the mixture was cooled and filtered to give 4.6 g. of O-methyl benzothiazole-2-carboxaldoxime, m.p. 65–68°.

Anal. Found: C, 55.7; H, 4.4.

This product (4.0 g.) and 10 ml. of methyl iodide in 75 ml. of methanol were refluxed for 85 hr. Ether was added to give 0.6 g. of an orange solid, m.p. 201–203° dec.

Anal. Calcd. for $C_{10}N_{11}IN_2OS$: C, 35.9; H, 3.3. Found: C, 35.6; H, 3.3.

N-Methyl-2-formyl-3-methylbenzothiazolium Iodide Oxime (V).—A similar procedure as described for VI (except that N-methylhydroxylamine was used) gave 26% of an orange solid, m.p. 233–235° dec.

Anal. Calcd. for $C_{10}H_{11}IN_2OS$: C, 35.9; H, 3.3. Found: C, 35.7; H, 3.4.

Nuclear Magnetic Resonance Studies.—The spectra were obtained using a Varian Model HR-60 high resolution n.m.r. spectrometer equipped with an electronic integrator. All chemical shifts are reported in cycles per second at 60 Mc./sec. downfield from the reference signals used. Tetramethylsilane was used as a reference for spectra obtained in acetonitrile and the methyl resonance of sodium 2,2-dimethyl-2-silapentane-5-sulfonate was used as a reference for the spectra obtained in D_2O.[17] All chemical shifts were determined using the side band technique.[18]

Acknowledgment.—The authors wish to express their gratitude to the Analytical Research Branch of the Research Directorate, U. S. Army Chemical Research and Development Laboratories, for part of the analyses reported here.

[17] G. V. D. Tiers and R. I. Coon, *J. Org. Chem.*, **26**, 2097 (1961).

[18] J. T. Arnold and M. E. Packard, *J. Chem. Phys.*, **19**, 1608 (1951).

Bridged Polycyclic Compounds. XXII. The Carbenoid Decomposition of Nortricyclenone *p*-Toluenesulfonylhydrazone

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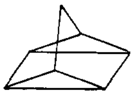
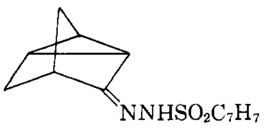
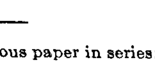
An attempt to prepare quadricyclo[2,2,1,$0^{2,6}$,$0^{3,5}$]-heptane (I) by treatment of the *p*-toluenesulfonylhydrazone of nortricyclenone (II) using the general procedure described by Friedman and Shechter[2] (heating with sodium methoxide in diglyme at 160°) gave hydrocarbon material (19% yield) which apparently did not contain any I,[3] but instead was a mixture of 69% of 4-ethynylcyclopentene (III), and 29% of 4-vinylidenecyclopentene (IV). The mixture of these two materials was separated by vapor phase chromatography.



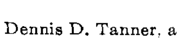
I



II



III



IV

Compounds III and IV were characterized and identified as follows. III gave the correct C,H analysis and decolorized bromine in carbon tetrachloride and 2% aqueous potassium permanganate instantaneously. Catalytic hydrogenation of III with palladium-on-charcoal catalyst in ethanol at room temperature led to rapid absorption of three moles of hydrogen per mole of compound. The boiling point of III was approximately 92° (628 mm.) and indicates a monomer. The infrared spectrum of III clearly showed the presence of an acetylenic function, exhibiting a strong, sharp absorption peak at 3.02 μ and a sharp, but less intense peak at 4.73 μ. Sharp peaks at 3.27 and 6.21 μ are ascribed to the ethylenic hydrogens and carbon–carbon double-bond stretching vibrations. The nuclear magnetic resonance spectrum of III exhibited a singlet at 4.42 τ, a complicated multiplet between 6.8 and 7.8 τ, and a clear doublet at 8.12 τ with relative areas of the peaks being 1.94, 5.09, and 1.00, respectively. The singlet at 4.42 τ is ascribed to the ethylenic hydrogens. Cyclopentene itself has a sharp singlet at 4.40 τ. The doublet at 8.12 τ (J = 2.0 c.p.s.) is assigned to the acetylenic hydrogen which is split by the methinyl hydrogen. Several examples of such 1,3 splittings are known.[4]

It was expected that the spin–spin splitting pattern of the olefinic hydrogens in the nuclear magnetic resonance spectrum of the acetylene would distinguish between the symmetrical compound III and its unsymmetrical isomer, 3-ethynylcyclopentene. However, when the nuclear magnetic resonance spectra of similar isomers, Δ^2 and Δ^3-cyclopentenylacetamide,[5] were obtained, it was found that the splitting pattern of the olefinic hydrogens of the isomers was essentially the same, although the appearance of the over-all spectrum clearly indicated two isomers.

