24.8; 163 ± 1.5°—1.90, 58.7; 3.00, 43.7; 4.50, 27.3; 6.00, 13.8; 7.00, 10.3.

Thermolysis of *trans*-1-Acetyl-2-methylcyclopropane (Attempt). After 12 hr at 160°, a sample of *trans*-1-acetyl-2-methylcyclopropane was unchanged. A sample heated to 179–180° for 24 hr did discolor, but neither vpc nor infrared analysis detected any rearrangement.

Thermolysis of *cis*-1-Acetyl-2-methylcyclopropane. A tube containing *cis*-1-acetyl-2-methylcyclopropane was subjected to 160° temperature concurrently with the *trans* isomer above for 12 hr. Almost total conversion to allylacetone was achieved, as evidenced by vpc analysis and an infrared spectrum which was almost identical with that of authentic material (Borden Chemical Co.).

Thermolysis of 4-Pentenophenone-2-d_2. Thermal rearrangements were performed using 0.3–0.5-g samples which were heated at 202 ± 2°. Progress of reactions was monitored by nmr. The doublet absorption noted at δ 2.4 collapsed to a complex multiplet as deuterium was exchanged for hydrogen. The amounts of deuterium per position after the various reaction periods are listed in Table I. Absorption peak areas were derived from the average values obtained from three electronic integrations per sample. Mass spectral analysis of the sample heated 72 hr revealed the following distribution of deuterium-labeled species: 5.6% d_4 molecules, 18.0% d_3 molecules, 37.4% d_2 molecules, 18.4% d_1 molecules, and 20.6% d_0 molecules.

Thermolysis of 3-Methyl-4-pentenophenone-2-d_2. The nmr data obtained after heating 0.5–0.6-g samples at 202 ± 2° are summarized in Table II. The starting material contained 1.72 deuterons per molecule; after 120 hr of heating, the value was 1.61 per molecule (see footnote *b*, Table II).

Thermolysis of 1:1 Mixture of 4-Pentenophenone-2-d_2 and 3-Methyl-4-pentenophenone. The 0.6-g sample was heated for 17 hr at 202 ± 2°. The higher molecular weight compound picked up 1.5 deuterons per molecule on the average; the specific composition was as follows: 9.5% d_4 molecules, 11.3% d_3 molecules, 23.5% d_2 molecules, 30.8% d_1 molecules, and 24.8% d_0 molecules. The 4-pentenophenone retained 0.3 deuterium per molecule on the average; the specific composition was: 29.9% d_1 molecules and 70.1% d_0 molecules.

Thermolysis of 4-Methyl-4-pentenophenone-2-d_2. Samples of the deuterated material (0.3–0.5 g) were subjected to thermal rearrangement at 202 ± 2°. Reaction times longer than 90 hr gave rise to considerable decomposition and polymerization which interfered with electronic integration of the nmr spectrum. Use of diphenyl ether in one experiment as a solvent did not slow the interfering processes. Usable data were obtained from samples distilled from a "kugelrohr" at less than 100° (1.3–2.3 mm). As deuterium from the α carbon exchanged for protons on the δ methylene, the nmr absorption at δ 2.4 broadened into a doublet with shoulders. The absorption at β-CH_2 was taken as an internal standard for two protons, and deuterium distributions after various heating periods were as listed in Table III. Absorption peak areas were derived from the average values obtained from three electronic integrations per sample.

Reactions of Active Nitrogen with Organic Substrates. V. Resynthesis and Rearrangement in the Reaction of Propylene. The Molecular Mechanism[1]

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Contribution from the Chemistry Department of Boston University, Boston, Massachusetts 02215. *Received August 11, 1966*

