sorbance. To avoid prior neutralization, a modified procedure was also used for reactions at pH 0.6–2.0. To a 2-ml aliquot of reaction mixture was added 1 ml of a solution made up from 4 *M* hydroxylamine hydrochloride and 3.5 *M* NaOH (1:2). After 10 min at 30°, 1 ml of 30% $FeCl_3 \cdot 6H_2O$ in 1 *N* HCl was added and the absorbance at 540 mμ read exactly 10 min later. When the yield of methyl acetate was low, cells of 5-cm light path were used.

Acknowledgment. We wish to thank Mr. Tad S. Stashwick for carrying out much of the synthetic work.

Camphene Racemization. III. The *endo*-Methyl Migration Problem[1]

Carl W. David,[2] Bruce W. Everling,[2] Robert J. Kilian,[1] J. B. Stothers,[3] and Wyman R. Vaughan*[2]

Contribution from the Departments of Chemistry of The University of Connecticut, Storrs, Connecticut 06268, and The University of Western Ontario, London, Ontario, Canada. *Received April 7, 1972*

Abstract: By means of ^{13}C labeling at the 8 position of camphene, it has been possible to effect simultaneous analysis by nmr for the amount of the isotope label at each of the possible positions (8, 9, and 10) after partial racemization. With these data it is possible to make full use of integrated rate equations developed earlier and thus obtain a more precise and significant value for the extent of *endo*-methyl migration during racemization. It is also possible to provide reasonably exact rate constants for all of the various processes contributing to racemization, including tricyclene formation. The *endo*-methyl migration appears to be very small: certainly less than 5% (as compared with the previously reported 22%) but very likely not actually zero.

The use of isotopic labeling to help elucidate the mechanism (or mechanisms) of racemization of camphene was first reported simultaneously from the laboratory of J. D. Roberts and that of the senior author of the present paper in 1953. Professor Roberts' study clearly showed that at least two mechanisms were operative: methyl migration (Nametkin rearrangement) and Wagner–Meerwein, 2,6-hydride shift; and the other paper first suggested the cyclical character of the overall racemization process. Then in 1963, the present senior author undertook to examine the individual involvement of each of three processes in the overall racemization:[4] *exo*-methyl migration, *endo*-methyl migration, and Wagner–Meerwein 2,6-hydride shift. To this end, the differential rate equations for the cyclical process were set up and integrated, and by appropriate Taylor's series approximations the integrated equations were solved for the fractional participation of each of the three processes.[4]

In order to obtain numerical values, camphene was labeled with ^{14}C at C-10, and the concentration of the isotope at C-8 was determined as a function of time. But it was also necessary to have corresponding data for camphene initially labeled at C-8, and to this end it seemed permissible to use the earlier data of Roberts[5] for X/X_0 since we[4] wished to avoid extensive repetition of his work. In the event, this proved a poor decision on our part, since the present work has revealed a need for careful solvent–catalyst purification and for lower reaction temperature to avoid demonstrable deterioration of the solvent–catalyst system in periods exceeding 3 hr, even at the lower temperature herein reported. The fortuitous agreement for our calculation of X/X_0 for Roberts' work and the present X/X_0 at 3 hr is just that. We attribute the high value previously reported for α to incompatibility of our original data[4] with Roberts' data[5] assignable to both a real temperature discrepancy and probable inconsistencies in the makeup and stability of the solvent–catalyst system. It was indeed a justifiable objection to using disparate sources of crucial data for the solution of the kinetic equations which in part impelled us to undertake the present investigation, and in part it was the 22% value for α (*endo*-methyl migration) leading to an apparently unique exception to the general absence of such 3,2-*endo*-alkyl migrations as noted by Berson.[6] In addition, at about the same time, Hirsjarvi[7] called attention to the large error inherent in the experimental method and also offered convincing evidence that one should not discount the possibility that racemization could occur *via* tricyclene formation. Thus it was clear that the problem rested in a rather unsatisfactory condition, and particularly because of increasing interest in the exo *vs.* endo migration problem, it seemed highly desirable to reinvestigate the extent of involvement of all logical processes.

Previous work using ^{14}C required starting with the label in two different positions,[4] since analysis for the label was possible only *via* degradation, and only the 8 position was amenable to such a degradative analysis. But the availability of ^{13}C nmr rendered the ^{14}C approach obsolete and provided an elegant method for determining the amount of the isotopic label at all three

(1) This paper also represents part XXVII in the series ^{13}C NMR Studies; part XXVI: J. L. Gough, J. P. Guthrie, and J. B. Stothers, *J. Chem. Soc., Chem. Commun.*, 979 (1972).

