hydrochloride (14.1 g), m.p. 150–160° (a butanol–1 mixture) which was fractionally crystallized from ethanol– ether to give similar mixtures together with a pure crop of 2a hydrochloride (0.8 g), m.p. and mixed m.p. 185–187° (i.r. and p.m.r. spectra identical with those of authentic sample).

Anal. Calcd. for C₁₅H₂₆ClNO: C, 66.3; H, 9.6. Found: C, 66.55; H, 9.6.

The total base (10 g) was dehydrated in a mixture of acetic acid and hydrochloric acids as before and the following products isolated:

The *cis* prop-1-ene **3** hydrochloride, (0.58 g), m.p. and mixed m.p. $242-243^{\circ}$ (i.r. and p.m.r. spectra identical with those of authentic sample).

The cis (t-Bu/H) but-2-ene 5 hydrochloride, (0.39 g), m.p. 208–210°.

Anal. Calcd. for $C_{16}H_{24}Cl_3N$: C, 57.1; H, 7.2; N, 4.2. Found: C, 57.4; H, 7.4; N, 4.1.

The *trans* (*t*-Bu/H) but-2-ene **5** hydrobromide, (0.25 g), m.p. 223°.

Anal. Calcd. for $C_{16}H_{24}BrCl_2N$: C, 50.4; H, 6.35; N, 3.7. Found: C, 50.7; H, 6.5; N, 3.5.

The Mannich base 1 hydrochloride (1.11 g) was also recovered.

The purity of the sample of 2,6-dichlorobenzyl bromide m.p. 55°, identical with reported value (8), used in this experiment was checked by its g.l.c. behavior in an F and M Scientific 700 laboratory chromatograph (hydrogen flame ionization detector, 6 ft 1% silicon gum rubber, diameter 1/8 in. column with OV-17, 80–100 mesh DMCS stationary phase). It gave rise to a single peak of retention time 20.5 min at 120°. Under the same conditions, the retention time of bromobenzene (a probable contaminant which could lead to 2a and 3) was 1.2 min, while a 50:50 mixture of the 2 halides displayed peaks corresponding with those of the pure materials.

1-(2,6-Dichlorophenyl)-4-dimethylamino-2phenylbutan-2-ol

The Mannich base 6 (9) (16 g) was treated with a

Grignard reagent prepared from 2,6-dichlorobenzyl bromide (35.9 g) and magnesium (4.9 g) as before. The base product after acidification with ethanolic hydrogen chloride yielded hydrochlorides of 6 (0.6 g) and *t*-butanol 7 (11.2 g), m.p. 234–235°.

Anal. Calcd. for $C_{18}H_{22}Cl_3NO$: C, 57.7; H, 5.9. Found: C, 57.6; H, 5.65.

Its p.m.r. spectrum in DMSO- d_6 (10% w/v) displayed a characteristic 8-proton aryl signal at 2.65 τ and a 2-proton methylene signal at 6.61 τ (both broad singlets). The hydroxyl signal was at 4.70 τ (broad singlet, which collapsed after the addition of a drop of D₂O).

The authors thank the Medical Research Council of Canada for financial support.

- 1. A. F. CASY and A. P. PARULKAR. Can. J. Chem. 47, 423 (1969).
- 2. A. F. CASY, A. H. BECKETT, and M. A. IORIO. Tetrahedron, 23, 1405 (1967).
- 3. A. F. CASY and P. POCHA. Tetrahedron, 23, 633 (1967).
- 4. M. S. KHARASCH and O. REINMUTH. Grignard reactions of non-metallic substances. Prentice-Hall, Englewood Cliffs, 1954.
- 5. A. F. CASY and R. R. ISON. Tetrahedron, 25, 641 (1969).
- F. A. ANET and M. ST. JACQUES. J. Amer. Chem. Soc. 88, 2586 (1966); F. A. ANET, M. ST. JACQUES, and G. N. CHNURNY. J. Amer. Chem. Soc. 90, 5243 (1968); J. P. N. BREWER, H. HEANEY, and B. A. MARPLES. Chem. Commun. 27 (1967); A. RIEKER, N. ZELLER, and H. KESSLER. J. Amer. Chem. Soc. 90, 6566 (1968); W. E. HEYD and C. A. CUPAS. J. Amer. Chem. Soc. 91, 1559 (1969).
- 7. A. F. CASY, J. L. MYERS, and P. POCHA. Tetrahedron, 22, 1001 (1966).
- 8. F. KROHNKE, K. ELLEGAST, and E. BERTRAN. Ann. 600, 176 (1956).
- 9. A. POHLAND and H. R. SULLIVAN. J. Amer. Chem. Soc. 75, 4458 (1953).

