far, prevented isolation; other systems (n = 2, 4, 5, 6) are predicted to be nonplanar, judging from molecular models.

Further work in progress (X-ray diffraction, C^{13} nmr) should provide more information about the properties and character of this molecule.

Acknowledgments. The authors are grateful to Mr. R. Rabinowitz for his able technical assistance, to Mr. R. E. Rhodes for obtaining the mass spectrometric measurements, to Mr. R. Pitcher of Varian Associates for the C^{13}–H coupling constants, and to Dr. A. A. Bothner-By for helpful discussions.

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1,5,9-Tridehydro[12]annulene[1]

Sir:

It has been reported by our group[2] that treatment of 1,3,7,9-cyclododecatetrayne (I, $C_{12}H_8$) with potassium *t*-butoxide leads to two different dehydro[12]annulenes. The elemental analysis[2b] of each of these substances indicated the anticipated empirical formula $C_{12}H_8$, and they were therefore both considered to be bisdehydro[12]annulenes. The dehydroannulene obtained in larger amount ("isomer A," complex nmr spectrum) was assigned structure II, while the one obtained in lesser amount ("isomer B," nmr singlet at τ 5.58 in CCl_4)[3] was assigned structure III.
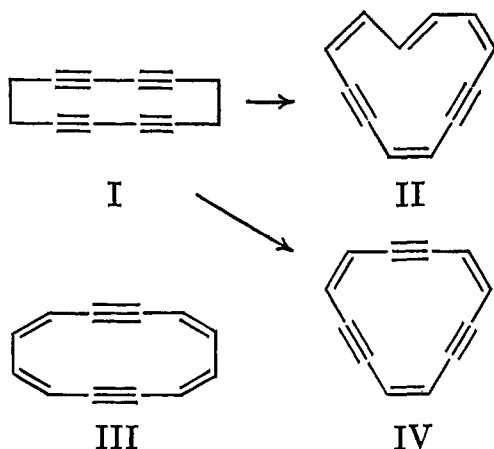
Very recently, Untch and Wysocki[5] have carried out an elegant synthesis of 1,5,9-tridehydro[12]annulene

(1) Part XLI in the series Unsaturated Macrocyclic Compounds. For part XL, see R. Wolovsky and F. Sondheimer, *J. Am. Chem. Soc.*, **88**, 1525 (1966).

(2) (a) F. Sondheimer, *Pure Appl. Chem.*, 7, 363 (1963); (b) R. Wolovsky and F. Sondheimer, *J. Am. Chem. Soc.*, **87**, 5720 (1965).

(3) Whereas the nmr spectrum of isomer A provided confirmation for a $C_{12}H_8$ formulation, such confirmation could not be provided by the spectrum of isomer B. The fact that the latter spectrum showed only a sharp singlet was disturbing (since III possesses two different types of protons), although this type of observation is not without precedent.[4] Separation can occur by change of solvent,[4] but the spectrum of isomer B, determined in different solvents, in all cases exhibited only a singlet ($CDCl_3$, τ 5.52 at 20°, 5.44 at −60°; $(CD_3)_2CO$, 5.34 at 20°, 5.20 at −80°; C_6D_6, 6.00 at 20°).

(4) *Inter alia*, G. Farges and A. S. Dreiding, *Helv. Chim. Acta*, **49**, 552 (1966); F. Sondheimer and P. J. Garratt, unpublished observations.

(5) K. G. Untch and D. C. Wysocki, *J. Am. Chem. Soc.*, **88**, 2608 (1966).

(IV, $C_{12}H_6$)[6] and have observed that this compound possesses properties essentially identical with those reported by us for isomer B. Dr. Untch kindly informed us of his work prior to publication, and we therefore reexamined the structure of isomer B. The mass spectrum was determined (AEI MS9 spectrometer), and the molecular ion (found 150.048) revealed that the empirical formula was in fact $C_{12}H_6$ (calcd 150.047) and not $C_{12}H_8$ (calcd 152.063).[7] Consequently, dehydrogenation must have taken place during the base treatment of I.[8] Isomer B was then shown to be identical with Untch's compound by direct comparison (thin layer chromatography, mass and ultraviolet spectra), and thus is 1,5,9-tridehydro[12]annulene (IV).[10]

The mass spectrum of "isomer A" (molecular ion, found 152.063) clearly showed the $C_{12}H_8$ formula to be correct, and the arguments[2] for assigning structure II to this compound remain unchanged.