(2) The University of Connecticut. For papers I and II, *cf.* ref 4 and 9.

(3) The University of Western Ontario.

(4) W. R. Vaughan, C. T. Goetschel, M. H. Goodrow, and C. L. Warren, *J. Amer. Chem. Soc.*, **85**, 2282 (1963).

(5) J. D. Roberts and J. A. Yancey, *ibid.*, **75**, 3165 (1953).

(6) J. A. Berson, R. G. Bergman, J. H. Hammons, A. W. McRowe, A. Remanic, and D. Houston, *ibid.*, **87**, 3246 (1965).

(7) P. Hirsjärvi, K. Heinonen, and L. Pirila, *Suomen Kemistilehti B*, 37, 77 (1964).

substituent positions simultaneously, regardless of the original position of the label.

Accordingly we undertook to prepare camphene of high optical activity, with the label at C-8 as the most convenient substrate for study. The starting material was commercially available optically pure "nopol" (10-hydroxymethyl-α-pinene or 2,7,7-trimethylbicyclo-[3.1.1]hept-2-ene-10-methanol) (**1**). This was hydrochlorinated at ice–salt bath temperature to give 10-hydroxymethylbornyl chloride[8] (2-*endo*-chlorobornane-10-methanol) (**2**) which was then dehydrochlorinated with silver acetate in refluxing glacial acetic acid[8] to give camphene-8-methyl acetate (**3**) with a rotation somewhat higher than that previously recorded. Alkaline permanganate oxidation of **3** afforded camphenilone (3,-3-dimethyl-2-norbornanone) (**4**) with an optical rotation of 75% of the maximum recorded rotation[9] for **4**.

Various conditions for a Wittig reaction to convert **4** to camphene (**5**) afforded but 30% **5** with 10% other products and 60% recovered **4**. It was also found that dehydration of methylcamphenilol (methylmagnesium iodide on **4**) (**6**) in dimethyl sulfoxide at 150° was unsatisfactory, yielding appreciably racemized **5** contaminated with 5% tricyclene.

The simplest method for converting **4** to **5** was *via* **6** which, converted to its lithium salt (with methyllithium), was treated with acetyl chloride to give the acetate of **6**, methylcamphenilyl acetate (**7**). Pyrolysis of **7** at 550° then yielded camphene with 80% of the maximum recorded rotation,[9] suggesting that no appreciable racemization occurs between **4** and camphene. However, the ^{13}C nmr spectrum indicates that *ca.* 2% of the label is redistributed prior to explicit racemization, and consequently appropriate corrections for this have been made in the isotope concentrations used in calculations.

In studying the experimental conditions for racemization, it was discovered that the solvent–catalyst system previously used by Roberts[5] and by the present senior author[4] (acetonitrile–pyruvic acid) failed to give satisfactorily reproducible results in refluxing bromobenzene vapor (154–156°) with the smaller samples used in the present work, with still larger divergence from reproducibility occurring if the pyruvic acid were not freshly redistilled just prior to use. Consequently it may well be that the effective temperature in our earlier work[4] was less than the recorded 154–156° owing to a lag in complete thermal equilibration and that the rate constant for racemization itself may be in error (see below).

To minimize this type of error, it was determined that reproducibility could best be achieved if the pyruvic acid was always redistilled just prior to use, that the acetonitrile should be of best spectral grade, and that samples such that thermal equilibration would require ~150 sec be used for all racemization runs. The optimum temperature appeared to be 137–138° (refluxing xylene vapor). In this way reasonably reproducible results for the racemization rate constant were obtained, and it may be inferred that all contributory processes are likewise occurring in a reproducible manner. The effective racemization rate constant (pseudo-first-order kinetics) is $k_{rac} = 0.188\ hr^{-1}$ under the conditions used at 137–138°, $t^{1/2} = 3.70$ hr.