Acid-catalyzed rearrangement of 3-carene-2,5-dione (3,7,7-trimethylbicyclo[4.1.0]hept-3-ene-2,5-dione)

I. W. J. STILL¹ AND G. W. NATHAN Department of Chemistry, University of Toronto, Toronto 181, Ontario Received October 14, 1969

The reaction of 3-carene-2,5-dione (2) with acetic anhydride – concentrated sulfuric acid at 25° has been shown to lead exclusively to the formation of 2-methyl-6-isopropenylhydroquinone diacetate (3*b*). Canadian Journal of Chemistry, 48, 1013 (1970)

The recently published findings of Bellamy and Whitham (1) on the reductive and mineral acid catalyzed rearrangements of 3-methylcar-4-en-2one (1) led us to examine the effect of acid on 3carene-2,5-dione (2). In the case of compound 1 it was found that preferential acid-catalyzed cleavage of the C_1 — C_7 bond occurred, with exclusive formation of *p*-menthane derivatives. In the case of 3-carene-2,5-dione the presence of a second carbonyl group might be expected to lead,

¹Author to whom enquiries should be addressed.

via protonation of a carbonyl group in acidic media, either to C_6 — C_7 or C_1 — C_7 cleavage and production of a tertiary carbonium ion, or as a less likely alternative, to C1-C6 cleavage and formation of a secondary carbonium ion. Loss of a proton from one of the methyl groups at C-7 and enolization of the remaining carbonyl group would lead in the first two instances to the aromatic derivatives 3a or 4a respectively, while C_1 — C_6 cleavage would have the additional disadvantage energetically of leading to nonbenzenoid products. We have used the same reaction conditions as Bellamy and Whitham (concentrated sulfuric acid in acetic anhydride), as it was felt that the diacetates (3b or 4b) would be less labile than the parent hydroquinones (3aor **4***a*).



Treatment of **2** under these conditions led to the formation of a single liquid product (68% after distillation), the homogeneity of which was established by thin-layer chromatography (t.l.c.) and gas-liquid chromatography (g.l.c.). The product showed no hydroxylic absorption in the infrared (i.r.) and a single carbonyl band at 1764 cm^{-1} . In addition, there were bands present characteristic of a benzenoid ring, a phenolic (or

enolic) acetate and the grouping $C = CH_2$. The

ultraviolet (u.v.) spectrum combined the main absorption bands observed for α -methylstyrene and hydroquinone diacetate. Elemental analysis and mass spectral data were in accord with the formula C₁₄H₁₆O₄, as was the nuclear magnetic resonance (n.m.r.) spectrum (see Experimental). This spectroscopic evidence could be accommodated by either **3***b* or **4***b*.

A decision between the two possibilities was

made possible by catalytic hydrogenation of the rearrangement product over palladium which resulted in the uptake of 1.14 moles of hydrogen. The reduced acetate which resulted (75% after distillation) was shown by t.l.c. to be a single compound, the purity of which was not less than 97% by g.l.c. analysis. The acetate revealed i.r. bands at 1767, 1215, and 1174 cm⁻¹ and aromatic region bands similar to those in the precursor, but

the band at 910 cm⁻¹ due to the C=CH₂ group-

ing had disappeared. This liquid acetate was clearly different from the previously described solid thymoquinol diacetate 6, an authentic sample of which was prepared from thymoquinone by reductive acetylation (2, 3). Table 1 compares the i.r., u.v., and n.m.r. spectra of 5 and 6. As would be expected for two such positional isomers, the differences between the respective u.v. and i.r. spectra are extremely small, and are only slightly more marked in the case of the n.m.r. data. Furthermore, since 3b and 4b are the only aromatic structures which are mechanistically likely for the rearrangement product itself, it follows that our reduced acetate is actually 5 and the rearrangement product must therefore be 2-methyl-6-isopropenylhydroquinone diacetate (3b).



Several attempts have been made to convert **5** into the corresponding quinone **7** by mild hydrolysis followed by oxidation. Although in one instance i.r. evidence suggested the presence of a quinone in the crude oxidation product, we were unable to isolate **7** in pure form. Examination of the literature has revealed that 2,6-dialkyl *p*-quinones are relatively rare, the 2,6-diethyl derivative (4) being the closest analogue of **7** that we could find.

1014

TABLE 1

Spectral comparison of diacetates 5 and 6

Compound	Spectrum (solvent)		
	Nuclear magnetic resonance (pyridine- d_5) δ , p.p.m.	Infrared (CCl ₄) cm ⁻¹	Ultraviolet (MeOH) nm
5	1.10 (6H, d, $J = 6.8$ Hz) 2.05 (3H, s) 2.16 (3H, s) 2.24 (3H, s) 3.01 (1H, sept, $J = 6.8$ Hz) 6.93 (2H, m)	1767 1215 1174	216 (ε, 10800) 274 (ε, 2400)
6	1.11 (6H, d, <i>J</i> = 6.5 Hz) 2.06 (3H, s) 2.23 (3H, s) 2.26 (3H, s) 3.05 (1H, sept, <i>J</i> = 6.5 Hz) 7.11 (2H, m)	1767 1215 1160	215 (ε, 7800) 274* (ε, 950)

*Fine structure of slightly lower intensity at 265-270 nm.