Acknowledgment. We wish to thank Dr. K. G. Untch for kindly providing a sample of IV, and to C.S.I.R.O. for an Overseas Postgraduate Studentship (to I.C.C.).

(6) See T. J. Sworski, *J. Chem. Phys.*, **16**, 550 (1948).

(7) The previously reported microanalysis (Found: C, 95.02; H, 5.01.[2b] Calcd for $C_{12}H_8$: C, 94.70; H, 5.30. Calcd for $C_{12}H_6$: C, 95.97; H, 4.03) must have been in error. This points to the inherent danger in assigning an empirical formula merely on the basis of microanalytical data.

(8) Analogous dehydrogenations have already been observed to occur in the C_{14}[2a,9a] and the C_{18} series.[9b]

(9) (a) F. Sondheimer, Y. Gaoni, L. M. Jackman, N. A. Bailey, and R. Mason, *J. Am. Chem. Soc.*, **84**, 4595 (1962); (b) R. Wolovsky, *ibid.*, **87**, 3638 (1965).

(10) It is of interest that the tribenzo analog of IV has been prepared very recently by two groups (H. A. Staab and F. Graf, *Tetrahedron Letters*, 751 (1966); I. D. Campbell, G. Eglinton, W. Henderson, and R. A. Raphael, *Chem. Commun.*, 87 (1966)).

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Electron Spin Resonance Determination of the Heat of Reaction for Triphenylmethyl Radical and Oxygen[1]

Sir:

We wish to report an experimental determination of the heat of reaction for the formation of a peroxy radical from a hydrocarbon radical and oxygen. This value has been obtained for triphenylmethyl radicals trapped in a crystal lattice permeable to oxygen.

Triphenylmethyl radicals were produced in the solid state by radiolysis of triphenylmethyl chloride, triphenylmethyl bromide, or triphenylacetic acid.[2]

$$Ph_3CX \xrightarrow{\quad} PH_3C\cdot \qquad (1)$$

$$X = Cl, Br, COOH$$
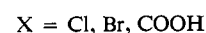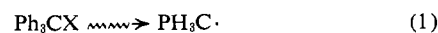
(1) Electron Spin Resonance Studies of Thermal Decomposition Mechanisms. Peroxides. I.

(2) γ-Radiation from cobalt-60 was used. The total dose was 4–10 × 10^{18} ev/g. The dose rate was 5 × 10^{15} ev/g sec^{-1}.

It is known that ionizing radiation produces alkyl radicals in solid alkyl halides.[3] The production of *t*-butyl radicals from radiolysis of pivalic acid has also been reported.[4]

A polycrystalline sample of triphenylmethyl chloride, triphenylmethyl bromide, or triphenylacetic acid subjected to radiation under vacuum[5] gives a symmetrical esr signal without hyperfine structure (g = 2.0024[6]; total line width = 10.7 gauss measured from maximum to minimum of first derivative curve). The signal is readily saturated at normal microwave powers. Upon admission of air or oxygen to the sample a new peak appears at lower field (g = 2.014; total line width = 7.4 gauss). The intensity of this peak increases with time at the expense of the triphenylmethyl radical. The new signal cannot be saturated. Since the observed g value is in good agreement with those reported by Ingold and Morton[7] for peroxy radicals, the new signal is attributed to the triphenylmethylperoxy radical.[8]

At 25° and at atmospheric oxygen pressure the conversion to the peroxy radical is at least 95% complete within 30 min in triphenylacetic acid. For triphenylmethyl chloride and bromide the reaction is much slower, the conversion after 2 hr being approximately 20 and 56%, respectively. There is evidently a marked difference in the rates of diffusion of oxygen in the crystal lattice of the three compounds.