Abstract: Propylene was recovered after contact of each of the three ^{14}C-labeled isomers with excess active nitrogen in a fast flow apparatus at 3 torr. With $(N)/(C_3H_6)$ equal to 6, the mean changes in total molar activity of recovered propylene and their standard deviations were from C_3H_6-1-^{14}C, $-7.7 \pm 1.3\%$; from C_3H_6-2-^{14}C, $+5.9 \pm 0.85\%$; from C_3H_6-3-^{14}C, $-3.8 \pm 1.2\%$. Mean changes in atomic activity at C-1 which occurred under the same conditions were from C_3H_6-1-^{14}C, $-15.3 \pm 1.8\%$; from C_3H_6-2-^{14}C, $+7.0 \pm 3.0\%$; from C_3H_6-3-^{14}C, $+12.5 \pm 1.6\%$. Similar data were obtained with $(N)/(C_3H_6)$ equal to 12. The changes in total molar activity establish that part of the recovered propylene is reconstituted from fragments of two or more molecules of reactant propylene. The changes in atomic activity at C-1 indicate that interconversion of C-1 and C-3 is superimposed on the resynthesis process. Resynthesis is best interpreted as involving recombination of a two-carbon fragment which is composed of one original C-2 atom plus either a C-3 or a C-1 atom with a one-carbon fragment which may be derived from any of the original carbon atoms. The latter always becomes C-1 of the reconstituted molecule. Several plausible mechanisms capable of rationalizing the interconverson of C-1 and C-3 are described. One of these involves reversible addition of $N(^4S)$ to the double bond followed by reversible rearrangement of the excited adduct to an excited azacyclobutyl radical, $(CH_2)_3N^*$. Consideration of the decomposition modes of the two intermediates and of the attack of one of the decomposition products, methylcarbene, or $N(^4S)$ on the intermediates provides a mechanistic scheme which correlates not only the resynthesis data but also previously reported data on the molecular origins of CH_3CN, C_2H_6, C_2H_4, C_2H_2, and C_3H_8 which are formed in this reaction.

A previous paper in this series[3] reported an investigation of the molecular origins of a number of the products of the reaction of active nitrogen with propylene variously labeled with ^{14}C. Within the limits of accuracy of that work, the recovered propylenes appeared to have molar activities identical with those of the original substrates. Application of a more accurate static counting procedure has, however, established that when excess active nitrogen is employed, original and recovered propylenes differ significantly in specific activity. These data have been supplemented by selectively removing the methylene carbon (C-1)

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[1] This work was supported in part by the U. S. Atomic Energy Commission Contract AT(30-1)2383 and in part by U. S. Army Research Office Grant DA-ARO(D)-31-124-G171.

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[3] Y. Shinozaki, R. Shaw, and N. N. Lichtin, *J. Am. Chem. Soc.*, **86**, 341 (1964).

from the original and recovered propylene and comparing their specific activities.

Experimental Section

The reaction system was substantially the same as that used in earlier work.[3] A Raytheon Model CMD-10 microwave generator was used to dissociate Matheson prepurified nitrogen, which had been further purified by passage over copper gauze at 450°, followed by passage through a liquid nitrogen cooled trap. The concentration of active nitrogen was measured by nitric oxide titration.[4] Controversy[5-12] regarding the validity of this procedure as a measure of active nitrogen concentration is not important to the present work. The main purpose in carrying out titrations was to ensure that a large excess of $N(^4S)$ was employed. The analytical uncertainty could not have led to deviation from this condition. The three propylene isomers which were used as substrates (1-^{14}C from Research Specialities Co., 2- and 3- isomers from New England Nuclear) were purified on a 0.25 in. × 4 ft silica gel column at room temperature with a helium flow of 35 cc/min to remove traces of ethylene and were then diluted with Phillips Research Grade propylene. Propylene was introduced into the nitrogen stream through a countercurrent nozzle, and all products were trapped at $-196°$ in a large spiral trap. By warming the trap up to $-78°$, propylene and other hydrocarbon products could be roughly separated from nitrogeneous products. The hydrocarbon mixture was further separated using on-line gas chromatography as described above. Propylene was collected in a small spiral trap very close to the detector; other products were diverted to a second trap and discarded.

The following reaction system parameters were constant during the work: flow rate of N_2, 150 μmole sec^{-1}; linear flow rate, 230 cm sec^{-1}; flow rate of $N(^4S)$, 1.4 ± 0.2 μmole sec^{-1}; system pressure, 3 ± 1 torr; distance from discharge to substrate inlet, 20 cm; distance from reactant inlet to trap, 50 cm; duration of reaction, 1 hr unless otherwise indicated; molar ratio of propylene to $N(^4S)$, 1:6 or 1:12; propylene consumption, $92 \pm 2\%$ at 1:6 ratio of reactants; propylene consumption, $96 \pm 2\%$ at 1:12 ratio of reactants.

All samples were counted as CO_2 in a Bernstein–Ballentine proportional counter tube[13] filled with Matheson P-10 gas at 1-atm pressure with the aid of a Tracerlab P30 preamplifier and SC72 scaler. Counting rates of all samples were at least ten times background. When the over-all activity of recovered or original propylene was to be determined, about 50 μmoles of olefin was heated with a large excess of Matheson Research Grade oxygen in a copper oxide packed furnace at 450° for 30 min. Preliminary tests showed that after 20 min of this treatment propylene was no longer chromatographically detectable. Product CO_2 was trapped at $-196°$ in a calibrated U tube, after passage through a trap at $-78°$ to remove water. Measured aliquots were then condensed in the counter tube using liquid nitrogen.

