

to leave a white, rubbery polymer containing 10.4% boron with ν_{min} 2620 cm^{-1} (B-H stretching). Under identical conditions no terpolymer was formed when 1-methyl-2-nitrosocarborane was used.

Acknowledgment.—We are indebted to the Atomic Energy Commission, Lawrence Radiation Laboratory, Livermore, Calif., for the support of this work under Contract No. W-7405-ENG 48, and to Mr. Richard Crooker, Mr. Raymond Storey, and Mr. Fred G. Hoffman of this laboratory for analyses and spectra.

THIOLKOL CHEMICAL CORPORATION
REACTION MOTORS DIVISION
DENVER, NEW JERSEY

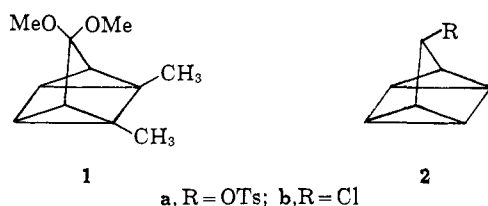
JOEL M. KAUFFMAN
JOSEPH GREEN
MURRAY S. COHEN
MARVIN M. FEIN
ERNEST L. COTTRILL

RECEIVED JULY 23, 1964

2,3-Dimethyl-7,7-dimethoxyquadracyclo- [2.2.1.0^{2,6}.0^{3,5}]heptane

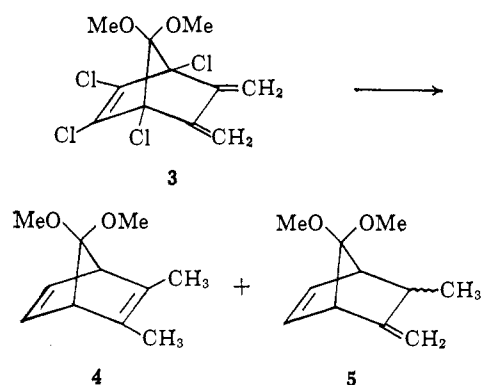
Sir:

Although numerous publications have been devoted to the one-step syntheses of quadracyclane derivatives,¹⁻⁶ relatively little is known about the chemical reactions of this highly strained system. As part of a general program in the area of quadracyclane chemistry we desired to elucidate the nature and ultimate fate of carbonium ions generated on this quadracyclic skeleton. This communication reports the synthesis of 2,3-dimethyl-7,7-dimethoxyquadracyclo[2.2.1.0^{2,6}.0^{3,5}]heptane (1) and the subsequent acid-catalyzed rearrangement of this tetrasubstituted quadracyclane. This rearrangement gives the first positive evidence for the type of bond cleavage postulated by Richey and Buckley⁵ and by Story and Fahrenholtz⁶ in accounting mechanistically for the conversion of 7-substituted quadracyclanes (2) to 7-substituted norbornadienes in the solvolysis of 2.



The synthesis of 1 originated with the known triene 3.⁷ Dehalogenation according to published procedures⁸ yielded 4 through a novel 1,4 reduction. The structure of 4 was substantiated in several ways. Catalytic hydrogenation over palladium on carbon resulted in the rapid uptake of one mole of hydrogen and the relatively slow uptake of a second mole of hydrogen. Near-infrared spectroscopy confirmed the presence of a norbornadiene structure with two olefinic hydrogens as indicated by the absorption at 1.655 μ with a molar absorptivity of 0.676.^{9,10} The final defini-

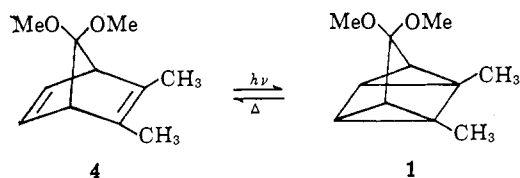
- (1) S. J. Cristol and R. L. Snell, *J. Am. Chem. Soc.*, **76**, 5000 (1954).
- (2) S. J. Cristol and R. L. Snell, *ibid.*, **80**, 1950 (1958).
- (3) W. G. Dauben and R. L. Cargill, *Tetrahedron*, **15**, 197 (1961).
- (4) G. S. Hammond, N. J. Turro, and A. Fischer, *J. Am. Chem. Soc.*, **83**, 4674 (1961).
- (5) H. G. Richey, Jr., and N. C. Buckley, *ibid.*, **85**, 3057 (1963).
- (6) P. R. Story and S. R. Fahrenholtz, *ibid.*, **86**, 527 (1964).
- (7) P. E. Hoch, *J. Org. Chem.*, **26**, 2066 (1961).
- (8) P. G. Gassman and P. G. Pape, *ibid.*, **29**, 160 (1964).
- (9) P. G. Gassman and W. M. Hooker, unpublished work.
- (10) The ultraviolet spectrum of 4 showed end absorption at 214 $\text{m}\mu$ (ϵ 1350). Norbornadiene gives an end absorption at 214 $\text{m}\mu$ (ϵ 1480).



tive proof was the nuclear magnetic resonance spectrum of 4 which showed the six allylic methyl hydrogens as a singlet at τ 8.30, two methoxy methyls as singlets at τ 7.02 and 6.92, two bridgehead hydrogens as a triplet at τ 6.81, and the two olefinic hydrogens as a triplet at τ 3.42. In addition to this major product, the diene 5 was isolated as the principal side product.

