The Photodecomposition of the Dianion of Tetramethylcyclobutane-1,3-dione Di-*p*-tosylhydrazone

PETER K. FREEMAN[1] AND RICHARD C. JOHNSON

Department of Chemistry, University of Idaho, Moscow, Idaho 83843

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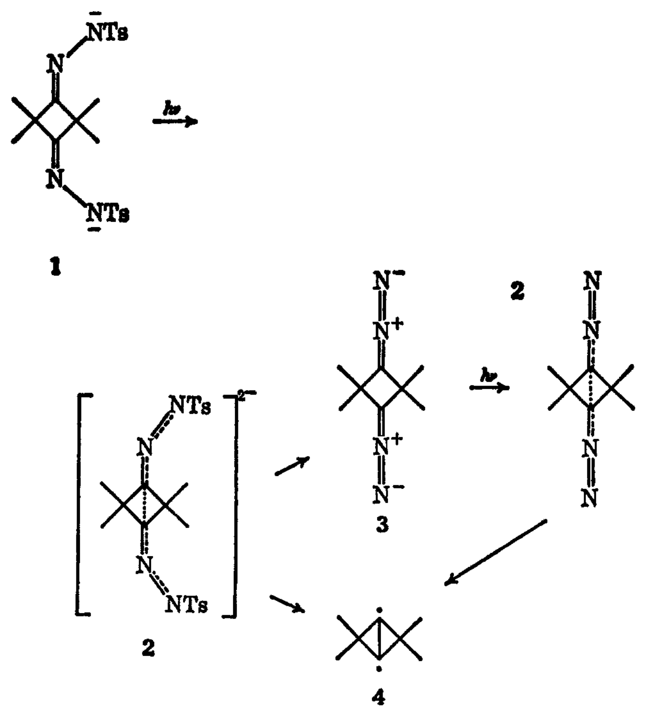
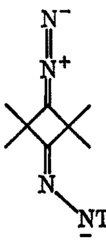
Irradiation of the disodium salt of the di-*p*-tosylhydrazone of tetramethylcyclobutane-1,3-dione in methanol generates 2,2,4-trimethylpent-3-enal dimethyl acetal and 2,2,4-trimethylpent-3-enal, accompanied by methyl 2,2,4-trimethylpent-3-enoate, which was subsequently found to be due to an impurity of the mono-*p*-tosylhydrazone of tetramethylcyclobutane-1,3-dione in the starting material. The mechanism of decomposition is discussed.

A study of the photodecomposition of the disodium salt of the ditosylhydrazone of tetramethylcyclobutane-1,3-dione (1) was undertaken concurrently with our investigation of the photodecomposition of the dianions of the ditosylhydrazones of biacetyl and benzil,[2] prompted by the thought that, if transannular conjugation is assumed, molecular orbital theory predicts that excitation of 1 to the first excited state should result in decreasing the bond order at the S–N and N–C linkages, while increasing the C-1–C-3 transannular bond order.[2] If these bond-order changes are chemically significant, the excited state (2) might undergo a bis elimination, shedding two molecules of nitrogen and two *p*-toluenesulfinate anions to yield an intermediate with bicyclobutane character (4). Alternatively, excited state 2 might lose just two *p*-toluenesulfinate anions to generate the didiazo compound 3. Here, again, a consideration of the nodes in the highest occupied molecular orbital (ψ_4) and lowest unoccupied molecular orbital (ψ_5), assuming transannular conjugation, suggests that excitation of 3 might also proceed by a bis elimination process to generate a bicyclobutane intermediate 4[2] (Scheme I).

SCHEME I



The geometry of the ditosylhydrazone salt 1 is advantageous for testing for a bis elimination process, when compared with the analogous salts of the ditosylhydrazones of biacetyl and benzyl, since the linear arrangement of functional groups in probable intermediates 3 and 5 would be expected to prevent cyclization in a fashion analogous to that of the salts of the ditosylhydrazones of 1,2-diketones (reaction 1).



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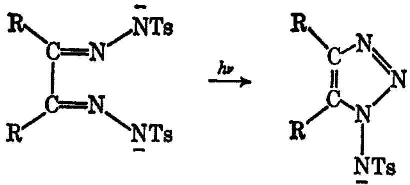
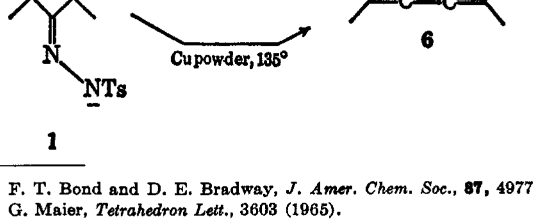


(1)

R = CH_3, or C_6H_5

Although, here, we are benefiting to some extent from hindsight, since this study and the one reported in the previous paper[2] were carried out concurrently.

While this investigation was in progress, two closely related studies of the thermal decomposition of 1 were reported by Bond and Bradway[3] and by Maier.[4] The major product found in both studies was tetramethylbutatriene (6) (eq 2). The nature of the product does not allow a choice to be made between a 1,3-dicarbenacyclobutane intermediate, favored by Maier,[4] and a process in which the bivalent carbon centers are



(2)

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(1) To whom correspondence should be addressed: Department of Chemistry, Oregon State University, Corvallis, Ore.

(2) P. K. Freeman and R. C. Johnson, *J. Org. Chem.*, **34**, 1746 (1969).

(3) F. T. Bond and D. E. Bradway, *J. Amer. Chem. Soc.*, **87**, 4977 (1965).

(4) G. Maier, *Tetrahedron Lett.*, 3603 (1965).

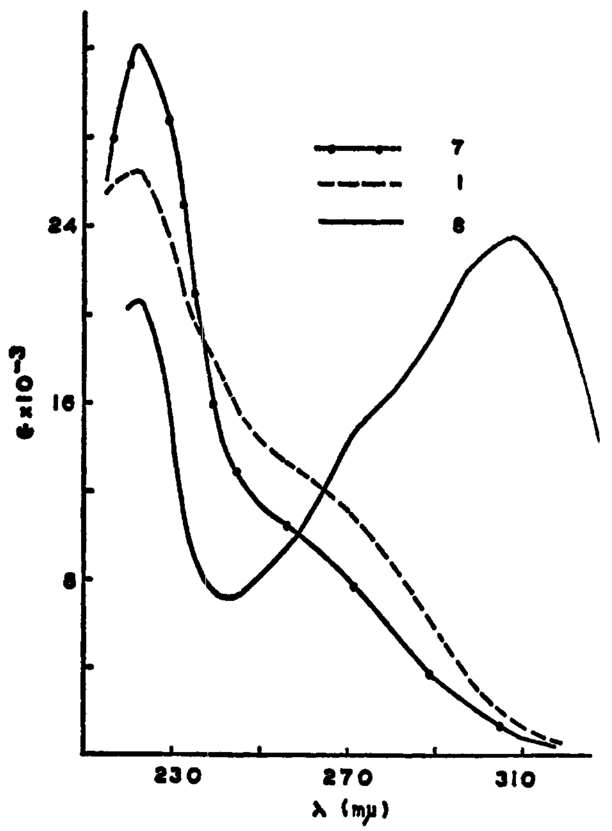
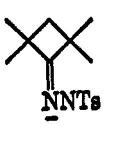


Figure 1.—Comparison of the uv absorption curves for the sodium salts of tetramethylcyclobutanedione ditosylhydrazone, tetramethylcyclobutanone tosylhydrazone (2ε), and biacetyl ditosylhydrazone.

generated in consecutive steps, favored by Bond and Bradway, although the latter alternative would seem to be the more reasonable one.

Results and Discussion

Appropriate models for examination of transannular conjugation in **1** appeared to be the anion of tetramethylcyclobutanone tosylhydrazone (**7**) and the dianion of biacetyl ditosylhydrazone (**8**). The spectra of **1**, **7**, and **8** are shown in Figure 1. The curve for **1** is seen to be a definite compromise between the curves for **7** and **8**. In the region of <235 mμ, the dominant characteristic is the presence of maxima which are found at approximately the same wavelength for all three anions. The intensity of the absorption bands, however, varies and it is especially notable that ε for **1** falls between ε for **7** and **8**. In the region of >235 mμ, the spectrum of **8** shows a high-intensity, long-wavelength maximum at 307 mμ (ε 23,600). The spectra of **1** and **7** show only shoulders in this region. However, the curve for **1** distinctly shows a hyperchromic effect relative to that for **7**.