To investigate intramolecular rearrangement of the recovered propylene it is necessary to degrade the olefin atom by atom. Removal of C-1 was achieved by permanganate oxidation. The procedure of Fries and Calvin[14] was modified so as to be compatible with the small samples (50–100 μmoles) and vacuum-line handling technique used in the present work. Oxidation for 3–4 hr was followed by gas chromatography on the previously described column. Oxidation was usually 50–70% complete; unreacted olefin was discarded, while CO_2 was trapped out, measured, and counted. Attempts were made to further degrade the product of permanganate oxidation, which was presumed to be acetic acid, by subjecting it to a Schmidt degradation. Despite extensive trials, and the availability of explicit experimental directions for performing the reaction using vacuum-line techniques,[15] it was not found possible to recover CO_2 with activity of the right magnitude. That this failure was related at least partially to the problems inherent in the small scale of the experiments was shown by employing known carboxyl-labeled (New England Nuclear) acetic acid in the Schmidt degradation on a scale four times that possible with the product of permanganate oxidation but still much smaller than that employed in reported[15] work. The specific activity of the resulting CO_2 fell short of the calculated level by an amount which was substantial but less than that observed on degradation of the product of permanganate oxidation of C-2-labeled propylene. The possibility that permanganate oxidation gives product(s) other than acetic acid and CO_2 was suggested by the observation that the residue remaining after removal of CO_2 produced by Schmidt degradation of the product of permanganate oxidation of C-2-labeled propylene was radioactive while the residue from Schmidt degradation of authentic acetic acid-1-^{14}C was not.

A sixfold excess of $N(^4S)$ was employed in most experiments. It was expected that recovered propylene would show larger isotopic changes the greater the excess of $N^4(S)$. For this reason some experiments employed a 12-fold excess of $N(^4S)$. Work at this high ratio is, however, more difficult. Because of the very high olefin consumption long (2 hr) reaction times were necessary. It was found that in continuous reactions of this length the rate of consumption of olefin diminished with time. To counter this, the reactions were divided into 30-min segments with 15-min intervals during which the olefin flow was stopped but the active nitrogen flow continued while the product trap was by-passed. Using this technique, consumption during the first and fourth half hours was constant to within 2%. Similar behavior has been observed with other substrates in this laboratory, but the phenomenon has not been investigated systematically.

Data. Observed changes in over-all activity and in activity at C-1 are presented in Table I. The molar activity of CO_2 produced by CuO oxidation of original propylenes achieved in preliminary work fell short of the expected value (one-third of the molar activity of the propylene) by $\sim$5%. The magnitude of this deficiency was not highly reproducible, and exact correction was not possible. A substantial part of the variance in the change in total molar activity (determined by counting CO_2 from original and recovered propylene) is probably due to this factor. In the column entitled "Relative activity at C-1" the values for original and recovered propylene are normalized to the activity of CO_2 obtained by CuO oxidation of original propylene. Were the propylene isomers radiochemically pure, the permanganate oxidation specific for C-1, and contamination by adventitious CO_2 negligible, the relative activity at C-1 of original propylene would be unity for the 1-^{14}C isomer and zero for the other isomers. The actual values obtained imply that one or more of these assumptions is not true. Contamination by adventitious CO_2 is only imperfectly compensated by normalization of the specific activity of CO_2 from permanganate oxidation to that obtained by combustion of original propylene over CuO. If contamination were generally heavier in the more complicated permanganate oxidation, values in columns 3 and 4 of Table I would generally err by being too small. In the absence of independent data on the radiochemical purity of the olefins, no firm conclusions can be drawn as to whether nonspecificity of oxidation or radiochemical impurity are important reasons for the nonideal activities of the original propylene isomers. The fact that the (negative) deviations from unit relative activity of CO_2 from 1-^{14}C-labeled original propylene substantially exceed the sums of the (positive) deviations from zero of the relative activities of CO_2 from 2-^{14}C and 3-^{14}C original propylenes could be due to nonspecificity of oxidation coupled with contamination of product CO_2 as discussed above. It might also be, at least in part, a consequence of radiochemical impurity of the propylene-1-^{14}C. The kinetic isotope effect may also be responsible for a minor part of the deviation from ideal behavior in the case of the 1-^{14}C compound since oxidations were incomplete (*cf.* Experimental Section). It must be emphasized, however, that the comparative procedure used in this work renders inconsequential uncertainties arising from lack of oxidative specificity, isotope effects, or minor contamination of product CO_2. Possible consequences of nonspecificity of ^{14}C labeling are discussed below.