The selective formation of 2-methyl-6-isopropenylhydroquinone diacetate rather than the 2,5-isomer 4 may be attributed to steric and electronic factors. If the electrophile R^+ leading to the presumed intermediate carbonium ion 8 is the acetylium ion rather than a proton, then attack at the C₅-carbonyl would be preferred on steric grounds. The same result might reasonably be predicted on the basis that electron release from the C₃-methyl group should selectively enhance the basicity of the C₅-carbonyl group. Loss of a proton from one of the C₇-methyl groups in 8, enolization, and acetylation then lead to 3b.

Experimental

Infrared spectra were recorded neat or in CCl₄ on a Perkin–Elmer Model 237B grating spectrophotometer and the u.v. spectra in methanol on a Unicam SP800 recording spectrophotometer. The n.m.r. spectra were obtained on a Varian HA-100 instrument with tetramethylsilane as internal standard. Mass spectra were measured on an AEI MS-902 spectrometer and elemental analyses were carried out in the laboratory of A. B. Gygli, Toronto. The g.l.c. analyses were carried out on a 10 ft \times 3/4 in., 10% SE-30 column, using the Aerograph Autoprep A-700 instrument. All melting points and boiling points are uncorrected.

3-Carene-2,5-dione (2)

This compound was prepared by deoximation of 3carene-2,5-dione-5-oxime (5) using the sodium nitrite – acetic acid procedure (6), and purified by sublimation.

2-Methyl-6-isopropenylhydroquinone Diacetate (3b)

Concentrated sulfuric acid (1.25 g, 0.012 mole) in acetic anhydride (36 ml) was added slowly with vigorous stirring to a solution of 3-carene-2,5-dione 2 (4.0 g, 0.025 mole) in acetic anhydride (120 ml). The mixture was stirred for 1 h at 25° before adding to water (800 ml) and shaking to hydrolyze excess acetic anhydride. Solid sodium carbonate was then added until the solution was slightly alkaline. The aqueous solution was extracted thoroughly with ether and the combined ether extracts filtered through a cone of anhydrous sodium sulfate before final drying (MgSO₄). Evaporation afforded a thick yellow oil (83%), which on distillation gave a viscous light yellow liquid (4.1 g, 68%), b.p. 136°/0.8 mm, n_D^{25} 1.5086. This liquid showed only a single spot on t.l.c. in several solvent systems and was at least 95% pure by g.l.c. analysis. The u.v. spectrum showed λ_{max} (MeOH) 273 (ϵ , 818), 234 (ϵ , 7920) and 216 nm (ϵ , 10 300). The i.r. spectrum (neat) showed bands at 1764 (C=O), 1642 (C=C), 1597, 1473, and 1435 (benzenoid), 1209 and 1170 (C=O), and 910 cm⁻¹

($C = CH_2$). The n.m.r. spectrum (CCl₄) had signals at

δ 1.98 (3H, s), 2.08 (6H, s), 2.10 (3H, s), 4.99 (1H, m), 5.12 (1H, m) and 6.84 (2H, m) p.p.m. The mass spectrum revealed a molecular ion at *m/e* 248 in agreement with the formula C₁₄H₁₆O₄.

Anal. Calcd. for C₁₄H₁₆O₄: C, 67.70; H, 6.51. Found: C, 67.51; H, 6.70.

2-Methyl-6-isopropylhydroquinone Diacetate (5)

2-Methyl-6-isopropenylhydroquinone diacetate (3b) (1.6 g, 0.0065 mole) was hydrogenated in ethanol over 10% Pd/C (45 mg). Hydrogen uptake was complete after 3.5 h. Filtration and concentration of the reaction mixture gave on distillation a viscous, pale yellow liquid (1.20 g, 75%), b.p. 115°/0.3 mm, n_D^{25} 1.4937. The essential homogeneity and purity (>97%) of the reduced acetate was again revealed by t.l.c. and g.l.c. The u.v. spectrum showed λ_{max} (MeOH) 216 (ε , 10 800) and 274 nm (ε , 2400). The i.r. spectrum (CCl₄) showed bands at 1767 (C=O), 1215 and 1174 cm⁻¹ (C=O). The n.m.r. spectrum (pyridine- d_5) had signals at δ 1.10 (6H, d, J = 6.8 Hz), 2.05 (3H, s), 2.16 (3H, s), 2.24 (3H, s), 3.01 (1H, sept, J = 6.8 Hz) and 6.93 (2H, m) p.m. The mass spectral data showed the expected molecular ion at m/e 250.