The integrated rate equations[4] may be written without approximation in terms of α and β, the fractions of camphene reacemizing *via endo*-methyl and *exo*-methyl migration, respectively, with $1 - \alpha - \beta$ representing the fraction racemizing *via* Wagner–Meerwein 2,6-hydride migration *and via* tricyclene formation, which necessarily results in the same isotope repositioning as the Wagner–Meerwein 2,6-hydride process. In eq 1–3,

$$\alpha + \beta = \frac{1}{3}\left\{2 - \frac{p[C_x - 2\cosh(ktp)]}{\sinh(ktp)}\right\} \quad (1)$$

$$\alpha = \frac{1}{3}\left\{1 + \frac{p[C_y + \cosh(ktp)]}{\sinh(ktp)}\right\} \quad (2)$$

$$\beta = \frac{1}{3}\left\{1 + \frac{p[C_z + \cosh(ktp)]}{\sinh(ktp)}\right\} \quad (3)$$

k = racemization rate constant (hr^{-1}), t = time (hr), $p = [1 - 3(\alpha + \beta - \alpha\beta - \alpha^2 - \beta^2)]^{1/2}$, $C_x = [3(X/X_0 - 1]e^{kt}$, $C_y = [3Y/X_0 - 1]e^{kt}$, $C_z = [3(Z/X_0 - 1]e^{kt}$, and X/X_0, Y/X_0, and Z/X_0 = respectively the mole fraction of isotope label at positions 8, 9, and 10 at time t.

Initial trial values for α, β, and $\alpha + \beta$ may be obtained from the original *approximate* equations.[4] The

$$\alpha + \beta = \frac{1}{3}\left\{2 - \frac{C_x - 2}{kt}\right\}$$

$$\alpha = \frac{1}{3}\left\{1 + \frac{C_y + 1}{kt}\right\}$$

$$\beta = \frac{1}{3}\left\{1 + \frac{C_z + 1}{kt}\right\}$$

values of α, β, and $\alpha + \beta$ are then used to obtain the value of p, which is inserted in eq 1, 2, and 3 to obtain new values for α, β, and $\alpha + \beta$, which in turn are used to obtain a new value for p, and the process is repeated until no further improvement is obtained. This is accomplished by a simple iterative procedure using an IBM 360-65 computer, and the final value of $\alpha + \beta$ affords an internal check on the results. Table I records the results obtained in this manner.

Next the values for α, β, and $\alpha + \beta$ were averaged to give single experimental values, and theoretical curves were obtained for X/X_0, Y/X_0, and Z/X_0 against time, again with the use of the computer. The general character of these curves is exactly what one expects for concurrent production of Y and Z from X, but most significant is the good agreement of the experimental (corrected) mole fractions with those predicted at the experimental reaction times by the curves. These data appear in Table II. As might be expected, the largest error occurs in the values for Y/X_0 which means that the value for α (see eq 1–3) also is in error by the largest amount. The numerical value for α is 0.026 with an error nearly but not quite as large, ±0.019. Parenthetically, the assignment of zero value to α does not give a good agreement of experimental mole fractions for X/X_0 with the predicted value. Thus α is considerably smaller than the previously reported value of 0.22 but very likely is not zero *under the conditions used.*

It should be pointed out here that the least precise measurement in this investigation is the value for the

(8) W. R. Vaughan, J. Wolinsky, R. R. Dueltgen, S. Grey, and F. S. Seichter, *J. Org. Chem.*, **35**, 400 (1970).

(9) W. R. Vaughan and R. Perry, *J. Amer. Chem. Soc.*, **75**, 3168 (1953).

Table I. Isotope Distribution at 137–138° and $k = 0.188\ hr^{-1}$

Expt no.	Time, hr	Label at C-8: % $^{13}C^{a,3}$	Label at C-8: % $^{13}C^{b}$	Label at C-8: X/X_0^c	Label at C-9: % $^{13}C^{a,3}$	Label at C-9: % $^{13}C^{b}$	Label at C-9: Y/X_0^c	Label at C-10: % $^{13}C^{a,3}$	Label at C-10: % $^{13}C^{b}$	Label at C-10: Z/X_0^c	α	β
15[d]	0	46.3 ± 0.5	46.3 ± 0.5	1.00	0.1 ± 0.05	0	0	1.3 ± 0.2	0	0		
16	1.5	39.2 ± 0.5	39.2 ± 0.5	0.8578	1.0 ± 0.1	0.9 ± 0.1	0.0197	6.9 ± 0.3	5.6 ± 0.3	0.1225	0.050	0.533
17	1.5	40.3 ± 0.5	40.3 ± 0.5	0.8741	0.9 ± 0.1	0.8 ± 0.1	0.0173	6.3 ± 0.3	5.0 ± 0.3	0.1086	0.040	0.468[e]
18	3.0	35.5 ± 0.5	35.5 ± 0.5	0.7701	1.4 ± 0.2	1.3 ± 0.2	0.0282	10.6 ± 0.4	9.3 ± 0.4	0.2017	0.002	0.535
19	3.0	35.6 ± 0.5	35.6 ± 0.5	0.7655	1.6 ± 0.2	1.5 ± 0.2	0.0323	10.7 ± 0.4	9.4 ± 0.4	0.2022	0.012	0.536
										Av	0.026	0.534