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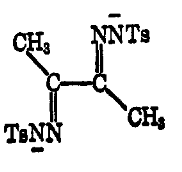

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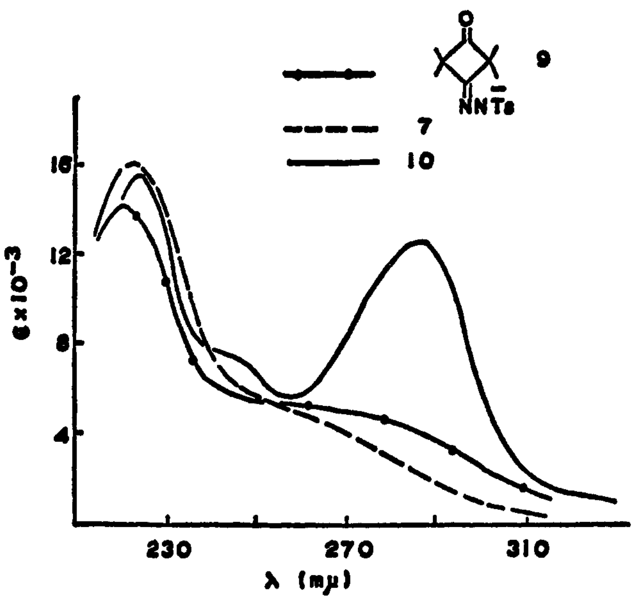
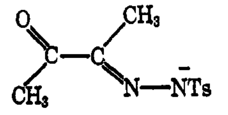


Figure 2.—Comparison of the uv absorption curves for the sodium salts of the monotosylhydrazones of biacetyl, tetramethylcyclobutanone, and tetramethylcyclobutanedione.

In a second comparison, we found it worthwhile to consider the ultraviolet (uv) spectra of the anion of tetramethylcyclobutane-1,3-dione monotosylhydrazone (**9**) and the spectra of appropriate model compounds **7** and **10** (Figure 2). The curve for **10** shows a long-wavelength, high-intensity maximum [287 mμ (ε 12,200)] similar to the one observed in the curve for **8**. The maximum is associated with increasing the length of conjugation of a tosylhydrazone chromophore by the addition of two p orbitals. The short-wavelength maxima for **7**, **9**, and **10** are closely grouped but, in the region of >235 mμ, the shoulder in the curve for **9** clearly appears shifted to longer wavelengths and enhanced over that for **7**. Although the effect is not large for either **9** or **1**, it does not appear unreasonable to ascribe the enhancement of the shoulders in the region of >235 mμ to transannular conjugation and to look for further evidence in the photochemistry of ditosylhydrazone dianions **1** and **9**.



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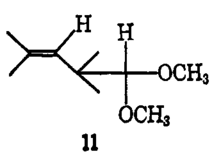
Irradiation of **1** in methanolic sodium methoxide solution resulted in a smooth decomposition producing a nearly quantitative evolution of nitrogen. A mixture of volatile products separated from the reaction medium was shown to consist of two major components (A and B, 49 and 17%, respectively) and a multiplicity of minor components by vapor phase chromatography (vpc). Components A and B and one of the minor components (C, 5%) were subsequently identified as 2,2,4-trimethylpent-3-enal dimethyl acetal (**11**), methyl 2,2,4-trimethylpent-3-enoate (**12**), and 2,2,4-trimethylpent-3-enal (**13**), respectively. The remaining



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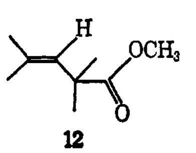

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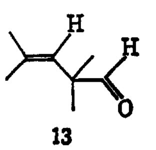
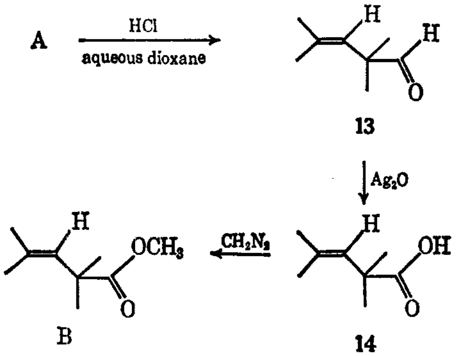


13

minor components were quite difficult to separate by vpc[5] and no individual structural assignments were made. Spectral analysis of various fractions of the mixture separated by vpc indicated the presence of unsaturated materials. One fraction apparently contained a compound or compounds having an allenic structure as indicated by the characteristic doublet at 2010 and 1995 cm^{-1}.[6]

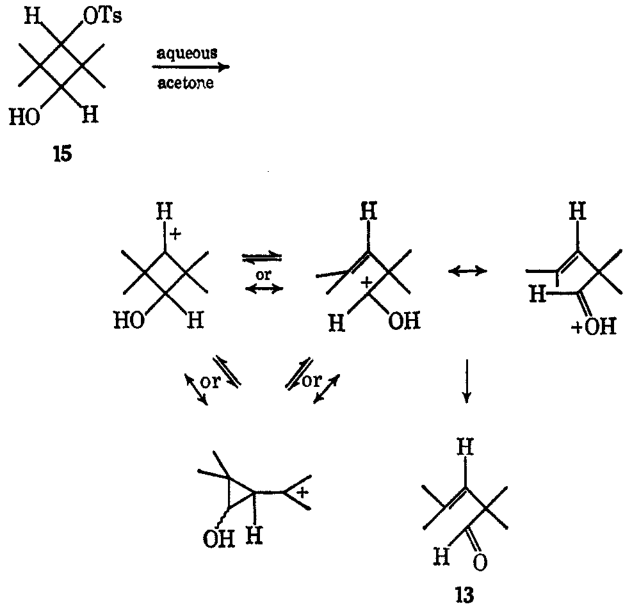
Component C was identified as the aldehyde **13** by comparison of its infrared (ir) spectrum with that of an authentic sample.[7] The structural assignments for A and B follow by virtue of the similarities of their ir and nmr spectra with the corresponding spectra of C. Both A and B show ir absorptions due to a trisubstituted carbon-carbon double bond (A, 1663 and 825 cm^{-1}; B, 1666 and 820 cm^{-1}) and nmr signals attributable to a single vinyl hydrogen and two allylic methyl groups [A, τ 4.88 (multiplet) and 8.32 (broadened singlet) in the ratio 1:6; B, τ 4.88 (multiplet), 8.32, and 8.48 (broadened singlets) in the ratio 1:3:3]. The ir spectrum of B showed an ester carbonyl absorption at 1735 cm^{-1} and the nmr spectrum of A showed a one-proton singlet whose chemical shift (τ 6.18) is appropriate for an acetal hydrogen.[8] Ultimate confirmation of the structures of A and B was achieved through the chemical transformations, outlined in Scheme II, which establish relationships between these compounds and the known aldehyde **13**. Component A was shown to be acetal **11** by its ready hydrolysis to **13**. Oxidation of **13** with silver oxide afforded acid **14** which yielded B on treatment with diazomethane.

SCHEME II



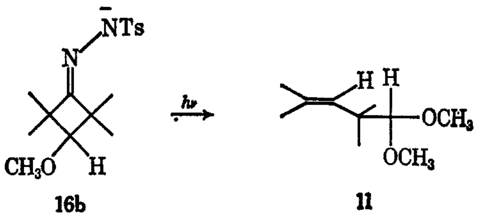
The structure of products **11–13** suggests that the photodecomposition of **1** in methanol occurs by way of a carbonium-ion mechanism. Thus Hasek, *et al.*,[9] discovered that treatment of *trans*-tetramethylcyclobutane-1,3-diol with hot dilute sulfuric acid yields **13**. In related work, Wilcox and Nealy[10] solvolyzed the monotosylate of this diol (**15**) obtaining again **13**. The formation of **13** from **15** was explained in terms of a cyclobutyl–allylcarbinyl rearrangement (Scheme III).

SCHEME III

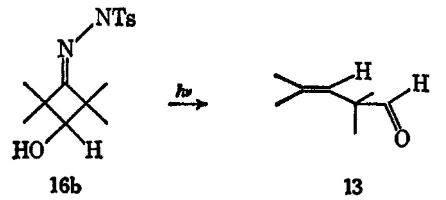


Since the thermal decomposition of the anions of monotosylhydrazones has been shown to occur largely *via* a cationic process in solvents of high "protonicity," [11] the mechanism proposed in Scheme IV views the formation of **13** and closely related **11** from **1** by the sum of two processes (a and b), each similar to that of Scheme III. The operation of this mechanism is supported by the isolation of 3-methoxytetramethylcyclobutanone tosylhydrazone from a reaction in which **1** was incompletely decomposed. In addition, irradiation of the anion **16b**, under the conditions used for **1**, produced **11** (eq 3). Similarly, irradiation of **16a** gave **13** (eq 4). Although the irradiation of **1** was carried out under anhydrous conditions, the source of hydroxide ion giving rise to **16a** may be traced to a small amount of hydroxide formed on the surface of freshly cut sodium on brief exposure to air.

A clue to the source of **12** was disclosed on examination of the ir spectrum of tetramethylcyclobutane-1,3-dione monotosylhydrazone, which exhibited a carbonyl absorption whose intensity is only moderate relative to the strong carbonyl absorption observed in



(3)



(4)

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(5) One fraction representing 12% of the total chromatogram area due to products was separated into two components: an apparently pure compound whose identity still remains unknown and toluene.

