cipitate weighed 31 mg. and melted above 230°. The ether extract was distilled, the residue being heated at 100° at 5 mm. A small amount of oil was collected in the trap and a few crystals collected in the condenser. Further attempts to isolate pure products were unsuccessful but it is certain that no more than a trace of the bromonitrile survived the experiment.

Acknowledgment.—We are indebted to the National Science Foundation for the support of these studies. O. D. T. was also privileged to hold a Procter and Gamble Summer Fellowship.

AMES, IOWA

[A CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

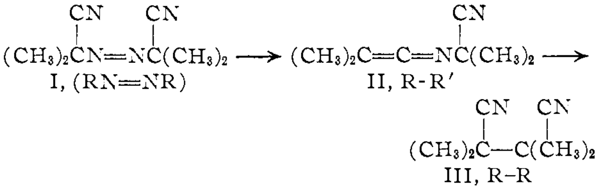
Isolation and Study of the Intermediate [Dimethyl-N-(2-cyano-2-propyl)-ketenimine] Formed in the Decomposition of α,α'-Azoisobutyronitrile

BY GEORGE S. HAMMOND,[1] ORLIN D. TRAPP, RICHARD T. KEYS AND DAVID L. NEFF

RECEIVED JANUARY 20, 1959

Dimethyl-N-(2-cyano-2-propyl)-ketenimine (R–R') has been isolated and characterized. The ketenimine reacts with halogens, water and butyl mercaptan. Decomposition of the compound, which produces tetramethylsuccinonitrile in the absence of free radical scavengers, follows first-order kinetics. Involvement of free radicals is demonstrated by the ability of the compound to initiate autoxidation of cumene and polymerization of styrene. The efficiency of R–R' as an initiator is less than that of α,α'-azoisobutyronitrile (ABN). The results are best accommodated by a free radical mechanism with a substantial cage effect.

Talât-Erben and Bywater[2] have shown that dimethyl-N-(2-cyano-2-propyl)-ketenimine (II) is an intermediate in the decomposition of α,α'-azoisobutyronitrile (ABN),[3] I. The ketenimine itself isomerizes forming tetramethylsuccinonitrile (III) which was previously known to be the principal end-product of ABN decomposition.[5–7] The ketenimine henceforth will be referred to as R–R' and the isomeric dinitrile will be called R–R.



$$(CH_3)_2\overset{\overset{CN}{|}}{C}N{=}N\overset{\overset{CN}{|}}{C}(CH_3)_2 \longrightarrow (CH_3)_2C{=}C{=}N\overset{\overset{CN}{|}}{C}(CH_3)_2 \longrightarrow (CH_3)_2\overset{\overset{CN}{|}}{C}{-}\overset{\overset{CN}{|}}{C}(CH_3)_2$$

I, (RN=NR) II, R-R' III, R-R

Since the decomposition of ABN is known to involve free radicals it was of interest to study the isomerization of R–R'. If the reaction also involves a free radical mechanism it would provide an excellent case for the study of cage effects.

Results and Discussion

Since R–R' is a liquid which is very soluble in petroleum solvents, in which ABN and R–R are sparingly soluble, we were able to develop a convenient preparative method for R–R'. ABN was decomposed by heating it in the presence of refluxing cyclohexane. After an appropriate time interval, the solids were removed by filtration and nearly pure R–R' was recovered by concentration of the filtration and nearly pure R–R' was recovered by concentration of the filtrate. The product was further purified by distillation *in vacuo*. The ketenimine reacts with water as previously reported[2] and reacts rapidly with iodine, bromine and concentrated solutions of butyl mercaptan. Direct titration with bromine in carbon tetrachloride was finally adopted as the best criterion of purity and was used as a basis for standardization of ultraviolet and infrared methods of analysis. The infrared band at 2020 cm.$^{-1}$ and the ultraviolet band having a maximum at 2900 Å. follow Beer's law except that the ultraviolet absorption is appreciably affected by oxygen.

Measurement of the rate of decomposition of R–R' was carried out using the infrared analysis. Runs were made at three temperatures, in several solvents, and in the presence of oxygen, both with and without anti-oxidants. The data give a good fit to the first-order law and are summarized in Table I. The rate of decomposition is increased substantially in the presence of oxygen.

