Reactions of Norbornyl-Type Ketones with Diazomethane[1]

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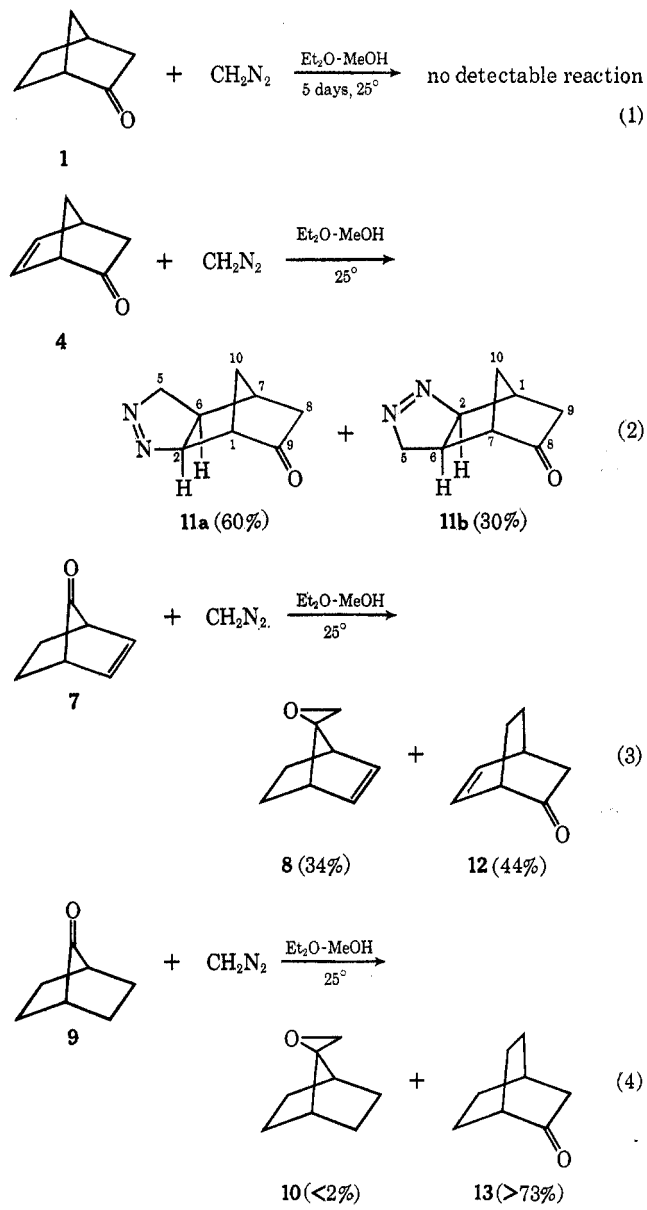
Ethereal diazomethane containing 10% methanol reacts stereoselectively with norbornen-7-one to produce a mixture of spiro[norborn-2-en-*anti*-7,2′-oxacyclopropane] (34%) and bicyclo[2.2.2]oct-5-en-2-one (44%). Under similar conditions norbornan-7-one is four times less reactive and yields spiro[norbornan-7,2′-oxacyclopropane] (<2%) and bicyclo[2.2.2]octan-2-one (>73%). Dehydronorcamphor is much less reactive and produces a mixture of the ketopyrazolines *exo*-3,4-diazatricyclo[5.2.1.0^{2,6}]dec-3-en-8-one (~30%) and *exo*-3,4-diazatricyclo-[5.2.1.0^{2,6}]dec-3-en-9-one (~60%). The probable mechanism of each of these reactions is discussed and explanations are offered for the differing reactivity of these norbornyl-type ketones with diazomethane.

Norbornyl-type ketones show a surprising diversity in their reactivity toward the neutral nucleophile dimethyloxosulfonium methylide. Norcamphor (**1**) reacts predominantly from the *exo* side to yield a 90:10 mixture of saturated oxides: spiro[norbornan-*endo*- and *exo*-2,2′-oxacyclopropane], **2** and **3**, respectively.[2] Dehydronorcamphor (**4**) reacts about twice as rapidly but is attacked preferentially from its more hindered *endo* side to produce a 29:71 mixture of unsaturated oxides: spiro[norbornen-*endo*- and *exo*-5,2′-oxacyclopropane], **5** and **6**, respectively.[2] Bicyclo[2.2.1]-hept-2-en-7-one (**7**) reacts very rapidly from the side of the double bond to give the unsaturated spirooxide **8** as the sole product.[3] Bicyclo[2.2.1]heptan-7-one (**9**) also reacts rapidly to yield some of the expected spirooxide **10**, but, in addition, produces large amounts of sulfoxides: methyl 7-(7-hydroxynorbornyl)carbinyl sulfoxide and bis[7-(7-hydroxynorbornyl)carbinyl sulfoxide.[4]

These reactivity differences toward dimethyloxosulfonium methylide have been attributed to an electronic effect of the double bond in **4** and **7** which stabilizes the transition state for *syn* attack and fixes the resulting zwitterion in the proper conformation for oxide formation[2,3] to a steric effect of the *endo*-5,6-hydrogens in **1** which hinders *endo* attack,[2] and to the cumulative steric effect of the *exo*-hydrogens in **9** which makes it difficult for the intermediate to attain the preferred *trans*-coplanar conformation for the displacement of dimethyl sulfoxide.[4] In order to test these conclusions and to determine whether these norbornyl-type ketones exhibit a similar pattern of behavior with other neutral nucleophiles, we have examined their reactivity toward diazomethane.