[a] Experimental value. [b] Corrected for initial isotope distribution. [c] Mole fraction corrected for initial isotope distribution: ±1.5% for X/X_0, ±10% for Y/X_0, ±5% for Z/X_0. [d] Duplicate runs coincide exactly. [e] Omit in average.

Table II. Comparison of Theoretical[a] and Experimental Mole Fractions of Labeled Camphene

Expt no.	Time, hr	X/X_0^b	X/X_0^c	Y/X_0^b	Y/X_0^c	Z/X_0^b	Z/X_0^c
15	0	1.00	1.00	0.00	0.00	0.00	0.00
16	1.5	0.863	0.858	0.0142	0.0199	0.123	0.123
17	1.5	0.863	0.874	0.0142	0.0173	0.123	0.109
18	3.0	0.761	0.770	0.0373	0.0282	0.202	0.202
19	3.0	0.761	0.766	0.0373	0.0323	0.202	0.202

[a] For $k = 0.188\ hr^{-1}$, $\alpha = 0.026$, $\beta = 0.534$, $1 - \alpha - \beta = 0.440$. [b] Theoretical (from theoretical curve). [c] Experimental (corrected for initial isotope distribution, *cf.* Table I).

racemization rate constant (k or k_{rac}), which we obtained for the four runs made with labeled camphene and calculated by the least-squares method using the origin as an additional data point. This lack of precision is inherent in the nature of the experimental technique used, and obviously it could be problematical if the dependence on k_{rac} of α, β, and $\alpha + \beta$ were very critical. The value for k as experimentally determined is $0.188 \pm 0.015\ hr^{-1}$ or an average deviation of approximately 8%. When one increases k by $^1/_6$ the consequent changes in the theoretical values of the mole fractions (Table II) are within the experimental limits as recorded, and consequently it follows that the 8% experimental error in k is not sufficient to cause any major variations in the distribution of the racemization mechanisms constituting the complete racemization process.

By using the average values for the fractions racemizing *via* the various mechanisms, the following rate constants can be calculated: $k_{rac} = 5.2 \times 10^{-5}\ sec^{-1}$, $k_{endo\text{-}methyl} = 1.4 \times 10^{-6}\ sec^{-1}$, $k_{exo\text{-}methyl} = 2.8 \times 10^{-5}\ sec^{-1}$, and $k_{other} = 2.3 \times 10^{-5}\ sec^{-1}$. The last of these includes both the Wagner–Meerwein 2,6-hydride mechanism and racemization *via* tricyclene. Table III contains data relevant to the tricyclene racemization, from which it may be seen that the rate of tricyclene formation is of the same order of magnitude as the rate of *endo*-methyl migration or about 0.08 of the value of k_{other}. Since the conversion of tricyclene to camphene proceeds considerably faster, one must agree with Hirsjärvi[7] that some of the racemized camphene indeed arises *via* this route, but the amount is not appreciably more significant than the amount experiencing *endo*-methyl shift.

Table III. Camphene–Tricyclene Interconversion[a]

Expt no.	Time, hr	% initial	% final	10^6k, sec^{-1}
		Camphene	Tricyclene	
16	1.5	99.4	1.6	1.8
17	1.5	99.4	1.9	2.4
18	3.0	99.4	2.4	1.7
19	3.0	99.4	2.5	1.8
Av				1.9
		Tricyclene	Camphene	
20	3.0	100	84.1	16.0

[a] 137–138°, same conditions as for isotope studies.