Since the decomposition of R–R' initiates the autoxidation of cumene and the polymerization of styrene, it is virtually certain that decomposition of the ketenimine produces free radicals.

Acceleration by oxygen cannot be attributed to a direct reaction of oxygen with R–R' since the inclusion of a small amount of an antioxidant removes the effect completely. The most acceptable explanation of the results is found in the assumption that peroxy radicals are formed in the presence of oxygen and attack the ketenimine unless they are scavenged rapidly by an antioxidant. Study of the phenomenon is being continued. The scheme (1) to (9) probably represents the decomposition mechanism. Primary decomposition products which are still resident in the same solvent cage are represented by $\overline{2R\cdot}$.

$$R{-}R' \longrightarrow \overline{2R\cdot} \qquad (1)$$

$$\overline{2R\cdot} \longrightarrow R{-}R \qquad (2)$$

$$\overline{2R\cdot} \longrightarrow 2R\cdot \qquad (3)$$

$$2R\cdot \longrightarrow R{-}R \qquad (4)$$

$$2R\cdot \longrightarrow R{-}R' \qquad (5)$$

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[1] Division of Chemistry, California Institute of Technology, Pasadena, Calif.

[2] M. Talât-Erben and S. Bywater, THIS JOURNAL, **77**, 3244 (1955).

[3] We have previously referred to this compound as AIBN but suggest the adoption of ABN as a designation in conformity with the terminology of Mayo.[4]

[4] F. R. Mayo, THIS JOURNAL, **80**, 2465 (1958).

[5] J. Thiele and K. Heuser, *Ann.*, **290**, 1 (1896).

[6] A. F. Bickel and W. A. Waters, *Rec. trav. chim.*, **69**, 1490 (1950).

[7] G. S. Hammond, J. N. Sen and C. E. Boozer, THIS JOURNAL, **77**, 3244 (1955).

TABLE I

RATES OF DECOMPOSITION OF DIMETHYL-(N-2-CYANO-2-PROPYL)-KETENIMINE

Solvent	Series[a]	Temp., °C.	Conditions	$k \times 10^5$, sec.$^{-1}$
Carbon tetrachloride	B	62.5	Degassed	0.84
Carbon tetrachloride	A	62.5	Degassed	1.03
Carbon tetrachloride	A	80.9	Degassed	9.64
Carbon tetrachloride	B	62.5	Degassed, 4.05×10^{-4} DPPH[b]	1.00
Carbon tetrachloride	C	62.5	O_2, one atmosphere	2.54
Carbon tetrachloride	C	62.5	Air	2.01
Carbon tetrachloride	C	62.5	Nitrogen	1.02
2:1 carbon tetrachloride–cumene	B	62.5	Degassed	0.96
2:1 carbon tetrachloride–cumene	B	62.5	Degassed	.97
2:1 carbon tetrachloride–cumene	B	62.5	$O_2 + 0.0143$ *M* DTBC[c]	.92
2:1 carbon tetrachloride–cumene	B	62.5	$O_2 + 0.0233$ *M* DTBC[c]	1.01
2:1 carbon tetrachloride–cumene	B	62.5	$O_2 + 0.0112$ *M* DTBC[c]	0.93
Benzene	A	62.5	Degassed	1.71
Benzene	B	70.0	Degassed	3.92
Benzene	A	80.9	Degassed	16.3
2:1 benzene–cumene	B	70.0	Degassed	3.49
2:1 benzene–cumene	B	70.0	$O_2 + 0.0095$ *M* DTBC[c]	2.94
2:1 benzene–cumene	B	70.0	$O_2 + 0.0192$ *M* DTBC[c]	2.92
Styrene	B	70.0	Degassed	6.22
5.79 *M* styrene in benzene	B	70.0	Degassed	6.31
2.59 *M* styrene in benzene	B	70.0	Degassed	5.41

[a] Series A, B and C were carried out by different workers. Variations in rate constants in duplicate runs within a series were smaller than the differences between series. [b] α,α-Diphenyl-β-picrylhydrazyl. [c] 2,6-Di-*t*-butyl-*p*-cresol.