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Table I. Changes in Activity of ^{14}C-Labeled Propylenes upon Reaction with Active Nitrogen

Expt[a]	Change in total molar activity, %	Relative activity at C-1[b]		Change in atomic activity at C-1, %
		Original C_3H_6	Recovered C_3H_6	
1-^{14}C; $(N)/(C_3H_6) = 6$				
A	...	0.83	0.66	−17
1	−6	...	...	...
2	−5	...	...	...
30	−13	0.81	0.66	−15
31	−8	0.71	0.57	−14
32	−17, −7, −9	...	...	...
33	−2	...	...	...
Mean[c]	−7.7 ± 1.3			−15.3 ± 1.8
1-^{14}C; $(N)/(C_3H_6) = 12$				
45	−9.5, −3	...	...	...
47	−5	0.76	0.64	−12
48	−8.5	0.76	0.56	−20
49	−9	0.74	0.40	−34
Mean[c]	−7.0 ± 1.3			−22 ± 6
2-^{14}C; $(N)/(C_3H_6) = 6$				
B	...	0.01	0.03	+2
C	...	0.01	0.07	+6
D	...	0.01	0.14	+13
8	+6	0.05	0.13	+8
9	+6	0.08	0.12	+4
11	+8	0.01	0.03	+2
12	...	0.04	0.17	+13
13	...	0.04	0.24	+20
14	+5	0.04	0.07	+3
15	+2	0.05	0.13	+8
16	+9	0.07	0.11	+4
17	...	0.07	0.09	+2
18	+5	0.07	0.12	+5
Mean[c]	+5.9 ± 0.85			+7.0 ± 3.0
2-^{14}C; $(N)/(C_3H_6) = 12$				
41	+9, +5	...	...	...
42	+7	0.10	0.20	+10
43	...	0.11	0.20	+9
44	+9.5	...	...	...
Mean[c]	+7.6 ± 1.0			+9.5 ± 0.8
3-^{14}C; $(N)/(C_3H_6) = 6$				
E	...	0.01	0.14	+13
4	+2	...	...	...
7	−6	...	...	...
8	−12	...	...	...
20	+2, −1	0.01	0.12	+11
21	...	0.01	0.12	+11
22	−3	0.01	0.10	+9
23	0	0.01	0.11	+10
24	−8	0.05	0.27	+22
25	−6, −1	...	...	...
26	−3, −13	0.01	0.13	+12
27	−6, −2	0.01	0.13	+12
Mean[c]	−3.8 ± 1.2			+12.5 ± 1.6
3-^{14}C; $(N)(/C_3H_6) = 12$				
36	−10	...	...	...
37	−6	...	...	...
38	−5.5	...	...	...
39	−5.5	...	...	...
40	−7.5	...	...	...
Mean[c]	−6.9 ± 0.85			

[a] Letters identify experiments by Y. T., numbers those by P. T. H. [b] Normalized to total molar activity of original propylene counted as CO_2. [c] Indicated uncertainties are standard deviations of the mean value.

It can be concluded from the data of Table I that the over-all activity of both the 1- and 3-^{14}C isomers decreases during reaction while the over-all activity of propylene-2-^{14}C increases. The activity at C-1 decreases during reaction for propylene-1-^{14}C but increases for the 2-^{14}C and 3-^{14}C isomers. It was anticipated that data obtained at $(N)/(C_3H_6)$ equal to 12 would show larger changes, both in total molar activity and in activity of C-1. This is generally borne out, although the percentage increases for different runs on the same isomer vary rather widely, and in the case of 1-^{14}C material there is apparently a smaller change in total activity at 12:1 than at 6:1. Because of the smaller number of experiments and experimental difficulties described in the Experimental Section, the data at 12:1 are appreciably less accurate. While the latter generally support results with $(N)/(C_3H_6) = 6$, subsequent discussion of the qualitative and quantitative significance of the results is in the main based on the data obtained at the lower ratio. A possible explanation of the surprisingly small variation in the changes in total molar activity is, however, offered below.

