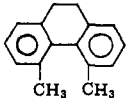
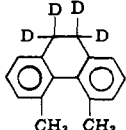
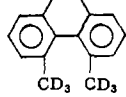
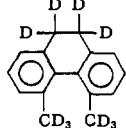


TABLE I
COMPOSITION AND RACEMIZATION RATES OF DEUTERATED 9,10-DIHYDRO-4,5-DIMETHYLPHENANTHRENES

No.	Formula ^a	Mass spectrometric composition (%) of deuterated species ^b	Av. no. D-atoms/molecule		Relative integrated areas of n.m.r. peaks ^d			Rate constants of racemization, ^e $k_1 \times 10^4$ (sec. ⁻¹)	k_D/k_H
			From mass spectra	From combustion ^c	A	B	C		
I		—	—	—	6.0	4.0	6.0	5.92 ± 0.02	—
II		d_4 (92.4), d_3 (7.3) d_2 (0.3)	3.92	3.90	6.0	≤ 0.1	6.0	6.21 ± 0.02	1.05
III		d_6 (73.3), d_5 (23.2) d_4 (3.3), d_3 (0.2)	5.70	5.63	6.0	4.0	0.32	6.70 ± 0.01	1.13
IV		d_{10} (69.7), d_9 (25.0) d_8 (3.9), d_{5-7} (1.4)	9.60-9.63	9.59	6.0	≤ 0.1	0.35	6.99 ± 0.01	1.18

^a Corresponding to the major constituent. ^b Measurements were kindly performed by Mr. E. Miller, using a CEC type 21-103C instrument operated at 7-8 e.v. ^c Determined by Mr. J. Nemeth, Urbana, Ill., using the falling drop method. ^d A = aromatic multiplet with center peak at $\tau = 2.8-2.9$; B = methylene peak, $\tau = 7.4$; C = methyl singlet, $\tau = 7.7-7.8$. Measurements were made using a Varian A-60 spectrometer and $\sim 10\%$ w./v. solutions in CDCl_3 with TMS as internal standard. ^e Determined polarimetrically (λ 435 $\text{m}\mu$, l 2 dm.) on benzene solutions (c 1-5) at $42.0 \pm 0.1^\circ$. In each case the listed average and standard error were computed by a non-linear least squares analysis of readings taken over a span of three half-lives.

mole.^{3,4} We now wish to report the observation of isotope effects in this system.

Salient results are summarized in Table I. The compositions of II-IV were calculated from the mass spectral parent peaks and the location of the deuterium atoms could be unequivocally assigned from the n.m.r. spectra. These analyses are in full accord with the analytical information which was obtained in the course of the syntheses and which will be described in the detailed paper. Precision and reproducibility of the first-order rate constants of racemization were excellent. The data were programmed by linear and by non-linear least squares codes,⁵ with identical results within standard error. The observed inverse isotope effects are therefore unquestionably real and further exemplify the operation of *conformational kinetic isotope effects*.⁶

It is seen that replacement of the methyl groups in the 4,5- or blocking positions by the less bulky tri-deuteriomethyl groups results in a 13% increase in the rate of racemization. Although only approximately 73% of the molecules in III and IV contain two $-\text{CD}_3$ groups, a further 23% contain a $-\text{CD}_3$ and a $-\text{CHD}_2$ group so that the maximum isotope effect is not expected to be much larger than 13%. The effect is the same for the two cases studied (III/I and IV/II) and is essentially solvent-independent (heptane, benzene, ethanol). Since the process studied is exceptionally free of complicating features, these observations would appear to offer unambiguous support for the view⁷ that

(4) Inspection of Stuart-Briegleb models suggests that I is not significantly overcrowded in the ground state. This impression is strengthened by the essential identity of the absorption spectra of I ($\lambda_{\text{max}}^{\text{EtOH}}$ 261 $\text{m}\mu$, $\log \epsilon$ 4.16) and of 9,10-dihydrophenanthrene ($\lambda_{\text{max}}^{\text{EtOH}}$ 264 $\text{m}\mu$, $\log \epsilon$ 4.23).

