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THE ACID-INDUCED DECOMPOSITION OF 7-SUBSTITUTED 3-DIAZO-2-NORBORNANONES. THE STRUCTURES OF THE PRODUCTS AND THEIR DISTRIBUTION

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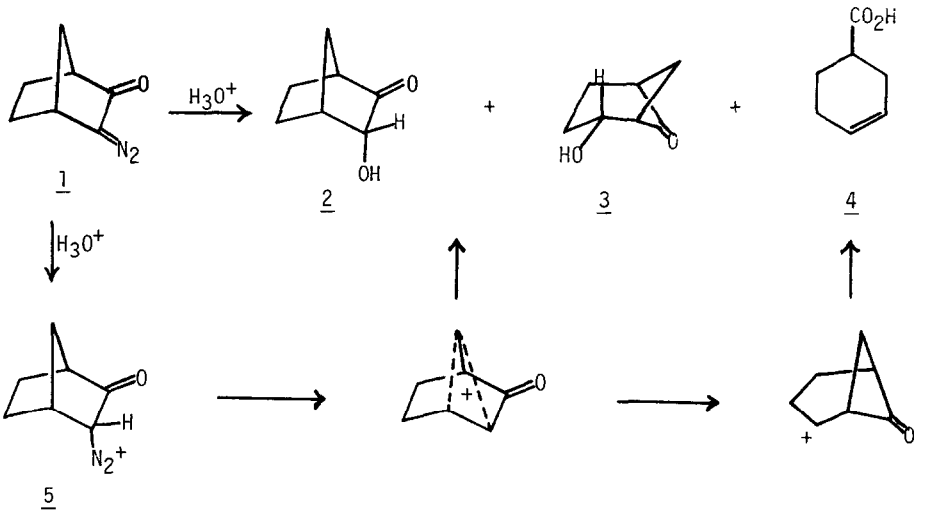
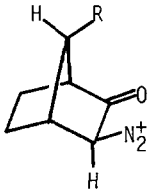
Abstract. Introduction of a syn-7 isopropyl or t-butyl substituent in 3-diazo-2-norbornanone results in both endo and exo protonation in aqueous acid and a marked decrease in α-ketol and increase in tricyclanone formation.

The decomposition of 3-diazo-2-norbornanone (1) in aqueous acid has been shown to give ketols 2 and 3 and the carboxylic acid 4.[1] The effects of methyl substituents on the nature and distribution of the products and other observations led to the proposal of the reaction pathways shown in Scheme 1.[1-3] Central to this proposal is the postulate that 1 undergoes irreversible exo protonation in aqueous acid to give endo diazonium ion 5, which rapidly decomposes to give the products (A-S_E2 mechanism).[4-6] We have therefore examined the acid-induced decomposition of



Scheme 1

derivatives of 1 in which retardation of exo protonation might be expected to lead to the occurrence of endo protonation to give an exo diazonium ion of type 6, and now report on an investigation of the acid-induced decomposition of syn-7-isopropyl-3-diazo-2-norbornanone (7) and syn-7-t-butyl-3-diazo-2-norbornanone (8) and their anti epimers 9 and 10.[7] In this



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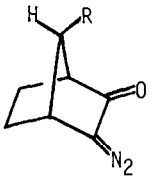
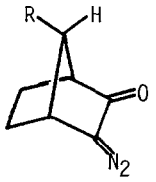


7 R = $CHMe_2$

8 R = CMe_3

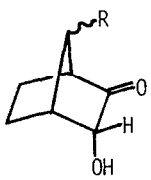


9 R = $CHMe_2$

10 R = CMe_3

Communication we describe the distribution of the products and in the accompanying Communication[8] kinetic studies are reported.

Each of the α-diazo ketones was stirred with dilute hydrochloric acid until the yellow color had been discharged and evolution of nitrogen had ceased. The products formed were of types 11-15, and their distribution is given in Table 1. The structures of compounds 11-14



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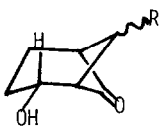

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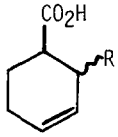

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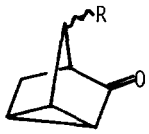

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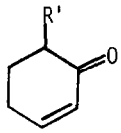

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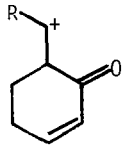
Table 1. Products from the Acid-Induced Decomposition of α-Diazo Ketones