When the temperature of the sample open to atmospheric oxygen is increased, the amount of peroxy radical decreases and the amount of triphenylmethyl radical increases. Upon cooling the same amount of peroxy radical reappears. With triphenylacetic acid as host the essentially complete conversion from triphenylmethyl radical to peroxy radical may be reversed repeatedly without any significant decrease in total radical concentration within the temperature range 25–130°. These observations demonstrate the existence of an equilibrium between triphenylmethylperoxy radical and triphenylmethyl radical and oxygen.[9]

$$Ph_3COO \cdot \; \rightleftarrows \; Ph_3C \cdot \; + \; O_2 \qquad (2)$$
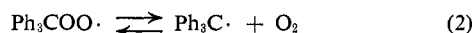
Further evidence for this equilibrium is the observation that the amount of peroxy radical decreases and the triphenylmethyl radical increases when the sample previously open to atmosphere is evacuated.

Equilibrium constants at atmospheric oxygen pressure were evaluated as a function of temperature in terms of the signal intensities of the peroxy radical.

(3) P. B. Ayscough and C. Thomson, *Trans. Faraday Soc.*, **58**, 1477 (1962); P. B. Ayscough and H. E. Evans, *J. Phys. Chem.*, **68**, 3066 (1964).

(4) H. Shields and P. Hamrick, *J. Chem. Phys.*, **42**, 443 (1965).

(5) Approximately 0.03 g was irradiated in tubes of high purity quartz (Supersil or Varian esr sample tubes) for 15–30 min. Signals resulting from irradiation of quartz were removed by annealing.

(6) A Varian 4502 epr spectrometer with 12-in. magnet was used. A dual cavity was used for *g*-value determinations.

(7) K. U. Ingold and J. R. Morton, *J. Am. Chem. Soc.*, **86**, 3400 (1964).

(8) Polycrystalline samples of tris-(*p*-nitrophenyl)methyl radical react slowly with oxygen to give a new radical (g = 2.006) attributed to tris-(*p*-nitrophenyl)methylperoxy radical: F. M. Schimmel and F. W. Heineken, *Physica*, **23**, 781 (1957).

(9) The possibility of a rapid equilibrium between triphenylmethylperoxy radical and triphenylmethyl radical and oxygen has been previously suggested: D. G. Hendry and G. A. Russell, *J. Am. Chem. Soc.*, **86**, 2371 (1964). Radicals resulting from γ-radiation of polytetrafluoroethylene have been shown to react reversibly with oxygen: T. Matsugashita and K. Shinohara, *J. Chem. Phys.*, **32**, 954 (1960); **35**, 1652 (1961).
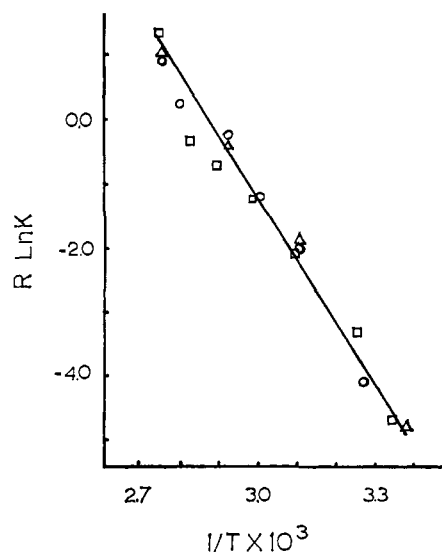

Figure 1. Plot of $R \ln K$ vs. $1/T$ for $Ph_3COO \cdot \rightleftarrows Ph_3C \cdot + O_2$. K is K(apparent) as defined in the text. The symbols O, □, and △ are different heating sequences of the same sample.

$$K(\text{apparent}) = \frac{(Ph_3COO \cdot)_0 - Ph_3COO \cdot}{Ph_3COO \cdot} \qquad (3)$$

$(Ph_3COO \cdot)_0$ represents the peroxy signal response with less than 1% of the radical present in the triphenylmethyl form and $Ph_3COO \cdot$ represents the equilibrium signal due to the peroxy radical at the temperature of the experiment. A plot of the logarithm of the equilibrium constant vs. the reciprocal of the absolute temperature gives a heat of reaction for the process in eq 2 of ΔH = 9.0 ± 0.4 kcal/mole (Figure 1). The ΔH for the reaction of the benzyl radical with oxygen (ΔH = 13 ± 2.5 kcal/mole) has been estimated by Benson.[10] If the resonance energy for the trityl radical is 3 kcal/mole greater than that for the benzyl radical,[11] the estimated ΔH for reaction 2 is 10 ± 2 kcal/mole.