Discussion

Resynthesis and Rearrangement. It must be emphasized that Table I summarizes the isotopic composition of residual propylene, *i.e.*, approximately 8% of reactant propylene when a sixfold excess of N(^{4}S) was employed and 4% with a 12-fold excess. Examination of such small residues is necessary in order to minimize the fraction of recovered propylene which has not interacted in any way with active nitrogen. The changes in total molar activity summarized in Table I show that a significant fraction of the residual propylene isolated after reaction with excess N(^{4}S) has an isotopic composition different from that of reactant propylene. This change in isotopic composition can only arise from resynthesis of propylene molecules from "fragments"[16] as a consequence of attack by the reagent. It can be further concluded from these data that, on the average, more than one original C-2 atom and less than one original C-1 or C-3 is incorporated in a resynthesized molecule of propylene. Although these qualitative conclusions are fully supported by the data, quantitative aspects are less satisfactory. *A priori*, the algebraic sum of the changes in total activity must equal zero. This sum is approximately −6% at both ratios of reagents employed and about twice the sum of the standard deviations of the mean values for individual isotopic isomers under both sets of conditions. The discrepancy must be attributed, at least in part, to one or more systematic errors. Contamination of propylene-1-^{14}C by its isotopic isomers, which is suggested above, cannot account for the discrepancy. On the basis of the data of Table I, contamination by either propylene-2-^{14}C or propylene-3-^{14}C would cause the magnitude of the measured decrease in total activity of the 1-^{14}C compound to fall short of the true value. The use of pure propylene-1-^{14}C could, according to this analysis, only increase the magnitude of the discrepancy.

Because the data of this research provide no way of estimating the proportion of recovered propylene which has actually been resynthesized, the absolute selectivity of the resynthesis reaction cannot be determined. The fact that the changes in activity at the C-1 position and in total molar activity are essentially identical for propylene initially labeled at C-2 can, however, be explained most efficiently by a resynthesis process in which two carbon "fragments" which always contain one original C-2 atom are united with "fragments" containing one carbon atom, the latter always becoming C-1 of the resynthesized compound. Only that fraction of the resulting resynthesized molecules in which

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[16] It is not meant to imply that these "fragments" are necessarily free entities.

the one carbon "fragment" originated at C-2 would, in the case of propylene initially labeled at C-2, show (equal) increases in C-1 and total activity. On this basis, the data for C-2-labeled propylene correspond to production of approximately 20% resynthesized propylene [with a sixfold excess of $N(^4S)$] if the molecular origin of the one-carbon "fragment" is random or to a minimum of about 6.5% in the event that there is unique derivation of the one-carbon "fragment" from C-2. If the proportion of original C-1 and C-3 in the one-carbon "fragment" is greater than random, the fraction of recovered propylene which is resynthesized is greater than 20%. The formation of two-carbon "fragments" containing one original C-2 atom is supported by the composition of the major two-carbon *products* formed in the reaction,[3] ethylene, acetylene, and acetonitrile, each of which contains approximately one original C-2 atom per molecule.

The changes in C-1 activity for propylene initially labeled at C-1 or at C-3 can be examined in the light of the models outlined above. If C-1 of resynthesized propylene is specifically derived from C-2 of original propylene, then C-1 activity of recovered propylene from initially C-1-labeled propylene should change by about −7% while no change should be observed in the product from the C-3-labeled reactant. If C-1 of resynthesized propylene is randomly derived from all the carbon atoms of original propylene, then the corresponding changes should be approximately −14% for propylene initially labeled at C-1 and +7% for propylene initially labeled at C-3. The latter prediction corresponds more closely to the facts than the former. As both models predict, the magnitude of the change for C-1-labeled propylene appears to be greater than for the C-3-labeled substrate. The small observed difference would be smaller than the true value if the C-1-labeled substrate were contaminated by either C-2 or C-3 labels. Either model of the resynthesis process coupled with the additional assumption of some degree of intramolecular interconversion of C-1 and C-3 fits the data. Only the amount of interconversion which must be assumed varies with the model, being greater for the "specific" model than for the "random" one, and the data are not capable of distinguishing among such models.[17] Scrutiny of the consequences of other assumed origins for C-1 of resynthesized propylene, *e.g.*, 50% from original C-1 or C-3 and 50% from original C-2, leads to the same conclusion. In every case some intramolecular interconversion of C-1 and C-2 must be assumed. It must be noted that there is a fundamental difference between the evidence for resynthesis and that for rearrangement. Occurrence of resynthesis is securely founded on primary facts. The assumption of interconversion of C-1 and C-3 is introduced because resynthesis does not completely account for the observed changes in activity at C-1.

The significance of resynthesis and rearrangement relative to earlier conclusions[3] concerning the molecular origins of the products (other than propylene) of the reaction of propylene with active nitrogen will be discussed in the next paper of this series.[18]

Mechanistic Speculation Concerning Resynthesis and Rearrangement. The assumption that $N(^4S)$ is the only component of active nitrogen significantly involved in chemical transformations has been made in the interpretation of our earlier work[3,19–21] and is supported to some degree by evidence.[20,22] This assumption underlies most of the speculative interpretation of the present work although potential roles of other energetic species are discussed explicitly.

