

not there established, but, since recent work¹⁴ shows that electron attachment to O₂ is a fast process, the discontinuity may be attributed to electron attachment to molecular oxygen product with accompanying reduction in DEA. The identical reductions in rate by 1% Ag⁺ and by interstitial molecular oxygen, alone or in combination with 0.4% Ag⁺, are then most readily explained by total scavenging of low-energy electrons by these concentrations of Ag⁺ and/or O₂. Maximum reductions of DEA processes would be predicted for AgNO₃ on mechanism B and, in fact, G_{NO₂-} experimental values for that salt fall (30 ± 10)% below the value predicted from the linear relationship between "free-space" and log G_{NO₂-} for other univalent nitrates.¹⁵

We are continuing studies on the radiolysis of ionic solids to assess the relative importance of mechanisms A and B, and the possible role of localization and ionization of superexcited states close to impurity centers.

(14) S. Gordon, E. J. Hart, J. Matheson, and J. K. Thomas, *J. Am. Chem. Soc.*, **85**, 1375 (1963).

(15) J. Cunningham and L. R. Steele, *Phys. Rev. Letters*, **9**, 47 (1962).

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Cyclobutane Formation from Mercury-Photosensitized Reactions of Ethylene

Sir:

It is now generally agreed that Hg 6³P₁ photosensitization of ethylene produces this molecule in one or more electronically excited states, presumably of triplet character.¹ Earlier work has not indicated a gross amount of C₄ products which might result from addition of a triplet diradical ethylene to a molecule of ethylene in the ground state^{2,3}; knowledge of such reactivity of other triplet species, e.g., oxygen and sulfur atoms,^{4,5} toward double bonds indicated the possibility of an excited molecule addition reaction in low yield for triplet ethylene. In the work being reported here the photosensitized reactions of ethylene were reinvestigated at higher pressures and lower conversions than hitherto employed to obtain information concerning the bimolecular reactivity of the triplet ethylene.

Matheson Research Grade ethylene at pressures between 18 and 140 cm. was circulated through a closed loop system consisting of a mercury saturator and a trap at 0° to maintain a constant mercury pressure and then through a fused silica photolysis cell at ca. 30°. After irradiation with a mercury resonance lamp, the pressure of noncondensable gas was measured to determine the extent of decomposition to hydrogen and acetylene. The photolyses were carried to a maximum of 0.1% decomposition to noncondensables. A primary product separation using a 0.5-in. diameter silicone oil on firebrick g.l.p.c. column at 0° removed the bulk of the unreacted ethylene. The C₄ and higher product mixture, obtained by heating and backflushing this column, was then subjected to g.l.p.c. analysis using a flame ionization detector. Silicone oil and silver nitrate in glycerol columns, whose temperatures were separately variable, were operated in series. A low holdup grease-free valve before the flame permitted the rescue of selected larger peaks for mass spectra.

(1) D. W. Setser, B. S. Rabinovitch, and D. W. Placzek, *J. Am. Chem. Soc.*, **85**, 862 (1963).

(2) B. de B. Darwent, *J. Chem. Phys.*, **20**, 1673 (1952).

(3) J. R. Majer, B. Mile, and J. C. Robb, *Trans. Faraday Soc.*, **57**, 1342 (1962).

(4) R. J. Cvetanović, *Can. J. Chem.*, **38**, 1678 (1960).

(5) O. P. Strausz and H. E. Gunning, *J. Am. Chem. Soc.*, **84**, 4080 (1962).

The principal products observed were butane, butene-1, butadiene, cyclobutane, hexene-1, and hexane. Acetylene is not eluted from the silver nitrate column.