Results

Each of the ketones was dissolved in ether containing 10% methanol, combined with an excess of ethereal diazomethane, and allowed to stand in the dark at room temperature for 1–5 days. The reaction mixtures were analyzed by gas–liquid partition chromatography (glpc) on a Quadrol–SAIB column.[2] The results are summarized in eq 1–4.



The structures of the volatile products **8**, **10**, **12**, and **13** were established by spectral comparison of collected samples with the authentic compounds.[3-5]

The structures of the two ketopyrazolines, **11a** and **11b**, obtained as a mixture from the reaction of diazomethane and dehydronorcamphor (**4**), were inferred as follows. Both the elemental analysis, $C_8H_{10}ON_2$, and the mass spectrum, $[M]\cdot^+ = 150$, indicate that **11** corresponds to the addition of one molecule of diazomethane to each molecule of the ketone. The presence of strong C=O stretches (1757 and 1722 cm^{-1}) in the

(1) Portions of this work were presented at the 14th Southeastern Regional Meeting of the American Chemical Society, Gatlinburg, Tenn., Nov 1962; *cf.*, "The Branched Chain," Vol. XVIII, No. 3, 1962, p 71.

(2) R. S. Bly, C. M. DuBose, Jr., and G. B. Konizer, *J. Org. Chem.*, **33**, 2188 (1968).

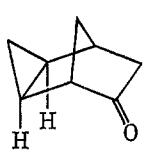
(3) R. K. Bly and R. S. Bly, *ibid.*, **28**, 3165 (1963).

(4) R. K. Bly and R. S. Bly, *ibid.*, **34**, 304 (1969).

(5) (a) W. C. Wildman, and R. R. Saunders, *ibid.*, **19**, 381 (1954); (b) H. M. Walborsky and D. F. Loncrini, *J. Amer. Chem. Soc.*, **76**, 5396 (1954).

infrared spectrum of the product mixture and the fact that a *p*-nitrophenylhydrazone can be prepared indicate that the keto group remains intact in the product(s). The Δ^1-type pyrazoline ring is suggested by the absence of C=C, C=N, and N—H stretches in the infrared and Raman spectra and by the presence of a strong N=N stretch at 1553 cm^{-1} in the infrared[6] and 1549 cm^{-1} in the Raman.[7] That the pyrazoline ring is fused *exo* to the norbornane skeleton is indicated by the large difference in the chemical shifts of the methano hydrogens at C-10, δ 1.53 and 0.83 ppm, respectively, in the nmr spectrum of this material.[8] Finally, it is clear from the two perturbed singlets at δ 3.18 (W_H = 7.5 Hz) and 3.03 (W_H = 4 Hz) which together integrate for one hydrogen and correspond to norbornane-type bridgehead protons on the side nearest the azo group,[9-11] that this material is a mixture of the two ketopyrazolines **11a** and **11b**. Since the broader of these two resonances, *i.e.*, at δ 3.18, corresponds to a bridgehead proton flanked by carbonyl-adjacent methylene hydrogens, *i.e.*, to the C-1–H of **11b**,[12] it is apparent from integrations of these two bridgehead-hydrogen resonances that the ketopyrazoline mixture **11** consists of about one-third **11b** and two-thirds **11a**.

In spite of the fact that the mass spectrum of the ketopyrazoline mixture **11** exhibits a fragment of low intensity corresponding to the loss of nitrogen from the molecular ion, *e.g.*, $[M]\cdot^+ - 28 = 122$, all attempts to isolate a cyclopropanonorbornanone, **14**, from its pyrolysis were unsuccessful. A similar failure has been reported in the case of the pyrazoline **15** formed from the addition of diazomethane to norbornene.[6]



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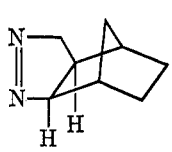

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In order to estimate the relative reactivity of ketones **7** and **9**, an equimolar mixture of the two was allowed to react with a less-than-stoichiometric amount of diazomethane. After the yellow color of the unreacted diazomethane had disappeared, the composition of the reaction mixture was determined by glpc analysis on a Quadrol–SAIB column. From these data it was calculated[13] that the unsaturated ketone **7** is about four times *more* reactive than the saturated ketone **9**.

