at 1730–1760 cm^{-1}, diphenyluretidinedione absorbs at 1775 cm^{-1}, di-*tert*-butyldiazetidinedione absorbs at 1813 cm^{-1},[9] and 2,4-azetidinediones absorb at 1725–1750 cm^{-1}.[10]

It is interesting to note that treatment of *tert*-butylamine with phosgene–pyridine gives *tert*-butyl isocyanate[11] and only small amounts of the urea and the uretidinedione. Treatment of *tert*-butylamine with phosgene in the absence of pyridine gives the urea in good yield. No tri-*tert*-butyl isocyanurate was found in these reactions.

The ring compound is quite stable. At 200° it readily cleaves to give 2 mol of *tert*-butyl isocyanate in high yield.[12] Infrared analysis of a sample which had been heated at 200° showed isocyanate and remaining dimer but no trimer. The convenience of this preparation of *tert*-butyl isocyanate is comparable with other good methods.[13] The ring is rapidly opened by sodium methoxide in methanol to give methyl *N,N'*-di-*tert*-butylallophanate.

Photolysis of the di-*tert*-butyluretidinedione gave only *tert*-butyl isocyanate. Di-*tert*-butyldiaziridinone[8a] was not detected[14] and was shown to be stable to the photolysis conditions.

Comparison of the photochemical and mass spectra results are of interest. The principal ions in the mass spectrum are M −15 (loss of CH_3), M −15 − 56 (loss of CH_3 and of C_4H_8), and M − 15 − 99 (the base peak, loss of CH_3 and of C_4H_9NCO). These fragmentations are similar to those observed with acyclic ureas.[15] Completely absent are *m/e* 99 (cleavage of molecular ion into two *tert*-butyl isocyanates), 170 (decarbonylation), and 142, 141 (loss of isobutylene, loss of *tert*-butyl).

Experimental Section

Di-*tert*-butyluretidinedione.—A solution of 4.05 g (0.0410 mol) of phosgene in 50 ml of benzene was added dropwise with stirring and ice-bath cooling to 25 ml of pyridine, giving a yellow precipitate. *N,N'*-Di-*tert*-butylurea (6.43 g, 0.0373 mol) was added at once, giving a thick yellow mixture. This was stirred for 1 hr at room temperature, during which it became more fluid and the yellow color faded. Water (200 ml) was added and the benzene layer was separated. No solid was present, and infrared analysis showed carbodiimide (2095 and 2130 cm^{-1}) and the uretidinedione. The water layer was extracted with pentane and the combined pentane and benzene solution was extracted with 50 ml of dilute HCl to remove the pyridine and to hydrate the carbodiimide. The precipitated *N,N'*-*tert*-butylurea was filtered. The solvent was distilled and the residue taken up in 50 ml of pentane. Filtration gave the remainder of the urea (total 1.70 g, representing a 26% yield of di-*tert*-butylcarbodiimide). The pentane was evaporated and the residue sublimed at 15 mm and 75° to give 3.84 g (52%) of white crystals, mp 87–90°. Recrystallization from a small amount of pentane gave mp 89–90°; ir (CCl_4) 1760 cm^{-1}; nmr (CCl_4) 1.37 (singlet); uv (cyclohexane) 240 nm (ε 96); mass spectrum (70 eV) *m/e* (rel intensity) 198 (M, 2.8), 183 (16.5), 127 (21), 85 (5.9), 84 (100), 70 (4.4), 57 (23), 56 (11.3), 55 (3.8).

Anal. Calcd for $C_{10}H_{18}N_2O_2$: C, 60.57; H, 9.15; N, 14.13. Found: C, 60.37; H, 9.14; N, 14.14.

***tert*-Butyl Isocyanate.**—Di-*tert*-butyluretidinedione (1.00 g) was placed in a distilling flask with a boiling stone and heated at 200°. For about 30 min the colorless liquid isocyanate distilled (0.95 g, 95%): ir (neat) 2251 cm^{-1}, nmr (CCl_4) 1.37 (singlet).