The cyclobutane yield appeared to increase linearly with ethylene pressure, although the yields of the other products decreased roughly as the reciprocal of the ethylene pressure. Addition of 99 and 224 cm. of argon on two runs to reactant ethylene at a pressure of 18 cm. had the effect of decreasing the yields of all products except cyclobutane; the product mixture composition at 224 cm. of argon and 18 cm. of ethylene was typical of that observed with 36 cm. of ethylene alone. The low-voltage mass spectrum of the butene-1, produced from a run starting with 73 cm. of an ethylene mixture containing 32% C₂D₄, showed major contributions at *m/e* = 63 and at other mass numbers corresponding to an odd number of deuterium atoms in the parent molecule ion. It is concluded from this analysis that the bulk of the butene-1 is not produced by an intramolecular rearrangement of an ethylene dimer, which would yield butene-1 as C₄H₈, C₄H₄D₄, and C₄D₈, but must arise from radical addition and disproportionation processes involving vinyl and butenyl radicals. It is known that vinyl radicals are a product of the primary quenching process in small yield at lower ethylene pressures, but the importance of this mode of ethylene decomposition at the pressures employed in this study has not been reported previously. The ethylene fraction recovered from the work with the C₂H₄-C₂D₄ mixture was examined for the presence of C₂H₂D₂ which would result from the decomposition of cyclobutane C₄H₄D₄. Low-voltage mass spectra gave the ^{30/32} mass ratio of 0.015 ± 0.001 for the reactant C₂D₄, and 0.015 ± 0.001 for the recovered ethylene mixture. This indicates that any C₂H₂D₂ formed was less than 0.1% of the C₂D₄ present. Analysis (g.l.p.c.) of this recovered ethylene mixture using a 100-ft. silver nitrate in glycerol column, which was capable of separating isotopically different ethylenes, further reduced the limit for C₂H₂D₂ content to less than 0.01%.⁶ Measurements of relative quantum yields by Callear and Cvetanović⁷ up to 74 cm. may be combined with Darwent's² absolute measurements at lower pressures for ethylene saturated with mercury at 0° to give a hydrogen quantum yield of 3.9 × 10⁻³ at 70 cm. The quantum yields for other products found in the current work at this ethylene pressure may then be calculated. The quantum yields for cyclobutane, butene-1, butane, butadiene, hexene-1, and hexane are then found to be 3.8 × 10⁻⁶, 48 × 10⁻⁶, 1.34 × 10⁻⁴, 46 × 10⁻⁶, 2.3 × 10⁻⁴, and 1.3 × 10⁻⁴, respectively. Absolute values are probably not valid to better than ±50 or 100%. At a typical total light input of 0.14 einstein/mole of ethylene, the limits of detection set for C₂H₂D₂ correspond to a quantum yield for this species of less than 7 × 10⁻⁴, or less than 100 molecules of C₂H₂D₂ formed per molecule of cyclobutane C₄H₄D₄ found as a product at a total ethylene pressure of 74 cm. The 112 kcal./einstein mercury excitation gives 131 kcal./mole as a maximum possible value for the excess energy of a cyclobutane molecule, 68 kcal. above the barrier to decomposition to ethylene, assuming no partial deactivation of excited ethylene or tetramethylene intermediates. Thus, if the addition of triplet ethylene to ground state ethylene is an efficient process, followed by an efficient triplet-singlet transition of the tetramethylene to a highly vibrationally excited cyclobutane, this cyclobutane would be expected to have a very short and pressure-dependent lifetime before reversion to ethylene. The upper bound of 7 × 10⁻⁴

(6) We are indebted to Dr. Colin MacKay for this analysis.