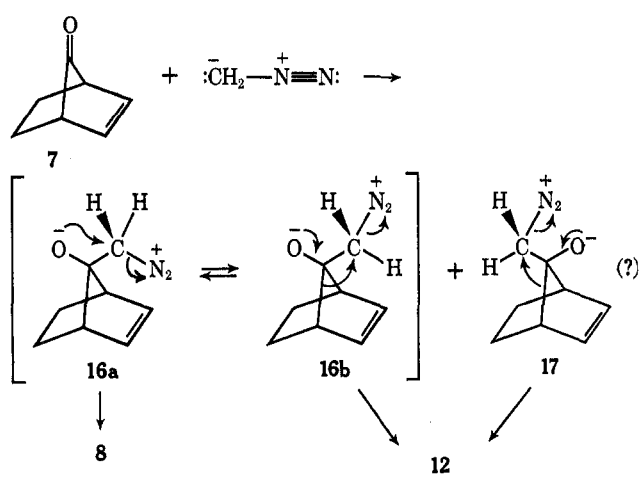
From the relative rates of reaction of norbornene and dehydronorcamphor (**4**) with alcoholic, ethereal diazomethane,[6,14] it is estimated that the former is about three times *less* reactive than the latter under similar conditions.

Although the data of Sauers and Tucker[15] indicate that norcamphor (**1**) reacts slowly with diazomethane to produce a complex mixture containing the 2- and 3-ketobicyclo[3.2.1]octanes in the ratio of 1.0:1.6, it is clear from our data that **1** is the least reactive of the ketones examined here toward this neutral nucleophile.

Discussion

The reaction of 7-ketonorbornene (**7**) with diazomethane is notable in three respects: it is more facile than that of the saturated analog 7-ketonorbornane (**9**), it produces a much higher proportion of epoxide than does that of **9**, and it yields the *anti*-oxide **8**, stereoselectively. The reaction may be formulated as shown in Scheme I.

SCHEME I



Although **17** is a possible intermediate on the route to the unsaturated ketone **12**, it appears that little if any of the ring-enlarged ketone is formed from this zwitterion. Assuming that the rate of conversion of **9** to **18** (Scheme II) is at least twice as great as the rate of *anti* attack on **7** to form **18**,[2] it may be estimated that no more than $(0.98 \times 0.5)/(0.56 \times 4)$ or about one-fifth of the total ketone, **12**, is produced from the "*anti*" zwitterion **17**.

The tendency of **7** to react with diazomethane from the side of the double bond may simply reflect the fact that this path is less hindered. Certainly **7** reacts with other nucleophiles predominantly or exclusively from the *syn* direction[2] and, in the case of the 7-carbometh-

(6) N. S. Zefirov, P. Kadziauskas, and Yu. K. Yuriev, *J. Gen. Chem. USSR*, **36**, 23 (1966); *Zh. Obshch. Khim.*, **36**, 23 (1966).

(7) (a) *Cf.* L. J. Bellamy "The Infra-red Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1958, p 272, and references cited therein. (b) We thank Dr. James R. Durig and Mr. John Casper for this determination.

(8) The effect of the azo group on chemical shifts of the C-10 hydrogens of **11** is similar to, though of smaller magnitude than, the effect of the etheno bridge on the positions of the C-9 hydrogen resonances in 1,4,4a,5,6,7,8,8a-octahydro-1,4-*exo*,*endo*-5,8-dimethanonaphthalene; *cf.* A. P. Marchand and J. R. Rose, *J. Amer. Chem. Soc.*, **90**, 3724 (1968), compound VI. Similar shifts are apparent in the *exo* adducts of phenylazide and norbornadiene,[9a] and diazomethane and norbornene.[6,9b]

(9) (a) S. McLean and D. M. Findlay, *Tetrahedron Lett.*, 2219 (1969); (b) R. K. B., unpublished work.

(10) The effect of the azo group on the chemical shift of the norbornane bridgehead hydrogens in **11** is much greater than that of the carbonyl. In norcamphor the C-1 hydrogen appears at δ 2.48, the C-4 hydrogen at δ 2.62.[11]

(11) (a) R. R. Sauers and P. E. Sonnet, *Chem. Ind.* (London), 786 (1963); (b) E. J. Corey, L. Casanova, Jr., P. A. Vatakencherry, and R. Winter, *J. Amer. Chem. Soc.*, **85**, 169 (1963); (c) see also, K. D. Berlin and R. Ranganathan, *Tetrahedron*, **25**, 793 (1969).