The camphene case is as significant for substituted norbornanes, and for basically the same reasons, as is the discrete norbornyl cation for the "simple" norbornane system; any of the mechanisms which involves migration or skeletal rearrangement of one bicyclo[2.2.1]-heptyl system into another involves no net change in free energy, since the initial ion and product ion are enantiomers. Consequently, the distribution among various pathways or mechanisms of racemization is necessarily a function of the relative ease of reaching a particular transition state and subject in no way to purely thermodynamic parameters. The paucity of any clear-cut cases of 3,2-endo migrations strongly suggests some common factor inhibiting them. Berson has suggested the nonclassical ion as the cause and has admirably documented and supported his suggestion.[6] We do not disagree with his cogent arguments; however, it seems desirable to focus attention on a possible geometrical factor which should be operative whether or not a particular ion is nonclassical. Specifically, the geometry at C-3 is such that the sp^3 orbital involved in bonding the exo substituent at C-3 is more nearly perpendicular to the sp^2 or quasi-sp^2 orbital system at C-2 than is the sp^3 orbital involved in the bonding of the endo substituent at C-3. This clearly would give preference to exo-3,2 migration, and such geometry may well be observable in a complete X-ray study of camphene (or camphenilone) even though it is not apparent in Dreiding or similar models.

If one accepts this as a working hypothesis, it follows that sufficiently large substituents on C-10 or C-9 (*endo*- and *exo*-methyls) of camphene can distort the geometry at C-3 by steric interactions with the endo hydrogen at C-5 or the syn hydrogen on C-7, respectively. Such distortions necessarily will be reflected in the extent of participation of the endo and exo migrations in the same manner that a substituent at C-8 (the methylene carbon) would inhibit either *endo*- or *exo*-methyl migration through destabilization of both product and transition state by the same steric interactions at C-5 endo hydrogen and C-7 syn hydrogen. The latter situation appears to have experimental support in the apparently exclusive Wagner–Meerwein 2,6-hydride rearrangement (racemization) of 8-substituted camphenes reported by Ritter and Vlases,[10] and the

(10) J. J. Ritter and G. Vlases, *ibid.*, 64, 583 (1942).

former appear to be deriving support from current research in the senior author's laboratory.[11]

Thus from the distribution among the various racemization mechanisms obtained in the present investigation, one has a "normal" basis from which deviations can be measured and one has accordingly a possible method for testing the hypothesis that the almost exclusive preference for exo 3,2-migration may be geometric in its origin.

In summary, the racemization of camphene embodies four mechanisms: two almost but not quite negligible ones, *endo*-methyl 3,2-migration and tricyclene formation, Wagner–Meerwein 2,6-hydride rearrangement (~41%), and *exo*-methyl 3,2-migration (53%). The conditions under which these values are applicable involve 137–138°, acetonitrile solvent, pyruvic acid catalyst (0.659 ± 0.022 *M*), and camphene (1.71 ± 0.02 *M*).

Experimental Section

General. Melting points were determined in capillary tubes with a Thomas–Hoover melting point apparatus and are uncorrected. Proton magnetic resonance spectra were run in carbon tetrachloride solution on a Varian A-60 and chemical shifts are reported in parts per million (δ) measured from an internal tetramethylsilane reference. All vapor phase chromatography was performed on an Aerograph Model 90-P gas chromatograph using a 5 ft × 0.25 in. copper column packed with 4% Carbowax 20M on Chromosorb G 60–80 AW-DMCS. The flow rate of helium was 40 ml/min and the injector and detector were maintained at 240 and 220°, respectively. All peak areas were measured by direct weighing of the chart paper. Silica gel from Gebruder Hermann, Cologne, Germany, was used for all column chromatographies. Rotations were obtained on a Rudolph Precision Model 70 polarimeter.

(−)-10-Hydroxymethylbornyl Chloride (2). This was prepared in 50% yield as previously reported[8] from (−)-nopol, $[\alpha]^{26.1}D$ −37.49° (Aldrich Chemical Co.). (−)-10-Hydroxymethylbornyl chloride (2) had bp 118–150° (1.2–1.3 mm); $[\alpha]^{26.5}D$ −27.4° (95% ethanol, 8.27 g/100 ml, l = 2.0 dm) [lit.[12] mp 39.8–40.6°; $[\alpha]^{25}D$ −35.6° (95% ethanol, 9.9 g/100 ml)]; nmr δ 4.50–4.10 (multiplet, 2, OH and exo H on carbon bearing chlorine), 4.10–3.30 (multiplet, 2, CH_2OH), and 3.0–0.8 (multiplet, 15).