Photolysis of Di-*t*-butyluretidinedione.—A solution of 452 mg (2.28 mmol) of the uretidinedione in 4.0 ml of cyclohexane in a quartz tube was placed in a quartz flask filled with methylene chloride (to cut out radiation below 230 mm) and irradiated with a Hanovia mercury lamp for 25 hr. Glc and infrared analysis showed *tert*-butyl isocyanate (11%) and unchanged starting material (88%). Di-*tert*-butyldiaziridinone[8a] was not detected.

Control Experiment on Irradiation of Di-*t*-butyldiaziridinone.—A solution of 0.808 g of the diaziridinone[8a] in 20 ml of cyclohexane was irradiated for 20 hr under the conditions described above. The course of the photolysis was followed by ir, which showed an undiminishing diaziridinone carbonyl band and the appearance at the end of two very small bands, one at 2250 cm^{-1} assignable to *tert*-butyl isocyanate and one at 1680 cm^{-1}. Fine needles, 18 mg (2% yield), mp 240–241°, of di-*tert*-butylurea were collected by filtration and identified by mixture melting point and infrared spectrum.

Methyl *N,N'*-Di-*tert*-butylallophanate.—Di-*tert*-butyluretidinedione (1.00 g, 5.05 mmol) was dissolved in 10 ml of methanol, and about 50 mg of sodium was added. After 5 min the solution was poured into 100 ml of water. The resulting precipitate was filtered, washed with water, and dried to give 0.396 g (34%) of white solid. Recrystallization from cyclohexane followed by sublimation at 0.15 mm and 40° gave mp 132–133°; nmr (CCl_4) 1.32 (9 H), 1.40 (9 H), 3.65 (3 H), 5.2 (1 H, broad); ir (CCl_4) 1710, 1730, 3423 cm^{-1}.

Anal. Calcd for $C_{11}H_{22}N_2O_3$: C, 57.36; H, 9.63; N, 12.17. Found: C, 57.05; H, 9.57; N, 12.06.

Registry No.—Di-*tert*-butyluretidinedione, 30885-14-4; *tert*-butyl isocyanate, 1609-86-5; methyl *N,N'*-di-*tert*-butylallophanate, 30885-16-6.

---

(9) J. C. Stowell, *J. Org. Chem.*, **32**, 2360 (1967).

(10) A. Ebnöther, E. Jucker, E. Rissi, J. Rutschmann, E. Schreier, R. Steiner, R. Süess, and A. Vogel, *Helv. Chim. Acta*, **42**, 918 (1959).

(11) Carbamoyl chlorides are known to react with pyridine to give isocyanates: R. J. Slocombe, E. E. Hardy, J. H. Saunders, and R. L. Jenkins, *J. Amer. Chem. Soc.*, **72**, 1888 (1950).

(12) Diphenyluretidinedione also gives phenyl isocyanate, while triphenyl isocyanurate gives CO_2 and diphenylcarbodiimide: R. Stollé, *Ber.*, **41**, 1125 (1908).

(13) H. Ulrich and A. A. R. Sayigh, *Angew. Chem., Int. Ed. Engl.*, **5**, 724 (1966).

(14) Photolysis of 1,3-cyclobutanediones effects successive decarbonylation to the corresponding cyclopropanones and olefins: N. J. Turro, *Accounts Chem. Res.*, **2**, 25 (1969).

(15) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco, Calif., 1967, pp 503–506.

