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SUBSTITUENT EFFECTS ON THE ACID-CATALYZED DECOMPOSITION OF 3-DIAZO-2-NORBORNANONES

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Decomposition of 3-diazonorbornanone (I) in aqueous acid gives the α-ketol II, the β-ketol III, and the acid IV (1,2). We report now on an investigation of the effect of methyl substituents on the product distribution, that has illuminated the course of these interesting transformations. Decomposition of α-diazo ketones V-X in 0.1 N sulfuric acid gave products analogous to II-IV (Table 1). We propose the following reaction scheme to account for the product distributions: irreversible exo protonation of I to give the endo diazonium ion XI (3), followed by rapid loss of nitrogen giving the bridged ion XII, which is attacked by water to give the α- and β-ketols, II and III, or is transformed to the ion XIII, which gives the carboxylic acid IV (4).

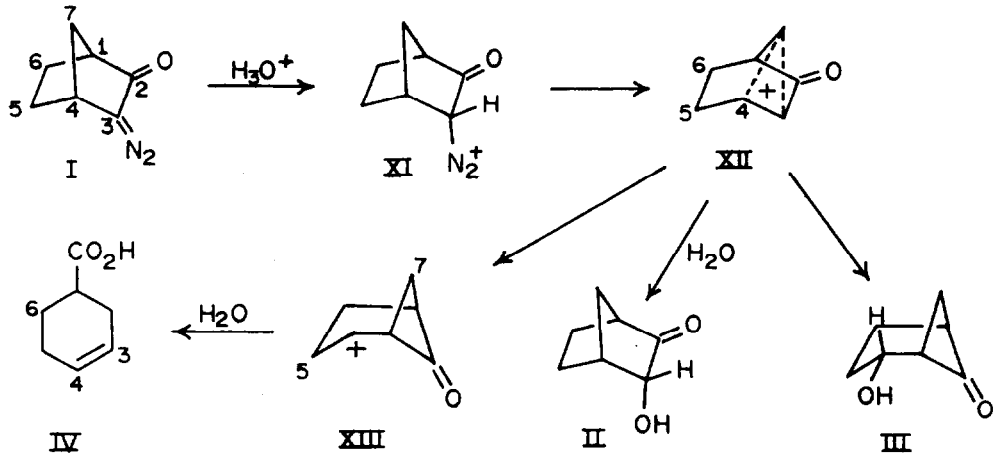


Table 1

Products from the Acid-Catalyzed Decomposition of 3-Diazo-2-norbornaones[a]

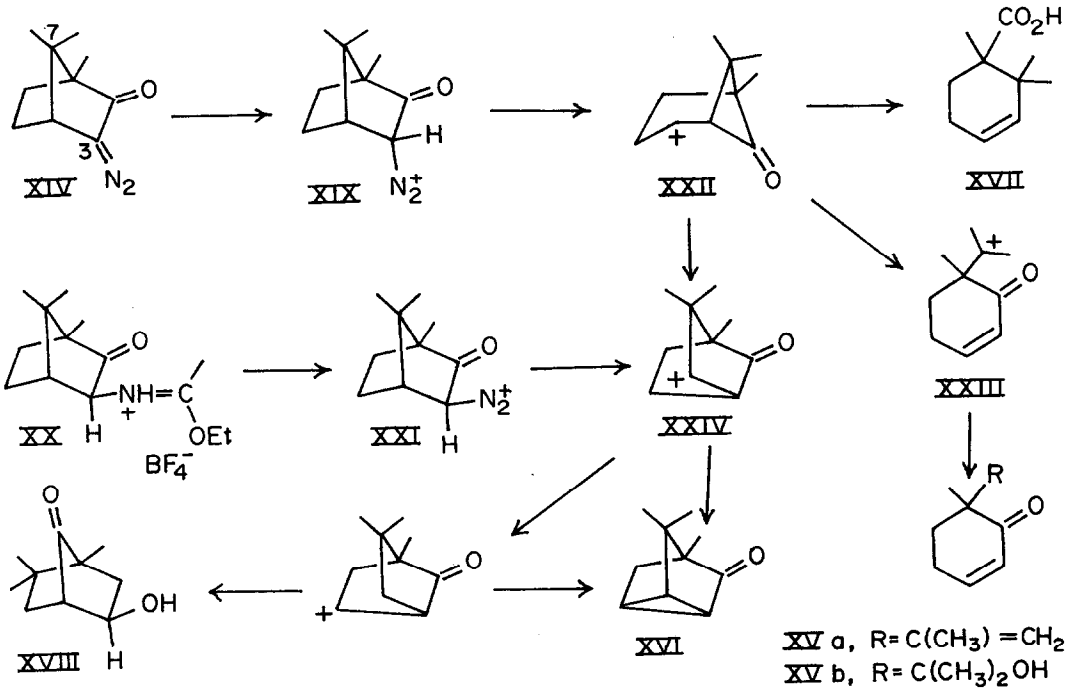
3-Diazo-2-norbornanone		Yields[b]		
Compound	Substituents	α-Ketol	β-Ketol	Acid
I[c]	None	45	30	25
V	6,6-dimethyl	32	35	33
VI	exo-5-endo-6-dimethyl	52	38	10
VII	endo-5-exo-6-dimethyl	85	-	15
VIII	5,5-dimethyl	84	-	16
IX	1,5,5-trimethyl	84	-	16
X	4,6,6-trimethyl	-	-	100

[a]The diazo ketones were stirred with 0.1 N sulfuric acid until nitrogen evolution ceased. [b]Relative yields determined by pmr spectroscopic and vpc analyses; the pmr spectra showed no significant amounts of other products. [c]Refs. (1) and (2).