$$R\cdot + O_2 \longrightarrow RO_2\cdot \qquad (6)$$

$$RO_2\cdot + R\text{–}R' \longrightarrow \text{products} \qquad (7)$$

$$2RO_2\cdot \longrightarrow \text{termination products} \qquad (8)$$

$$RO_2\cdot + \text{antioxidant} \longrightarrow \text{termination products} \qquad (9)$$

Reaction 4 is, of course, inferred from the fact that R–R is the principal reaction product in inert solvents. Reactions 6, 8 and 9 have been studied previously in connection with the decomposition of ABN in the presence of oxygen.[8,9] The inference of reaction 7 from the kinetic data was described above. Production of radicals by reactions 1 and 3 is inferred from the fact that R–R′ initiates free radical chain reactions.

Since R–R′ decomposes at a rate very close to that of ABN, the efficiencies of radical production from two initiators may be compared in perfectly controlled experiments. Efficiencies were compared in both autoxidation, using the inhibitor lifetime method,[7] and polymerization, by comparison of polymerization rates. Table II shows the results obtained in the oxidation experiments and Table III shows those derived from polymerization rates. The oxidation runs were made in the presence of 2,6-di-*t*-butyl-*p*-cresol, an inhibitor having a known stoichiometric factor,[8] so the results yield absolute figures for efficiencies. The values for ABN efficiency (*a*) agree well with the average figure of 0.48 which was measured previously. The average value for the efficiency of R–R′ is 0.41, which is significantly lower than the ABN efficiency.

TABLE II

EFFICIENCIES OF INITIATION OF CUMENE OXIDATION IN 2:1 CARBON TETRACHLORIDE–CUMENE AT 62.5°

Run	Initiator	Initial moles initiator $\times 10^4$	Initial moles DTBC[a] $\times 10^5$	Induction period, min.	Efficiency, factor, *a*[b]
IV	ABN	6.19	1.35	66	0.469
VI	ABN	6.14	1.35	62	.514
VII	ABN	6.12	1.47	68	.511
V[c]	R–R′	6 48	1.35	133	.40
VIII	R–R′	3.38	1.47	200	.42

[a] 2,6-Di-*t*-butyl-*p*-cresol. [b] Calculated from the formula, $2[\text{DTBC}]_0 = 2a[\text{ABN}]_0(1 - e^{-k_1T_i})$; $k_{1(\text{ABN})} = 1.18 \times 10^{-5}$ sec.$^{-1}$, $k_{1(\text{R–R}')} = 0.97 \times 10^{-5}$ sec.$^{-1}$, T_i = induction period. [c] The temperature fell to 60° for 14 minutes during this run.

TABLE III

COMPARISON OF INITIATORS IN STYRENE POLYMERIZATION AT 70.0°

Initiator	$[\text{Initiator}]_0 \times 10^2$	$R_p \times 10^4$, moles l.$^{-1}$ sec.$^{-1}$	$\dfrac{R_p^2}{k_1[\text{In}]_0}$
ABN	1.000	2.12	0.098
R–R′	1.161	2.35	.077
R–R′	1.167	2.37	.078
R–R′	0.198	0.964	.076

Comparison of initiator efficiencies in styrene polymerization was carried out in bulk styrene in parallel experiments at 70°. Under these circumstances the ratio of the relative rates should be dependent only on the relative rates of initiation.

$$\frac{R^2_{p(\text{ABN})}}{R^2_{p(\text{R–R}')}} = \frac{k_{1(\text{ABN})}a[\text{ABN}]}{k_{1(\text{R–R}')}a'[\text{R–R}']}$$

That polymerization initiated by R–R′ follows the usual half-order dependence on initiator concentration[10] is demonstrated by the invariance of the quantity, $R^2_p/k_1a[\text{R–R}']$, with fivefold variation in the R–R′ concentration. The *a* factor for R–R′ is 0.79 times that of ABN.

The demonstration that two initiators which decompose to give the same radicals have measurably different efficiencies shows unambiguously

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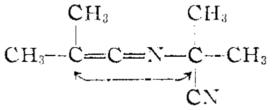
(8) C. E. Boozer, G. S. Hammond, C. E. Hamilton and J. N. Sen, THIS JOURNAL, **77**, 3235 (1955).

(9) C. E. Boozer, G. S. Hammond, C. E. Hamilton and C. Peterson, *ibid.*, **77**, 3380 (1955).

