** and **1b**

Starting material	D/ molecule[a]	Product	D/ molecule in **5**[a]	Fraction of D at C-5–C-8[b]	Selectivity
Ia, X = OBs	1.334	**2**, Z = OAc	0.549	0.411	1.4
Ia, X = OBs	1.334	**2**, Z = OAc	0.547	0.410	1.4
Ib, X = OBs	1.414	**2**, Z = OAc	0.872	0.616	1.6
Ia, X = NH_2	1.460	**2**, Z = OH	0.193	0.132	6.6
Ib, X = NH_2	1.461	**2**, Z = OH	1.242	0.850	5.7

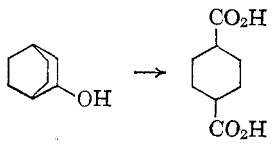
[a] Falling drop analyses by Mr. Joseph Nemeth, Urbana, Ill. [b] Relative uncertainty in this figure is about 5%.

potassium azodicarboxylate[6] and acetic acid-O-*d* on *syn*- and *anti*-2-norbornene-7-carbinols. Acetolysis of **1a** and **1b**, X = OBs, followed by cleavage with lithium aluminum hydride, or nitrosation of **1a** and **1b**, X = NH_2, and preparative vapor chromatography give compound **2**, Z = OH. Nitric acid oxidation of **2** gives *cis*-3-carboxycyclopentaneacetic acid, which upon heating with hydrochloric acid at 180° is transformed to the *trans* isomer (**5**). The deuterium content of **5** (Table I) represents that of C-5–C-8 of compound **2**.[2a]





2 **5**



3 **6**

That transannular hydride shifts are not a factor is established by reductive deacetylation and oxidative degradation of the 2-bicyclo[2.2.2]octyl product **3** to *cis*-cyclohexane-1,4-dicarboxylic acid (**6**), which is found to contain all (100 ± 2% from **1a**, X = OBs, 99 ± 3% from **1b**, X = OBs, and 102 ± 2% from **1a** and **1b**, X = NH_2) of the deuterium present in the starting material.

The results show that: (1) Any secondary kinetic isotope effect must be negligibly small, since the migratory aptitude of a *syn*- or *anti*-$C_2D_2H_2$ bridge is the same within experimental error as that of a *syn*- or *anti*-C_2H_4 bridge, respectively. (2) There is a memory effect in that the *anti* bridge is the better migrating group in the second rearrangement step (see the adjacent scheme). In this system, the memory is preserved more efficiently in deaminative than in solvolytic ring expansion (Table I). (3) In contrast to the cases of norbornyl and substituted norbornyl cations, in which 6,2-hydride shift is observable even in strongly nucleophilic media,[7] the corresponding process in the next higher homolog, which is one of the *a priori* conceivable mechanisms for the observed[2b,4] racemization of the 2-bicyclo[2.2.2]octyl cation, does not occur at a rate competitive with solvent capture.

As a working hypothesis for the mechanism of the memory effect, we suggest that twisted cation **8** is trapped intramolecularly by follow-up rearrangement. Type **x** trapping is more effective than type **y** because of orbital geometry[2,3] about the cationic site (the p orbital axis in **8** is indicated by the dotted line). The lack of complete specificity (crossover) may be due to some type y trapping directly in **8**, to symmetrization of **8** by relaxation[8] to classical ion **9** before trapping,

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(6) For a review of the chemistry of diimide, see S. Hünig, H. R. Müller, and W. Thier, *Angew. Chem. Intern. Ed. Engl.*, **4**, 271 (1965).

(7) For a review, see J. A. Berson in "Molecular Rearrangements," Part 3, Vol. I, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963.