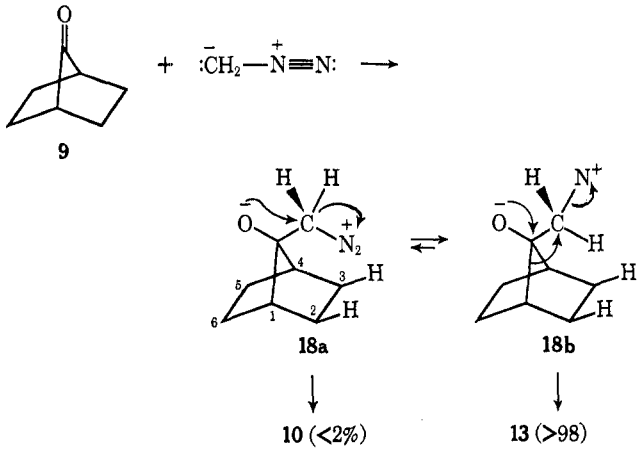
(12) We base this conclusion upon the fact that in the nmr spectrum of the keto–pyrazoline mixture which results from the reaction of diazomethane with dehydronorcamphor containing 1.6 equiv of deuterium at the C-3 position, the W_H of the higher field resonance, *i.e.*, δ 3.03, remains unchanged at ~4 Hz while that of the lower field resonance at δ 3.18 is decreased from 7.5 to ~5 Hz; *cf.* Experimental Section.

(13) T. S. Lee in "Technique in Organic Chemistry," Vol. VIII, S. L. Friess and A. Weissberger, Ed., Interscience Publishers, New York, N. Y., 1953, p 100 ff.

(14) C. H. Norton, Ph.D. Dissertation, Harvard University, 1955, pp 151–152.

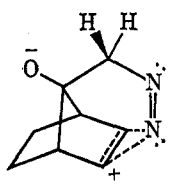
(15) R. R. Sauers and R. J. Tucker, *J. Org. Chem.*, **28**, 876 (1963).

SCHEME II



oxynorbornenes, at least, the *syn* isomer is the more stable.[16]

Whether the increased reactivity of 7-ketonorbornene (**7**) with respect to 7-ketonorbornane (**9**) can also be attributed to a decrease in steric hindrance is less certain. Brown and Muzzio[17] have shown that **7** is less reactive than **9** toward reduction with sodium borohydride and have attributed the decreased rate to the inductive effect of the double bond. Our previous studies of the reaction of **7** with sulfur ylides indicate that the double bond may decrease the rate of *anti* attack and increase the rate of *syn* attack.[2] We have ascribed the latter effect to charge delocalization. Similar delocalization may also act to enhance the reactivity of **7** toward diazomethane by stabilizing any positive charge which develops on the terminal nitrogen in the transition state, *i.e.*



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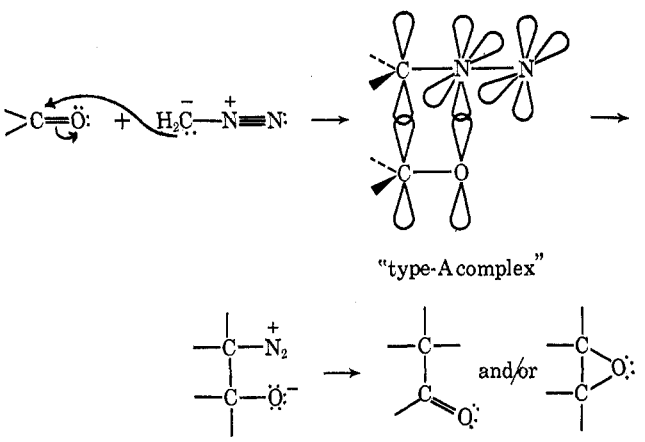
The relatively greater tendency of 7-ketonorbornene to produce epoxide rather than ring-enlarged ketone (*cf.* eq 3 and 4) can probably be attributed to the absence of *exo* hydrogens at C-2 and C-3. Thus the intermediate "*syn*" zwitterion is able to adopt a conformation, **16a**, which is favorable for the intramolecular displacement of nitrogen by the nucleophilic oxide (Scheme I). In the corresponding zwitterion **18** (Scheme II), formed in the reaction of 7-ketonorbornane (**9**) and diazomethane, the *exo* hydrogens at C-2 and C-3 destabilize **18a** with respect to **18b** and ring enlargement is the preponderant reaction. A related effect on the extent of hydrogen migration *vs.* ring enlargement has been observed in the acetolyses of *syn*- and *anti*-7-brosyloxymethylnorbornenes and to a lesser extent in the acetolysis of 7-brosyloxymethylnorbornane.[18]

(16) R. R. Sauers and R. M. Hawthorne, Jr., *J. Org. Chem.*, **29**, 1685 (1964).
(17) H. C. Brown and J. Muzzio, *J. Amer. Chem. Soc.*, **88**, 2811 (1966).
(18) (a) J. A. Berson and J. J. Gajewski, *ibid.*, **86**, 5020 (1964); (b) R. K. Bly and R. S. Bly, *J. Org. Chem.*, **31**, 1577 (1966); (c) J. A. Berson and M. J. Poonian, *J. Amer. Chem. Soc.*, **88**, 170 (1966); (d) J. A. Berson, J. J. Gajewski, and D. S. Donald, *ibid.*, **91**, 5550 (1969); (e) J. A. Berson, M. S. Poonian, and W. J. Libbey, *ibid.*, **91**, 5567 (1969); (f) J. A. Berson, D. S. Donald, and W. J. Libbey, *ibid.*, **91**, 5580 (1969).