(5) M. H. Lietzke, Oak Ridge National Laboratory Report No. 3259, Oak Ridge, Tenn., March 21, 1962. We are obliged to Drs. C. J. Collins and M. H. Lietzke for bringing this program to our attention and for performing the computations.

(6) K. Mislow, E. Simon and H. Hopps, *Tetrahedron Letters*, No. 22, 1011 (1962).

(7) E.g., L. S. Bartell, *J. Am. Chem. Soc.*, **83**, 3567 (1961); *Iowa State J. Sci.*, **36**, 137 (1961).

secondary kinetic isotope effects may arise from differences in steric requirements of protium and deuterium. Nevertheless it may be hazardous to draw this obvious and attractive conclusion since the replacement of the protons in the 9,10- or bridge positions by deuterons *also* results in a far from negligible (5%) increase in the rate of racemization. This effect, which is the same for the two cases studied (II/I and IV/III), appears to be associated with torsion about the 9,10-bond⁸ and it is believed that steric repulsion of adjacent hydrogens is not to any major extent responsible for the torsional barrier about σ -bonds.⁹

The temperature dependence of $k_{\text{III}}/k_{\text{I}}$ in heptane gives $\Delta H_{\text{H}}^\ddagger - \Delta H_{\text{D}}^\ddagger \sim 0.2$ kcal./mole and $\Delta S_{\text{H}}^\ddagger - \Delta S_{\text{D}}^\ddagger \sim 9.3$ e.u.; the putative steric isotope effect thus manifests itself in the surprisingly small value of 30-50 cal./D-atom. Further discussion is reserved for the detailed paper.

Acknowledgment.—We thank Drs. C. J. Collins and M. Wolfsberg for valuable discussions.

(8) In a related situation, the potential barrier to internal rotation in ethane fluctuates within about 10% of the average barrier height of 3030 cal./mole for variously deuterated species (D. R. Lide, *J. Chem. Phys.*, **29**, 1426 (1958)).

(9) E. B. Wilson, Jr., "Advances in Chemical Physics," Vol. 2, Interscience Publishers, Inc., New York, N. Y., 1959, p. 367.

(10) Fellow of the Alfred P. Sloan Foundation.

DEPARTMENT OF CHEMISTRY
NEW YORK UNIVERSITY
NEW YORK 53, N.Y.

KURT MISLOW¹⁰
ROLF GRAEVE
ARNOLD J. GORDON
GEORGE H. WAHL, JR.