(6) The presence of a compound having an allenic structure suggests that a small fraction of **1** decomposes by way of a carbenoid process.[3,4]

(7) The ir spectrum of 2,2,4-trimethylpent-3-enal was kindly provided by Dr. Edward Elam of the Tennessee Eastman Co., Kingsport, Tenn.

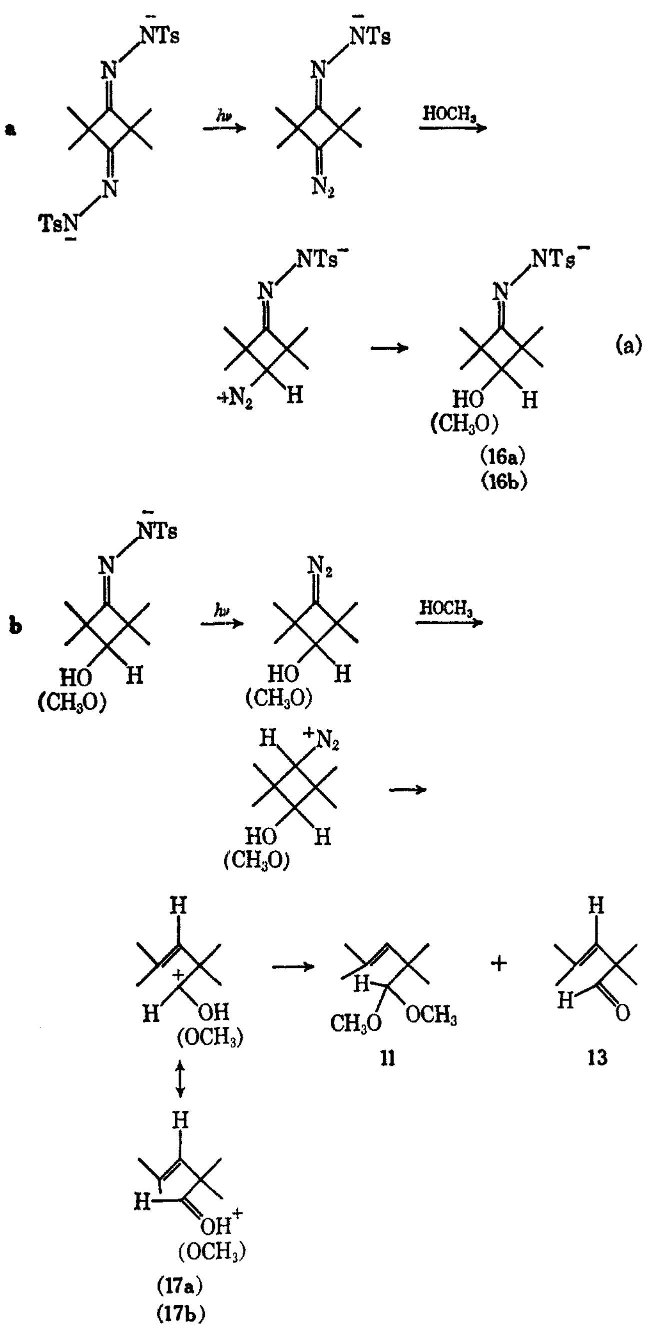
(8) H. U. Hostettler, *Helv. Chim. Acta*, **49**, 2417 (1966).

(9) R. H. Hasek, R. D. Clark, and J. H. Chaudet, *J. Org. Chem.*, **26**, 3130 (1961).

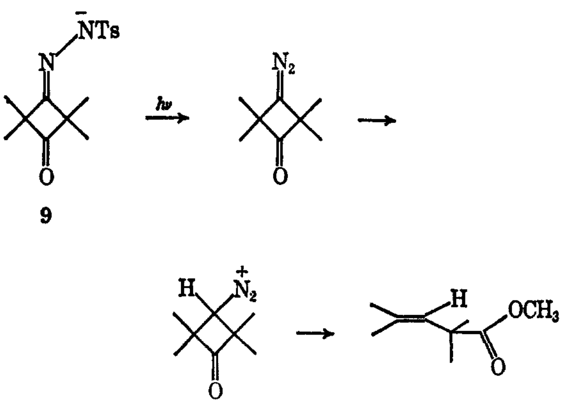
(10) C. F. Wilcox, Jr., and D. L. Nealy, *ibid.*, **28**, 3450 (1963).

(11) (a) J. H. Bayless, L. Friedman, F. B. Cook, and H. Shechter, *J. Amer. Chem. Soc.*, **90**, 531 (1968). (b) J. A. Smith, H. Shechter, J. Bayless and L. Friedman, *ibid.*, **87**, 659 (1965). (c) L. Friedman and H. Shechter, *ibid.*, **81**, 5512 (1959). (d) J. W. Powell and M. C. Whiting, *Tetrahedron*, **7**, 305 (1959).

Scheme IV

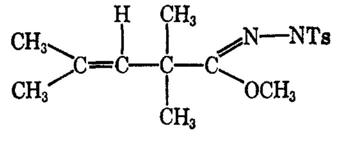


the spectra of most ketones. Consequently, the quantity of monotosylhydrazone contaminating the ditosylhydrazone as determined from the ir spectrum of the latter was always underestimated. Indeed, examination of the crude ditosylhydrazone by nmr revealed that the amount of contaminant was about 15 mol % which made monotosylhydrazone a ready suspect as the parent of **12**. This was reinforced by the fact that irradiation of a sample of **1**, in which the amount of contaminant was reduced to 5% by an intensive purification procedure, gave a product mixture containing a higher ratio of **11** to **12** (62:8 instead of 49:17). Finally, irradiation of anion **9** under the same conditions used for **1** gave **12** (eq 5).



(5)

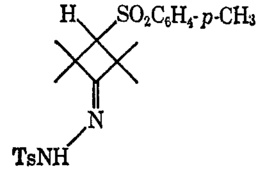
The substitution pattern found for the carbonium-ion intermediates generated in the photodecomposition of **1** whether the ions are delocalized in a nonclassical sense or not, would be expected to be dictated by the substituents on the carbon skeletons of the particular intermediates involved.[12] Thus in process b (Scheme IV), the production of end products **11** and **13** is most likely due to the stabilization of the allylcarbinyl form, relative to the cyclopropylcarbinyl and cyclobutyl forms, by electron delocalization by α-methoxyl[13] and hydroxyl.[10] In process a, the cyclobutyl form should be more stable than the cyclopropylcarbinyl form owing to the energy increase imposed by the trigonal carbon atom in the cyclopropane ring. The relative stability of the cyclobutyl over the allylcarbinyl form, however, is not clear and one might consider an alternate pathway between **1** and **11** in which the allylcarbinyl structure **18** is formed in the first step by a process analogous to that for the transformation of **9** to **12**. While it is conceivable that this mechanism is competitive with that of process a (Scheme IV), we have no evidence which supports it, while we do have evidence supporting reaction *via* **16a** and **16b**.



$(CH_3)_2C{=}CH{-}C(CH_3)_2{-}C(OCH_3){=}N{-}NTs$

18

The extent to which mechanisms competitive with process a (Scheme IV) are possible, may be judged by the fact that, when the irradiation of **1** was carried out employing a Vycor filter, the acid form of **16b** accounted for 43% of the methanol-soluble intermediates formed in the reaction.[14] A second tosylhydrazone (**19**) was isolated in addition to the conjugate acid of **16b**; however, the amount of this material was minor, constituting only 4% of the methanol-soluble substances.[15]



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[12] *Cf.* R. Breslow in "Molecular Rearrangements," P. de Mayo, ed, John Wiley & Sons, Inc., New York, N. Y., p 266 and references therein.

[13] R. H. Martin and R. W. Taft, *J. Amer. Chem. Soc.*, **88**, 1353 (1966); B. G. Ramsey and R. W. Taft, *ibid.*, **88**, 3058 (1966).

[14] Tetramethylcyclobutane-1,3-dione ditosylhydrazone is insoluble in methanol in contrast with the solubility of most monotosylhydrazones, so that extraction of recovered solid material with methanol was a convenient means of isolating substances such as the conjugate acid of **16b**.

[15] Sulfones have been isolated in other tosylhydrazone photolyses. See D. M. Lemal and A. J. Fry, *J. Org. Chem.*, **29**, 1673 (1964).

The remaining solid components were present as a complex mixture which resisted further attempts at separation. A second and clearer view of the composition of methanol-soluble materials was obtained from a similar reaction in which **1** was irradiated through Corex. The conjugate acid of **16b** and tosylhydrazone **19** were obtained in approximately equal amounts, accounting for 70% of the extracted material. Only minor amounts of other substances were present.

Thus, in summary, we find that in spite of the spectral data supporting possible transannular conjugation and the favorable geometry of this system, which should allow the observation of a bis elimination process, there is no evidence which suggests or requires a bicyclobutane-type intermediate such as **4**. Instead the experimental results are rationalized most simply in terms of a stepwise carbonium-ion process.

Experimental Section

In addition to the general comments made earlier,[2] the following apply.