2,3-Dimethyl-7,7-dimethoxybicyclo[2.2.1]heptadiene (4) is extremely unstable to acidic conditions. Reaction with dilute acid at -20° gave violent gas evolution with *o*-xylene being formed in high yield. This transformation probably occurs through the initial formation of 2,3-dimethylnorbornadienone (6) and subsequent decarbonylation. All attempts to trap 6 have been unsuccessful. It is interesting to note that *o*-xylene also results from the pyrolysis of 4. This possibly occurs through the expulsion of dimethoxycarbene.¹¹

Photolysis at *ca.* 10° of a pentane solution of 2,3-dimethyl-7,7-dimethoxybicyclo[2.2.1]heptadiene and 2,4-dimethylbenzophenone¹² with a 150-watt Sylvania "blacklite" source gave good conversion of 4 to the



tetrasubstituted quadracyclane, 1. The photolysis product exhibited less thermal stability than previously reported quadracyclane derivatives. Although 1 is stable at Dry Ice temperature, it slowly reverts to the starting diene at 0° and rapidly isomerizes at more elevated temperatures.¹³ Very pure samples, m.p. $18-19^\circ$, could be prepared by low temperature recrystallization from pentane. The quadracyclane could also be distilled at low temperature but this resulted in considerable thermal isomerization. In addition to the thermal reversal of 1 to 4 and the low boiling point of 1 (indicative of its monomeric character) there exists conclusive spectral evidence for the structure of 1. The nuclear magnetic resonance spectrum showed the six methyl protons as a singlet at τ 8.78, three methoxy protons as a singlet at τ 6.70, three methoxy protons at

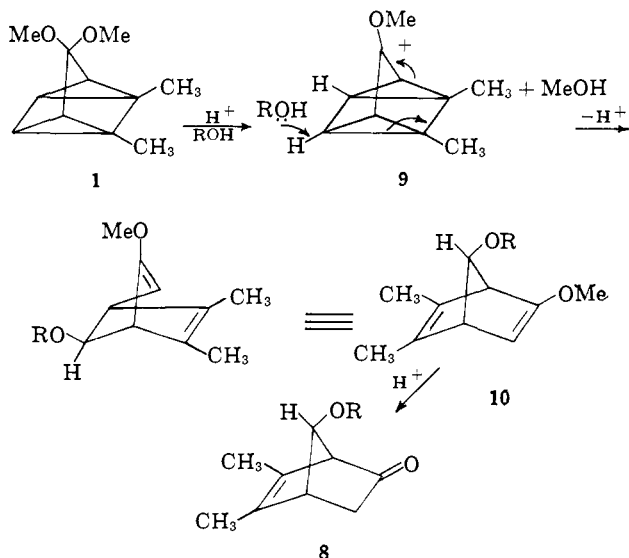
(11) J. Diekmann, *J. Org. Chem.*, **28**, 2880 (1963); R. W. Hoffmann and H. Hauser, *Tetrahedron Letters*, **No. 4**, 197 (1964); D. M. Lemal, E. P. Gosselink, and A. Ault, *ibid.*, **No. 11**, 579 (1964); P. G. Gassman and T. H. Koch, unpublished work.

(12) We have found that 2,4-dimethylbenzophenone is an excellent photosensitizer for low temperature photolyses.

(13) Because of the lability of this compound we did not obtain a carbon-hydrogen analysis on 1. Correct analyses have been obtained on all other compounds.

τ 6.67 (singlet), two protons at τ 8.82 (doublet), and two protons as a doublet at τ 8.51. The doublet at τ 8.51 was assigned to the hydrogens α to the ketal function and the doublet at τ 8.82 was attributed to the remaining two cyclopropyl hydrogens. The near-infrared spectrum, $\lambda_{\text{max}}^{\text{CCl}_4}$ 1.667 μ (ϵ 1.587), and the ultraviolet spectrum, end absorption 210 $m\mu$ (ϵ 380), were also consistent with the postulated structure.

Attempts to hydrolyze **1** to 2,3-dimethylquadri-cyclanone (**7**) led to an unexpected and intriguing result. Under the conditions of acid catalysis **1** was converted to the keto ether **8**. This conversion most likely occurs through a complex rearrangement of the initially formed carbonium ion **9**, as shown below. The manner in which **9** rearranges sheds considerable light on the fate



of a carbonium ion in the 7-position on the quadri-cyclanone skeleton. The theoretical implications of this rearrangement in relation to nonclassical carbonium ion theory will be discussed in a future publication.