RECEIVED FEBRUARY 2, 1963

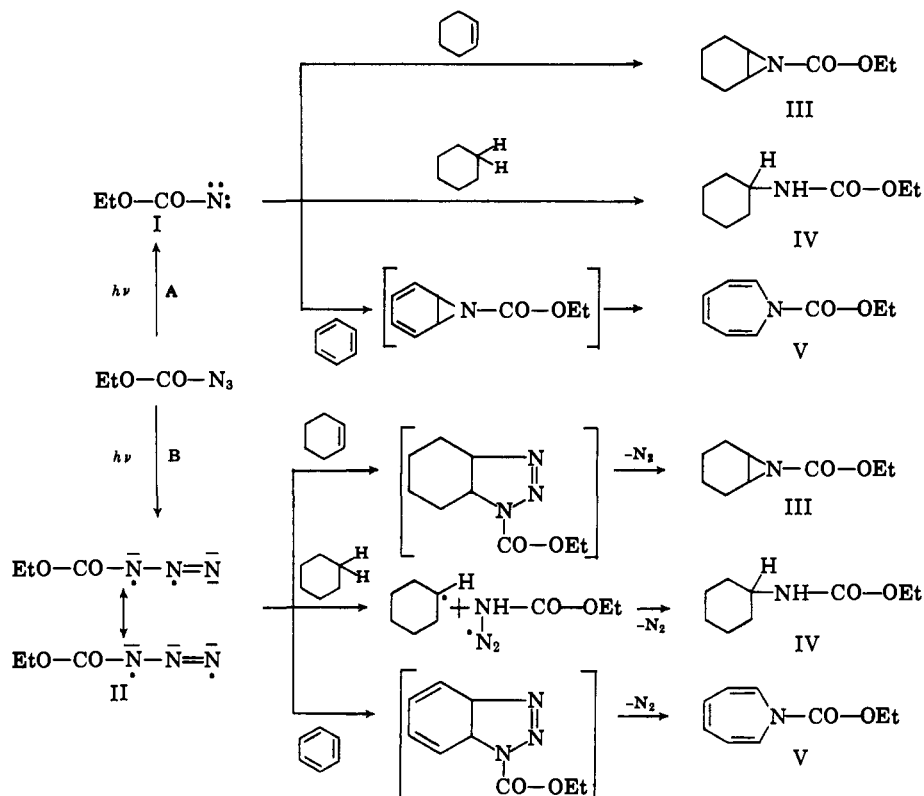
CARBETHOXYNITRENE

Sir:

The photodecomposition of ethyl azidoformate in the presence of cyclohexane, cyclohexene or benzene leads to the formation of cyclohexylurethane,¹ 7-carbethoxy-7-aza-bicyclo[4.1.0]heptane¹ and N-carbethoxyazepine,²

(1) W. Lwowski and T. W. Mattingly, *Tetrahedron Letters*, 277 (1962).

(2) K. Hafner and C. Koenig, *Angew. Chem.*, **76**, 89 (1963).

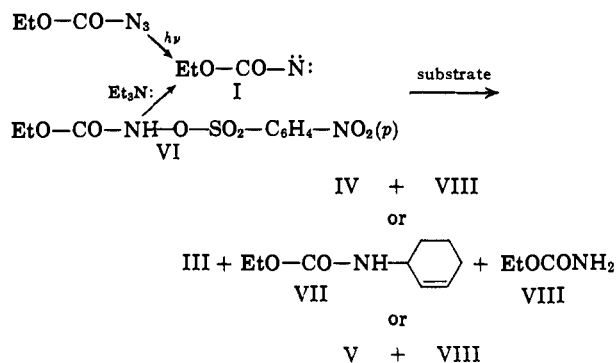


respectively. These reactions can be explained by assuming a nitrene intermediate (I) (mechanism A). Other possible mechanisms, such as B, involve intermediates or transition states containing all three nitrogen atoms of the azido group. Such mechanisms have to be seriously considered, since Huisgen³ found that benzazide adds to norbornene forming a triazoline which at 40° loses nitrogen to give an aziridine. Furthermore, the decomposition of arylazides in indene, leading to aziridines, proceeds at a rate much higher than that in saturated hydrocarbons. This suggests participation of the double bond in the step determining the rate of loss of nitrogen.⁴

We can now show that intermediates or transition states containing three nitrogen atoms (as II) are not necessary for the formation of (III), (IV) and (V). α -Elimination of *p*-nitrobenzenesulfonic acid from its *N*-hydroxyurethane ester (VI) in cyclohexane, cyclohexene or benzene leads to the same products as does the photodecomposition of ethyl azidoformate in these substrates. Moreover, in the reactions in cyclohexene, 3-cyclohexenylurethane (VII) is formed as a by-product in about the same amount, relative to the main product (III). The ratio (VII) to (III) was 1:6 with *N*-*p*-nitrobenzenesulfonoyurethane as starting material and 1:4.5 with ethyl azidoformate. Controls were run to exclude the formation of (VII) from (III) during vapor phase chromatography. Another by-product common to all the reactions is urethane (VIII). We therefore conclude that carbethoxynitrene (I) is formed first, from both starting materials. (I) either combines with the unsaturated substrate, or abstracts a hydrogen atom, forming a radical pair. This can lead to (IV) and (VII), or can dissociate. A further hydrogen abstraction then gives urethane (VIII).