(10) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953.

that, *at least the difference in the efficiencies must be due to complexities in the decomposition mechanism.* It has been pointed out[7,11] that the inefficiency of ABN could be attributed to a non-radical decomposition rather than to recombination of primary products before they escape the solvent cage. The same type of explanation could be evoked to account for the behavior of R–R′ but is chemically unpalatable. The ketenimine group must be linear so it is hard to conceive of a concerted process (such as is indicated in IV) which will bring together the two carbon atoms which must form the new bond in R–R. Other mechanisms, in which the migrating cyanopropyl group slides along the unsaturated system without any unpairing of electron spins, might be considered and called concerted. We do not see any basis for distinguishing between such mechanisms and mechanisms involving dissociation to give radicals with uncorrelated electron spins. Ionic mechanisms are untenable because of the relative insensitivity of the decomposition rate to solvent effects.



$$CH_3{-}\overset{\overset{\textstyle CH_3}{|}}{C}{=}C{=}N{-}\underset{\underset{\textstyle CN}{|}}{\overset{\overset{\textstyle CH_3}{|}}{C}}{-}CH_3$$

IV

The fact that cage effects are more important in the decomposition of R–R′ than in the same reaction of ABN may be due to a number of factors. The nitrogen molecule which is released in the decomposition of ABN may exert either a physical or chemical control over the process or the radicals from ABN may have a higher recoil energy than those from R–R′. Study of the relative amounts of R–R′ and R–R formed in the cage during ABN decomposition also provides evidence for the deviant behavior of the fragments[12,13] from ABN.

Reaction 5, the regeneration of R–R′ from free radicals, *must be of very little consequence in the decomposition of the ketenimine.* Otherwise the net rate of disappearance of R–R′ should be increased in the presence of effective scavengers for cyanopropyl radicals. Comparison of runs taken from series B show that the addition of diphenylpicrylhydrazyl or oxygen and an antioxidant does not increase the rate by more than 10%. There is actually no consistent indication that there is any increase.

If the mechanism outlined is complete, all of the inefficient decomposition of R–R′ should lead to the production of R–R. The dinitrile has been isolated in considerable amounts from reaction mixtures produced in the presence of oxygen. Further experiments of this type are in progress.

Regeneration of ketenimine by recombination of radicals in the cage cannot be detected unless decomposition is carried out in the presence of sufficiently high concentrations of reactive scavengers to permit the scavenging of caged radical pairs. Most highly reactive scavengers, such as bromine, react rapidly with R–R′ when they are present in high concentration. It is possible that the high rate of decomposition of R–R′ in styrene may be due to scavenging from the cage. The rate is 78% higher in styrene than in benzene whereas the rate of decomposition of ABN is increased by only 10%.[14] It has been recognized for some time that the propagation reaction of vinyl polymerization is not sufficiently fast to compete with diffusion controlled processes[15] so scavenging by the monomer would have to occur by way of reversible formation of a loose complex. The mechanism is shown in eqs. 10 and 11.

$$\overline{2R\cdot} + C_8H_8 \longrightarrow R\cdot + C_8H_8 \rightarrow R\cdot \qquad (10)$$

$$C_8H_8 \rightarrow R\cdot \rightleftharpoons C_8H_8 + R\cdot \qquad (11)$$

Cyanopropyl radicals must be electron acceptors and should form complexes with electron-rich aromatic compounds. Such complexes recently have been suggested to account for the capture of peroxy radicals by antioxidants[11] and the deactivation of chlorine atoms in aromatic solvents.[16] Consideration of reversible complex formation with monomer as a factor in determining initiator efficiencies permits resurrection of the explanation suggested by Matheson[17] for the anomalous increases, with increasing monomer concentration, in the rates of peroxide-initiated polymerization of styrene.