α-Diazo Ketone	Product Yields (%)					
	11	12	13	14	15	Unidentified
7	10	48	34	6	1	1
8	-	52	37	8	-	3
9	61	-	24	0.5	11.5	3
10	60	-	31	1	5	3
1[a]	45	30	25	-[b]	-	-

[a]Ref. 2. [b]Edwards et al.[4] have observed the formation of ∿1% of nortricyclanone in the autocatalytic decomposition of 1 in water.

were established by spectroscopic comparison with analogous compounds obtained previously,[1-3] and, in the case of 14, by spectroscopic comparison with authentic samples obtained by the copper-catalyzed decomposition of the corresponding α-diazo ketones. The 2-cyclohexenones 15 were identified by the characteristic vinyl proton signals [δ 5.9-6.1 (dt, J 10, 2 Hz, 1H), 6.9-7.0 (dt, J 10, 4 Hz, 1H)] in their ^{1}H n.m.r. spectra; the nature of the substituent R' varied but the formation of all of these products could be interpreted in terms of the intermediacy of ions of type 16.



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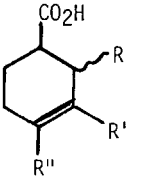
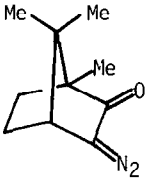


17 R' = D, R" = H

18 R' = H, R" = D



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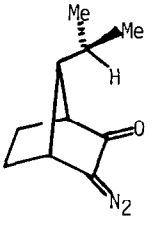

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The occurrence of endo protonation was detected by examination of the deuterium labelling pattern in the cyclohexenecarboxylic acids of type 13 obtained on decomposition of the α-diazo ketones in D_2O/D_2SO_4. While exo protonation gives rise to labelled products of type 17, endo protonation leads to products of type 18.[1-3] The observed distributions of the deuterium label are given in Table 2. These values taken in conjunction with the product distributions in Table 1 give only a minimum value for the extent of endo protonation, since the tricyclanones 14 can also arise via either exo or endo protonation, although the reactions in D_2O/D_2SO_4 do not reveal their source. It is possible to estimate ranges of the overall extent of endo vs. exo protonation by combining the minimum values above with maximum values derived by assuming that all of the tricyclanones 14 are formed via endo protonation. These ranges are given in Table 2.

Table 2. Direction of Protonation of α-Diazo Ketones

α-Diazo Ketone	Yield of 13 (%) via exo protonation	Yield of 13 (%) via endo protonation	Overall direction of protonation (%) exo	Overall direction of protonation (%) endo
7	31	3	91-97	3-9
8	23	14	78-86	14-22
9	23	1	98-99	1-2
10	30	1	98-99	1-2
1	24	≤1	99-100	0-1

These results show that introduction of a syn-7 isopropyl or t-butyl group in 1 results in the occurrence of endo protonation, which is negligible in the case of 1 itself. The effect of the isopropyl group is small; this is in accord with the earlier observation that the effect of the syn-7 methyl group in 3-diazocamphor (19) on the direction of its protonation in aqueous acid is very small,[2,3] if, as expected, the preponderant conformation of 7 is 20, in which the isopropyl group would not exert a much greater steric obstacle to exo protonation than a methyl group. The effect of the t-butyl group, which cannot adopt a conformation that avoids steric interaction between a methyl group and a hydronium ion attacking the exo face, is significantly greater. The most noteworthy effect on product distribution of syn-7 vs. anti-7 substitution of an isopropyl or t-butyl group in 1 is a marked decrease of α-ketol and increase of tricyclanone formation in the former case and a marked decrease of β-ketol and increase of cyclohexenone formation in the latter. These results can readily be accommodated in terms of the effects of these substituents on the transition states for the reactions postulated to account for the formation of these products.

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References and Notes

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2. R.A. Blattel and P. Yates, Tetrahedron Lett., 1073 (1972).
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5. Cf. H. Dahn and M. Ballenegger, Helv. Chim. Acta, 52, 2417 (1969); G. Fierz, J.F. McGarrity, and H. Dahn, Helv. Chim. Acta, 58, 1058 (1975).
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7. The 3-diazo-2-norbornanones were prepared by treatment of the monotosylhydrazones of the corresponding 2,3-norbornanediones with alumina [cf. J. Meinwald, P.A. Gassman, and J.J. Hurst, J. Am. Chem. Soc., 84, 3722 (1962)]. The latter compounds were obtained by selenium dioxide oxidation of the corresponding 2-norbornanones.
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