Anal. Calcd. for C₁₄H₁₈O₄: C, 67.26; H, 7.28. Found: C, 67.44; H, 7.39.

Thymoquinol Diacetate (6)

This compound was obtained by reductive acetylation of thymoquinone (2) in an acetic anhydride - zinc dust hydrochloric acid mixture by a modification of a standard procedure (3). The product was obtained as a white solid (79% yield) m.p. 70-71° (lit. (7) m.p. 73-75°) from petroleum ether (b.p. $60-70^{\circ}$).

Financial support of this work by the National Research Council of Canada is gratefully acknowledged. We wish to acknowledge also the valuable experimental contributions of Mr. R. W. Mulligan.

- 1. A. J. BELLAMY and G. H. WHITHAM. Tetrahedron **24**, 247 (1968).
- 2. E. KREMERS, N. WAKEMAN, and R. M. HIXON. Organic syntheses. Coll. Vol. I, 2nd Ed., John Wiley and Sons, Inc., New York, 1941. pp. 511-513. L. F. FIESER. Organic experiments. 2nd Ed., Ray-
- theon Education Co., Lexington, Massachusetts, 1968. pp. 221–222. 4. E. C. S. Jones and J. KENNER. J. Chem. Soc. 1842
- (1931).
- 5. È. J. COREY and H. J. BURKE. J. Amer. Chem. Soc. 78, 174 (1956).
- 6. G. L. BUCHANAN, R. A. RAPHAEL, and I. W. J. STILL.
- J. Chem. Soc. 4372 (1963).
 Dictionary of organic compounds. 4th Ed., Vol. 3. Eyre and Spottiswoode, London, 1965. p. 1958.

Wavelength dependency of the relative proportions of singlet/triplet methylenes from the photolysis of diazomethane¹

G. W. TAYLOR² AND J. W. SIMONS

Chemistry Department, New Mexico State University, Las Cruces, New Mexico 88001 Received August 21, 1969

Results of a high pressure study of the photolysis of diazomethane/cis-butene-2/ethylene mixtures at 4358 and 3660 Å under various conditions are reported. These results indicate that the proportion of ground triplet state methylene radicals, produced in the primary photolysis of diazomethane, is independent of photolysis wavelength.

Canadian Journal of Chemistry, 48, 1016 (1970)

The separate reactivities of singlet and triplet electronic state methylene radicals toward C—H bonds and C=C bonds have been extensively investigated (1-12). The presence of both electronic states of methylene in the photolysis of ketene and diazomethane has been established (1-15). It has been found that the ratio of triplet to singlet methylenes varies significantly with wavelength in the photolysis of ketene (7, 8). A study of the wavelength dependence of the relative amounts of triplet and singlet methylenes from the photolysis of diazomethane/cis-2butene/ethylene mixtures at high total pressures is presented here.

The experimental and analytical procedures used have been reported (16). The limited vapor pressure of *cis*-2-butene made it necessary to add ethylene in order to increase total pressures above ~ 100 cm. Photolyses were carried out in 4 different sized reactors; 2 of relatively small volume (4.3 and 5.9 cc) and 2 of larger volume

(15.0 and 19.6 cc). Identical pressure runs were made at each of the photolysis wavelengths of 4358 and 3660 Å for each reactor employed. In order to test the effect of varying the diazomethane (DM) concentration relative to the total pressure (P_t) , several sets of experiments were performed with $DM/P_t \sim 1/10$ and $\sim 1/30$. In addition, a series of packed vessel experiments were performed in 5.8 and 26.7 cc glass woolpacked reactors with $DM/P_t \sim 1/10$ and $\sim 1/30$, respectively. Dark reactions in the 5.9 cc reactor at high total pressure with added ethylene gave none of the C_5 -products of interest.

The pertinent reaction scheme and kinetic parameters for singlet methylene radicals have been reported (16). Plots of the ratio of *trans*- to cis-1,2-dimethylcyclopropane (TDMC/CDMC) vs. pressure are presented in Figs. 1 and 2. The data in Fig. 1 were taken from photolysis runs in which $DM/P_{t} \sim 1/10$ while Fig. 2 presents data taken from photolysis runs with DM/P, $\sim 1/30$. The lower solid curves in Figs. 1 and 2 represent the predicted behavior of TDMC/CDMC vs. pressure if only singlet methylenes were present;

¹This work was supported by National Science Foundation under Grant No. GP-6124.

²National Defence Education Act Predoctoral Fellow.