

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

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The decomposition of 3-diazoisofenphone (3-diazo-1,5,5-trimethyl-2-norbornanone, I) in aqueous sulfuric acid to give the carboxylic acid II and the α -ketol III has been postulated to proceed via exo protonation of I to give the endo-diazonium ion IV and loss of nitrogen to give the bridged ion V, which is either attacked by water to give III or is converted to the ion VI, which gives II (1). An investigation of the effects on product distribution of carrying out the decomposition in acetic acid and aqueous acetic acid and of the addition of salts to the reaction mixture has given results that can be interpreted in terms of these postulates. In addition to II and III, the acetate VII of III and the dienone VIII were found in the product mixtures, which are summarized in Table 1.

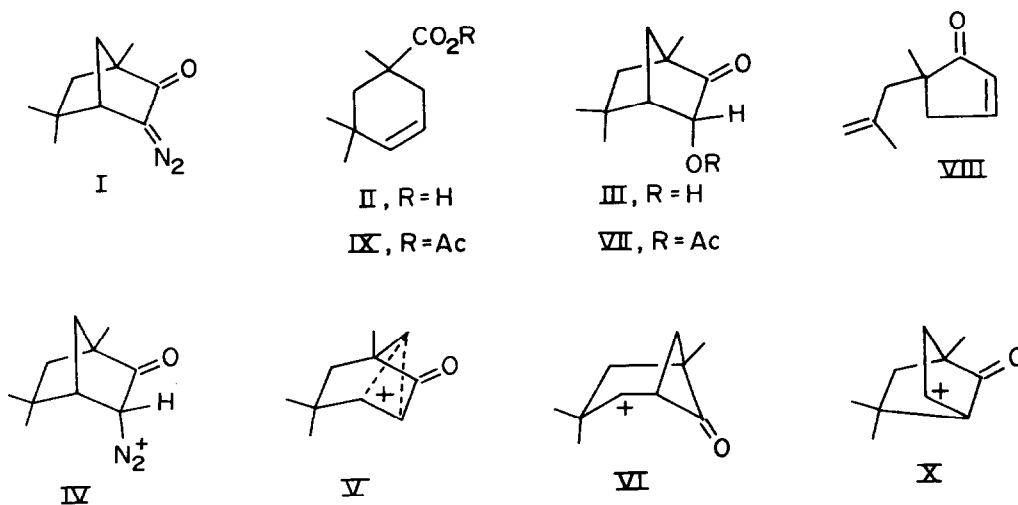


Table 1
Relative Yields of Products from the Decomposition
of 3-Diazoisofenphone (I) in Aqueous Acid^a

% Acetic Acid (v/v)	Yields ^b				% Acetic Acid (v/v)	Salt (1m)	Yields ^b			
	II	III	VII	VIII			II	III	VII	VIII
0 ^c	16	84	-	-	50	NaCl	31	45	24	-
6	21	79	-	-	50	CCl ₃ CO ₂ Na	38	41	21	-
25	31	60	9	-	50	HCO ₂ Na	47	42	11	-
50	28	47	25	-	50	CH ₃ CO ₂ Na	51	31	12	6
75	32	27	41	-	100	CH ₃ CO ₂ Na	51	-	38	11
90	32	11	57	<u>d</u>						
100	51	-	38	11						

^aA solution of I (50 mg.) in 10 ml. of solvent was stirred for 30 min. ^bRelative yields determined by pmr spectroscopic and vpc analyses; the pmr spectra showed no significant amounts of other products. ^cRef. (1). ^dTrace.

The solvent effects can be interpreted in terms of the counterion of V. In acetic acid, where the protonating agent is molecular acid, V would be formed in a tight ion pair with an acetate ion on the exo face (2). Because V is bridged, this ion pair cannot collapse until the counterion has become re-oriented, permitting, in addition to attack by solvent, rearrangement to an ion pair corresponding to VI, which forms IX, the anhydride of II with acetic acid (3), and also rearranges to an ion pair corresponding to X, which forms VIII and IX (4). In aqueous sulfuric acid the protonating agent is hydronium ion, which would give the free carbonium ion V or a corresponding solvent-separated ion pair. Such cations are more susceptible to nucleophilic attack than those in tight ion pairs (5), accounting for the formation of III as the major product, nucleophilic attack occurring rapidly relative to rearrangement to VI. Further, the rearranged ion is more susceptible to nucleophilic attack than the corresponding ion pair, accounting for the failure to form VIII. In aqueous acetic acid protonation by both hydronium ion and molecular acid would be expected; that there is little change in these distributions in the 25-90% range is attributable to the relatively slow change in the ratio of the two

acids in this range and the much higher acidity of the hydronium ion. The effects of the addition of salts to 50% aqueous acetic acid corroborate these proposals. Addition of sodium acetate results in a ratio of II to III + VII that is very similar to that in 100% acetic acid, in accord with its effect in lowering the concentration of hydronium ion. The effects of sodium formate and trichloroacetate show that, as expected, the stronger the conjugate acid of the counterion the less the rearrangement of the tight ion pair. The fact that sodium chloride has no effect shows that these results are not due to ionic strength effects, and the failure of sodium acetate to affect the product distribution in 100% acetic acid shows they are not due to the basicity of the added salts.