N-*p*-Nitrobenzenesulfonoyurethane (VI) was made from *N*-hydroxyurethane and *p*-nitrobenzenesulfonyl chloride by controlled addition of triethylamine, m.p. 116.5°. Calcd. for $\text{C}_9\text{H}_{10}\text{N}_2\text{O}_7\text{S}$: C, 37.24; H, 3.47;

N, 9.65. Found: C, 37.43; H, 3.34; N, 9.65. The n.m.r. spectrum in CDCl_3 showed a triplet at 8.83 τ (3.00), a quartet at 5.86 τ (1.99) and complex absorption around 1.54 τ (5.01; aromatic C-H and N-H). The infrared spectrum (in KBr) showed the N-H at



3187 cm^{-1} , the CO at 1697 cm^{-1} . The decompositions of (VI) were carried out in the substrates as solvents, with one to two equivalents of triethylamine at room temperature. The triethylamine salt of *p*-nitrobenzenesulfonic acid separated in about 90% yield within a few hours. It was identified by comparison with an authentic sample. The runs in cyclohexene and cyclohexane were heterogeneous and gave (III) in 12% and (IV) in 5.4% of the theoretical yield. (III) and (IV) were identified by comparison of their v.p.c. retention times and their infrared spectra with those of authentic samples.¹ 3-Cyclohexenylurethane (VII) was synthesized by an independent route: 3-bromocyclohexene⁵ was treated with potassium phthalimide and the product hydrolyzed to the amine. Treatment of the amine with ethyl chloroformate gave a product identical with (VII) in its infrared spectrum, n.m.r. spectrum and vapor phase chromatography retention time. The n.m.r. spectrum shows the olefinic protons at 4.28 τ (2.0), N-H at 5.28 τ (1.0), ethyl CH_2 and C_α -

(3) R. Huisgen and G. Mueller, *Angew. Chem.*, **73**, 371 (1960).

(4) P. Walker and W. A. Waters, *J. Chem. Soc.*, 1632 (1962).

(5) H. J. Schaeffer and C. J. Collins, *J. Am. Chem. Soc.*, **78**, 124 (1956).

H at 5.95 τ (2.8); CH₂ groups and ethyl CH₃ at 8.05, 8.28 and 8.87 τ (8.8). The infrared spectrum in CCl₄ shows N-H at 3454 cm.⁻¹ (sharp) and 3348 cm.⁻¹ (hydrogen bonded, broad); olefinic C-H at 3030 cm.⁻¹; CO at 1720 cm.⁻¹; double bond at 1648 cm.⁻¹. Urethane (VIII) was identified by comparison of its infrared spectrum and its vapor phase chromatography retention time with those of an authentic sample.

N-Carboethoxyazepine was obtained in 50% of the theoretical yield from a homogeneous solution of (VI) in benzene and 1.1 equivalents of triethylamine. It was identified by its ultraviolet spectrum (λ_{\max} at 210 m μ ($\log \epsilon$ 4.37) and λ_{\max} 329 m μ ($\log \epsilon$ 2.74)), its infrared spectrum (no NH; H-H at 3051, 3033, 2984, 2933 cm.⁻¹, CO at 1717 cm.⁻¹, double bonds at 1651 cm.⁻¹), its n.m.r. spectrum (triplet at 8.71 τ ; quartet at 5.81 τ ; multiplet from 3.9 to 4.8 τ). It was also hydrogenated² to the hexahydro compound, the infrared spectrum of which was identical with that of a sample prepared from hexamethyleneimine and ethyl chloroformate. The formation of phenylurethane in the nitrene reaction could not be proven, since N-carboethoxyazepine itself readily isomerizes to phenylurethane.