(+)-Camphene-8-methyl Acetate (3). This was prepared in 81% yield from **2** as reported:[8] bp 88–93° (1.8–2.1 mm); $[\alpha]^{22.5}D$ +101.0° (neat liquid, l = 2.0 dm) (lit.[8] bp 75° (0.03 mm); $[\alpha]^{27}D$ +93.72); nmr δ 5.00 (broad triplet, J = 7 Hz, =CH), 4.37 (broad doublet, J = 7 Hz, CH_2OAc), 1.79 (s, acetate CH_3), and 0.88 (d, *gem*-dimethyl group). Vpc at 190° on comparable material from another run showed one major component and one very minor component at 3.5 and 4 min, respectively.

(−)-Camphenilone (4). In a typical run, a mixture of 60.2 g (0.289 mol) of camphene-8-methyl acetate (3) and 3300 ml of water was cooled, with stirring, in an ice–salt water bath to 3°. To this was added, with stirring, over a period of 10 min, 133.0 g (2.02 mol) of 85% potassium hydroxide. The temperature rose to 10°. After 10 min, the temperature fell to 8° and then 319.2 g (2.02 mol) of potassium permanganate was added, with stirring, over a period of 10 min. The ice–salt water bath was removed and the mixture was stirred at room temperature for 158 hr. The resulting mixture was cooled in an ice–salt water bath to 5° and then sulfur dioxide was added at a rate to maintain the temperature at 15–20° until the pH of the mixture was 4.0–6.0. The mixture was then steam distilled until 1 l. of distillate had been collected. The distillate was extracted with pentane, and the combined pentane extracts were washed with saturated sodium bicarbonate solution and dried. Most of the pentane was removed by distillation and the remaining material was sublimed at 0.9–1.0 mm to yield 14.838 g (37%) of (−)-camphenilone as a white solid: $[\alpha]^{23.0}D$ −56.99° (benzene, 7.95 g/100 ml, l = 2.0 dm) [lit.[9] $[\alpha]^{20}D$ 76.1° (benzene)]. Vpc at 188° showed only one component. Nmr on comparable material from another run showed an eight-proton complex absorption at δ 2.6–1.1 and a six-proton doublet centered at 0.99.

Methylcamphenilol-8-^{13}C (6). In a typical run, a solution of 2.00 g (0.0140 mol) of methyl-^{13}C iodide (obtained from Merck Sharp and Dohme of Canada, Ltd., Lot. No. C-521, 65.7 atom % ^{13}C) in 24 ml of ether was added dropwise, with stirring, over a period of 10 min, to 0.433 g (0.0178 g-atom) of magnesium ribbon cooled in an ice–water bath, under nitrogen. The resulting mixture was heated, under nitrogen, at reflux for 1 hr and then cooled in an ice–water bath. To this was added, over a period of 5 min, a solution of 1.978 g (0.0143 mol) of (−)-camphenilone (4) in 15 ml of ether. The resulting mixture was heated at reflux, under nitrogen, for 5 hr. Then, an additional amount of Grignard reagent, prepared by adding a solution of 2.008 g (0.0141 mol) of unlabeled methyl iodide in 15 ml of ether to 0.455 g (0.0195 g-atom) of magnesium ribbon, was added. The resulting mixture was heated at reflux, under nitrogen, for an additional 15 hr. During the reflux period additional ether was added as necessary to replace that lost by evaporation. The reaction mixture was cooled in an ice–water bath and 20 ml of saturated ammonium chloride solution was added dropwise, with stirring. An additional 10 ml of water was added and the mixture was stirred for 3 hr. The resulting clear two-phase mixture was poured into water and this mixture was extracted with ether. The combined ether extracts were washed first with saturated ammonium chloride solution and then with saturated sodium bicarbonate solution and then dried. The ether was removed under reduced pressure to yield 2.43 g of crude methylcamphenilol-8-^{13}C as a white solid: nmr δ 1.10 (s, CH_3 on carbon bearing alcohol) and 2.15 and 0.05 (s, ^{13}C satellite peaks associated with methyl on carbon bearing alcohol).