Vapor phase chromatographic analyses and analytical separations were made using an Aerograph A-90 P chromatograph equipped with a thermal conductivity detector or an F & M Model 609 flame ionization chromatograph. A 5 ft by 0.25 in. column of aluminum (column C) containing 15% Carbowax 20M on 60–80 Gas-Chrom P was employed along with columns A and B specified earlier.[2] Product ratios and percentage yields calculated from chromatographic data were made on the basis of relative peak area and are uncorrected for variations of thermoconductivity with molecular weight.

Ultraviolet Spectral Analyses.—Ultraviolet spectra were obtained using a Cary Model 14 recording spectrometer. The samples used were, except for tetramethylcyclobutane-1,3-dione ditosylhydrazone, analytically pure. Tetramethylcyclobutanedione ditosylhydrazone was purified by precipitation from a solution of its dianion in methanol by the addition of methanolic hydrochloric acid.[16] The ditosylhydrazone contained the monotosylhydrazone as a contaminant after repeated precipitation and recrystallization from both aqueous and methanolic dimethylformamide. The spectral data reported for **1** are corrected for an estimated 5% monotosylhydrazone (ir).

The uv spectra, run either in 10^{-3} *N* sodium hydroxide solution or Spectrograde methanol, were reproducible with minor deviations in two separate trials.

Preparation of the Tosylhydrazones.—Tosylhydrazine was prepared according to "Organic Syntheses."[17] Unless obtained in relatively pure state (mp >100°), the product was recrystallized from 50% aqueous methanol, which gave purified material melting generally in the range 105–108°. The recrystallized tosylhydrazine was then subsequently used in the preparation of the tosylhydrazones. An analytical grade sample was obtained after three recrystallizations from 50% aqueous methanol (mp 107.8–109.8°).

Tetramethylcyclobutane-1,3-dione Ditosylhydrazone.—A modification of the method of Bamford and Stevens was used.[18] Tetramethylcyclobutane-1,3-dione (15.1 g, 0.108 mol) was placed with 125 ml of absolute ethanol in a 1-l. round-bottom flask. The dione was brought into solution by heating on a steam bath and a solution of 40.0 g (0.215 mol) of tosylhydrazine in 250 ml of absolute ethanol was added. The flask was fitted with a water condenser and the mixture was heated to gentle reflux, then allowed to cool slightly, whereupon 7 ml of concentrated hydrochloric acid was added in portions. Reflux was resumed and after 5 to 10 min, the solution became cloudy. At the end of 2.5 hr, the product was collected by filtration of the hot reaction mixture, washed with hot absolute ethanol, and air dried. The yield of crude product [mp 270° dec (lit.[4] mp 268°)] was 34.7 g (68%). The crude product contained monotosylhydrazone as an impurity (ir 1798 cm^{-1}). The nmr spectrum of this material exhibited aromatic methyl absorptions due to mono- and ditosylhydrazone in the area ratio 3:44 and ring methyl signals in the ratio 8:50 corresponding to an approximate composition of 13% mono- and 87% ditosylhydrazone. The quantity of monotosylhydrazone could be reduced but not removed by repeated recrystallization from aqueous or methanolic dimethylformamide or by repeated precipitation from a stirred solution of the dianion in methanol (0.3 *M*) at 0° by the slow dropwise addition of methanolic hydrochloric acid (2 ml of concentrated acid to 20 ml of methanol). The ir spectrum (Nujol mull) of the purified material (containing *ca.* 5% monotosylhydrazone) exhibited ν_{max} 3270 (m, NH), 1798 (w, C=O, monotosylhydrazone), 1595 (w, C=C, aromatic), 1397 (m), 1338 (s, SO_2N, asymmetric), 1188 (m), 1157 (s, SO_2N, symmetric), 1120 (w), 1097 (w), 1080 (w), 1020 (m), 927 (w), 827 (m), 819 (m), and 780 cm^{-1} (w). The nmr spectrum (D_2O containing 1 drop of concentrated aqueous sodium hydroxide solution)[19] displayed signals at τ 2.32, 2.45, 2.71, and 2.85 (A_2B_2 quartet, aromatic, 8.0 H), 7.76 (singlet, $ArCH_3$, 6.65 H), and 8.78 (singlet, ring CH_3, 12.3 H).

Anal. Calcd for $C_{22}H_{28}N_4O_4S$: C, 55.43; H, 5.92. Found: C, 55.63; H, 5.94. The calculated percentages for a mixture of 13% mono- and 87% ditosylhydrazone are C, 55.70; H, 5.85.

In variations of procedure in which a solution (100 ml) of the dione (0.0280 mol) was added dropwise to a stirred refluxing solution (250 ml) of tosylhydrazine (0.0591 mol) containing concentrated hydrochloric acid (1.7 ml) or in which a solution (100 ml) of the dione (0.00860 mol), tosylhydrazine (0.0258 mol), and concentrated hydrochloric acid (0.7 ml) was allowed to stand overnight always resulted in product contaminated with >10% monotosylhydrazone.

Tetramethylcyclobutane-1,3-dione Monotosylhydrazone.—A solution of the dione (17.4 g, 0.124 mol) and tosylhydrazine (23.06 g, 0.124 mol) in ethanol (450 ml) was heated at near reflux on a steam bath for 30 min and then poured over ice. After the mixture was allowed to come to room temperature, the product was separated by filtration and recrystallized from absolute ethanol. The yield of tetramethylcyclobutane-1,3-dione monotosylhydrazone (mp 178–180.5°) was 24.2 g (63.5%). The ir spectrum (Nujol mull) displayed ν_{max} 3270 (m–w, NH), 1798 (m–w, C=O), 1675 (w, C=N), 1596 (w, C=C, aromatic), 1399 (w), 1343 (s, SO_2N, asymmetric), 1273 (w), 1188 (w), 1162 (s, SO_2N, symmetric), 1070 (w), 1036 (w), 987 (w), 897 (w), and 820 cm^{-1} (m). Signals were observed in the nmr spectrum ($CDCl_3$–CCl_4) at τ 2.06, 2.18, 2.59, and 2.71 (A_2B_2 quartet, aromatic), 7.53 (singlet, $ArCH_3$), and 8.67 and 8.75 (singlets, ring CH_3).

Anal. Calcd for $C_{15}H_{20}N_2O_3S$: C, 58.41; H, 6.53. Found: C, 58.27; H, 6.70.

Tetramethylcyclobutanone Tosylhydrazone.—Tetramethylcyclobutane-1,3-dione was reduced to tetramethylcyclobutanone in 5% over-all yield by the Wolff–Kishner method described by Herzog and Buchman.[20] Tetramethylcyclobutanone was converted into the tosylhydrazone in 63% yield by the procedure outlined by Meinwald.[21] Infrared and nmr spectral data for the tosylhydrazone were in accord with those reported.[21]

Biacetyl Monotosylhydrazone.—The procedure of Meinwald, *et al.*,[21] was employed omitting the use of hydrochloric acid. After several hours, the product was induced to crystallize by seeding. After 12 hr, the solid was removed by filtration, washed with chilled methanol, and air dried giving material melting at 134.0–134.5°. A second crop (mp 133–134°) was obtained by diluting the mother liquor with water. The over-all yield was 85%. One recrystallization of the crude product from aqueous ethanol afforded an analytical sample melting at 135° dec. The ir spectrum (Nujol mull) of this material showed absorptions at 3240 (m, NH), 1693 (s, C=O, conjugated), 1587 (m, C=C, aromatic), 1488 (w), 1342 (s, SO_2N, asymmetric), 1300 (m), 1290 (m), 1186 (s), 1172 (s, SO_2N, symmetric), 1123 (w), 1102 (m), 1086 (s), 908 (m), 812 (s), and 741 cm^{-1} (s). The nmr spectrum ($CDCl_3$) showed signals at τ 2.08, 2.21, 2.60, and 2.75 (A_2B_2 quartet, aromatic, 4.0 H), 7.43 (singlet, $ArCH_3$, 3.0 H), 7.55 (singlet, CH_3C=O, 2.7 H), and 7.98 (singlet, CH_3C=N, 3.2 H).

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[16] This method was kindly suggested to us by Dr. F. T. Bond.

[17] L. Friedman, R. Little and W. Reichle, *Org. Syn.*, **40**, 93 (1960).

[18] W. R. Bamford and R. S. Stevens, *J. Chem. Soc.*, 4735 (1952).

[19] Methanol was used as an internal reference assigning the position of the $-OCH_3$ signal a value of τ 6.66 relative to tetramethylsilane.

[20] H. L. Herzog and E. R. Buchman, *J. Org. Chem.*, **16**, 99 (1951).

[21] J. Meinwald, J. W. Wheeler, A. A. Nimetz, and J. S. Liu, *ibid.*, **30**, 1038 (1965).

Anal. Calcd for $C_{11}H_{14}N_2O_3S$: C, 51.95; H, 5.55. Found: C, 51.95; H, 5.52.