The occurrence of changes in total activity exclude the possibility that all "product propylene" is formed *via* an intermediate in which all carbon atoms are equivalent, *e.g.*, an excited cyclopropane molecule. Such a process could, however, be responsible for part of the observed rearrangement since it would lead to increases in atomic activity at C-1 for the substrates initially labeled at C-2 and C-3 which would be identical in magnitude and one-half the magnitude of the decrease for the C-1-labeled substrate, a result not greatly different from that observed. Alternatively, the rearrangement reaction may occur in part *via* abstraction of a hydrogen atom to form an alkyl radical (in which the terminal carbon atoms are equivalent) followed by readdition of hydrogen. On the basis of bond energies, $N(^4S)$ is a plausible reagent for the forward process since the reaction would be approximately 8 kcal/mole exothermic according to one set of estimates of bond energies[23,24] and approximately thermally neutral according to another.[23,25] Abstraction by hydrogen atom, which is approximately 18 kcal/mole more exothermic, is known to be rapid and apparently occurs at the allylic position of propylene.[26] The presence of substantial quantities of hydrogen atoms in mixtures of active nitrogen with ethylene has recently been demonstrated,[12] and it is likely that they are also formed in the reaction with propylene. They can presumably also add to allyl radical to complete the rearrangement. Some reagent capable of hydrogenating propylene is apparently present in mixtures of propylene and active nitrogen since propane is formed in about 10% yield with $(N)/(C_3H_6)$ equal to 6, and its total isotopic content differs little from that of reactant propylene.[3] The possibility that the reagent is hydrogen atom is supported by the observation[26] that addition of hydrogen atom to propylene is 2.5 times as fast as abstraction at both 25 and 205°.

Vibrational and/or electronic excitation of propylene *via* energy transfer from vibrationally or electronically excited N_2 or as a result of propylene serving as the third body in recombination of nitrogen atoms constitutes a potential basis for wholly intramolecular rearrangement. (Such excitation has been considered else-

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[17] Consideration of second generation resynthesis and rearrangement is not justified by the data although such processes probably occur.

[18] Y. Titani and N. N. Lichtin, to be submitted for publication.

[19] A. Tsukamoto and N. N. Lichtin, *J. Am. Chem. Soc.*, 84, 1601 (1962).

[20] A. Fujino, S. Lundsted, and N. N. Lichtin, *ibid.*, **88**, 775 (1966).

[21] T. Hanafusa and N. N. Lichtin, *Can. J. Chem.*, **44**, 1230 (1966).

[22] In as yet unpublished work performed in this laboratory, J. Goldberg has shown that NH_3 has no effect on the monomeric products of reaction of active nitrogen with 1,3-butadiene.

[23] The energy of the bond of N–H is quoted as approximately 85 kcal/mole. *Cf.* T. L. Cottrell, "The Strengths of Chemical Bonds," Academic Press Inc., New York, N. Y., 2nd ed, 1958, pp 270–294, for this and other relevant energy values.

[24] The dissociation energy of the CH_2CHCH_2–H bond has been reported to be 77 kcal/mole. *Cf.* A. H. Sehon and M. Szwarc, *Proc. Roy. Soc.* (London), **A202**, 263 (1950).

[25] J. W. Simons, B. S. Rabinovitch, and F. H. Dorer, *J. Phys. Chem.*, **70**, 1076 (1966), suggest 83 kcal/mole as the dissociation energy of the methyl C–H bond of propylene.

[26] B. de B. Darwent and R. Roberts, *Discussions Faraday Soc.*, **14**, 55 (1953).