Methylcamphenilyl-8-^{13}C Acetate (7). In a typical run, 17–18 ml of 2.1 *M* methyllithium in ether was added dropwise, with stirring, over a period of 5 min, to a solution of 2.63 g (0.0169 mol) of methylcamphenilol-8-^{13}C in 30 ml of ether, cooled in an ice–water bath, under nitrogen. Immediate gas evolution was noted and the resulting cloudy solution was heated at reflux, under nitrogen, for 3 hr. The solution was cooled in an ice–water bath and then 3.5 ml of freshly distilled acetyl chloride was added dropwise, with stirring, over a period of 10 min. The resulting yellow mixture was heated at reflux, under nitrogen, for 2 hr and then the orange mixture was cooled in an ice–water bath, 40 ml of water and 20 ml of ether were added, and the mixture was stirred for 3 hr. The resulting clear two-phase mixture was poured into water and extracted with ether. The combined ether extracts were washed with saturated sodium bicarbonate solution and dried. The ether was removed under reduced pressure to yield 3.07 g (92%) of crude methylcamphenilyl-8-^{13}C acetate as a red oil: nmr δ 1.25 (s, CH_3 on carbon bearing acetate) and 2.32 and 0.20 (s, ^{13}C satellite peaks associated with methyl on carbon bearing acetate).

(−)-Camphene-8-^{13}C (5). In a typical run, a solution of 3.00 g of crude methylcamphenilyl-8-^{13}C acetate (7) in 25 ml of pentane was filtered to remove the insoluble material and was then added dropwise over a period of 30 min to a 1.5 × 45.0 cm tube of 0.125-in. glass helices at 540–550° in a stream of dry nitrogen. An additional 50 ml of pentane was added dropwise, and the tube was allowed to cool to room temperature, and then another 25 ml of pentane was added dropwise. The combined pentane fractions were washed with saturated sodium bicarbonate solution and dried. Most of the pentane was removed by distillation and the resulting concentrated orange pentane solution was chromatographed on 120 g of silica gel using 300 ml of pentane as eluent. This pentane fraction was combined with similar pentane fractions from two other runs and the pentane was removed *via* distillation and subsequently at reduced pressure to yield 3.00 g (0.219 mol) (51% based on camphenilone) of (−)-camphene-8-^{13}C: $[\alpha]^{25.0}D$ −87.41° (benzene, 2.81 g/100 ml, l = 2.0 dm) [lit.[9] for unlabeled material $[\alpha]^{20}D$ +109.0° (benzene, 4 g/100 ml]. Vpc at 78° showed a camphene:tricyclene ratio of 99.4:0.6.

Partial Racemization of (−)-Camphene-8-^{13}C (5). In a typical run, a mixture of 0.612 g of (−)-camphene-8-^{13}C, 0.13 ml of freshly distilled (*in vacuo*) pyruvic acid, and 2.5 ml of acetonitrile was heated under nitrogen in a sealed tube at 137–138° by immersion in refluxing xylene vapor for 1.5 hr. The mixture was then quenched in ice–water and then poured into a mixture of pentane and water. The resulting mixture was extracted with pentane and the combined pentane extracts were washed with saturated sodium bicarbonate solution and dried. The pentane solution was chromatographed on 40 g of silica gel, using 150 ml of pentane as additional eluent, to yield 0.360 g (59% recovery) of white solid, $[\alpha]D$ −63.47°. Vpc at 78° showed a camphene:tricyclene ratio of 98.4:1.6.

(11) D. M. Teegarden, Ph.D. dissertation, The University of Michigan, 1972.

(12) J. P. Bain, A. H. Best, B. L. Hampton, G. A. Hawkins, and L. J. Kitchen, *J. Amer. Chem. Soc.*, 72, 3124 (1950).

Four runs were made and the data are summarized as expt 16–19 in Table I.

^{13}C Nmr.[3] The ^{13}C spectra were obtained under steady-state (cw) conditions using a Varian XL-100-15 instrument equipped with a V-3512 proton decoupler and a C-1024 time-averaging device. The camphene samples were examined as 10% (w/v) solutions in benzene-d_6. With normal samples, operating conditions were adjusted so that the signals for each carbon bearing hydrogen exhibited the same integrated intensity; these conditions were then employed for each enriched sample. The signals for the four carbons absorbing at highest field were recorded using a 250-Hz sweep width and 500–800 scans to obtain relatively high signal to noise ratio. These signals are (in parts per million downfield from TMS): 24.2 (C-5), 26.0 (*endo*-Me), 29.2 (C-6), 29.7 (*exo*-Me). Off-resonance decoupling was employed to establish these assignments and it may be noted that these differ from those reported previously.[13] Careful integration of the four signals allows one to follow the increase in ^{13}C at the methyl carbons quantitatively since the two methylene signals (C-5, C-6) provide a measure of the natural-abundance ^{13}C as an internal standard. In addition, proton spectra of the olefinic region of the enriched samples were carefully integrated (HA-100). Because of the large ^{13}C–H coupling constants, the ^{13}C satellites are readily observed and their intensities relative to those of the main absorption bands (^{12}C–H) were determined to obtain values for the ^{13}C content at C-8. Integrated intensities were determined, in triplicate, for each sample and the results averaged; these data are listed in Table I.