On the Dehydration of Bicyclo[2.2.1]-2-heptanols in the Mass Spectrometer

KREŠIMIR HUMSKI* AND LEO KLASINC

Department of Organic Chemistry and Biochemistry and Department of Physical Chemistry, Institute "Rudjer Bošković," Zagreb, Croatia, Yugoslavia

Received January 26, 1971

The mass spectra of bicyclo[2.2.1]-2-heptyl derivatives have been reported in a number of papers. The behavior under electron impact was studied in order to find methods for structure elucidations[1] and also in connection with the investigation of some well-known reactions in the gas phase and solutions as Wagner–Meerwein rearrangement,[2] retro-Diels–Alder reaction,[3] and the classical–nonclassical controversy. In these studies deuterium labeling was often necessary to get precise information regarding the fragmentation in the mass spectrometer and structures of obtained fragments. Kwart and Blazer[3] recently published an

---

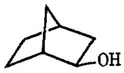
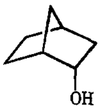
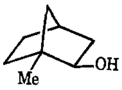
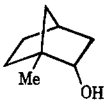
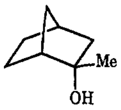
(1) D. D. Dimmel and J. Wolinsky, *J. Org. Chem.*, **32**, 410, 2087, 2735 (1967).

(2) C. A. Bunton and T. W. Del Pesco, *Org. Mass Spectrom.*, **2**, 81 (1969).

(3) H. Kwart and T. A. Blazer, *J. Org. Chem.*, **35**, 2726 (1970).

TABLE I

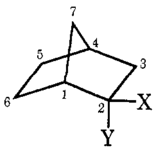
DEHYDRATION OF BICYCLO[2.2.1]-2-HEPTANOL DERIVATIVES BY ELECTRON IMPACT

Compd	No.		Relative intensities[a]				Deuterium contents, %	HOD loss, %
			[M − 17]	[M − 18]	[M − 19]	[M − 20]		
	I		10	100	5			
I-3-3-d_2		Expt[b]	11	97	8		97 D_2 3 D_1	<1
		Calcd[c]	10	97	8			
	II		9	100	5.5			
II-2-d_2		Expt[b]	9	99	6.5		99.5 D	<1
		Calcd[c]	9	99	6			
II-3,3-d_2		Expt[b]	10	95	9.5		96 D_2 4 D_1	<1
		Calcd[c]	9.5	96	9			
	III		10	100	3			
III-7,7-d_2		Expt[b]	8	22	50	33	3 D_3 21 D_2 52 D_1 24 D_0	>5
		Calcd[c]	5	26	55	26		
	IV		10	100	4			
IV-7,7-d_2		Expt[b]	7.5	21	51	33	3 D_3 21 D_2 50 D_1 26 D_0	>5
		Calcd[c]	5	26	54	28		
IV-*endo*-5,6-d_2		Expt[b]	13	63	33	5	4 D_3 86 D_2 10 D_1	~25
		Calcd[c]	13	87	13	1		
	V		16	100	6			
V-*exo*-5,6-d_2		Expt[b]	19	80	23		4 D_3 80 D_2 16 D_1	~2
		Calcd[c]	17	83	21			

[a] Including ^{13}C; accurate within 1%. [b] Normalized to the corresponding undeuterated compound. [c] Assuming that only H_2O is lost; normalized as "b".

analysis of mass spectral fragmentation patterns in various bicyclic alcohols, where bicyclo[2.2.1]-2-heptanol was examined employing the deuterium-labeling technique. It was stated that the alcohols undergo dehydration *via* the formation of an intermediate carbonium ion which then experiences extensive scrambling of hydrogen (and deuterium) atoms on the skeleton before completing elimination of water.

We have also studied the mass spectral behavior of bicyclo[2.2.1]-2-heptanols using a number of specifically deuterated compounds. The results indicate that



bicyclo[2.2.1]-*exo*-2-heptanol (I), X = OH; Y = H
bicyclo[2.2.1]-*endo*-2-heptanol (II), X = H; Y = OH

the dehydration of the molecular ion is a stereospecifically preferred 1,3 (and possibly 1,4) single-step elimination process which occurs prior to hydrogen scrambling.