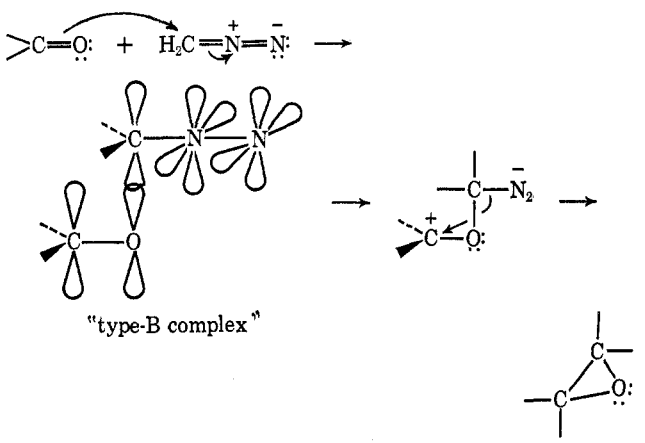
Charge delocalization as depicted in **19** could also act to increase the epoxide-to-ketone ratio in the unsaturated case, **7**, by further stabilizing **16a** with respect to **16b**.

Gutsche, *et al.*,[19] following an earlier suggestion of Bradley, Cowell, and Ledwith,[20] postulate that some cyclic ketones may react with a diazoalkane by either or both of two paths: nucleophilic attack of the diazoalkane at the carbonyl carbon of the ketone to produce a "type-A complex" which is converted *via* the usual zwitterion to a mixture of epoxide and ketone (Scheme III), or by electrophilic attack of diazomethane on the carbonyl oxygen of the ketone to produce a "type-B complex" (Scheme IV) which yields only epoxide.

SCHEME III



SCHEME IV



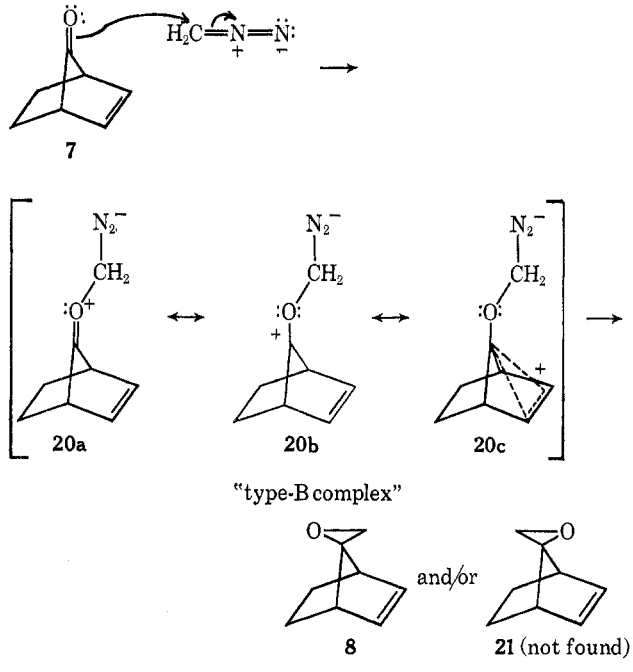
They argue that the well-known tendency of a hindered ketone to produce a high proportion of epoxide-to-ketone[21] reflects its greater propensity to react *via* the less hindered type-B complex.

We doubt that the increased tendency of 7-ketonorbornene (**7**) relative to 7-ketonorbornane (**9**) to produce epoxide when treated with diazomethane can be due to type-B complex formation, since such a complex, **20**, even though it might involve relatively little π-electron delocalization[22] (*e.g.*, **20c**) would not be expected

(19) (a) C. D. Gutsche and J. E. Bowers, *J. Org. Chem.*, **32**, 1203 (1967); (b) C. D. Gutsche and D. Redmore, "Carbocyclic Ring Expansion Reactions," Academic Press, New York, N. Y., 1968, p 81 ff.
(20) J. N. Bradley, G. W. Cowell, and A. Ledwith, *J. Chem. Soc.*, 4334 (1964).
(21) C. D. Gutsche, *Org. React.*, **8**, 364 (1954), and references cited therein.
(22) Because most of the stabilization is expected to be achieved by delocalization of the positive charge to oxygen, *e.g.*, **20a**.

to decompose *exclusively* to the *anti* oxide, **8** (Scheme V).[23]

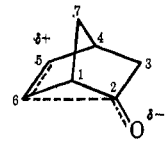
SCHEME V



The exclusive double bond attack that is observed when diazomethane reacts with dehydronorcamphor (**4**) is reminiscent of the unique formation of pyrazoline which is typically observed in the non-Lewis acid-catalyzed reactions of this "1,3-dipole"[24] with α,β-unsaturated aldehydes and ketones.[21] Attempts to induce carbonyl attack on **5** by the addition of boron trifluoride etherate or aluminum trichloride[25] were unsuccessful.[26]