(8) Whether 2-bicyclo[2.2.2]octyl cations would be more stable in a symmetrical, eclipsed conformation or a twisted, staggered one is debatable. The parent hydrocarbon, bicyclo[2.2.2]octane, would benefit by some relief of nonbonded hydrogen–hydrogen repulsions if twisted,[9] but present physical evidence on this substance and its 1,4-diaza analog are at least equally compatible with an eclipsed conformation.[10]

(9) R. B. Turner, W. R. Meador, and R. E. Winkler, *J. Am. Chem. Soc.*, **79**, 4116 (1957)

(10) J. J. McFarlane and I. G. Ross, *J. Chem. Soc.*, 4169 (1960); A. H. Nethercot, Jr., and A. Javan, *J. Chem. Phys.*, **21**, 363 (1953); M. P. Marzocchi, G. Sbrana, and G. Zerbi, *J. Am. Chem. Soc.*, **87**, 1429 (1965); G. S. Weiss, A. S. Parkes, E. R. Nixon, and R. E. Hughes, *J. Chem. Phys.*, **41**, 3759 (1964); T. Wada, E. Kishida, Y. Tomia, H. Suga, S. Seki, and I. Nitta, *Bull. Chem. Soc. Japan*, **33**, 1317 (1960).

and/or to reversible formation of **9**[2b] from its nonclassical counterparts **9x** and **9y** after trapping.

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Received September 3, 1965

Spectroscopy and Photolysis of a Ground-State Triplet Molecule, Diphenylmethylene

Sir:

Recent electron spin resonance (esr) studies of a number of aromatic methylenes[1,2] resulted in the assignment of a triplet ground state to these species. As part of a program designed to study the reactivity of these latter species, it was of interest to study their optical spectroscopy. The only methylenes which have been observed by ultraviolet and visible spectroscopy are methylene[3] and certain halogenated methylenes.[4] A previous attempt to obtain the electronic absorption spectrum of diphenylmethylene was unsuccessful.[5] We wish to report that we have obtained the emission and excitation spectra of diphenylmethylene in a variety of organic matrices at 77°K.[6]

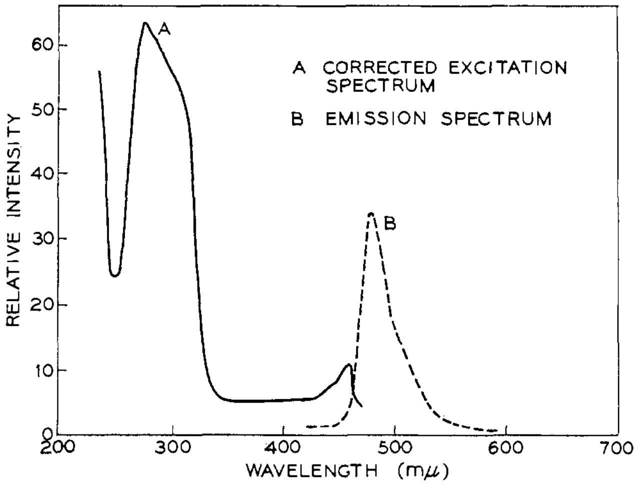

Figure 1. Electronic spectra of diphenylmethylene in methylcyclohexane at 77°K.

The emission consists of a broad band in the region 470 to 600 mμ with λ_{max} 480 mμ (see Figure 1). The position and structure of this band are independent of the wavelength of the exciting light in the range 240 to 460 mμ. The corrected excitation spectrum corresponding to the 480-mμ emission shows that *diphenylmethylene absorbs in the range 240 to 470 mμ with principal maxima at 280 and 465 mμ* (see Figure 1). The position and structure of the excitation spectrum is independent of wavelength for emission in the range 470 to 600 mμ. When the phosphoroscope was placed in the spectrophotofluorometer,[6] both the excitation and emission spectra disappeared.