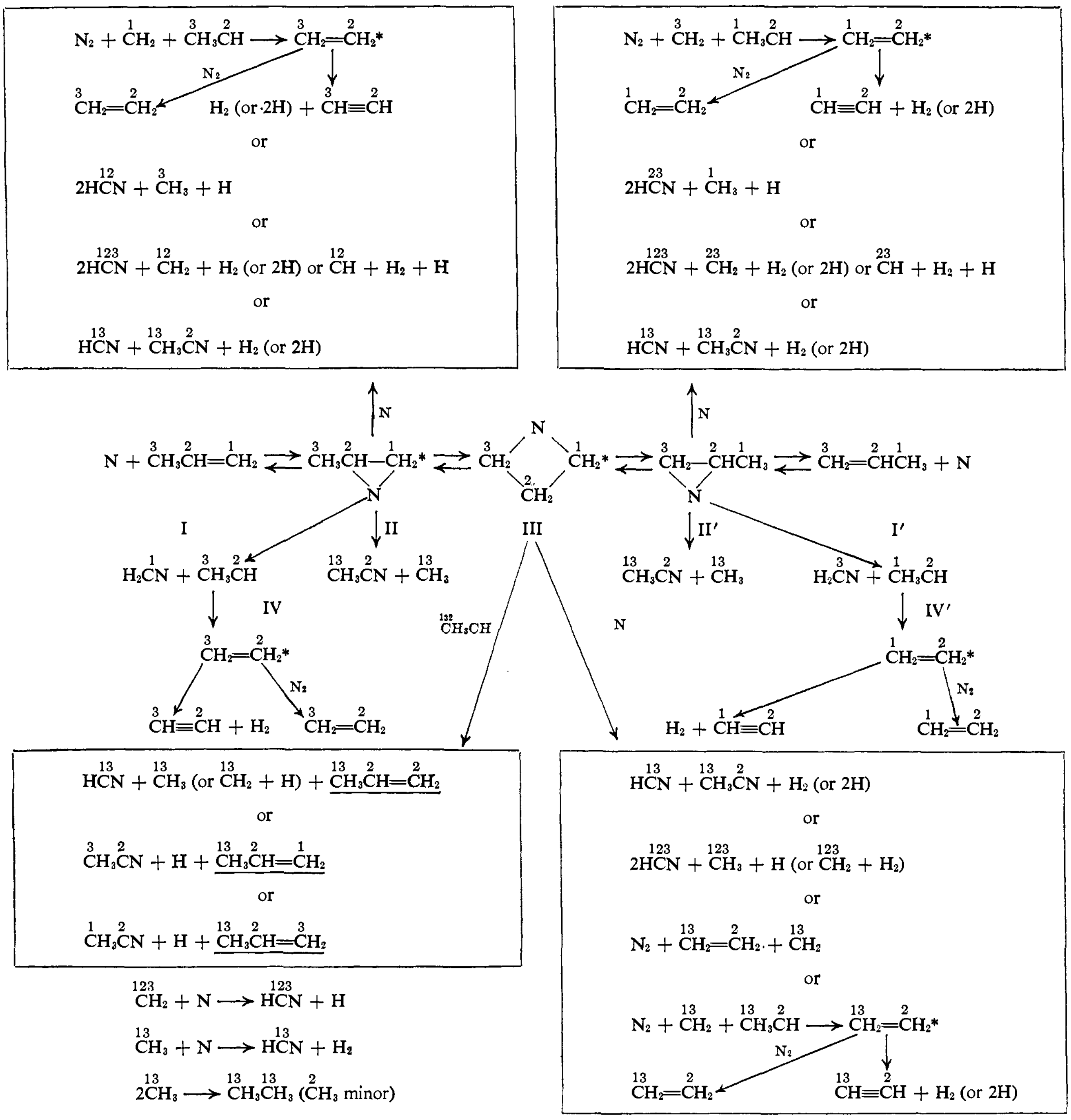


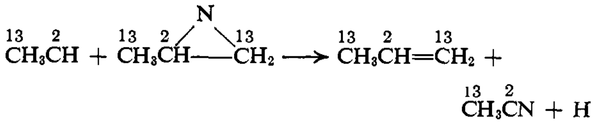
Figure 1. A possible partial mechanism of reaction of N(^{4}S) with propylene. Superscripts designate initial positions of carbon atoms.

where[20] relative to the reaction of 1,3-butadiene with active nitrogen, and the arguments marshalled there against its significance are partially relevant to the present case.) Alternatively, excitation of propylene might lead to its dissociation to allyl radical and hydrogen atom, as has been observed[25] for excited propylene formed by the addition of methylene to ethylene. The energy required for this reaction, approximately 80 kcal/mole,[24,25] is probably considerably greater than that required for intramolecular hydrogen transfer and its accumulation by transfer of vibrational energy from N_2 ($V = 1$)[20] accordingly less likely to be a significant process. Energy available from recombination of nitrogen atoms (225 kcal/mole) or from quenching of N_2 ($A^3\Sigma$) (142 kcal/mole) is more than sufficient, however, for either process.