(7) A. B. Callear and R. J. Cvetanović, *J. Chem. Phys.*, **24**, 873 (1956).

set for the quantum yield for $C_2H_2D_2$ is evidence that efficient cyclobutane formation and decomposition is not taking place. The increase in cyclobutane yield with increased pressure of ethylene or inert gas indicates, however, that some collisional stabilization of vibrationally excited cyclobutane is occurring. It has been noted⁸ that excited ethylene appears to undergo efficient electronic as well as vibrational energy relaxation on collision with other ethylene molecules. At 70 cm. a quantum yield of 3.8×10^{-6} for cyclobutane formation then becomes to an order of magnitude the lower limit for the collision efficiency for addition of excited ethylene to a carbon-carbon double bond. This is between the efficiencies of 1.1×10^{-3} and 3.1×10^{-9} reported⁹ for the addition of hydrogen atoms and methyl radicals to ethylene at *ca.* 25°. Thus, the excited ethylene species does not appear to be exceedingly more reactive than these monoradicals in their ground states.

Acknowledgment.—This work was performed under the support of the USPHS, grant GM 11344-01. The use of the University of Pennsylvania mass spectrometric facilities and the assistance of Mr. Jonathan Kabat in part of the calculations and experimental work are gratefully acknowledged.

(8) D. W. Setser, D. W. Placzek, R. J. Cvetanovic, and B. S. Rabinovitch, *Can. J. Chem.*, **40**, 2179 (1962).

(9) A. F. Trotman-Dickenson, "Gas Kinetics," Butterworths Scientific Publications, London, 1955, pp. 287, 296.

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The Synthesis of 7-Substituted Adenines through the Use of a Blocking Group at the 3-Position. Site of Alkylation of 7-Substituted Adenines¹

Sir:

The recent communication by Montgomery and Thomas² of the synthesis of 7- α -D-ribofuranosyladenine, the nucleoside moiety of pseudovitamin B₁₂, and its anomer, starting from 3-benzyladenine prompts us to record a direct, general synthesis which we have employed for 7-substituted adenines.³ Treatment of adenine with benzyl,² allyl, and γ,γ -dimethylallyl bromide in dimethylacetamide furnished, after basification, the corresponding 3-substituted adenine (I) as the major product (55–66%): 3-benzyladenine, m.p. 278–280^{4,5}, pK_a' 5.0 \pm 0.1 in 50% DMF; 3-allyl-adenine, m.p. 204–205°, pK_a' 5.2; 3-(γ,γ -dimethylallyl)-adenine (*triacanthine*), m.p. 230–231°, pK_a' 5.4.⁷ *The efficient formation of the last of the group constitutes the most direct synthesis of triacanthine.*^{6,8} Characterization of all as 3-substituted adenines is readily achieved by determination of their acid dissociation constants and their ultraviolet spectra in neutral and acid

(1) Supported by a research grant (USPHS-RG5829, currently GM-05829-05) from the National Institutes of Health, U. S. Public Health Service.

(2) J. A. Montgomery and H. J. Thomas, *J. Am. Chem. Soc.*, **85**, 2672 (1963).

(3) Reported at the Second International Symposium on the Chemistry of Natural Products, Prague, Czechoslovakia, August, 1962, and in the Reilly Lectures, University of Notre Dame, November, 1962.

(4) R. Denayer, *Bull. soc. chim. France*, 1358 (1962).

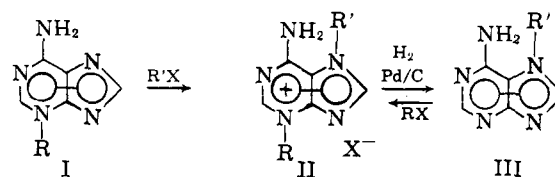
(5) We have ascertained that the material obtained according to the directions of M. Krüger, *Z. physiol. Chem.*, **18**, 423 (1894), and G. Thoiss, *ibid.*, **13**, 395 (1889), namely, treatment of adenine with benzyl chloride in the presence of potassium hydroxide, is a mixture of 3-benzyladenine and 9-benzyladenine, m.p. 233–235°.

(6) See N. J. Leonard and J. A. Deyrup, *J. Am. Chem. Soc.*, **84**, 2148 (1962), and references therein.

(7) Correct analyses have been obtained for all of the compounds reported herein.