The mass spectra of bicyclo[2.2.1]-2-heptanol, *exo*- (I) and *endo*- (II), 1-methylbicyclo[2.2.1]-2-heptanol, *exo*- (III) and *endo*- (IV), 2-methylbicyclo[2.2.1]-*endo*-2-heptanol (V), as well as of I-3,3-d_2, II-2-d, II-3,3-d_2, III-7,7-d_2, IV-7,7-d_2, IV-*endo*-5,6-d_2, and V-*exo*-5,6-d_2 have been measured. A survey of the results concerning the loss of water from bicyclo[2.2.1]-2-heptanols is given in Table I. Unfortunately, not all deuterium-labeled compounds were deuterated to a high degree and some calculations were necessary in order to get the distribution of HOD–H_2O. Assuming that only H_2O is lost from the partially deuterated molecules (*i.e.*, [M′ − 17], [M′ − 18], and [M′ − 19] ions obtained; M′ being molecular mass of the species) and regarding the water loss from the undeuterated analog, a pattern for [M − 17], [M − 18], [M − 19], and [M − 20] ions (M′ being the molecular mass according to formula) was calculated and is given in Table I. This pattern is compared with the experimentally obtained pattern. An increase in abundancy of lower masses [M − 19] and [M − 20] accompanied by a simultaneous decrease in higher masses [M − 17] and [M − 18] gives then the extent of HOD loss. A loss of HOD (*m/e* 19) was found with III-7,7-d_2, IV-*endo*-5,6-d_2, IV-7,7-d_2, and V-*exo*-5,6-d_2. All other deuterated compounds lost only H_2O (*m/e* 18). Deuterium randomization would require a ratio of ions [M − HOD]/[M − H_2O] of about 1:10 for monodeuterated and of about 1:5 for the dideuterated compounds, respectively, regardless of the position of deuteration. The fact that I-3,3-d_2, II-2-*d*, and II-3,3-d_2 do not lose HOD at all rules out a 1,1 and 1,2 elimination process. However, a 1,2 elimination including H from position 1 cannot be excluded on the basis of these results, but it seems unlikely to occur for steric reasons (Bredt's rule). The difference in HOD elimination from IV-*endo*-5,6-d_2 and V-*exo*-5,6-d_2 (which can be 1,3 as well as 1,4 elimination) confirms the stereospecificity of the dehydration. A similar result was obtained in the 1,4 elimination of cyclohexane-1,4-diol-1,4-d_2 where the loss of HOD from the molecular ion was due to 1,4 elimination, the proportion of ion yield associated with the [M − HOD] peak in the spectrum of trans compound being eight times greater than the corresponding peak from the spectrum of cis compound.[4] The loss of HOD in IV-*endo*-5,6-d_2 of 25% indicates that hydrogens from other positions are also contributing to the elimination. No evidence is available whether one or both hydrogens in positions 5 and 6 are involved in dehydration.

A substantial loss of HOD (>5%) was observed in the case of III-7,7-d_2 and IV-7,7-d_2. These compounds were 50% deuterated but these results are good indications that hydrogens from position 7 are involved in dehydration. On the other hand, it is interesting that in these compounds no difference between exo and endo position of the hydroxyl group was found.

The lack of contribution from hydrogens in position 3 in the case of I-3,3-d_2 and II-3,3-d_2 compared with substantial contribution from hydrogens in position 7 is an additional proof that positions 3 and 7 are not equivalent as one would expect in the case of involvement of nonclassical carbonium ion in the process of dehydration.

Experimental Section

Technique.—All spectra were recorded under identical operating conditions with a CEC 21-110C mass spectrometer at about 100° with 70 eV, using a direct inlet (rod).

Origin of Samples.—The samples III, IV, V, III-7,7-d_2, IV-7,7-d_2, IV-*endo*-5,6-d_2, and V-*exo*-5,6-d_2 were prepared in the Physical Organic Chemistry Laboratory, Institute "Rudjer Bošković," by Dr. J. Jerkunica, whereas I, II, I-3,3-d_2, and II-3,3-d_2 were prepared as described earlier.[5]

Registry No.—I, 497-37-0; I-3,3-d_2, 10503-35-2; II, 497-36-9; II-2-*d*, 24867-16-1; II-3,3-d_2, 10503-34-1; III, 766-25-6; III-7,7-d_2, 30469-68-2; IV, 3588-21-4; IV-7,7-d_2, 30469-70-6; IV-*endo*-5,6-d_2, 30469-71-7; V, 3212-16-6; V-*exo*-5,6-d_2, 30469-72-8.