The equilibrium constant defined in eq 3 is an apparent constant based upon the reasonable assumption that the activity of the oxygen to which the samples are exposed and, therefore, the activity in the solid is constant. This apparent K may be used directly in the calculation of $\Delta H°$. In order to estimate $\Delta G°$ and $\Delta S°$, one must assume a value for this activity. Using a value of 0.2 atm, one obtains at 298°K $\Delta G°$ = 2.2 kcal/mole. With $\Delta H°$ = 9.0 kcal/mole⁻¹, $\Delta S°$ = 23 gibbs/mole.

A significant decrease in radical concentration resulted from heating triphenylmethyl chloride and bromide. The radicals may be reacting with the host to give nonradical products or with each other at temperatures where increased rates of diffusion are likely. In crystalline solids which do not undergo phase transition below the temperature of fusion (T_f), the critical temperature at which recombination of radicals begins is about $0.8–0.9T_f$.[12] For triphenylmethyl chloride and bromide this critical temperature is in the range

(10) S. W. Benson, *J. Am. Chem. Soc.*, **87**, 972 (1965). Benson has calculated ΔH for the reaction of benzyl radical with oxygen from the heats of formation for benzyl hydroperoxide and the benzyl radical assuming the ROO–H bond strength to be the same as that for HOO–H.

(11) S. W. Benson, *J. Chem. Educ.*, **42**, 502 (1965).

(12) R. Bensasson, M. Durup, A. Dworkin, M. Magat, R. Marx, and H. Szwarc, *Discussions Faraday Soc.*, **36**, 177 (1964).

where triphenylmethylperoxy radical decomposes. Triphenylacetic acid was found most suitable because its critical temperature is above the temperatures used in this study.

The solid state appears to be a promising medium for obtaining thermochemical and kinetic data for stable radicals and oxygen. Preliminary results have been obtained for other radicals, e.g., 9-phenylfluorenyl.

Acknowledgment. This work was supported in part by a grant from the Division of Radiological Health of the U. S. Public Health Service and the Director of General Research of the University of Georgia.

(13) University of Georgia Alumni Foundation Fellow, 1965–1966.

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Substitution Reaction of 3-Ev Tritium Atoms with Methane[1]

Sir:

We have produced 3-ev tritium atoms by the photolysis of TBr with 1849-A radiation and have observed both the abstraction and substitution reactions 1 and 2

$$T^* + CH_4 \longrightarrow HT + CH_3 \qquad (1)$$
$$T^* + CH_4 \longrightarrow CH_3T + H \qquad (2)$$
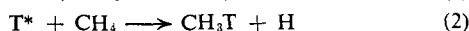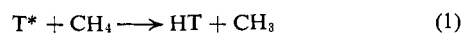
with methane. Previous experimenters have demonstrated that deuterium atoms from the photolysis of DI with 2537-A radiation, and from the photolysis of DBr with 1849-A radiation, undergo hot reactions with methane,[2,3] but the experimental systems did not permit the separation of the contributions of the reactions corresponding to (1) and (2), or even to demonstrate the qualitative presence of both reactions.[4] Tritium atoms formed with much higher energy by nuclear-recoil processes react by both reactions 1 and 2 in the yield ratio of approximately 0.8–1.0 for halogen or oxygen-scavenged methane.[5-7] Our experiments indicate that the yield ratio of reactions 1 and 2 is approximately 3.5–4.0 for 3-ev atoms in methane and depends to some extent on the ratio of scavenger molecule to methane.

The abstraction and substitution reactions cannot be separated in these photolytic systems if the photolytic source also serves as the scavenger molecule in this system; the CH_3 radical from (1) abstracts T from TBr and forms CH_3T, while the H from (2) forms HT by abstraction. Such combination photolytic source and scavenger experiments have been used in successful measurements of the total hot reaction in methane for D