Irradiations.—Irradiations were conducted in the same manner described previously.[2] Volatile products were isolated by diluting the reaction mixture with an equal volume of water followed by extraction with four–five portions of pentane. The combined extracts were washed with three portions of water and the pentane was removed by distillation. A Vycor filter was employed unless otherwise stated. Gas evolution was measured using either a wet test meter or an inverted cylinder.

Irradiation of the Dianion of Tetramethylcyclobutane-1,3-dione Ditosylhydrazone.—Tetramethylcyclobutane-1,3-dione ditosylhydrazone (23.3 g containing *ca.* 13% monotosylhydrazone and thus 0.0445 mol of ditosylhydrazone) was dissolved in methanolic sodium methoxide solution prepared by dissolving 7.92 g (0.146 mol) of commercial sodium methoxide in 192 ml of methanol. The resulting slightly yellow solution was irradiated without filter[22] until gas evolution retarded (4 hr, 90% of theoretical volume). The lemon-yellow, pleasant-smelling reaction mixture was processed giving 6.61 g of residual liquid after removal of pentane. Vapor phase chromatography (column A at 60–120°, column C at 50–60°) indicated that the residual liquid was a complex mixture consisting of at least 13 components. Three components (A, B, and C in the ratio 49:17:5) were separable from the remainder of the products. Component C was identified as 2,2,4-trimethylpent-3-enal by a comparison of its ir spectrum with one of an authentic sample.[7]

Component A (2,2,4-trimethylpent-3-enal dimethyl acetal) exhibited the following absorptions in the ir (neat): 2990–2915 (unresolved, s, CH), 2832 (s, OCH_3), 2700 (w), 2635 (w), 1663 (w, C=C, trisubstituted), 1445 and shoulder 1465 (s, CH), 1389 and 1360 (s, doublet, *gem*-dimethyl), 1375 (s, CH_3), 1343 (s), 1190, 1140, 1113, 1080, and 1023 (s, acetal), 1008 (s), 983 (s), 966 (s), 927 (m), 841 (m), and 825 cm^{-1} (m, C=CH, trisubstituted). The nmr showed absorption bands at τ 4.88 (multiplet, nonconjugated olefinic, 1.0 H), 6.18 (singlet, acetal, 1.0 H), 6.62 (singlet, OCH_3, 6.0 H), 8.32 (broadened singlet, CH_3C=C, 5.7 H), and 8.97 (singlet, saturated CH_3, 6.1 H).

Anal. Calcd for $C_{10}H_{20}O_2$: C, 69.72; H, 11.70. Found: C, 69.91; H, 11.50.

The structures of components A and C were related by the following experiment. A sample (0.50 g) of the crude product mixture obtained by processing the photolysate was placed in a 5-ml flask along with 0.60 g of 4% aqueous hydrochloric acid and 1.20 g of purified dioxane. The reaction mixture was heated at reflux for 45 min,[23] cooled, and extracted twice with pentane. A sample of the first extract was analyzed by vpc (column C at 61°). The essential feature was that no peak corresponding to component A was present, but the peak due to component C had increased by an equal proportion. The combined pentane extracts were washed with three portions of water and the pentane was removed by distillation leaving a residual liquid. Material corresponding to the new peak having retention time equal to that of component C was separated by vpc and identified as 2,2,4-trimethylpent-3-enal by a comparison of ir spectra.

Component B (methyl 2,2,4-trimethylpent-3-enoate) exhibited the following peaks in the ir (neat): 2990–2930 (s, CH), 2710 (w), 1735 (s, C=O, ester), 1666 (w, C=C, trisubstituted), 1468 (s), 1440 (s), 1389 (s) and 1362 (m, doublet *gem*-dimethyl), 1377 (s), 1268 (s, COC, asymmetric), 1228 (s), 1206 (s), 1195 (s), 1145 (s, COC, symmetric), 1077 (m), 1020 (m), 996 (m), 947 (w), 901 (m), 820 (s, C=CH, trisubstituted), and 773 cm^{-1} (m). The nmr spectrum gave absorptions at τ 4.88 (multiplet, nonconjugated olefinic, 0.8 H), 6.38 (singlet, OCH_3, 2.5 H), 8.32 and 8.48 (broadened singlets of equal area, CH_3C=C, 6.0 H), and 8.75 (singlet, saturated CH_3, 5.9 H).

Anal. Calcd for $C_9H_{16}O_2$: C, 69.19; H, 10.32. Found: C, 69.32; H, 10.47.

The structures of components B and C were related by the following procedure. A sample of 2,2,4-trimethylpent-3-enal dimethyl acetal (2.50 g) isolated in 98% purity by spinning-band distillation of the processed photolysate was hydrolyzed to 2,2,4-trimethylpent-3-enal by the above-described procedure. Analysis of the product by vpc indicated complete conversion into the aldehyde. The initial steps in the procedure described by Clark, *et al.*,[24] were followed in converting the aldehyde into 2,2,4-trimethylpent-3-enoic acid. After stirring for 3 hr, the reaction mixture was extracted with pentane. The extract showed no traces of the aldehyde by vpc. The reaction mixture was acidified with dilute sulfuric acid and extracted with several portions of ether. The combined extracts were dried over anhydrous magnesium sulfate and the ether was removed by distillation leaving a yellow oil. The ir spectrum of the oil indicated the presence of an acid (broad absorption 3700–2400, carbonyl at 1707, and an OH out-of-plane bending absorption at 920 cm^{-1}). The oil was cooled in an ice bath and treated with an excess of ethereal diazomethane prepared according to the method of DeBoer and Backer.[25] The mixture was allowed to stand at ice-bath temperature until nitrogen evolution had ceased. Excess diazomethane was destroyed by the dropwise addition of acetic acid. Ether was removed by distillation leaving a yellow oil. Analysis of the oil by vpc indicated the presence of a component with retention time equal to that of component B under the same column conditions. An ir spectrum of a sample of this component separated by vpc was superimposable on a spectrum of component B.

Incomplete Photodecomposition of the Dianion of Tetramethylcyclobutane-1,3-dione Ditosylhydrazone. Isolation of 3-Methoxytetramethylcyclobutanone Tosylhydrazone.—The dianion was prepared from the ditosylhydrazone (23.3 g, 0.0445 mol) according to the standard method. Irradiation was interrupted after 53 min. After volatile reaction products had been removed in the usual manner, the reaction mixture was acidified with 80 ml of 2 *N* hydrochloric acid. The precipitate was collected by filtration and dried. The dry solid (16.19 g) was extracted with methanol in a Soxhlet apparatus for a period of 24 hr. Removal of methanol using a rotary evaporator left a solid residue (3.35 g). The residue was dissolved in chloroform and placed on a column prepared using 80 g of Camag alumina (pH 4.5) previously moistened with 3.2 ml of water. The column was eluted with 420 ml of 10% ethyl acetate–chloroform and the eluate was collected in 40-ml fractions. Solid residues remained on evaporation of solvent from all of the fractions. The nmr spectra of the residues from fraction 3 (1.65 g) and fraction 4 (0.72 g) were similar in gross features to a spectrum of 3-methoxytetramethylcyclobutanone tosylhydrazone prepared by the procedures described below. The nmr spectra of residues from the other fractions were dissimilar. Recrystallization of the residue from reaction 3 gave a purified material whose ir and nmr spectra were essentially identical with corresponding spectra of 3-methoxytetramethylcyclobutanone tosylhydrazone. The yield of this tosylhydrazone based on the nmr spectra of residues 3 and 4 was 1.43 g (43% of the methanol-soluble solids isolated by extraction).

Irradiation of the Dianion of Tetramethylcyclobutanedione Ditosylhydrazone Using a Corex Filter.—The standard method was used employing 23.0 g (0.0439 mol) of the ditosylhydrazone, 2.22 g (0.0965 g-atom) of sodium metal, and 200 ml of methanol. Irradiation for 1.58 hr through Corex resulted in the evolution of 48% of the theoretical volume of gas. After processing in the usual manner, the reaction mixture was acidified with 51 ml of 2 *N* hydrochloric acid. The precipitate was collected by filtration and dried. The dry solid (13.5 g) was stirred with 300 ml of methanol for 30 min and the undissolved solid was separated by filtration and dried giving 9.35 g. The filtrate was concentrated by removal of solvent using a rotary evaporator giving a solution from which white crystals were deposited on cooling in an ice bath. The crystals were removed by filtration and dried affording 1.56 g. The solid behaved peculiarly on heating, appearing first to melt (<100°) and then to solidify once more (100–160°) melting finally at >170°. The solid was tentatively identified as 3-toluenesulfonyltetramethylcyclobutanone tosylhydrazone. The ir spectrum (Nujol mull) showed absorptions at 3700 (w), 3530 (w), 3250 (shoulder, w, NH), 1675 (w, C=N), 1607 (w), 1598 (C=C, aromatic), 1322 (s, SO_2N, asymmetric), 1282 (s, SO_2, asymmetric), 1186 (m), 1162 (s, SO_2N, symmetric), 1142 (s, SO_2, symmetric), 1091 (m), 1019 (m), 888 (w), 848 (w),

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[22] The results of this experiment were the same regardless of whether uv radiation was unfiltered or filtered through Vycor, also whether sodium methoxide solutions were prepared using commercial sodium methoxide or freshly cut sodium metal.