---

[4] C. G. Macdonald, J. S. Shannon, and G. Sugowdz, *Tetrahedron Lett.*, **13**, 807 (1963).

[5] J. P. Shaefer, M. J. Dagani, and D. S. Weinberg, *J. Amer. Chem. Soc.*, **89**, 6938 (1967).

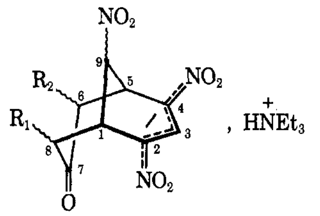
Condensation Cyclization Reactions of Electron-Deficient Aromatics. III. *N*-Bromosuccinimide Oxidation of Bicyclic Dinitropropenides to Isoxazoline *N*-Oxides

MICHAEL J. STRAUSS* AND STEPHAN P. B. TAYLOR

Department of Chemistry, University of Vermont,
Burlington, Vermont 05401

Received February 12, 1971

We have previously reported the preparation of a new class of stable bicyclic anions **1** which form spontaneously from appropriately structured Meisenheimer complexes.[1−5] We report here the unusual NBS oxidation of these anions to isoxazoline *N*-oxides and a detailed pmr analysis which provides evidence for the proposed structures.



1a, $R_1 = R_2 = C_6H_5$ (cis)
b, $R_1 = EtO_2C$; $R_2 = H$

Reaction of 2 equiv of NBS with 1 equiv of **1a**[3] or **1b**[3] in methanol solution at 25° results in immediate disappearance of the intense dinitropropenide absorption at 500 nm.[1] Two equivalents of NBS are required, as the first reacts with $HNEt_3^+$ (*vide infra*).[6] Quenching the yellow methanolic solution in a large excess of distilled water yields a voluminous white precipitate, which when filtered and recrystallized from ethanol gives colorless crystals of the oxidation product (*ca.* 50% yield).

The oxidation product obtained from NBS treatment of **1a** melts at 211–213° and analyzes correctly for $C_{21}H_{15}N_3O_7$. This corresponds to a formal loss of hydrogen and triethylamine from **1a**, and is consistent with the parent peak of 421 in the mass spectrum. The product readily forms a dinitrophenylhydrazone, mp 184–185°, rapidly decolorizes permanganate, but does not add bromine. It shows a broad band from 235 to to 290 nm (ϵ 6 × 10^3) in the uv and strong carbonyl and weak olefinic absorption at 1721 and 1653 cm^{-1} in the ir. Base treatment with alcoholic hydroxide or methoxide yields a solution with an intense absorption at 500 nm, indicating that the dinitropropenide function has probably been regenerated. These chemical and spectral properties, coupled with the observed disappearance of one of the benzylic proton resonances and induced nonequivalence of the phenyl groups in the pmr

---

[1] Previous papers: M. J. Strauss, T. C. Jensen, H. Schran, and K. O'Conner, *J. Org. Chem.*, **35**, 383 (1970); H. Schran and M. J. Strauss, *ibid.*, **36**, 856 (1971).

[2] M. J. Strauss and H. Schran, *J. Amer. Chem. Soc.*, **91**, 3974 (1969).

[3] M. I. Foreman, R. Foster, and M. J. Strauss, *J. Chem. Soc. C*, 2112 (1969).

[4] R. Foster, M. I. Foreman, and M. J. Strauss, *Tetrahedron Lett.*, 4949 (1968).

[5] M. J. Strauss, *Chem. Rev.*, **70**, 667 (1970).

[6] This was established by pmr analysis of the reaction of $HNEt_3^+$, Br^-, and NBS.