The reaction of diazomethane with a double bond to produce a Δ^1-pyrazoline can probably be formulated as a [2 + 3] cycloaddition.[27] Even though such reactions are thought to occur in a concerted manner by way of an "isopolar" transition state,[28] the formation of the two new σ bonds need not be completely synchronous, and such additions usually respond to electronic effects in a predictable manner.[24,27] In particular, the substitution of electron-withdrawing groups such as cyano, carbalkoxy, carbonyl, or carboxyl on the double bond of the 1,3-dipolarophile enhances the rate of addition and causes diazoalkanes to produce predominately 3- rather than 4-substituted Δ^1-pyrazolines.[24]

Though such effects are predictably smaller in a β,γ-unsaturated ketone such as dehydronorcamphor (**4**), they are still apparent nevertheless. Not only does the nucleophilic carbon of diazomethane react twice as rapidly at the δ position (C-5) as it does at the γ (C-6), but the reaction is also enhanced by the electron-withdrawing effect of the carbonyl,[29] *viz.*



This result implies that in [2 + 3] cycloaddition reactions of diazoalkanes with double bonds, C–C bond formation is more important in the transition state than is N–C bonding.[24,27] The enhanced double bond reactivity of dehydronorcamphor (**4**) coupled with the decreased electrophilicity of its carbonyl (compared with that of **7**)[2,3,17] is apparently sufficient to render pyrazoline formation the exclusive reaction in this case.[30]

Experimental Section[31]

Reaction Products of Bicyclic Ketones with Diazomethane. A. 7-Ketonorbornene (7).—To a solution of 1.0 g (0.093 mol) of 7-ketonorbornene (**7**) in 10 ml of ether containing 10% methanol was added 30 ml of 0.45 *M* ethereal diazomethane. The mixture was allowed to stand in the dark at room temperature overnight. At this time the solution was still a pale straw color. The reaction mixture was analyzed by glpc at 110° on a Quadrol–SAIB column.[2] Two components with relative retention times and (abundance) of 1 (42%) and 5.3 (58%) were found to be present. A small sample of each of the products was collected from the Quadrol column. The ir and nmr spectra of the first component were found to be identical with those of authentic spiro[bicyclo[2.2.1]hept-2-en-*anti*-7,2′-oxacyclopropane] (**8**).[3] The second component was identical in all respects with authentic bicyclo[2.2.2]oct-5-en-2-one (**12**).[5a] The ethereal solution was concentrated under atmospheric pressure, and the residue was distilled in a short-path still at 100–110° (20 mm) to give a total of 0.873 g (78%) of product. An nmr analysis of the distillate showed the presence of epoxide **8** (44%) and ketone **12** (56%).

B. 7-Ketonorbornane (**9**) (1.0 g, 0.092 mol) was treated with ethereal diazomethane exactly as described for **7** (part A). After 24 hr, glpc analysis of the reaction mixture showed two components with relative retention times and (abundance) of 1 (<2%) and 5.0 (>98%). The major component was collected from the Quadrol column and was found to be identical with authentic bicyclo[2.2.2]octanone (**13**).[5b] The minor component was not isolated in pure form, but we believe it to be spiro[bicyclo[2.2.1]heptan-7,2′-oxacyclopropane] (**10**), since the glpc retention time of this component was identical with that of authentic **10**[4] on Quadrol–SAIB, Carbowax 20M, and Ucon (nonpolar) columns.[31] The remaining solution was concentrated at atmospheric pressure and the residue sublimed at 100° (15 mm) to give 0.845 g (75%) of product.

C. Dehydronorcamphor (**4**) (2.2 g, 0.020 mol) was allowed to react with the ethereal diazomethane solution (see part A) for ~3 days. The solvent was removed under reduced pressure and the residue distilled in a short-path still at 110° (0.08 mm). Redistillation of the reddish oil at 100° (0.08 mm) gave 2.6 g (93%)

(23) Actually, to the extent that **20c** contributes to its stability, **20** would be expected to yield **21** predominantly or exclusively; *cf.* (a) S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *J. Amer. Chem. Soc.*, **77**, 4143 (1955); (b) S. Winstein and M. Shatavsky, *ibid.*, **78**, 592 (1956); (c) A. Diaz, M. Brookhart, and S. Winstein, *ibid.*, **88**, 3133 (1966); (d) M. Brookhart, A. Diaz, and S. Winstein, *ibid.*, **88**, 3135 (1966).

(24) R. Huisgen, *Angew. Chem. Int. Ed. Engl.*, **2**, 565, 633 (1963), and references cited therein.