[23] R. Shriner, R. Fuson, and D. Curtin, "The Systematic Identification of Organic Compounds," Fourth Ed., John Wiley & Sons, Inc., New York, N. Y., and London, 1956, p 195.

[24] K. J. Clark, G. I. Fray, R. H. Jaeger, and R. Robinson, *Tetrahedron*, **6**, 217 (1959).

[25] T. J. DeBoer and H. J. Backer, *Rec. Trav. Chim.*, **73**, 229 (1954).

817 (s), 738 (m), and 708 cm^{-1} (m). The nmr spectrum (CD_3COCD_3) showed signals at τ 2.06, 2.20, 2.44, and 2.58 and 2.15, 2.31, 2.54, and 2.68 (two overlapping A_2B_2 quartets, aromatic, 8 H), 6.38 (singlet, ring H, 1 H), 7.54 and 7.56 (two overlapping broadened singlets, $ArCH_3$, 6 H), 8.36, 8.55, 8.71, and 8.92 (singlets of equal area, ring CH_3, 12 H). The uv spectrum (10^{-3} *N* aqueous sodium hydroxide solution) showed a maximum at 228 mμ (ϵ 29,000) and a shoulder extending from 245 mμ (ϵ 8600) to greater than 320 mμ. The intensity of the maximum is in accord with the presence of a *p*-tolylsulfonyl group (ϵ *ca.* 12,000) and a tosylhydrazone group (ϵ *ca.* 16,000).

Anal. Calcd for $C_{22}H_{28}N_2O_4S_2$: C, 58.90; H, 6.29. Found: C, 58.80; H, 6.49.

The filtrate obtained upon separation of the above-described sulfone was evaporated to dryness leaving 2.21 g of residue whose nmr spectrum showed the features of the spectrum of 3-methoxytetramethylcyclobutanone tosylhydrazone. The amount of this tosylhydrazone contained in the residue was estimated to be 1.5 g (*ca.* 36% of the methanol-soluble materials separated by extraction).

Irradiation of Purified Tetramethylcyclobutanedione Ditosylhydrazone Dianion.—The ditosylhydrazone containing 5% monotosylhydrazone (30.0 g, 0.0606 mol) was dissolved in 470 ml of sodium methoxide solution prepared with 4.50 g (0.195 g-atom) of sodium metal. The solution was placed in a quartz vessel and irradiated for 22 hr in a Rayonet photochemical reactor employing medium-pressure mercury arc lamps. In the course of this time, 90% of the theoretical volume of gas was liberated. The reaction mixture was processed in the usual manner giving 17.9 g of liquid residue. Analysis by vpc revealed that the composition of the residue was essentially the same as before except that the ratio of areas of peaks due to components A and B (A:B) was 62:8. Spinning-band distillation of the lower boiling components left 2,2,4-trimethylpent-3-enal dimethyl acetal as a residue (6.64 g, 72% based on a 90% conversion of starting material). Results similar to these were obtained when the irradiation was carried out in the immersion reactor.

Irradiation of the Anion of 3-Methoxytetramethylcyclobutanone Tosylhydrazone.—3-Methoxytetramethylcyclobutanone tosylhydrazone (10.0 g, 0.0308 mol) was dissolved in 200 ml of methanolic sodium methoxide solution and the irradiation, carried out according to the standard method for 1.6 hr, produced 93% of the theoretical volume of gas. Processing of the reaction mixture gave 11.81 g of residual liquid. Analysis of the liquid by vpc (column B) indicated the presence of a major component (54% of the chromatogram area due to products) and other minor materials. An ir spectrum of a sample of the major component separated by vpc was identical with a spectrum of 2,2,4-trimethylpent-3-enal dimethyl acetal obtained by photodecomposition of 1.

Irradiation of the Anion of 3-Hydroxytetramethylcyclobutanone Tosylhydrazone.—3-Hydroxytetramethylcyclobutanone tosylhydrazone (13.05 g, 0.0420 mol) was dissolved in 180 ml of methanolic sodium methoxide solution prepared using 1.50 g (0.0625 g-atom) of sodium metal. Irradiation according to the standard method for 2.6 hr was accompanied by the evolution of 85% of the theoretical volume of gas. Processing of the reaction mixture gave 5.67 g of residual liquid. Analysis of the liquid by vpc (column C) showed the presence of a major component (60%) and minor materials. Additional pentane (1.05 g) was removed by distillation at atmospheric pressure. Under reduced pressure (10 mm) lower boiling components (0.88 g) slowly distilled followed by the major component (0.20 g), leaving a residue (1.99 g), composed predominantly of the major component. An ir spectrum of a sample of the major component purified by vpc was identical with a spectrum of 2,2,4-trimethylpent-3-enal. The yield of the aldehyde was estimated to be 2.0 g by vpc (44% based on an 85% conversion of starting material).

Irradiation of the Anion of Tetramethylcyclobutane-1,3-dione Monotosylhydrazone.—Tetramethylcyclobutane-1,3-dione monotosylhydrazone (14.9 g, 0.0485 mol) was dissolved in 185 ml of methanolic sodium methoxide solution prepared using 1.65 g (0.0717 g-atom) of sodium metal. Irradiation according to the standard method resulted in a quantitative evolution of gas in 1.3 hr. Processing of the nearly colorless reaction mixture gave 8.4 g of yellowish liquid residue. Analysis of the liquid by vpc (column C at 73°) indicated the presence of a major component (82%) with the same retention time as that of methyl 2,2,4-trimethylpent-3-enoate under identical column conditions. Distillation of the residue under reduced pressure (23–18 mm) gave 4.63 g (bp 57–59°) of material (>95% major component by vpc) leaving a residue (0.56 g) with the same degree of purity. A sample of the major component purified by vpc furnished an ir spectrum superimposable on one of methyl 2,2,4-trimethylpent-3-enoate. The yield of ester based on vpc analyses of the collected fractions and the residue was 5.19 g (65%).

3-Hydroxytetramethylcyclobutanone Tosylhydrazone.—In a 500-ml, three-necked flask equipped with a water condenser, mechanical stirrer, and dropping funnel was placed 5.78 g (0.152 mol) of lithium aluminum hydride and 250 ml of dry tetrahydrofuran. A solution of 22.3 g (0.075 mol) of tetramethylcyclobutane-1,3-dione monotosylhydrazone in 175 ml of dry tetrahydrofuran was added dropwise with stirring. When addition was complete, the reaction was heated at reflux for 5 hr and allowed to cool, and excess hydride was destroyed by the dropwise addition of water. Sulfuric acid (10%) was added to dissolve the solids and the organic phase was separated. The aqueous phase was extracted with four portions of ether and the extracts were combined with the organic phase. After the mixture was dried, over anhydrous magnesium sulfate, ether was removed using a rotary evaporator yielding 18.80 g (84%) of crude product melting at 118–126°. Reduction using sodium borohydride gave material of higher purity only in a lower yield. A sample of this material recrystallized satisfactorily from aqueous ethanol yielding tosylhydrazone with mp 125–127° (lit.[26] mp 132–133°). The ir spectrum (Nujol mull) showed absorptions at 3432 (m, OH), 3285 (m, NH), 1670 (w, C=N), 1599 (w, C=C, aromatic), 1495 (m), 1399 (m), 1342 (s, SO_2N, asymmetric), 1295 (m), 1174 (s, SO_2N, symmetric), 1115 (m), 1095 (m), 1073 (m), 1000 (s–m), 933 (w), 875 (w), 838 (w), 821 (m), 813 (m), and 748 cm^{-1} (m). Signals were observed in the nmr spectrum (D_2O containing 1 drop of 40% aqueous sodium hydroxide solution) at τ 2.18, 2.33, 2.52, and 2.66 (A_2B_2 quartet, aromatic 4.0 H), 6.28 (singlet, ring H, 0.7 H), 7.58 (broad singlet, $ArCH_3$, 3.0 H), and 8.67, 8.75, 8.85, and 8.92 (singlets of equal area, ring CH_3, 9.2 H). The nmr sample seemed unstable evolving gas slowly which perhaps accounts for the lower than theoretical ratio of ring hydrogens to aromatic hydrogens.