Experimental

Preparation of Dimethyl-N-(2-cyano-2-propyl) ketenimine (R–R′).—In a typical preparation 3 liters of Phillips petroleum pure grade cyclohexane was placed in a 5-liter, three-neck, round-bottom flask fitted with a stirrer, reflux condenser (protected by a tube of Drierite), and a nitrogen bubbler. The liquid was purged with nitrogen (purified with hot copper turnings) for one hour. The liquid was then brought to the reflux temperature and 200 g. of ABN was added quickly. The mixture was heated under reflux for 145 minutes. The flask then was stoppered and cooled rapidly in an ice–salt-bath. The liquid was removed by decanting 700-ml. portions. The combined solution was concentrated by reduced pressure. The residue of 25 g. (15% yield) was nearly pure R–R′. Successive distillation with a Claisen head at 10^{-3} mm. and 35° pot temperature gave a water-white liquid, m.p. of various samples of 12.7–13.0° to 15.1–16.7°, $n^{25}\text{D}$ 1.4470 to 1.4473; mol. wt., calcd. for $C_8H_{12}N_2$ 136.2, found 136 ± 4 (cryoscopic in benzene); *Anal.* Calcd.: C, 70.55; H, 8.88; N, 20.57. Found: C, 70.63; H, 8.94; N, 20.69.

Determination of Residue on Hydration of R–R′.—The most probable contaminants in the ketenimine are ABN and the isomeric R–R. The hydration of R–R′ to water-soluble amides[18,19] is accomplished readily whereas ABN and R–R are insoluble in and inert toward dilute aqueous acid. Samples of R–R′ preparations were weighed in tared centrifuge tubes and treated with 10 ml. of distilled water and 2.5 ml. of 1*N* hydrochloric acid. The tube was closed and shaken vigorously for 24 hours. The residual precipitate was filtered, washed with distilled water and dried in the presence of Drierite. The residue was dried for several days and was weighed and considered as the impurity in the original ketenimine sample. In controls it was found that 11 mg. of ABN and 18 mg. of R–R were dissolved under the conditions. Therefore, the complete dissolution of a 500-mg. sample ensures that it contains no more than 2% ABN and 4% R–R. This procedure proved to be useful in the early stages of the work for following the progress of attempted purification.

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(11) J. C. Roy, J. R. Nash, R. R. Williams and W. H. Hamill, This Journal, **78**, 519 (1956).

(12) P. Smith and A. M. Rosenberg, *ibid.*, **81**, 2037 (1959).

(13) O. D. Trapp and R. T. Keys, unpublished observations.

(14) R. T. Keys, unpublished observations.

(15) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 76.

(16) G. A. Russell, This Journal, **79**, 2977 (1957).

(17) M. S. Matheson, *J. Chem. Phys.*, **13**, 554 (1945).

(18) H. Staudinger and E. Hauser, *Helv. Chim. Acta*, **4**, 887 (1921).

(19) M. Talât-Erben and A. N. Isfendiyaroglu, *Can. J. Chem.*, **36**, 1156 (1958).

Reactions of R–R′ with Halogens.—Weighed samples were dissolved in carbon tetrachloride to give concentrations of the order of $0.01M$ and 10-ml. aliquots were withdrawn and placed in a 250-ml. erlenmeyer flask. Small pieces of Dry Ice and a calculated excess of $0.1N$ iodine in carbon tetrachloride were added. A volume of acetic acid equal to that of the assay sample and two volumes of distilled water were added. The residual iodine was titrated with standard, $0.05N$ thiosulfate. As the end-point was approached a large excess of water and starch indicator were added. Assuming a 1:1 stoichiometric relationship, redistilled ketenimine assayed 103 ± 6% pure by the procedure. Bromine titrations were carried out as follows: 0.1-g. samples of R–R′ were weighed into 50-ml. erlenmeyer flasks and titrated with a standard, $0.03M$ solution of bromine in carbon tetrachloride. Titrant was added until the bromine color persisted. Bromine solution then was added dropwise to a blank until the color matched that in the assay mixture in order to determine the correction for excess titrant added. The correction amounted to about 0.5%. The excess bromine was also estimated spectrophotometrically by reading the absorption of the assay mixture at 4000 Å. The results of the two procedures for estimation of the overstepping of the end-point agreed very closely. Samples which were assayed by this procedure then were used to calibrate infrared and ultraviolet measurements. The product of the reaction has not been isolated, but the changes in the infrared spectrum indicate that simple addition occurs. The band at 2020 cm.$^{-1}$ disappears completely and a new band, attributed to the C=N stretch, appears at 1680 cm.$^{-1}$. Much of the work reported in this manuscript was carried out before the bromine titrations were developed. After the method was adopted as a standard, a large number of assorted samples were examined. The precision of ultraviolet analyses at 2900 Å. was ±3% and infrared measurements scatter by ±5%. However, the infrared errors originate almost exclusively in the instrumentation whereas precision in the ultraviolet analysis depends upon the absence of impurities.