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STERLING CHEMISTRY LABORATORY
YALE UNIVERSITY
NEW HAVEN, CONNECTICUT

WALTER LWOWSKI
TOM J. MARICICH
THOMAS W. MATTINGLY, JR.

RECEIVED MARCH 4, 1963

Rh₆(CO)₁₆ AND ITS IDENTITY WITH PREVIOUSLY REPORTED Rh₄(CO)₁₁

Sir:

A three-dimensional crystal structure investigation has shown that the compound previously analyzed as Rh₄(CO)₁₁¹ has the molecular formula Rh₆(CO)₁₆.

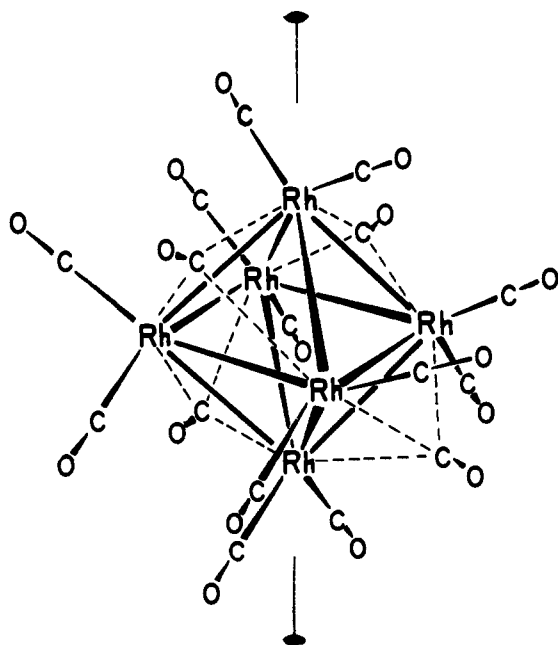


Fig. 1.—Molecular structure of Rh₆(CO)₁₆.

This is the first example of a hexanuclear metal carbonyl.

Crystals of this air-stable black rhodium carbonyl were prepared by the reaction of dry RhCl₃ and silver or copper powder at 80–230° and 200 atmospheres of carbon monoxide.¹ Rh₆(CO)₁₆ crystallizes in a mono-

(1) W. Hieber and H. Lagally, *Z. anorg. allgem. Chem.*, **251**, 96 (1943).

clinic unit cell of symmetry I2/a with dimensions $a = 17.00 \pm 0.03$ Å., $b = 9.78 \pm 0.02$ Å., $c = 17.53 \pm 0.03$ Å., $\beta = 121^\circ 45' \pm 30'$. The observed density of 2.87 g./cc. determined by the flotation method agrees well with the calculated density of 2.86 g./cc. based on four Rh₆(CO)₁₆ molecules per unit cell.

The structure was determined from an analysis of three-dimensional intensity data taken photographically with MoK α radiation. Final least-squares refinement² with an isotropic temperature factor for each atom gave discrepancy factor $R_1 = 7.1\%$ and $R_2 = 7.6\%$.

In each molecular unit (Fig. 1) the rhodium atoms are located at the corners of an octahedron with a weighted average metal-metal bonding distance of $2.776 \pm 0.001_4$ Å. Twelve of the sixteen carbonyl ligands are terminal groups while the remaining four are located on 3-fold axes above four of the octahedral faces. Each of these latter four carbonyls which are directed toward the vertices of a tetrahedron is bonded to three rhodium atoms. The eight-coordinated tetragonal antiprismatic rhodium atoms each have the same localized ligand environment: four adjacent rhodium atoms, two terminal carbonyl groups and two of the carbonyls that bridge three metal atoms. The idealized molecular point group symmetry is T_d- $\bar{4}3m$. One of the three molecular 4 axes lies on a crystallographic 2-fold axis. The following weighted average bond distances are found: for the terminally bonded carbonyls, Rh-C = 1.864 ± 0.015 Å., C-O = 1.155 ± 0.015 Å.; for the carbonyls bonded to three metal atoms, Rh-C = 2.168 ± 0.012 Å., C-O = 1.201 ± 0.022 Å.