Tetramethylcyclobutane-1,3-diol.—This procedure is based on one reported by Roberts and Sauer.[27] Lithium aluminum hydride (16.9 g, 0.423 mol) and anhydrous ether (750 ml) were placed in a 2-l. three-necked flask equipped with a water condenser, dropping funnel, and mechanical stirrer. A solution of tetramethylcyclobutane-1,3-dione (101.5 g, 0.725 mol) in a mixture of anhydrous tetrahydrofuran (450 ml) and anhydrous ether (300 ml) was added dropwise with stirring over a period of 2.5 hr. The reaction was exothermic. Stirring was maintained for 7.25 hr after addition was complete. Excess hydride was destroyed by the careful dropwise addition of water. Sulfuric acid (10%) was added to dissolve the solids. The reaction mixture was diluted with 500 ml of saturated sodium chloride solution and the organic phase was separated, dried over anhydrous magnesium sulfate, and stripped of solvent, using a rotary evaporator, yielding 69.1 g of crude product. An additional 15.6 g of product, obtained from an ether extraction of the aqueous phase, was combined with the main product giving 84.7 g (81%) of tetramethylcyclobutane-1,3-diol melting at 125.5–128.0° (lit.[28] mp 125–135°). The nmr spectrum displayed signals at τ 4.60 (singlet, OH, 2.2 H), 6.20 and 6.41 (singlets, ring H due to the *cis* and *trans* isomers respectively, 1.9 H), and 8.70, 8.83, and 8.78 (singlets, ring CH_3 due to *cis* and *trans* isomers respectively, 12.0 H). The ratio of areas of the ring-methyl absorptions in the two isomers was 0.775, indicating that the mixture consisted of 43.7% *cis*- and 56.3% *trans*-diols. In another reaction where stirring was less efficient, the ratio of *trans* to *cis* isomer formed was 4:1.

3-Methoxytetramethylcyclobutanol.—Sodium hydride dispersion (60.1%) in mineral oil (14.3 g, 0.358 mol) was washed with four portions of anhydrous ether. The mineral oil free reagent was transferred with the aid of 250 ml of anhydrous ether to a 1-l. three-necked flask provided with a water condenser and dropping funnel. A solution of tetramethylcyclobutane-1,3-diols (43.7% *cis* and 56.3% *trans*, 48.6 g, 0.338 mol) in anhydrous tetrahydrofuran (250 ml) was added with magnetic stirring over a period

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(26) J. R. Chapman, *Tetrahedron Lett.*, 113 (1966).

(27) J. D. Roberts and C. W. Sauer, *J. Amer. Chem. Soc.*, **71**, 3925 (1949)

(28) Tetramethyl-1,3-cyclobutanedione, "Properties. . .Reactions," Eastman Chemical Products, Inc., Kingsport, Tenn., May 1960.

of 0.5 hr. The reaction mixture was stirred while being heated at reflux for 18.5 hr. Heating was discontinued and the reaction mixture was allowed to cool to room temperature. Subsequently, methyl iodide (25 ml, 0.402 mol) was added dropwise, with stirring, to the light gray alcoholate slurry over a period of 1 hr. The reaction was exothermic. After addition was complete, the reaction mixture was heated at reflux for 2.5 hr. An additional 15 ml of methyl iodide was added and heating was continued at reflux for 6 hr more. The reaction mixture was diluted with saturated sodium chloride solution and the organic phase was separated. The aqueous phase was extracted with three portions of ether which were combined with the organic phase. After the mixture was dried over anhydrous magnesium sulfate, solvent was removed by distillation through a short Vigreux column leaving a residue (51.2 g) consisting of a liquid with suspended crystalline solid. Distillation under reduced pressure gave the following fractions: (I) 31–45° (155–73 mm) (0.30 g); (II) 66–77° (40 mm) (1.59 g); (III) 75–79° (40 mm) (4.74 g); (IV) 76–77° (33–35 mm); (V) 65–71° (20 mm) (5.51 g); (VI) 71–80° (20 mm) (3.54 g); (VII) 80–85° (20 mm) (1.17 g); (VIII) 85–91° (20 mm) (8.18 g); (IX) 89–91° (20 mm) (5.53 g); and a solid residue (15.40 g). Fractions VIII and IX showed a major peak (95 and 88%, respectively) by vpc (column C at 102°) which was subsequently shown to correspond to a mixture of *cis*- and *trans*-3-methoxytetramethylcyclobutanols. A sample of this isomeric mixture isolated from fraction IX by vpc furnished the following spectra: ir (CCl_4) 3490 (s, OH), 2970–2850 (s, CH), 1465 (s, CH), 1379 and 1368 (s, doublet, *gem*-dimethyl), 1310 (m), 1255 (m), 1204 (s), 1127 (s, COC, symmetric), 1073 (s, CO, alcohol), 1010–983 (s), 950 (m), and 860 cm^{-1} (m); nmr τ 6.60 (singlet, ring H in *trans* isomer, 0.8 H), 6.76 (singlet, OCH_3, 3.0 H), 6.99 (ring H in *trans* isomer, 0.7 H), 7.16 (singlet, ring H in *cis* isomer, 0.3 H), 8.28 (singlet, OH?, 1.0 H), 8.87 (singlet, axial ring CH_3 in *cis* isomer, 2.4 H), 8.99 (singlet, axial and equatorial ring CH_3 in *trans* isomer, 8.15 H), and 9.05 (singlet, equatorial ring CH_3 in *cis* isomer, 1.6 H). The ring hydrogen in the *cis* isomer, counterpart to the ring hydrogen in the *trans* isomer at τ 7.16, seems to overlap with the methoxyl hydrogen signal. The mole ratio of the two isomers (*cis/trans*) was calculated to be 32:68 on the basis of the areas of the ring-methyl signals.

Anal. Calcd for $C_9H_{18}O_2$: C, 68.31; H, 11.47. Found: C, 68.38; H, 11.32.

3-Methoxytetramethylcyclobutanol formed a brosylate as a mixture of *cis* and *trans* isomers melting at 65–75°. The *trans* isomer obtained by recrystallization melted at 60.5–62.5°.

Anal. Calcd for $C_{15}H_{21}O_4SBr$: C, 47.75; H, 5.61. Found: C, 47.65; H, 5.76.

Fractions I–VI showed two important peaks by vpc (column C at 65°) in varying area ratio. The peaks were subsequently shown to correspond to *trans*- and *cis*-1,3-dimethoxytetramethylcyclobutanes in order of increasing retention time.

trans-1,3-Dimethoxytetramethylcyclobutane furnished the following spectra: ir (CCl_4) 2995–2860 (s, CH), 2830 (s, OCH_3), 1463 (s, CH), 1386 and 1373 (s, doublet, *gem*-dimethyl), 1353 (s), 1204 (s), 1174 (m), 1151 (m), 1105 (s, COC, asymmetric), 1032 (m), 1005 (m), 994 (s), 982 (s), 950 (w), 875 (w), and 860 cm^{-1} (w); nmr τ 6.82 (singlet, OCH_3, 6.0 H), 7.12 (singlet, ring H, 2.2 H), and 9.03 (singlet, ring CH_3, 11.8 H).

Anal. Calcd for $C_{10}H_{20}O_2$: C, 69.72; H, 11.70. Found: C, 69.69; H, 11.72.

cis-1,3-Dimethoxytetramethylcyclobutane furnished the following spectra: ir (CCl_4) 2940–2875 (s, CH), 1458 (s, CH), 1388 and 1371 (s, doublet, *gem*-dimethyl), 1345 (s), 1235 (m), 1205 (s), 1191 (s), 1152 (m), 1135 (s), 1100 (s, COC, asymmetric), 1021 (s), 990 (m), and 972 cm^{-1} (s); nmr τ 6.76, (singlet, OCH_3, 6.0 H), 7.22 (singlet, ring H, 2.0 H), and 8.85 and 9.04 (singlets of equal area, axial and equatorial ring CH_3 respectively, 12.0 H).

Anal. Calcd for $C_{10}H_{20}O_2$: C, 69.72; H, 11.70. Found: C, 69.75; H, 11.84.

The residue consisted of a mixture of 3-methoxytetramethylcyclobutanol and starting material as indicated by its nmr spectrum which was superimposable on one of an isomeric mixture of tetramethylcyclobutanediols except for a signal at τ 6.76 due to the former compound. The composition of the residue calculated from the ratio of areas corresponding to ring methyl and methoxyl hydrogens was 87% tetramethylcyclobutane-1,3-diols (a mixture of 33% *cis* and 67% *trans*) and 13% 3-methoxytetramethylcyclobutanol. A sample of the residue injected as a solution in acetone on column C (128°) gave a peak with the same retention time as that of the starting material under identical column conditions. Analysis of the residue by nmr showed the following products and yields calculated from vapor phase chromatograms of the various fractions: 1,3-dimethoxytetramethylcyclobutanes, 8.96 g of *trans* (15.4%) and 12.9 g of *cis* (22.0%), and 3-methoxytetramethylcyclobutanols (a mixture of *ca.* 32% *cis* and 68% *trans*), 14.9 g (27.9%). The amount of starting material recovered was 13.4 g (27.5%).