Infrared Analysis.—Measurements were made with both Perkin–Elmer model 13 and model 112 instruments with lithium fluoride optics. Using a slit width of 0.500 mm., and the "cell in–cell out" method, measurements of absorbencies were made at 2020 cm.$^{-1}$ with a densitometer. The best values for molar extinction coefficients are shown in Table IV.

TABLE IV

INFRARED AND ULTRAVIOLET ABSORPTION MAXIMA OF R–R′

Solvent	Ultraviolet molar absorption coefficient	Infrared molar extinction coefficient at 2020 cm.$^{-1}$ Perkin–Elmer model 13	Perkin–Elmer model 112
Carbon tetrachloride	191[a]	553	604
Cyclohexane	149.5[b]	514	645

[a] Measured at 2850 Å. [b] Measured at 2900 Å.

Ultraviolet Spectra.—Ultraviolet extinction coefficients measured with Beckman DU and Cary model 12 instruments were in exact agreement. Best values are listed in Table IV. In cyclohexane the spectrum of R–R′ is symmetrical about a maximum at 2900 Å. In carbon tetrachloride the curve is unsymmetrical with a nearly horizontal point of inflection at 2850 Å. The spectrum was unchanged when measured in carbon tetrachloride which had been subjected to careful purification with concentrated sulfuric acid and with mercury. We believe, therefore, that the spectral shift is due to interaction between R–R′ and the solvent itself.

In the presence of air, R–R′ rapidly becomes yellow. Infrared analyses show that the coloration does not indicate extensive decomposition but the ultraviolet absorption in the vicinity of 2900 A. is changed significantly. The effect is readily detected if the spectrum in cyclohexane is scanned since the symmetry of the peak at 2900 Å. is destroyed with an increase of absorption on the short wave length side of the maximum.

Decomposition Rates.—Samples of R–R′ in various solvents were heated in individual tubes which had been degassed and sealed *in vacuo*. At intervals the tubes were opened and aliquots were removed and placed in the infrared cells. Absorbance at 2,020 cm.$^{-1}$ was read and the concentration of R–R′ was calculated using equations (based on Beer's law) appropriate for the particular cells and instrument alignment. Calibrations were repeated frequently. While the absolute values of concentration were unknown during much of the work, samples used ranged in purity from 85–95%. Scatter of points within kinetic runs varied but was such as to indicate probable errors in the rate constants of 15% or less. Runs, not reported in detail, showed that the rate constants were independent of initial concentrations over a fivefold range.

Inhibition periods in cumene oxidation were measured by the technique described previously.[8]

Decomposition of R–R′ in the Presence of Oxygen.—In a typical run 2.716 g. of R–R′ (estimated purity 89% with total ABN and R–R′ less than 5%) was dissolved in 1550 g. of carbon tetrachloride and stirred under one atmosphere of oxygen at 62.5°. Samples were removed periodically and analyzed for residual ketenimine by the infrared method. The solution was heated for a period of eight half-lives, based on the rate of decomposition in the absence of oxygen. A 780-g. fraction was freed of solvent through a two foot Oldershaw column at a reflux ratio of 17:1. After the volume of the pot residue was reduced to 35 ml. the residue was transferred to a 100-ml. beaker and the flask was washed out with two portions (5 ml. each) of acetone. The volume then was reduced to about 5 ml. by evaporation under an air jet. The residue now was poured onto a short column of activated alumina and the beaker was washed out with 4 ml. of acetone. The column was eluted with a total of 900 ml. of petroleum ether (Skellysolve A). The first fraction was yellow and cloudy. Some of the yellow material settled out on standing overnight and then was separated from the solution by decantation. The entire eluate was reduced to 35 ml. by distillation through a 3 ft., vacuum jacketed column containing randomly packed glass helices. Residual solvent was removed from the pot residue by evaporation. The residual solid weighed 0.997 g. A 0.121-g. sample from this residue was subjected to sublimation at room temperature at 0.2 mm. After four hours, 0.0426 g. of crystals was collected on the cold finger which was cooled with liquid nitrogen. While the infrared spectra of such samples matched that of R–R closely, the material melted over the range 118–135°. Despite the impurity of the product this was believed to be a minimum recovery since some losses occurred during evaporation and the sublimation was probably incomplete. The yield is equivalent to 20% of the original charge of ketenimine or 22% if correction is made for the estimated impurity of the sample. Up to 5% R–R could have been introduced in the sample. Since the rate constant for R–R disappearance in this experiment was 2.61×10^{-5} sec.$^{-1}$, about 40% of the decomposition occurred by way of spontaneous decomposition. Assuming that no R–R is produced by the induced reaction in the presence of oxygen, the results indicate a minimum value of 35–50% yield of R–R by recombination in the solvent cage. Other runs gave 12, 14 and 16% recovery of R–R based upon the weight of R–R′ used. In each case attempts were made to analyze the products by other procedures and unknown losses occurred. The results are considered to establish the existence of reaction 2 but are insufficient to measure its extent.