(8) R. Denayer, A. Cavé, and R. Goutarel, *Compt. rend.*, **263**, 2994 (1961).

media.^{6,8} Preferential 3-substitution on adenine^{9–11} was accompanied by formation of the corresponding 9-substituted adenines (10–14%) and 1-substituted adenines (7–13%), paralleling the experience of Pal¹⁰ in ethylation and methylation under different conditions.



The 3-substituted adenines described above underwent methylation mainly at the 7-position (II) (71–76% yield) when heated with methyl iodide in acetone or dimethylacetamide: 3-benzyl-7-methyladenine iodide, m.p. 261–262°; 3-allyl-7-methyladenine iodide, m.p. 256–258°; 3-(γ,γ -dimethylallyl)-7-methyladenine iodide (*triacanthine methiodide*),⁶ m.p. 236–239°. The salts were readily converted to perchlorates or chlorides and as such had similar ultraviolet spectra (*e.g.*, 3-(γ,γ -dimethylallyl)-7-methyladenine perchlorate: $\lambda_{\max}^{H_2O}$ 277 m μ (ϵ 17,100); λ_{sh} 223 (13,300); λ_{\min} 241 (4400) essentially unchanged in 0.1 N HCl; $\lambda_{\max}^{1.0N NaOH}$ 281 (15,800); λ_{\min} 242 (2500); isosbestic point, 282 m μ) indicative of identical positional disubstitution.¹² The location of the methyl group was established by hydrolysis, which led in each case to the formation of some 7-methyladenine (III), m.p. 349–350° dec.,¹³ produced most efficiently (72%), along with toluene, from 3-benzyl-7-methyladenine chloride. The synthesis of 7-methyladenine by benzyl blocking at the 3-position of adenine (I), followed by methylation on N-7 (II) and hydrogenolysis at N-3 (III), is only one representative of a *general 7-alkylation procedure*.

The preferred site of alkylation of 7-substituted adenines has been determined readily in the corollary experiment (III \rightarrow II) of heating 7-methyladenine with benzyl, allyl, and γ,γ -dimethylallyl bromide in dimethylacetamide to yield (71–84%) the corresponding 3-benzyl-7-methyladenine bromide, m.p. 254–255°; 3-allyl-7-methyladenine bromide, m.p. 241–243°; 3-(γ,γ -dimethylallyl)-7-methyladenine bromide, m.p. 230–231°. These salts, converted to a common anion, were identical with the separate 3,7-disubstituted adenine salts produced by the first route (I \rightarrow II).^{14,15} Further interest in the hydrolytic cleavage stems from the partially selective conversion, using hydrogen and palladium/charcoal, of 3,7-dibenzyladenine chloride (obtained from the bromide, m.p. 205–207°, which was made by benzylation of 3-benzyladenine), to 7-benzyladenine, m.p. 236–238° dec.

(9) J. W. Jones and R. K. Robins, *J. Am. Chem. Soc.*, **84**, 1914 (1962).

(10) B. C. Pal, *Biochemistry*, **1**, 558 (1962); also B. C. Pal and C. A. Horton, Abstracts of Papers, 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., September, 1962, p. 39c.

(11) N. J. Leonard and R. A. Laursen, *J. Am. Chem. Soc.*, **85**, 2062 (1963).

(12) Dr. R. K. Robins, Arizona State University, Tempe, Ariz., has kindly informed us of his similar results on the methylation of 3-methyladenine.

(13) We are grateful to Dr. R. K. Robins and to Dr. E. C. Taylor, Jr., of Princeton University, for providing us with authentic samples of 7-methyladenine, with which our product was identical.

(14) In the case of the 3-(γ,γ -dimethylallyl)-7-methyladenine salt, the structure of our triacanthine methiodide⁶ is thus confirmed (see above and ref. 6).

(15) The n.m.r. spectra of compound types I, II, and III will be discussed fully in a forthcoming joint publication from Dr. Robins' Laboratory and our own.

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