This is the first known polynuclear metal carbonyl that contains carbonyls bridged to three metal atoms. Similarly bridged groups have been shown conclusively by X-ray diffraction³ for (C₅H₅)₃Ni₃(CO)₂ in agreement with its infrared spectrum.⁴ A comparison of angles involving the bridge carbonyls in (C₅H₅)₃Ni₃(CO)₂ and Rh₆(CO)₁₆ shows close agreement: Ni-C-O angle = 134° vs. Rh-C-O angle = 132° (av.); Ni-C-Ni angle = 77° vs. Rh-C-Rh angle = 79.5° (av.). Carbonyl ligands bonded to triangular arrangements of metal atoms have been predicted from infrared data for (C₆H₅)₃CO₃(CO)₂¹⁺,^{3,5,6} and (C₇H₇)₃CO₃(CO)₂¹⁺,⁶ and by analogy for Fe₃(CO)₁₁^{2-3,7}

Octahedral arrangements of metal atoms similar to that in Rh₆(CO)₁₆ are found in the cations Mo₆Cl₈⁴⁺,⁸ Nb₆Cl₁₂²⁺,⁹ Ta₆Cl₁₂²⁺,⁹ and Ta₆Br₁₂²⁺,⁹ all of which can also be described on the basis of a tetragonal antiprismatic arrangement¹⁰⁻¹² of eight electron pairs about each metal atom.¹³

(2) W. R. Busing and H. A. Levy, "A Crystallographic Least-Squares Refinement Program for the IBM 704," Oak Ridge National Laboratory Report 59-4-37 (1959).

(3) A. A. Hock and O. S. Mills, "Advances in the Chemistry of the Coordination Compounds," edited by S. Kirschner, The Macmillan Co., New York, N. Y., 1961, pp. 640-648.

(4) E. O. Fischer and C. Palm, *Chem. Ber.*, **91**, 1725 (1958).

(5) E. O. Fischer and O. Beckert, *Angew. Chem.*, **70**, 744 (1958).

(6) P. Chini and R. Ercoli, *Gazz. chim. ital.*, **88**, 1171 (1959).

(7) W. Hieber and G. Brendel, *Z. anorg. allgem. Chem.*, **259**, 324 (1957).

(8) C. Brosset, *Arkiv Kemi, Mineral. Geol.*, **20A**, No. 7 (1945); **23A**, No. 11 (1946); C. Brosset, *Arkiv Kemi*, **1**, 353 (1950); P. A. Vaughan, *Proc. Natl. Acad. Sci. U.S.A.*, **36**, 461 (1950).

(9) P. A. Vaughan, J. H. Sturdivant and L. Pauling, *J. Am. Chem. Soc.*, **72**, 5477 (1950); R. B. Corey, R. H. Stanford, Jr., R. E. March, Y. C. Leung and L. M. Kay, *Acta Cryst.*, **18**, 1157 (1962).

(10) G. H. Duffey, *J. Chem. Phys.*, **19**, 963 (1951).

(11) R. J. Gillespie, *Can. J. Chem.*, **39**, 2336 (1961); R. J. Gillespie, in ref. 3, pp. 34-49.

(12) L. D. Crossman, D. P. Olsen and G. H. Duffey, *J. Chem. Phys.*, **38**, 73 (1963).

(13) The two rhodium-bridged carbonyl bonds presumably are "bent." Directed valence bond metal hybrid orbitals have been constructed by Duffey for both a regular tetragonal antiprismatic arrangement¹⁴ and a distorted version¹⁰ based on the Ta₆Cl₁₂²⁺ structure.

(14) C. H. Duffey, *J. Chem. Phys.*, **18**, 746 (1950).