(25) (a) H. O. House, E. J. Grubbs, and W. F. Gannon, *J. Amer. Chem. Soc.*, **82**, 4099 (1960); (b) E. Müller, M. Bauer, and W. Rundel, *Z. Naturforsch, B*, **15**, 268 (1960); *Tetrahedron Lett.*, No. 13, 30 (1960); No. 4, 136 (1961); (c) W. S. Johnson, M. Nieman, S. P. Birkeland, and N. A. Fedorak, *J. Amer. Chem. Soc.*, **84**, 989 (1962). (d) For a comprehensive review see E. Müller, H. Kessler, and B. Zeek, *Fortschr. Chem. Forsch.*, **7**, 128 (1966).

(26) The only product that could be isolated under these conditions was polymethylene, R. K. B., unpublished.

(27) E. M. Kosower, "An Introduction to Physical Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1968, p 209 ff.

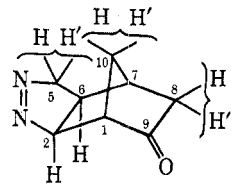
(28) Reference 27, p 195.

(29) Attack by the nucleophilic carbon of diazomethane occurs twice as rapidly at C-6 in **4** as it does at either end of the double bond in norbornene.

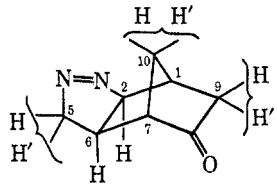
(30) A referee has suggested that the greater tendency of these bicyclic ketones to yield epoxides with ylides may reflect the displacement-promoting properties of the solvent DMSO. This may be a valid point for we have yet to investigate this aspect of the problem.

(31) Microanalyses were performed by Bernhardt Mikroanalitisches Laboratorium 5251 Elbach über Engelskirchen, Germany. Spectra were determined on a Perkin-Elmer grating spectrophotometer, Model 337, a Varian A-60A nmr spectrometer, and a Hitachi Model RMU-6E mass spectrometer. Gas chromatographic analyses were carried out in an F & M Model 500 chromatograph using 8 ft × 0.25 in. coiled copper columns packed with 20% Quadrol–SAIB[2] on 60–80 mesh Gas-chrom CL and 20% Carbowax 20M or Ucon oil (non polar) on Gas-chrom A.

of a viscous liquid (11): ir (neat) 2970, 2930 (sh), 2900 (sh) (CH); 1757, 1722 (C=O); 1553 cm^{-1} (N=N); Raman (neat) 1549 cm^{-1} (N=N)[7a]; mass spectrum $[M]\cdot^+ = 150$. The nmr (CCl_4) spectrum of the product mixture 11 exhibits a complex three-



11a



11b

hydrogen multiplet between δ 5.0 and 3.83 which we attribute to the hydrogens that flank the azo group.[9,10,32] The C-2 and the C-5 hydrogens apparently have similar chemical shifts in each isomer. One of the methylene hydrogens at C-5 is split by the other nonequivalent C-5 hydrogen,[33a] and by those at C-2 and C-6 into an eight-line multiplet centered at δ 4.63 that is superimposed on a second complex multiplet centered at $\sim\delta$ 4.7 which is due to the single hydrogen at C-2. The other C-5 hydrogen (H′) is also coupled to the three hydrogens at C-2, C-5 (H), and C-6, and appears as a pair of asymmetric quartets centered at $\sim\delta$ 4.18. The principal coupling is apparently between the nonequivalent C-5 hydrogens H and H′; $J = -18$ Hz.[33] The bridgehead hydrogens at C-1 in **11b** and **11a** respectively give rise to broad singlets at δ 3.18 (W_H = 7.5 Hz) and 3.03 (W_H = 4 Hz) corresponding to $^1/_3$ and $^2/_3$ of a hydrogen each.[10] The bridgehead hydrogen at C-7 in **11b** appears as a broad (W_H = 7.5 Hz) singlet at δ 2.44,[12] while the C-7 hydrogen of **11a** constitutes a portion of a complex $3^1/_3$ proton multiplet extending from δ 2.33 to 1.87 which includes the C-8 hydrogens of **11a**, the C-9 hydrogens of **11b**, and the C-6 hydrogen of each isomer. The C-10 hydrogens of both **11a** and **11b** have similar chemical shifts and appear as a 2 proton, AB quartet,[33b,34] $J_{H,H'} = -12$ Hz, centered at δ 1.18. This quartet collapses into two broad singlets when irradiated at δ 1.53 + 44 Hz or at δ 0.83 − 44 Hz.

Anal. Calcd for $C_8H_{10}ON_2$: C, 63.98; H, 6.71; N, 18.65. Found: C, 63.70; H, 6.74; N, 18.01.

A *p*-nitrophenylhydrazone was prepared in the usual manner, mp 221–223° dec.

Anal. Calcd for $C_{14}H_{15}N_5O_2$: C, 58.93; H, 5.30; N, 24.55. Found: C, 58.87; H, 5.40; N, 24.44.

D. Norcamphor (1) (1.0 g, 0.091 mol) was mixed with an ethereal solution of diazomethane as described in part A and allowed to stand at room temperature for 5 days. A glpc analysis of the still yellow solution revealed only the unreacted starting ketone 1. Removal of the solvent followed by sublimation of the residue at 100° (20 mm) led to the recovery of 0.865 g (87%) of unreacted norcamphor.

