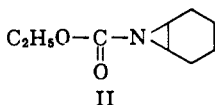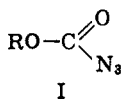# COMMUNICATIONS TO THE EDITOR

FLASH-PHOTOLYTIC DECOMPOSITION OF GASEOUS ALKYL AZIDOFORMATES

Sir:

We have studied the flash-photolytic decomposition of gaseous methyl and ethyl azidoformates, I. We have identified the principal, ultraviolet-absorbing transient

decomposition product of both compounds with flash ultraviolet absorption spectra. We have collected and identified the main product of the flash-photolytically-induced reaction of gaseous ethyl azidoformate, with cyclohexene vapor. The evidence from this work points firmly to the existence of a highly reactive and unstable nitrene of the form RO–CO–N.

Recent work has demonstrated that the photodecomposition of ethyl azidoformate in liquid cyclohexene leads to the formation, in good yield, of the aziridine II, 7-carbethoxy-7-azabicyclo[1.4.0]heptane.[1] This reaction and the photolytic decomposition of I in liquid cyclohexane leading to cyclohexylurethane[1] point strongly to the presence of a nitrene intermediate. The work reported here was undertaken to study the possible existence of a gaseous nitrene, and to investigate rapid reactions of such a species.

Photolysis and spectroscopy were carried out with apparatus differing only slightly from that reported previously.[2] A multiple-pass sample cell (path length up to 3.2 m.) was used for many of the spectra, a Mc-Pherson 2.217-m. grating spectrograph was used for the spectra from which the wave length measurements were made and a rotating-drum camera mounted behind medium quartz and glass spectrographs was used for some of the time-dependence measurements. Spectra were taken at times from 12 μsec. to several minutes after initiation of photolysis. Photolyses were carried out with partial pressures of azidoformate of 8 to 15 mm. and with the added inert gases CO_2, N_2 and Ar. The most effective condition for producing the principal transient absorber were p(azidoformate) 8–9 mm. and p(CO_2) 300 mm. Nitrogen and argon were less efficient than CO_2 as stabilizing media. In the absence of inert gas, the transient was detected, but only with difficulty.

The principal transient absorber is the radical NCO. This is unequivocally identified by a comparison of our spectra with those reported by Dixon.[3] We observe both the $^2\Pi$–$^2\Pi$ and $^2\Sigma^+$–$^2\Pi$ transitions. In the band system of the former, we have found the bands at 315.0, 314.8, 305.1, 304.5, 296.4, 295.9 and 294.8 mμ and in the latter, the bands at 440.3, 438.9, 438.4, 435.1, 435.0, 434.8, 416.7, 415.0, 413.7, 413.3, 399.3 and 397.7.

The NCO radical is detectable at times as short as 12 μsec. after initiation of photolysis of either azidoformate. The intensity of the bands reaches a maximum at about 20 μsec., at which time the photolysis lamp is

still intense, but is decaying. The intensity of NCO absorption is greater when the methyl compound is the source than when the ethyl compound is used. The half-life of NCO is about 200 μsec. with the methyl precursor, and about 50 μsec. with the ethyl. Intensity measurements as functions of time, made under the optimum conditions described above, indicate that the disappearance of NCO follows kinetics which are first order in the NCO concentration. If one adds NO at any partial pressure down to 15 mm., the NCO bands are not observed. When cyclohexene vapor is present at pressures of 20 mm. or more, the bands are not detected; if the cyclohexene pressure is as low as 0.3 mm., the NCO bands are weak but detectable.

From the photolysis of ethyl azidoformate in the presence of 20 mm. of cyclohexene, the aziridine (II) was isolated by vapor chromatography and identified by comparison of its retention time and infrared spectrum with an authentic sample prepared previously.[1] (The column was silicone, at 150°.)

We conclude that I loses N_2 to give an unstable and reactive nitrene RO–CO–N. This may be trapped if a suitable substrate is present; otherwise its C–O single bond breaks. The formation of NCO by attack of the nitrene on the alkyl group, followed by decomposition of a cyclic intermediate, is unlikely, because of the higher photolysis yield of NCO from the methyl compound than from the ethyl.

The transient spectra also show bands in the region of 2700 Å. which we have not identified, and which are now being investigated.

Acknowledgment.—We wish to thank the Directorate of Chemistry, U. S. Air Force Office of Scientific Research, for partial support of this work.