The structure of **8** was established on the basis of combined spectral and chemical evidence. The appearance of a carbonyl band at 5.72 μ coupled with the facile formation of a 2,4-dinitrophenylhydrazone confirmed the presence of a ketone function. The position of this ketone function relative to the rest of the molecule was obvious after measurement of the rearrangement product's ultraviolet spectrum (see Table I). The anomalous $n \rightarrow \pi^*$ absorption at 299 $m\mu$ (ϵ 487)

Structure	$\lambda_{\text{max}}^{\text{iso-octane}}$		$\lambda_{\text{max}}^{\text{c-hexane}}$	
	μ	ϵ	μ	ϵ
11	296.5	242	294	436
8	307.5	277	304	413
	319.5	177	316	242

could only be reconciled with the dehydronorcamphor skeleton,¹⁴ **11**. Since the absence of norbornenyl vinyl hydrogens was evident from both nuclear magnetic resonance and near-infrared spectroscopy, the vinylic positions must have been substituted. The presence of the methyl hydrogens at τ 8.33 and 8.41 in the nuclear magnetic resonance spectrum confirmed the placement of the methyl groups in the vinylic positions. The pres-

(14) A. Moscowitz, K. Mislow, M. A. W. Glass, and C. Djerassi, *J. Am. Chem. Soc.*, **84**, 1945 (1962).

ence of the methoxy group was obvious from the sharp singlet at τ 6.80 and from the infrared spectrum. Although the n.m.r. spectrum of **8** was extremely complex it was consistent with the methoxy in the 7-position being *anti* to the double bond. This was obvious from the complex nature (six broad peaks spread over 8 c.p.s.) of the single hydrogen at C-7 which appeared at τ 6.22. As was recently shown¹⁵ this requires that the C-7 proton be *syn* to the olefinic linkage with coupling to the bridgehead hydrogens and to the *endo*-hydrogen at C-6. Since there are no olefinic hydrogens, any C-7 proton *anti* to the double bond would only be split by the bridgehead hydrogens and hence would possess a simplified splitting pattern.

Acknowledgment.—The authors are indebted to the Petroleum Research Fund administered by the American Chemical Society for partial support of this work.

(15) P. Laszlo and P. von Ragué Schleyer, *ibid.*, **86**, 1171 (1964); E. I. Snyder and B. Franzus, *ibid.*, **86**, 1166 (1964).

(16) (a) The Ohio State University Undergraduate Research Scholar, 1962–1963; (b) The Ohio State University Undergraduate Research Scholar, 1963–1964; National Science Foundation Undergraduate Research Participant, Summer, 1963.

DEPARTMENT OF CHEMISTRY
THE OHIO STATE UNIVERSITY
COLUMBUS, OHIO 43210

P. G. GASSMAN
D. H. AUE^{16a}
D. S. PATTON^{16b}

RECEIVED JULY 27, 1964

The Photochemistry of 4,5-Diphenyl-2-pyrone. A Mechanistic Study

Sir:

In a recent publication¹ we reported that the photolysis of 3,4-diphenyl-4,5-epoxy-2-cyclopenten-1-one (I) gave, depending on the conditions of the irradiation, a number of products. Brief irradiation of I afforded in almost quantitative yield a compound which had been identified as 4,5-diphenyl-2-pyrone (II).¹ We now wish to present evidence which assigns structures to the remaining products and to report on the unusual photochemistry of 4,5-diphenyl-2-pyrone.

Photolysis of I in anhydrous ether at 25° with ultraviolet light of wave length above 260 $m\mu$ ² afforded a mixture of products. Consideration of the product distribution obtained in a number of photolyses *vs.* time showed an initial buildup of 4,5-diphenyl-2-pyrone (II) followed by a decrease in the amount present. Evidence that 4,5-diphenyl-2-pyrone (II) is an intermediate in the formation of the remaining products was confirmed by the finding that the photolysis of II itself in anhydrous ether afforded III, IV, and V in about the same distribution as found in runs beginning with 3,4-diphenyl-4,5-epoxy-2-cyclopenten-1-one (Table I).

TABLE I
PHOTOLYSIS OF 4,5-DIPHENYL-2-PYRONE (II)

Run	Time, hr.	Products, % yield			
		II	III	IV	V
1	0.16	96	0	0	0
2	1	52	24	0	0
3	2	38	19	10	6
4	4	10	14	25	17

(1) A. Padwa, *Tetrahedron Letters*, No. **15**, 813 (1964).

(2) The initial photolysis was conducted using an internal water-cooled mercury arc lamp (Hanovia, Type L-450 watts) with a corex filter to eliminate wave lengths below 260 $m\mu$.