The Rate of Polymerization of Styrene by RR′.—Styrene obtained from Eastman Kodak Co. was washed four times with 5% sodium hydroxide solution, two times with water, and dried over calcium chloride. It then was distilled under nitrogen at 65.1° and 50.5 mm. ABN was recrystallized once from methanol, once from ether and the solvent was pumped off under vacuum, m.p. 103.5–104.5° (uncor.). RR′ was prepared as described above. Initiator (ABN or RR′) was weighed into 50-ml. volumetric flasks and the dilutions with monomer were made in air.

The polymerization rates were measured dilatometrically using essentially the same dilatometer design as that employed by Bartlett and Kwart.[20] Over half the length of the capillaries was calibrated absolutely by filling the dilatometer volume cells with mercury and measuring the increase in height of mercury in the capillary for small increments of temperature change over a range of 60°.[20] All lengths were measured with a cathetometer to ±0.005 cm. The ratio

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[20] P. D. Bartlett and H. Kwart, THIS JOURNAL, **72**, 1051 (1950).

of the area of capillary to total volume was 8.24–10.52 × 10^{-4} cm.$^{-1}$ for the dilatometers used in the study. Samples were degassed before each run using high vacuum technique.

Reaction of R–R′ with Butyl Mercaptan.—The reaction was observed in the course of attempts to use the mercaptan as a scavenger for radicals produced in the decomposition of R–R′. Solutions initially containing about 0.016*M* R–R′ and about 0.9*M* mercaptan in benzene and carbon tetrachloride showed only 2–6% residual R–R′ by infrared analysis after heating for one hour at 80°. In similar experiments in which the initial concentration of mercaptan was 0.04*M* the apparent first-order rate constant for disappearance of R–R′ was increased by factors of 2–3. Insufficient data were gathered to permit quantitative documentation of the rate law involved or to resolve the "true" unimolecular contribution to the rates. The reaction products were not isolated.

Acknowledgment.—This work was supported by a grant from the National Science Foundation. Infrared spectroscopic service was provided by the Iowa State Institute for Atomic Research. We are especially indebted to Messrs. E. Miller Layton and Richard Knisely for programming infrared analyses.

AMES, IOWA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

Preparation of α-Nitroketones. C-Acylation of Primary Nitroparaffins[1]

BY G. BRYANT BACHMAN AND TAKEO HOKAMA[2]

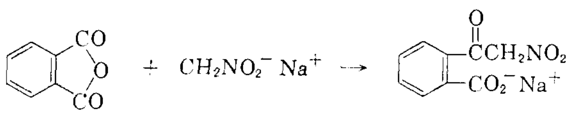
RECEIVED DECEMBER 27, 1958

C-Acylation of primary nitroparaffin salts to form α-nitroketones has been accomplished with the aid of acyl cyanides in 30–70% yields. No α-nitroketones were obtained from salts of secondary nitroparaffins. The mechanisms of acylations by acyl cyanides and by acid halides are discussed.