Preparation of 3,3-Dideuteriodehydronorcamphor.[35]—Dehydronorcamphor[2] (0.50 g, 4.6 mmol) was dissolved in 20 ml of a 1:2 D_2O–dioxane mixture containing 0.03 *N* sodium deuterioxide. The solution was heated at 85° for 4 days, cooled, and poured into a separatory funnel containing 20 ml of pentane and 10 ml of 0.4 *N* aqueous nitric acid. The aqueous solution was extracted with three additional portions of pentane. The pentane extract was dried (Na_2SO_4) and the solvent was removed at atmospheric pressure. Distillation of the residue in a short-path still at ~100° (30–40 mm) gave 280 mg (55%) of partially deuterated product: ir (CCl_4) 2235, 2175, 2125 cm^{-1} (C–D); mass spectrum $[M]\cdot^+ = 109$ (37%) and $[M]\cdot^+ = 110$ (63%). The nmr spectrum (CCl_4) showed a broad singlet at δ 1.85–1.65 (–COCHD–) with an area corresponding to ~0.4 hydrogen (compared to 2.0 hydrogens in dehydronorcamphor) but was otherwise identical with that of nondeuterated **4**.

Reaction of Mono- and Dideuterated Dehydronorcamphor with Diazomethane.—A mixture of 3-deuterio- and 3,3-dideuteriodehydronorcamphor (*vide supra*) was treated with ethereal diazomethane in the manner described for the nondeuterated ketone **4** to yield a mixture of the deuterated ketopyrazolines 8-deuterio- and 8,8-dideuterio-*exo*-3,4-diazatricyclo[5.2.1.$0^{2,6}$]dec-3-en-9-one and 9-deuterio- and 9,9-dideuterio-*exo*-3,4-diazatricyclo-[5.2.1.$0^{2,6}$]dec-3-en-8-one: ir(CCl_4) 2800, 2735, 2680, and 2630 cm^{-1} (C–D); mass spectrum $[M]\cdot^+ = 151$ (38%) and $]M]\cdot^+ = 152$ (62%). The nmr spectrum (CCl_4) of this mixture showed a complex multiplet at δ 2.2–1.8 corresponding to 2.4 hydrogens and a singlet at δ 3.17 (W_H = 5 Hz). In other respects the spectrum did not differ significantly from that of the nondeuterated ketopyrazoline mixture **11**.

Competitive Reaction of 7-Ketonorbornene (7) and 7-Ketonorbornane (9) with Diazomethane.—To a solution containing 42 mg (0.39 mmol) of **7** and 40 mg (0.36 mmol) of **9** in 2 ml of ether was added 2 drops of methanol and 1 ml of 0.4 *M* ethereal diazomethane. The solution was allowed to stand at room temperature for 2 hr and then analyzed on the Quadrol–SAIB column at 110°. The mixture was found to contain 16% **7**, 41% **9**, 14% epoxide **8**, 21% ketone **12**, and 8% ketone **13**; *i.e.*, the relative reactivity of ketones **7** and **9** is approximately 1:4.[13]

Relative Reactivity of Norbornene and Dehydronorcamphor (4) with Diazomethane.—Solutions containing (a) 75 mg (0.80 mmol) of norbornene and 0.03 ml of ethanol, and (b) 86 mg (0.80 mmol) of dehydronorcamphor (**4**), 0.03 ml of ethanol and 0.05 ml of anisole, in 4 ml of 0.25 *M* ethereal diazomethane were allowed to stand in the dark at room temperature. Samples were withdrawn at various times and analyzed on the Quadrol–SAIB column. The extent of each reaction was estimated by comparison of the peak area of the unreacted starting material with that of an unreactive component: ethanol in solution a, anisole in solution b. The time required to consume 75% of the starting material was 25 hr for norbornene and 7.5 hr for dehydronorcamphor.

Registry No.—Diazomethane, 334-88-3; **1**, 497-38-1; **4**, 694-98-4; **7**, 694-71-3; **9**, 10218-02-7; **11a**, 24627-23-4; **11b**, 24627-24-5.

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(32) We designate two magnetically nonequivalent hydrogens of a methylene group as H and H′ but make no attempt to attribute uniquely an observed chemical shift to either one of the two individual hydrogens.

(33) The geminal coupling constant of nonequivalent hydrogens on a methylene group adjacent to an azo linkage is reported to range from −16.8 to −19.6 Hz; *cf.* (a) R. Cahill, R. C. Cookson, and T. A. Crabb, *Tetrahedron*, **25**, 4681 (1969), and references cited therein; (b) *ibid.*, **25**, 4711 (1969).

(34) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, London, 1959, pp 89–90.

(35) We thank Dr. Thomas T. Tidwell for helpful advice on the preparation of this material.