Compounds VII-IX differ from I in giving mainly α-ketols and no β-ketols. The failure to form β-ketols is attributable to the steric effect of an endo C-5 methyl group in the bridged ion XII which prevents attack at C-4. An endo C-5 methyl group would also be expected to retard the conversion of XII to XIII, due to steric interaction with the carbonyl group, thus accounting for the reduced proportion of acid formed from VII-IX (5). Were the acid formed directly from XII (1), an endo C-5 substituent would not be expected to have this effect. Compound X forms only acid. This can be attributed to the C-4 methyl group, which exerts a greater stabilizing effect on XIII than on XII (6) and leads to exclusive conversion of the latter to the former. Compound V gives, like I, α- and β-ketols and acid in comparable amounts. This is in accord with expectation since neither the exo nor endo C-6 methyl groups should influence markedly the relative ease of attack of water on XII nor its ease of conversion to XIII, and again supports the view that the acid does not arise from XII, since this process would be hindered by an endo C-6 methyl group. Compound VI also gives all three types of product, but the ratio of acid to α- plus β-ketol is reduced relative to that for I and V. This is attributable to retardation of the conversion of XII to XIII, due to a gauche interaction

between the methyl groups.

The introduction of two methyl groups at C-7 in 3-diazonorbornanone, as in diazocamphor (XIV), brings about a profound change in the nature of the products formed on acid-catalyzed decomposition. Edwards and Lesage (7) have shown that treatment of XIV with aqueous acid gives the dienone XVa, the related enolone XVb, and cyclocamphanone (XVI). We obtained XVa (31%), XVb (31%), XVI (13%), the acid XVII (21%) and the β-ketol XVIII (4%). We, like Edwards and Lesage (7), have found that deamination of endo-3-aminocamphor leads to an identical product distribution indicating that the acid-catalyzed decomposition of XIV is initiated by irreversible exo protonation to give the endo diazonium ion XIX (8). This view is corroborated by the fact that treatment of the immonium salt XX with nitrous acid gives XVI (65%) and XVIII (19%), which are considered to arise from the exo diazonium ion XXI (9). The absence of products derived from attack by water on a bridged ion analogous to XII suggests that such an ion is not an intermediate in the case of 3-diazocamphor



and that XIX is converted directly to XXII. This can be attributed to the steric interaction between the syn C-7 methyl group and the C-3 hydrogen atom in the bridged ion (10). The ion XXII can give XVII (4), cleave to XXIII (11), which gives XVa and XVb, and rearrange to XXIV, which gives XVI and XVIII (12).

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REFERENCES

1. P. Yates and R.J. Crawford, J. Amer. Chem. Soc. 88, 1561 (1966).
2. P. Yates and C. Kashima, unpublished results.
3. Cf. H. Dahn and M. Ballenegger, Helv. Chim. Acta, 52, 2417 (1969); their conclusion that secondary α-diazo ketones are irreversibly protonated in aqueous acid has been corroborated by the observation that deamination of 3-endo-amino-6,6-dimethyl- and 3-endo-amino-1,5,5-trimethyl-2-norbornanone-3-d with aqueous nitrous acid gives product distributions identical with those from the action of aqueous acid on V and IX with retention of the deuterium.
4. Decomposition of V, IX, and XIV with D_3O^+/D_2O gave cyclohexenecarboxylic acids with >90% of the deuterium at C-3, demonstrating that these acids are formed largely, if not entirely, by migration of the C-4-C-7 bond rather than the C-4-C-5 bond. A similar conclusion could be reached in the case of X, which gave 4,6,6-trimethyl- rather than 3,6,6-trimethyl-3-cyclohexenecarboxylic acid.
5. An alternative transition state leading to the other conformation of the six-membered ring of XIII would introduce another unfavorable steric interaction, that between the hydrogen atom or exo methyl group at C-5 and the anti hydrogen atom at C-7.
6. Cf. P. Yates and J.D. Fenwick, J. Amer. Chem. Soc. 93, 4618 (1971).
7. O.E. Edwards and M. Lesage, Can. J. Chem. 41, 1592 (1963).
8. Cf. the base-catalyzed deuterium exchange of camphor, where exo exchange largely preponderates [A.F. Thomas, R.A. Schneider, and J. Meinwald, J. Amer. Chem. Soc. 89, 68 (1967); T.T. Tidwell, J. Amer. Chem. Soc. 92, 1448 (1970)]. In the present case endo protonation as a minor pathway cannot be excluded.
9. The reaction of XX with nitrous acid also gave XV (8%) and XVII (8%). The former is considered to arise via epimerization of XX before decomposition; this was corroborated by the fact that deamination in acetic acid-d gave XV-2-d.
10. Cf. P. von R. Schleyer, M.M. Donaldson, and W.E. Watts, J. Amer. Chem. Soc. 87, 375 (1965). Other work has confirmed that it is the syn C-7 methyl group that inhibits α-ketol formation (P. Yates and D.G.B. Boocock, unpublished results).
11. The ion XXIII could also be formed directly from XIX; this is contraindicated, however, by the failure of epibornylamine to give ring-opened products on deamination [J. Suszko and W.Z. Antkowiak, Bull. Acad. Polon. Sci., Ser. Sci. Chim. 13, 447 (1965).
12. The reaction schemes proposed here also serve as a basis for interpreting solvent effects on the acid-catalyzed decomposition of methyl substituted 3-diazonorbornanones (R.A. Blattel and P. Yates, accompanying communication).