(4) Alfred P. Sloan Fellow.
(5) National Institutes of Health Predoctoral Fellow.

STERLING CHEMISTRY LABORATORY   R. STEPHEN BERRY[4]
YALE UNIVERSITY   DOUGLAS CORNELL[5]
NEW HAVEN, CONNECTICUT   WALTER LWOWSKI

RECEIVED MARCH 4, 1963

A NOTE ON STERIC ISOTOPE EFFECTS. CONFORMATIONAL KINETIC ISOTOPE EFFECTS IN THE RACEMIZATION OF 9,10-DIHYDRO-4,5-DIMETHYLPHENANTHRENE
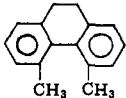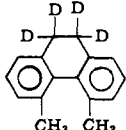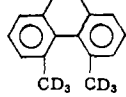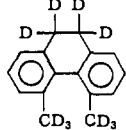
Sir:

The smaller amplitude of vibration of deuterium as compared to that of protium is reflected in a smaller van der Waals radius.[1] In a recent attempt to assess the importance of this factor in kinetics,[2] we concluded that highly crowded transition states would be required for the exhibition of secondary isotope effects arising from differences in non-bonded repulsions of the isotopes, *i.e.*, steric isotope effects. This requirement is eminently satisfied in the racemization of 9,10-dihydro-4,5-dimethylphenanthrene (I)[3]: in the transition state for racemization the extreme congestion of the two methyls, acting as classical blocking groups, results in molecular deformations which must be largely responsible for the observed activation energy barrier of 23 kcal./

(1) W. Lwowski and T. W. Mattingly, *Tetrahedron Letters*, 277 (1962).
(2) R. S. Berry, G. N. Spokes and M. Stiles, *J. Am. Chem. Soc.*, **84**, 3570 (1962).
(3) R. N. Dixon, *Can. J. Phys.*, **38**, 10 (1960); *Phil. Trans. Roy. Soc.* (London), **252**, 165 (1959); R. Holland, D. W. G. Style, R. N. Dixon and D. A. Ramsay, *Nature*, **182**, 336 (1958).

(1) *E.g.*, A. R. Ubbelohde, *Trans. Faraday Soc.*, **32**, 525 (1936).
(2) K. Mislow, R. E. O'Brien and H. Schaefer, *J. Am. Chem. Soc.*, **82**, 5512 (1960); **84**, 1940 (1962), and references cited therein.
(3) K. Mislow and H. B. Hopps, *ibid.*, **84**, 3018 (1962).

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 From mass spectra	Av. no. D-atoms/molecule From combustion[c]	Relative integrated areas of n.m.r. peaks[d] A	B	C	Rate constants of racemization,[e] $k_1 \times 10^4$ (sec.⁻¹)	k_D/k_H
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_2 (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 τ = 2.8–2.9; B = methylene peak, τ = 7.4; C = methyl singlet, τ = 7.7–7.8. Measurements were made using a Varian A–60 spectrometer and ∼10% w./v. solutions in $CDCl_3$ with TMS as internal standard. [e] Determined polarimetrically (λ 435 mμ, l 2 dm.) on benzene solutions (c 1–5) at 42.0 ± 0.1°. In each case the listed average and standard error were computed by a nonlinear 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 trideuteriomethyl groups results in a 13% increase in the rate of racemization. Although only approximately 73% of the molecules in III and IV contain two —CD_3 groups, a further 23% contain a —CD_3 and a —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 view[7] that

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-bond[8] 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_{III}/k_I in heptane gives $\Delta H_H^{\ddagger} - \Delta H_D^{\ddagger} \sim 0.2$ kcal./mole and $\Delta S_H^{\ddagger} - \Delta S_D^{\ddagger} \sim 9.3$ 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.

(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 (λ_{max}^{EtOH} 261 mμ, log ϵ 4.16) and of 9,10-dihydrophenanthrene (λ_{max}^{EtOH} 264 mμ, log ϵ 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).

(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   KURT MISLOW[10]
NEW YORK UNIVERSITY   ROLF GRAEVE
NEW YORK 53, N.Y.   ARNOLD J. GORDON
     GEORGE H. WAHL, JR.

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]heptane[1] and N-carbethoxyazepine,[2]

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

(2) K. Hafner and C. Koenig, Angew. Chem., 75, 89 (1963).