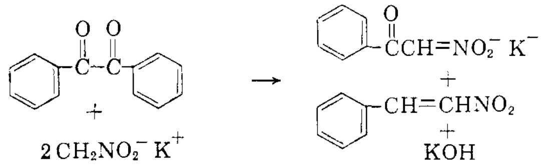
The nitroparaffins have attracted considerable theoretical interest since their initial discovery because of the ambivalency of their corresponding anions which permits substitution reactions to occur either at the oxygen of the nitro group or at the carbon attached to the nitro group. Numerous workers have investigated the acylation of nitroparaffins using acid halides,[3] acid anhydrides,[4] ketene,[3e,5] acylpyridinium chlorides[6] and acid esters[7] under a variety of conditions.

In all but one case, initial O-acylation was observed to occur exclusively with subsequent rearrangement of the nitronic anhydrides formed to acylated hydroxamic acids from primary nitroparaffins. A logical sequence of reactions for these paraffins and to nitroso acyloxy compounds from secondary nitro rearrangements has recently been proposed.[8]

The only case of C-acylation by an acid derivative was that reported by Gabriel[4a] in 1903 when he obtained poor and inconsistent yields of 2-(nitroacetyl)-benzoic acid from the reaction of phthalic anhydride with sodium methanenitronate in ether. Another exceptional case in which an α-nitroketone was obtained from a carbonyl compound (not an acid derivative) was reported by Jakubowitsch.[9] He obtained nitroacetophenone from the reaction of benzil with nitromethane in the presence of two molar equivalents of alcoholic potassium hydroxide.



(1)



(2)

We have found that C-acylation of primary nitroparaffins can be accomplished with acyl cyanides[10] under basic conditions. α-Nitroketones are obtained in 30–70% yields. No C-acylated product was obtained from secondary nitroparaffins although numerous attempts to do so were made under a variety of conditions. The results of these investigations are summarized in Tables I and II.

Discussion of Results

Good yields of α-nitroketones are highly dependent on various factors but especially on suitable solubilities of the reactants and on the suppression of side reactions which consume the acylating agent faster than the desired reaction. As a better understanding of these factors was gained through systematic evaluations of them, it became possible to formulate a mechanism for the reaction and to explain the suitability of acyl cyanides as acylating agents for nitroparaffins.

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(1) Taken from a thesis submitted by T. Hokama to the faculty of the Graduate School of Purdue University in partial fulfillment of the requirements for the Ph.D. degree, August, 1958.

(2) American Cyanamid Fellow, 1957–1958.

(3) (a) J. Kissel, *Ber.*, **15**, 727 (1882); (b) L. W. Jones, *Am. Chem. J.*, **20**, 1 (1897); (c) A. F. Holleman, *Rec. trav. chim., France*, **15**, 356 (1896); (d) A. van Raalte, *ibid.*, **18**, 378 (1899); (e) D. A. Isacescu and C. D. Nenitzescu, *Bull. soc. chim. Romania*, **14**, 53 (1953); (f) H. Wieland and Z. Kitasato, *Ber.*, **62**, 1252 (1929); (g) H. Wieland and A. Hochtlen, *Ann.*, **505**, 237 (1933); (h) J. T. Thurston and R. L. Shriner, *J. Org. Chem.*, **2**, 183, 560 (1937); (i) W. Wislicenus and K. Pfeilsticker, *Ann.*, **436**, 40 (1924).

(4) (a) S. Gabriel, *Ber.*, **36**, 570 (1903); (b) M. G. Foster, *J. Chem. Soc.*, **77**, 251 (1900); (c) T. Urbanski, *ibid.*, 3374 (1949); (d) E. P. Stefl and M. F. Dull, THIS JOURNAL, **69**, 3037 (1947).

(5) T. Urbanski and W. Gurzynska, *Roczniki Chem.*, **25**, 183 (1951); *C. A.*, **46**, 7994 (1952).

(6) R. H. Terss and W. E. McEwen, THIS JOURNAL, **76**, 580 (1954).

(7) R. Lin, M.S. Thesis, Purdue University, 1956.

(8) E. H. White and W. J. Considine, THIS JOURNAL, **80**, 626 (1958).

(9) A. J. Jakubowitsch, *J. prakt. Chem.*, **142**, 37 (1935).

(10) The use of acyl cyanides as acylating agents for other types of active methylene compounds was first reported by A. Dornow and H. Grabhöfer, *Chem. Ber.*, **91**, 1824 (1958).