Although IV was unstable, its structure was established unequivocally by spectral means. The infrared spectrum of IV clearly indicated the presence of the allene function by a sharp intense absorption peak at 5.10 μ. The allene function is reported[6] to absorb at 5.08 to 5.12 μ. Sharp peaks of medium intensity at 3.27 and 6.21 μ are again ascribed to the ethylenic hydrogen and carbon–carbon double-bond stretching vibrations. The nuclear magnetic resonance spectrum of IV consists of a sharp singlet at 4.48 τ, a pentuplet centered at 5.40 τ, and a triplet centered at 6.87 τ with relative peak areas of 0.95, 1.00, and 1.97, respectively. The relative intensities of the components of the triplet were 1:2:1 and of the pentuplet 1:4:6:4:1, indicating that the multiplicity is the result of groups of equivalent nuclei splitting with each other.[7] The spectrum is clearly compatible only with the structure IV for the allene. Finally, the fact that the acetylene isolated is isomerized to IV makes it most probable that it is the 4-ethynyl derivative. It is unlikely that the conditions employed are drastic enough to isomerize the carbon–carbon double bond concurrently with the acetylene–allene transformation.

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[1] Previous paper in series: S. J. Cristol, Dennis D. Tanner, and Robert P. Arganbright, *J. Org. Chem.*, **28**, 1374 (1963).

[2] (a) L. Friedman and H. Shechter, *J. Am. Chem. Soc.*, **81**, 5512 (1959); (b) **82**, 1002 (1960); (c) G. L. Closs, *ibid.*, **84**, 809 (1962).

[3] W. G. Dauben and R. L. Cargill, *Tetrahedron*, **15**, 197 (1961).

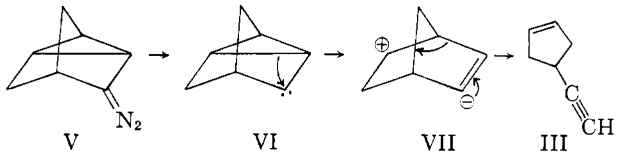
[4] N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, "NMR Spectra Catalog," Varian Associates, Palo Alto, Calif., 1962.

[5] S. J. Cristol and P. K. Freeman, *J. Am. Chem. Soc.*, **83**, 4427 (1961).

[6] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 61.

[7] The nuclear magnetic resonance spectrum of IV is being considered in detail elsewhere: M. W. Hanna and J. K. Harrington, *J. Phys. Chem.*, in press.

Friedman and Shechter[2b] have observed that acetylene and ethylene are formed in the carbenoid decomposition of cyclopropanecarboxyaldehyde *p*-toluenesulfonylhydrazone and methylacetylene and ethylene from the related reaction starting with cyclopropyl methyl ketone. It would appear that the formation of an acetylene and an olefin may be general for carbenes in which one of the substituents is a cyclopropane ring. The transformation involved in the formation of III can be represented as follows.



V VI VII III

There is, of course, no certainty regarding the existence of intermediates VI and VII. The formation of allene IV seems best rationalized on the basis that it is the result of base-catalyzed isomerization[8] of the acetylene III rather than a direct product of the carbene reaction. This rationalization is supported by the fact that only III was formed (in 42% yield) upon thermal decomposition of the potassium salt of II or upon irradiation of the salt of II according to the general procedure of Dauben and Willey.[9] It is also supported by the fact that III was isomerized to IV under conditions similar to those used in the decomposition of II.

Experimental

Elemental analyses were performed by Galbraith Microanalytical Laboratories, Knoxville, Tennessee. Infrared spectra were recorded on a Beckman IR-5 double beam spectrophotometer equipped with sodium chloride optics. Spectra were obtained in carbon tetrachloride solution. Nuclear magnetic resonance spectra were obtained in carbon tetrachloride solution with an A-60 analytical spectrometer of Varian Associates using tetramethylsilane as an internal standard. Vapor phase chromatograms were obtained with a Perkin-Elmer Model 154-D vapor fractometer. Analyses and separations were effected on a 1-m. glass column charged with 30% UCON Oil LB-550-X on Chromosorb W. All runs were made at 72° with a flow rate of 87 ml. of helium/min. Peak areas were determined by triangulation and corrected for variation in thermal conductivity except that thermal conductivities of III and IV were considered equal.