(1) This research has been supported by AFOSR Grant No. 62–15 at the University of Kansas, and by AEC Contract No. 34, Agreement No. 126, at the University of California, Irvine.
(2) R. J. Carter, W. H. Hamill, and R. R. Williams, Jr., *J. Am. Chem. Soc.*, 77, 6457 (1955).
(3) R. M. Martin and J. E. Willard, *J. Chem. Phys.*, 40, 3007 (1964).
(4) The yield of the substitution reaction has been shown to be quite small for 0.9–1.8-ev T atoms from the 2537-A photolysis of TI in the presence of I_2: M. C. Sauer, Jr., Ph.D. Thesis, University of Wisconsin, 1958.
(5) M. F. A. El-Sayed and R. Wolfgang, *J. Am. Chem. Soc.*, 79, 3286 (1957); M. Henchman, D. Urch, and R. Wolfgang, "Chemical Effects of Nuclear Transformations," Vol. 2, International Atomic Energy Agency, Vienna, p 83.
(6) A. A. Gordus, M. C. Sauer, Jr., and J. E. Willard, *J. Am. Chem. Soc.*, 79, 3284 (1957).
(7) J. W. Root, Ph.D. Thesis, University of Kansas, 1964; J. W. Root and F. S. Rowland, unpublished results.

Table I. Distribution of Tritium Radioactivity after 1849-A Photolysis of TBr in Methane

Sample no.	— Pressure of reactants,[a] mm —			Measured product ratios after photolysis, HT/CH_3T
	CH_4	Br_2	O_2	
31	220	86	...	3.37[b]
32	430	10	...	4.19[b]
65	350	32	...	3.57[c]
64	350	33	...	3.58[c]
63	350	32	...	3.57[d]
59	320	<3	30	3.75[e]
60	310	30	...	3.64[e]

[a] TBr present in carrier-free quantities; $\sim 10^{-3}$ mm. [b] 1-min irradiation with lamp current at 39 ma. [c] 1-min irradiation with lamp current at 49 ma. [d] Fused quartz lamp was used instead of Suprasil quartz lamp; irradiation at 50 ma for 1 min. [e] 2-min irradiation with fused quartz lamp at 50 ma.

atoms[2,3] and in hexane for T atoms.[8] We have carried out our experiments using carrier-free TBr and utilizing Br_2 as the scavenger molecule, thereby avoiding the formation of a radioactive molecule in the second reaction following (1) and (2).

Appropriate mixtures of TBr, CH_4, and Br_2 were introduced into Suprasil quartz photolysis cells, and irradiation was carried out in a nitrogen atmosphere with a low-pressure Hg lamp, also of Suprasil quartz. While the main output of the lamp is in the ultraviolet region at 1849 and 2537 A, the absorption of TBr at 2537 A is sufficiently small relative to that at 1849 A[9,10] that the irradiations were carried out without using any filters. The tritiated products were analyzed by radio gas chromatography. Similar experiments have also been carried out with C_2H_6. Typical results are shown in Table I.

Carrier-free TBr was prepared by passing an electric discharge between two gold electrodes in a vessel containing a mixture of T_2 and Br_2, and then by pumping off the unreacted T_2 at $-196°$. Mixtures of TBr, Br_2, and methane showed negligible radioactivity as molecular hydrogen or hydrocarbons, whether analyzed immediately, or after storage for 24–48 hr. Mixtures prepared as usual, but substituting Vycor glass for the Suprasil quartz in the reaction vessel, showed no radioactivity in either HT or CH_3T, confirming that the hot T atoms are formed almost entirely through photolysis with 1849-A radiation. The actual TBr pressure is estimated to be 10^{-3} mm.

Since the abstraction reaction of H atoms with methane is well established, the qualitative question of importance is whether or not the observed yield of CH_3T was formed by the substitution reaction 2. The most likely other source of CH_3T would be from the reaction with TBr of CH_3 radicals formed by some other process in the system.[11] An estimate of this contribution can

(8) D. Perner and R. H. Schuler, *J. Phys. Chem.*, 70, 317 (1966). These authors have demonstrated the equivalence in yield of HT and $C_6H_{13}T$ in the photolysis of TI in hexane.
(9) C. F. Goodeve and A. W. C. Taylor, *Proc. Roy. Soc.* (London), A152, 221 (1935).
(10) J. Romand, *Ann. Phys.* (Paris), 4, 527 (1948).
(11) There is no positive evidence for CH_3 radicals in our system. However, the absorption cross section for methane for 1849-A radiation is extremely small at low pressures but has been reported as nonnegligible at pressures approaching 1 atm; see A. B. F. Duncan and J. P. Howe, *J. Chem. Phys.*, 2, 851 (1934), and S. W. Leifson, *Astrophys. J.*, 63, 73 (1926).