3-Methoxytetramethylcyclobutanone.—This compound was prepared according to a procedure described by Holum[29] using an isomeric mixture of 3-methoxytetramethylcyclobutanols (16.4 g, 0.104 mol). Samples were withdrawn at 12-hr intervals, diluted with water, and extracted with ether, and the extract was subjected to vpc analysis after removal of ether. Following the reaction in this manner, the starting material was observed to decrease concomitant with the appearance of a product having a lower retention time on the column employed (column B at 150°). The reaction rate decreased after 2 days and the reaction was discontinued finally after 3 days when 84% of the starting material had disappeared. Distillation under reduced pressure through a short Vigreux column gave three fractions. The major fraction boiling at 84–88° (40 mm) (7.15 g) was 97% product and 3% starting alcohol by vpc. The ir spectrum (CCl_4) showed absorption bands at 2990, 2950, 2890 (s, CH), 2840 (s, OCH_3), 1773 (s, strained C=O), 1460 (s, CH), 1383 and 1361 (s, doublet, *gem*-dimethyl), 1272 (s), 1211 (m), 1200 (s), 1178 (m), 1149 (m), 1120 (s, COC, asymmetric), 1080 (m), 1012 (s), 993 (s), 954 (w), and 902 cm^{-1} (w). The nmr spectrum showed signals at τ 6.73 (singlet, OCH_3, ring H superimposed, 3.86 H), and 8.88 and 8.93 (singlets of equal area, ring CH_3, 12.0 H). An analytical sample was prepared by vpc separation on column B. The yield of 3-methoxytetramethylcyclobutanone based on vpc analysis of the collected fractions and residue was 10.5 g (61%).

Anal. Calcd for $C_9H_{16}O_2$: C, 69.19; H, 10.32. Found: C, 69.03; H, 10.29.

3-Methoxytetramethylcyclobutanone Tosylhydrazone.—This tosylhydrazone was obtained from 3-methoxytetramethylcyclobutanone (9.25 g, 0.0570 mol based on 97% purity) and tosylhydrazine (11.0 g, 0.0591 mol) as a succession of crystalline crops totaling 15.08 g (81.5%) employing the method of Meinwald.[21] A sample recrystallized from aqueous methanol had mp 132.5–133.5°. The nmr spectrum (CD_3COCD_3) of this material showed signals at τ 2.46, 2.59, 2.84, and 2.88 (A_2B_2 quartet, aromatic, 4.0 H), 6.85 (singlet, OCH_3, 3.0 H), 6.93 (singlet, ring H, 1.0 H), 7.73 (singlet, $ArCH_3$, 3.0 H), and 8.78, 8.89, 8.95, and 9.05 (singlets of equal area, ring CH_3, 12.0 H). The ir spectrum ($CDCl_3$) displayed absorption bands at 3290 (m, NH), 2973 (s), 2942 (s), 2913 (m), 2978 (m, CH), 2837 (m, OCH_3), 1678 (w, C=N), 1600 (m, C=C, aromatic), 1497 (m), 1397 and 1373 (s, doublet, *gem*-dimethyl), 1340 (s, SO_2N, asymmetric), 1308 (w), 1293 (w), 1223 (w), 1206 (w), 1188 (m), 1170 (s, SO_2N, symmetric), 1127 (m), 1097 (w), 1076 (w), 1022 (s), 1012 (s), 987 (s), and 816 cm^{-1} (s).

Anal. Calcd for $C_{16}H_{24}N_2O_3S$: C, 59.23; H, 7.46. Found: C, 59.39; H, 7.60.

Registry No.—**1,** 19203-14-6; **7,** 19203-15-7; **8,** 19185-60-5; **9,** 19203-17-9; **10,** 19203-18-0; tetramethylcyclobutane-1,3-dione ditosylhydrazone, 5530-15-4; tetramethylcyclobutane-1,3-dione monotosylhydrazone, 4930-35-2; biacetyl monotosylhydrazone, 19203-21-5; component A, 19203-22-6; component B, 19203-23-7; 3-toluenesulfonyltetramethylcyclobutanone tosylhydrazone, 19203-24-8; 3-hydroxytetramethylcyclobutanone tosylhydrazone, 1156-43-0; *cis*-3-methoxytetramethylcyclobutanol, 19206-06-5; *trans*-3-methoxytetramethylcyclobutanol, 19206-07-6; *cis*-3-methoxytetramethylcyclobutanol brosylate, 19206-08-7; *trans*-3-methoxytetramethylcyclobutanol brosylate, 19206-09-8; *trans*-1,3-dimethoxytetramethylcyclobutane, 19206-10-1; *cis*-1,3-dimethoxy-

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[29] J. R. Holum, *J. Org. Chem.*, **26**, 4814 (1961).

tetramethylcyclobutane, 19206-11-2; 3-methoxytetramethylcyclobutanone, 19203-26-0; 3-methoxytetramethylcyclobutanone tosylhydrazone, 19203-27-1.

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Kinetic Studies on the Autoxidation of Phenylhydrazones[1]

W. F. TAYLOR, H. A. WEISS, AND T. J WALLACE

Esso Research and Engineering Company, Government Research Laboratory, Linden, New Jersey 07036

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Detailed kinetic studies were carried out on the thermally initiated autoxidation of cyclohexanone phenylhydrazone (CHPH) and cyclopentanone phenylhydrazone (CPPH) to their corresponding phenylazoalkane hydroperoxides. The rate of oxidation was measured over the range of 0–35° in four different solvents, *i.e.*, benzene, *n*-heptane, acetone, and methanol. In all solvents, CHPH was oxidized more rapidly than CPPH, reflecting the sterochemistry of the cyclohexane and cyclopentane ring systems at the carbon–nitrogen linkage during the allylic rearrangement of the intermediate free radical which takes place in the autoxidation process. The rate of oxidation of both CHPH and CPPH is more rapid in nonpolar solvents than in polar solvents. A compensation effect was observed with CPPH; it has oxidized more rapidly in benzene than in acetone, but the observed activation energy was less (11.5 *vs.* 7.3 kcal/mol). These results suggest that solvent–phenylhydrazone interaction is greater than solvent–radical interaction.

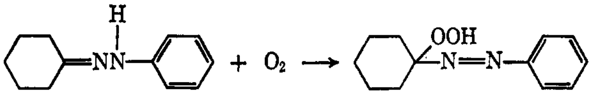
In recent years, studies in these laboratories have been concerned with the oxidation of thiols under a variety of conditions.[2] These studies aroused our interest in an "*in situ*" peroxidation technique for thiols. Phenylhydrazones looked attractive for this purpose since it has been reported that they are readily autoxidized to hydroperoxides.[3–5] A careful examination of the literature disclosed that there is a paucity of data on the mechanism of this reaction. Most studies have been qualitative in nature and have employed either unsubstituted or substituted benzaldehyde phenylhydrazones. Spectroscopic studies have established that the initial oxidation products are unstable phenylazoalkane hydroperoxides.[6–8] In view of this situation, we undertook a detailed study of the kinetics of the thermally initiated autoxidation of both cyclohexanone phenylhydroazone (CHPH) and cyclopentanone phenylhydarzone (CPPH).[9]

Results

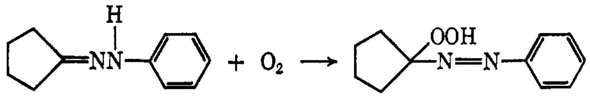
In preliminary experiments the reaction stoichiometry shown below (eq 1) was confirmed by a comparison of

$$\mathrm{PH} + \mathrm{O_2} \rightarrow \mathrm{POOH} \qquad (1)$$

oxygen consumption and phenylhydrazone (PH) disappearance by glpc for a number of runs. Direct evidence for hydroperoxide formation was obtained from the 60-MHz proton spectra of freshly oxidized Ia and IIa in benzene (eq 2 and 3). Both products



Ia Ib (2)



IIa IIb (3)

exhibited a diagnostic singlet resonance band at *ca.* τ 0.1 which is ascribed to the proton of the hydroperoxide group. Similar results were obtained by Bellamy and Guthrie.[6] Accordingly, proton spectroscopy afforded a complementary method for monitoring the formation of hydroperoxide formed from Ia and IIa.

An examination of the rates of oxidation of CPPH and CHPH indicated that the reaction was initially autocatalytic with the rate increasing exponentially with time.[9] As pointed out by Semenov, such initial autoacceleration is typical of many thermal (*i.e.*, noncatalyzed) hydrocarbon oxidations.[10] Initial reaction rates in terms of the moles of PH oxidized per liter per second were obtained from semilogarithmic plots of rate *vs.* time by extrapolating the linear portion of these curves to zero reaction time. The rate of oxidation at "lined-out" conditions was also obtained; however, a comparison of "lined-out" rates and initial rates indicated that both sets of data produced the same directional effects. Initial rates were employed to obtain kinetic parameters because such values can be directly associated with a given phenylhydrazone and oxygen concentration. A study was first made of the effect of phenylhydrazone concentration and oxygen

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[1] This work was carried out under U. S. Army Contract No. DA18-035-AMC-330(A) and was monitored by the Chemical Research Laboratory, Edgewood Arsenal, Md.

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