Nortricyclenone.—The preparation of nortricyclenone was accomplished according to the method of Schaefer.[10] The ultraviolet spectrum and melting point of its 2,4-dinitrophenylhydrazone agreed with the values given by Roberts, Trumbull, Bennett, and Armstrong.[11] The ketone was stored as the stable sodium bisulfite addition compound and regenerated as needed by hydrolysis with aqueous sodium carbonate.

Nortricyclenone *p*-Toluenesulfonylhydrazone.—To a solution of *p*-toluenesulfonylhydrazine (27.0 g., 0.145 mole) in 300 ml. of 1% ethanolic sulfuric acid, nortricyclenone (15.5 g., 0.144 mole) was added all at once. The mixture was heated to 55° for approximately 5 min., then poured into ice-water, and allowed to crystallize at 10°. Filtration yielded 37.4 g. (94%) of the dry *p*-toluenesulfonylhydrazone, m.p. 157–159° dec. An analytical sample was prepared by recrystallization from ethanol–water, m.p. 158.5–160° dec., λ_{max} (in ethanol), 275 mμ, ϵ 700; 225 mμ, ϵ 15,000.

Anal. Calcd. for $C_{14}H_{16}N_2O_2S$: C, 60.84; H, 5.84. Found: C, 60.93; H, 5.99.

Decomposition of Nortricyclenone *p*-Toluenesulfonylhydrazone with Excess Sodium Methoxide.—The decomposition was carried out by a modification of the procedure of Closs.[2c] A three-neck flask was equipped with dropping funnel, magnetic stirrer, fritted nitrogen inlet, and a 30-cm. Vigreux column. The Vigreux column was wrapped with electrical heating tape and connected with two receiving traps in series which were cooled in a mixture of Dry Ice and acetone. The jacketed Vigreux column was heated to 100° and the system purged with prepurified nitrogen which was used as a carrier gas to sweep out the products of the reaction. Dry reagent-grade sodium methoxide (7.71 g., 0.143 mole) was suspended in diglyme (distilled twice from lithium aluminum hydride) and the suspension was heated in a stirred oil bath at 160°. A solution of II (12.0 g., 0.044 mole) in diglyme (150 ml.) was added dropwise over a period of 3 hr. The contents of the two traps were diluted with a fivefold excess of water and extracted three times with 25-ml. portions of pentane. The combined extracts were dried and the pentane was removed by careful distillation through a 30-cm. coiled wire column. Hydrocarbon material, 748 mg. (19%), composed essentially of III and IV, was obtained. III and IV were then separated by vapor phase chromatography. III had a retention volume of 1650 ml. and IV a retention volume of 2300 ml. The ratio of III to IV was 71/29. III instantly decolorized bromine in carbon tetrachloride in a capillary test. III dissolved in acetone decolorized a drop of 2% aqueous potassium permanganate. A sample of III was purified for analysis by vapor phase chromatography, n^{20}D 1.4592.

Anal. Calcd. for C_7H_8: C, 91.25; H, 8.75. Found: C, 91.42; H, 8.55.

The boiling point of III, taken by Emrich's method,[12] was approximately 92° (628 mm.). Reduction of III (43.3 mg., 0.470 mmole) in 95% ethanol (20 ml.) was effected over 50 mg. of prereduced 10% palladium on charcoal in a low pressure apparatus at 632 mm. and 22.5°. Hydrogen (40.4 ml.) was taken up in 5–6 min., corresponding to an uptake of 2.95 moles of hydrogen per mole of III.

IV was obtained in pure form (a single peak on reinjection) by vapor phase chromatography but proved to be unstable. Upon standing at room temperature, IV changed to a yellow gum in a few hours and to a solid in approximately 24 hr. The structure of IV was established by analysis of its nuclear magnetic resonance spectrum.

Neutralization of Nortricyclenone *p*-Toluenesulfonylhydrazone with One Equivalent of Sodium Methoxide.—A dry 50-ml. two-neck flask was equipped with a nitrogen inlet and distilling head. The system was purged with prepurified nitrogen. To it was added II (5.913 g., 0.0214 mole), dry sodium methoxide (1.129 g., 0.0209 mole), and absolute methanol (15.0 ml.). A clear solution was obtained. Methanol was then removed by distillation under reduced pressure. The residue was ground in an agate mortar and pestle in a dry box under an atmosphere of prepurified nitrogen and dried under reduced pressure over phosphoric anhydride.