The emission is attributed to *fluorescence* arising from a radiative transition from the first excited triplet level of diphenylmethylene to the triplet ground level. This assignment is based upon the following evidence. (a) The emission is different from that of other possible products, *viz.*, tetraphenylethylene, benzophenone, benzophenone azine (which does not emit), alkyl-substituted diphenylmethanes, and the diphenylmethyl radical. (b) The intensity of the fluorescence band at 480 mμ correlates well with the intensity of the esr absorption at 1000 gauss of diphenylmethylene[1] obtained from the same sample tube. (c) The fluorescence disappears on warming and freezing indicative of the presence of a reactive intermediate. In the presence of dissolved oxygen a luminescent reaction occurs during warming giving rise to benzophenone phosphorescence. (d) The lifetime of the luminescence at 480 mμ is less than 1 msec. There is only one other published example of triplet–triplet emission from aromatic molecules.[7] Attempts to detect phosphorescence from diphenylmethylene have so far proven unsuccessful.

By studying the photolysis of diphenyldiazomethane as a function of exposure time in a rigid matrix, it should be possible to obtain some idea of the reactions of diphenylmethylene both in its ground state and in its excited state. Thus, at very low conversions, one could determine if free radicals were formed (with esr spectroscopy) and if molecular products were formed (identification by their luminescence spectra). These two types of products could arise by either abstraction or insertion reactions of diphenylmethylene or by photolysis of insertion products. Any major differences between the results at short exposure times and those at longer exposure times, when most of the incident light is being absorbed by diphenylmethylene, might be attributable to reactions of *excited* diphenylmethylene.

With light of wavelength 2537 A,[8] the only products initially detected in the photolysis of diphenyldiazomethane in methylcyclohexane at 77°K were diphenylmethylene and tetraphenylethylene (by its fluorescence at 425 mμ). Neither free radicals (corresponding to abstraction reactions) nor phosphorescence at *ca.* 370 mμ (corresponding to alkyl-substituted diphenylmethanes, possible insertion products) were detected. However, on warming and freezing one of these solutions, a phosphorescence at 370 mμ was detected.[9]

At prolonged photolysis times, the intensity of the esr and fluorescence signals from diphenylmethylene decreased rapidly with concomitant appearance of solvent

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(1) R. W. Murray, A. M. Trozzolo, E. Wasserman, and W. A. Yager, *J. Am. Chem. Soc.*, **84**, 3213 (1962); R. W. Brandon, G. L. Closs, and C. A. Hutchison, Jr., *J. Chem. Phys.*, 37, 1878 (1962).

(2) A. M. Trozzolo, E. Wasserman, and W. A. Yager, *J. Am. Chem. Soc.*, **87**, 129 (1965), and references cited therein.

(3) G. Herzberg and J. Shoosmith, *Nature*, **183**, 1801 (1959); G. Herzberg, *Proc. Roy. Soc.* (London), **A262**, 291 (1961).

(4) P. Venkateswarlu, *Phys. Rev.*, **77**, 79, 676 (1950); E. B. Andrews and R. F. Barrow, *Nature*, **165**, 890 (1950); R. K. Laird, E. B. Andrews, and R. F. Barrow, *Trans. Faraday Soc.*, **46**, 803 (1950); J. W. Johns, 7th International Symposium on Free Radicals, Padua, 1965.

(5) W. B. DeMore, H. O. Pritchard, and N. Davidson, *J. Am. Chem. Soc.*, **81**, 5874 (1959).

(6) The luminescence spectra were obtained on an Aminco-Bowman spectrophotofluorometer. Accurate fluorescence and excitation spectra were obtained with the assistance of Drs. J. W. Longworth and J. Ferguson.

(7) (a) F. Dupuy, G. Nouchi, and A. Rousset, *Compt. Rend.*, **256**, 2976 (1963). (b) A luminescence associated with diphenylmethylene has previously been observed: R. Harrell, unpublished results.

(8) A Rayonet photochemical reactor was used for all photolysis experiments. Unfiltered low-pressure mercury arcs were used for 2537-A irradiation and "Blaklite" lamps for irradiation at wavelengths >3100 A.

(9) A phosphorescence at *ca.* 370 mμ does not prove that an alkyl-substituted diphenylmethane is present. However, this is the most likely assignment to such a phosphorescence in the present case.