(13) J. B. Grutzner, M. Jautelat, J. B. Dence, R. A. Smith, and J. D. Roberts, *ibid.*, **92**, 7107 (1970).

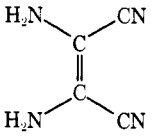
Spectroscopic and Photochemical Study of Diaminomaleonitrile and Diaminofumaronitrile[1]

Ralph S. Becker,* Jaroslav Kolc, and William Rothman

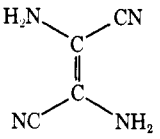
Contribution from the Department of Chemistry, University of Houston, Houston, Texas 77004. *Received July 3, 1971*

Abstract: Based on a wavelength study of the excitation of pure diaminofumaronitrile (DAF) in a polar solvent, we conclude that either (1) DAF cannot form 4-amino-5-cyanoimidazole (ACI) but can be converted to diaminomaleonitrile (DAM) which can or (2) there is a wavelength dependence for the formation of ACI from DAF. The highly dominant result of irradiation of DAF at wavelengths well within the absorption onset is trans (DAF) → cis isomerization to produce DAM. Irradiation of initially pure DAM in a polar solvent at wavelengths within (but relatively near) the absorption onset results in photoisomerization to DAF and production of the imidazole, ACI. The photochemical formation of ACI has an overall activation energy which is larger than that necessary for isomerization. There is evidence for the existence of an intermediate(s) between DAM (also potentially DAF) and ACI. Excitation of DAM or DAF in a rigid matrix at −196° produces a species which has been assigned as aminocyanocarbene, in addition to photoisomerization (but no ACI).

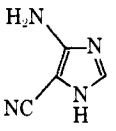
Diaminomaleonitrile (DAM) (I) and diaminofumaronitrile (DAF) (II) are respectively substituted cis and trans derivatives of ethylene. These can undergo photochemical interconversion.[2] Also, photochemical conversion of DAM to 4-amino-5-cyanoimidazole (ACI) (III) is believed to be an important step toward the chemical evolution of purines.[3–6]



I



II



III

A mechanistic proposal of the photochemical conversion of DAM (I) to ACI (III) has been given.[3–7] The trans isomer, DAF (II), was given as one of the intermediates in the transformation of DAM (I) to ACI (III).[3] Lamps with principal emissions at 253 and 350 nm have been successfully used to convert DAM to ACI (in the latter case, wavelengths other than 350 nm must be effective since DAM has no absorption at 350 nm). Yamada, *et al.*,[2] reported that irradiation with wavelengths longer than 320 nm enhanced the photochemical conversion of DAF back to DAM.[1] This was noted to be in contrast to the results of Ferris and Orgel[4] who indicated ACI was formed. Nonetheless, the former authors[2] maintained the opinion[3,4] that the photochemical rearrangement of DAM to ACI proceeds *via* DAF.

As a part of our continuing interest in photoisomerization and photochemistry, we have investigated DAM and DAF. In particular, we have studied the interconversion of DAM and DAF and the conversion of DAM and DAF to ACI as a function of temperature and exciting wavelengths.

Experimental Section

DAM was synthesized and purified by multiple crystallization.[7] DAF was prepared using the procedure described by Yamada, *et al.*[2]

All samples used for photochemistry and spectroscopy were care-

(1) Supported by the National Aeronautics and Space Administration, Grant No. NGR 44-205-091.

(2) Y. Yamada, N. Nagashima, Y. Iwashita, A. Nakamura, and I. Kumashiro, *Tetrahedron Lett.*, 4529 (1968).

(3) R. A. Sanchez, J. P. Ferris, and L. E. Orgel, *J. Mol. Biol.*, **30**, 223 (1967).

(4) J. P. Ferris and L. E. Orgel, *J. Amer. Chem. Soc.*, **88**, 1074 (1966).

(5) J. P. Ferris, J. E. Kuder, and A. W. Catalano, *Science*, **166**, 765 (1969).

(6) J. P. Ferris and J. E. Kuder, *J. Amer. Chem. Soc.*, **92**, 2527 (1970).

(7) J. P. Ferris and R. A. Sanchez, *Org. Syn.*, **48**, 60 (1968).