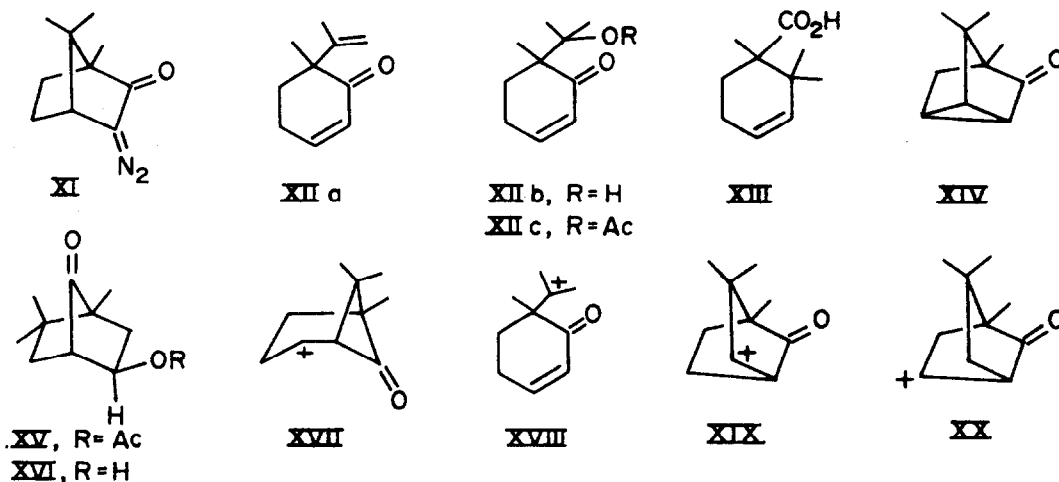
Related observations have been made for the reaction of 3-diazocamphor (XI) in aqueous acetic acid. The products, XII-XV, were the same as those obtained in aqueous sulfuric acid (1), except that XV (6) was obtained in place of XVI, and XIIC accompanied XIIa and XIIb. The product distributions are summarized in Table 2 and can be rationalized in terms of the intermediacy of the ions XVII-XX (1), which are free (or solvent-separated) when the protonating agent is hydronium ion but form part of tight ion pairs when it is molecular acid (4,7,8).

Table 2

Products from the Decomposition of 3-Diazocamphor (XI) in Aqueous Acetic Acid^a

% Acetic Acid (v/v)	Yields ^b				% Acetic Acid (v/v)	Salt (1m)	Yields ^b			
	XIIa-c	XIII	XIV	XV			XIIa-c	XIII	XIV	XV
0 ^c	62	21	13	4 ^d	50	NaCl	65	23	11	e
50	64	23	13	e	50	CH ₃ CO ₂ Na	22	16	57	5
90	54	26	9	11	100	CH ₃ CO ₂ Na	13	18	45	24
95	40	21	13	25						
100	15	18	32	34						

^aA solution of XI (50 mg.) in 10 ml. of solvent was stirred for 30 min. ^bRelative yields determined by pmr spectroscopic and vpc analyses. ^cRef. (1). ^dXVIII. ^eTrace.



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REFERENCES

1. R.A. Blattel and P. Yates, accompanying communication.
2. This assumes that loss of nitrogen from the initially formed tight diazonium ion pair is rapid and that the counterion lies on the exo face of the latter (1).
3. The work-up procedures used ensure that XI would be hydrolyzed to II, the yields of which thus represent the combined yield of acid and anhydride.
4. That II arises both by migration of the C-4-C-7 and the C-4-C-5 bonds of I was shown by the fact that I in CH_3COOD gave both II-3-d (59%) and II-4-d (41%). By contrast, in $\text{D}_2\text{O}/\text{D}_2\text{SO}_4$, where the rearranged carbonium ion X is believed to play a minor role at most, I gave II-3-d (>90%). Corresponding results were obtained for the acid XIII (vide infra).
5. Cf. C.M. Williams and D. Whittaker, J. Chem. Soc. B, 668, 672 (1971).
6. Cf. M. Ishidate and T. Isshiki, Bull. Soc. Chem. Jap. 17, 502 (1942); J.C. Crano, W.P. Wetter, and R.C. Little, Abstracts, 145th National Meeting of the American Chemical Society, New York, N.Y., Sept. 1963, p.3Q.
7. The effect of salts may be interpreted as before with the additional feature that, due to its basicity, acetate favors the formation of XIV over XV.
8. An alternative rationale involves both exo and endo attack by acetic acid to give an endo/exo diazonium ion ratio of ca 1:2. This is difficult to reconcile, however, with evidence that suggests there should be a high preponderance of exo attack. [A.F. Thomas, R.A. Schneider, and J. Meinwald, J. Amer. Chem. Soc. 89, 68 (1967); H.C. Brown and J.H. Kawakami, J. Amer. Chem. Soc. 92, 201 (1970); T.T. Tidwell, J. Amer. Chem. Soc. 92, 1448 (1970)].