Thermal Decomposition.—This dry product (most probably the salt of II, m.p. > 200°) and diglyme (25 ml., distilled from lithium aluminum hydride) were placed in a flask fitted with a nitrogen inlet and a heated Vigreux column connected with two receiving traps cooled in a mixture of Dry Ice and acetone. The apparatus was lowered into a stirred oil bath held at 160° and heated for two hours with nitrogen flowing through the system. The contents of the traps were analyzed by vapor phase chromatography and only III (42% using benzene as an internal standard) was found. No observable amounts of IV were detectable. The contents of the traps were poured into water (100 ml.) and extracted with pentane. The combined extracts were dried and the pentane removed by careful distillation to give III (687 mg., 36%) contaminated by a small amount of pentane. Analysis by vapor phase chromatography again showed IV to be absent.

Photolytic Decomposition.—A sample of the product (730 mg.) obtained by treating II with one equivalent of sodium methoxide was suspended in dry diglyme (10 ml.) in a quartz tube, stirred with a magnetic stirrer, and subjected to irradiation by a 450-w. Hanovia high pressure ultraviolet lamp for 1.75 hr. The contents of the quartz tube were analyzed by vapor phase chromatography and only the presence of III (in low yield) was detected.

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(8) R. A. Raphael, "Acetylenic Compounds in Organic Synthesis," Academic Press, Inc., New York, N. Y., 1955, pp. 134–39.

(9) W. G. Dauben and F. G. Willey, *J. Am. Chem. Soc.*, **84**, 1497 (1962).

(10) J. P. Schaefer, *J. Am. Chem. Soc.*, **82**, 4091 (1960).

(11) J. D. Roberts, E. R. Trumbull, W. Bennett, and R. Armstrong, *ibid.*, **72**, 3116 (1950).

(12) A. I. Vogel, "Practical Organic Chemistry," Longmans, Green and Co., New York, N. Y., 1956, p. 86.

Isomerization of 4-Ethynylcyclopentene to 4-Vinylidenecyclopentene.—To a small glass tube was added sodium methoxide (34.1 mg., 0.632 mmole), dry diglyme (0.30 ml.), and III (0.0147 g., 0.160 mmole) which was purified by vapor phase chromatography and contained no detectable amount of IV. The tube was sealed and heated at 160° for 8 min. in a stirred oil bath. The tube was quickly cooled in an ice bath, opened, and the contents analyzed by vapor phase chromatography. The ratio of III to IV was found to be 83/17.

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Reaction of Triphenylmethyl with Several Peroxides

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Wieland and Meyer[1] discovered that triphenylmethyl reacts with benzoyl peroxide in benzene to give trityl benzoate, benzoic acid, and tetraphenylmethane. Work on various aspects of the mechanism of this reaction has been relatively extensive.[2] It seems well established that trityl benzoate is formed by attack of triphenylmethyl on benzoyl peroxide and by combination of triphenylmethyl with benzoyloxy radicals.[2d]

$$(C_6H_5)_3C\cdot + (C_6H_5CO_2)_2 \xrightarrow{C_6H_6} (C_6H_5)_4C + C_6H_5CO_2C(C_6H_5)_3 + C_6H_5CO_2H$$

Several workers have shown that formation of tetraarylmethanes occurs in aromatic solvents other than benzene.[2a,c] Several mechanisms have been suggested to account for the formation of tetraarylmethanes. The most recent has been suggested by Benkeser and Schroeder,[2c] who have postulated that tetraphenylmethane is formed by reaction of a π-complex of triphenylmethyl and benzene with benzoyl peroxide or a benzoyloxy radical.