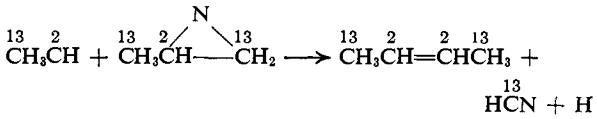
A fourth kind of mechanism for interconversion of C-1 and C-3 has been proposed in connection with evidence that these two atoms are equivalent in the precursor of HCN formed in the reaction of propylene with active nitrogen.[3] The proposed precursor is an unstable, four-membered ring adduct of propylene and N(^{4}S). Reversible formation of such an adduct would lead to the observed rearrangement. Elaboration of this model provides a speculative means of rationalizing resynthesis as well as rearrangement. The relevant reactions are outlined in Figure 1. This scheme, which was devised to correlate the facts reported in this paper, is, at the same time, consistent with much of our earlier data on product activities.[3] On the basis of standard bond energies, the reaction I → II should be 82 kcal/mole exothermic. Compound II would therefore be highly excited and its interconversion with III and its decomposition to N and propylene rapid processes. All other reactions shown in Figure 1 are probably exothermic,[23] at least in the versions where H_2 is formed rather than 2H, with the possible exception of II → IV which is energetically neutral in terms of standard bond energies.[23] (The coproduct of IV, H_2CN, would presumably disappear bimolecularly to give H_2 and HCN.) An alternative mechanism of formation of the essential intermediate, IV, is inherent in the proposed speculative scheme *via* the exothermic attack of N(^{4}S) on II, II′, or III to form N_2 and CH_2 along with $\overset{3}{C}H_3\overset{2}{C}H$ (where the superscripts designate the molecular origins of the carbon atoms), *i.e.*, IV of isotopic composition identical with that achieved by unimolecular decomposition of II and II′.

The abstraction of $\overset{123}{C}H_2$ from III by $\overset{13}{C}H_3\overset{2}{C}H$ meets the requirement imposed by the data that there be, on the average, more than one original C-2 per molecule of resynthesized propylene. It agrees with the fact that essentially all the excess ^{14}C in resynthesized propylene derived from the C-2-labeled reagent is in the CH_2 group of the product. The model corresponds to the simplifying assumption which was made above that all the C-2 in resynthesized propylene is derived from C-2 of reactant propylene. The assumption that CH_3CH has a sufficiently long lifetime to permit encounter with III is consistent with the reported trapping of methylcarbene by propylene[27] and cyclohexene.[28] On this basis *cis*- and *trans*-1,2-dimethylcyclopropane should be found among the products of reaction of active nitrogen with propylene when an appropriate ratio of reactants is employed, thereby providing a test of part of the scheme. Part of the methylcarbene would be expected[27] to rearrange to excited ethylene, some of which would be deactivated and some of which would dissociate to acetylene. The scheme predicts the isotopic compositions $H_2\overset{13}{C}{=}\overset{2}{C}H_2$ and $H\overset{13}{C}{\equiv}\overset{2}{C}H$, in essential agreement with the results of our earlier work on the isotopic composition of products.[3]

Equations 1 and 2 represent other potential reactions of IV and IV′. Reaction 1 provides propylene of composition consistent with the present data. Reaction 2



(1)



(2)

predicts the formation of 2-butene with a characteristic distribution of isotopic label. This as yet unobserved product provides another potential test of the reaction scheme.

The acetonitrile formed in the postulated scheme has the isotopic composition $\overset{13}{C}H_3\overset{2}{C}N$. This is in essential agreement with the results of our earlier work.[3] The predicted unique isotopic composition of the nitrile group is also subject to verification and can serve to test the reaction scheme. The scheme is consistent with the observed[3] very low original C-2 content of product ethane and its derivation from about equal amounts of initial C-1 and C-3 since, of the eight routes to CH_3, only one gives any $\overset{2}{C}H_3$ while the rest give equal amounts of $\overset{1}{C}H_3$ and $\overset{3}{C}H_3$. A number of the postulated reactions yield hydrogen atoms, as expected from Herron's study[12] of the reaction of ethylene with active nitrogen. These can serve to reduce propylene to propane of identical isotopic composition, as found in prior work.[3] Agreement of the postulated scheme with the observed isotopic composition of acetylene, ethylene, ethane, and acetonitrile extends to values of the ratio, $(C_3H_6)/(N)$, equal to or greater than unity since the predicted compositions are essentially the same whether they are formed with or without attack of N(^{4}S) on II, II′, or III, in agreement with experiment.[3,18] Finally, competition between N and CH_3CH for II, II′, and III provides a possible explanation of the failure to observe a substantial increase in the changes in total molar activity of recovered propylene when the ratio of reactants is increased from 6:1 to 12:1.

It is clear that the speculative mechanism summarized in Figure 1 is based on *ad hoc* reasoning. It is consistent with the available data and does not appear to be seriously at odds with relevant analogies. It has not, of course, been subjected to searching tests, such as, for instance, would be available if degradative studies had identified the fate of each carbon atom of reactant propylene. Such tests must await further work.

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[27] H. M. Frey, *J. Chem. Soc.*, 2293 (1961).

[28] V. Franzen, H. J. Schmidt, and Ch. Merz, *Ber.*, 94, 2942 (1961).