Interestingly, apparently no one has demonstrated that the tetraarylmethane-forming reaction can be effected by any peroxide other than benzoyl. It was the purpose of this work to investigate this point. Triphenylmethyl was allowed to react with benzoyl peroxide, cyclopropylformyl peroxide, hydrocinnamoyl peroxide, 3,3,3-triphenylpropanoyl peroxide, and *t*-butyl perbenzoate. Triphenylmethyl induced the decomposition at room temperature of all of the diacyl peroxides. It was necessary to boil the benzene-*t*-butyl perbenzoate-triphenylmethyl reaction mixture to effect decomposition of the perester. Even so the total time required for decomposition was considerably less than that required for the decomposition of *t*-butyl perbenzoate in the absence of triphenylmethyl. Only with benzoyl peroxide and cyclopropylformyl peroxide could the formation of tetraphenylmethane be detected. With benzoyl peroxide a 14% yield was obtained,[3] while cyclopropylformyl peroxide yielded *ca.* 1% of tetraphenylmethane. It cannot be definitely stated that no tetraphenylmethane was formed with the other peroxides but if any was formed it must have been very little. For example, three separate decompositions of hydrocinnamoyl peroxide gave no evidence for tetraphenylmethane formation.

The results of these experiments show that the formation of tetraphenylmethane is dependent upon the nature of the peroxide used. Of greater significance is the correlation between the stability of the acyloxy radical derived from the peroxide and the formation of tetraphenylmethane. It seems well established, mainly on the basis of radical trapping experiments, that the benzoyloxy radical[4] is more stable towards decarboxylation than a cyclopropylcarboxy radical,[5] both of which are more stable than simple acyloxy radicals.[6]

The results obtained with the various peroxides indicate that the formation of tetraphenylmethane probably does not involve a direct reaction with the peroxide. If this were the case, it seems reasonable to suppose that all diacyl peroxides should be capable of participating in the reaction.[7] The results are in accord with a reaction path in which an acyloxy radical reacts with a π-complex of triphenylmethyl and solvent,[2c] although this is not the only possibility. For example, triphenylmethyl may react with a π-complex of the acyloxy radical with solvent.

It is interesting that other radicals, *i.e.*, various alkyl radicals which were undoubtedly present during the decompositions with the diacyl peroxides, did not promote the formation of tetraphenylmethane. Indeed the reaction seems limited to relatively stable acyloxy radicals. The true requirement may be that an electrophilic radical be present. This may well be due to a necessity for strong electron transfer contributions to the transition state which leads to tetraarylmethane.[8]

Experimental

Reaction of Cyclopropylformyl Peroxide and Triphenylmethyl.—A solution of triphenylmethyl was prepared by stirring 10 g. (0.08 mole) of triphenylmethyl chloride dissolved in 75 ml. of benzene with 35 g. (0.18 g.-atom) of mercury for 8 hr. under an atmosphere of nitrogen. To this solution was added 5.1 g. (0.03 mole) of cyclopropylformyl peroxide in 75 ml. of benzene. After stirring for 1 hr., the infrared spectrum of the mixture indicated that all of the peroxide had been decomposed. The mixture was filtered and concentrated to a volume of 35 ml. and then chromatographed on 60 g. of alumina. Elution with 20% benzene in petroleum ether (30–60°) afforded a white crystalline substance in the first 150 ml. of eluate.[9] Recrystallization from

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[1] H. Wieland and A. Meyer, *Ann.*, **532**, 179 (1937).

[2] (a) H. Wieland and A. Meyer, *ibid.*, **551**, 249 (1942); (b) G. S. Hammond, J. T. Rudesill, and F. J. Modic, *J. Am. Chem. Soc.*, **73**, 3929 (1951); (c) R. A. Benkeser and W. Schroeder, *ibid.*, **80**, 3314 (1958); (d) W. E. Doering, K. Okamoto, and H. Krouch, *ibid.*, **82**, 3579 (1960).

[3] Hammond and co-workers, ref. 2b, obtained yields of 20–30% of tetraphenylmethane depending on the reaction conditions.

[4] G. S. Hammond and L. M. Soffer, *J. Am. Chem. Soc.*, **72**, 4711 (1950)

[5] H. Hart and D. P. Wyman, *ibid.*, **81**, 4891 (1959).

[6] This order of stability is based upon the amount of parent acid formed during the decomposition of the peroxide in the presence of iodine and water. Using this technique, 96% benzoic acid,[4] 47% cyclopropane carboxylic acid,[5] and 10% hydrocinnamic acid have been obtained (H. Weiss, thesis, Rutgers, The State University, 1962).

[7] Such a reaction might have involved electron or hydrogen transfer from a π-complex to the peroxide.

[8] Many radical reactions are subject to this effect. See C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 365–368, for a discussion of this matter.

[9] These conditions were determined as optimal from experiments with reaction mixtures obtained from the reaction of benzoyl peroxide and triphenylmethyl in benzene.