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Addition of Hydrogen Cyanide to Unsaturated Compounds

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The addition of hydrogen cyanide to unactivated carbon–carbon double bonds has been accomplished by the use of dicobalt octacarbonyl at 130° in sealed vessels. Best results were obtained with compounds of the type $RCH{=}CH_2$, where R is hydrogen, phenyl or an alkyl group, with conjugated dienes, and with Diels–Alder adducts of cyclopentadiene.

The addition of hydrogen cyanide to carbon–carbon double bonds has been accomplished in the liquid phase in the presence of an alkaline catalyst only with compounds in which the double bond is sufficiently activated by negative groups.[1] In the vapor phase, nitriles have been obtained from branched chain olefins, such as isobutylene and trimethylethylene, by reaction with hydrogen cyanide over alumina,[2] and from propylene over cobalt cyanide-on-alumina or cobalt-on-alumina.[3] Furthermore, hydrogen cyanide has been added to conjugated dienes in both liquid and vapor phase in the presence of cuprous salts[4,5] or nickel carbonyl,[6] and polymeric products containing nitrogen have been obtained from butadiene with Friedel–Crafts type catalysts.[7]

The present communication reports a new method for the preparation of nitriles by addition of hydrogen cyanide to unsaturated compounds in the presence of dicobalt octacarbonyl.[8] Best results were obtained with the following classes of compounds: (1) compounds containing terminal double bonds of the type $RCH{=}CH_2$, where R is hydrogen, phenyl or an alkyl group, (2) conjugated dienes, and (3) Diels–Alder adducts of cyclopentadiene. Secondary nitriles were formed as products from the olefins indicating "normal" addition of hydrogen cyanide to the double bonds.

For compounds in the first class, the addition of hydrogen cyanide became more difficult as the length of R increased. For example, under similar conditions, ethylene, propylene and 1-butene gave at least 65% conversions to nitriles, whereas 1-octene gave only 13% conversion. Styrene gave over 50% conversion to 2-phenylpropionitrile. 2-Butene, a compound having an internal double bond, gave only 9% conversion to 2-methylbutyronitrile. The following unsaturated compounds containing negative groups considerably removed from the double bond were hydrocyanated in fair yields: 5-hexenenitrile, 3-pentenenitrile and methyl 5-hexenoate. 4-Vinylcyclohexene underwent normal addition to the vinyl group as shown by hydrogenation and hydrolysis of the product to 2-cyclohexylpropionic acid, identical to a sample prepared by hydrogenation and hydrolysis of 2-phenylpropionitrile.

The second class of compounds included the open-chain dienes, butadiene and isoprene. The major products formed by these compounds with hydrogen cyanide resulted from 1,4-addition. However, butadiene gave minor amounts of both the "normal" and "reverse" 1,2-adducts, as well as dinitriles resulting from the addition of two moles of hydrogen cyanide. The amount of "reverse" 1,2-adduct (4-pentenenitrile) formed, as determined by infrared analysis, was about the same as the amount of "normal" 1,2-adduct (2-methyl-3-butenenitrile) isolated. In the case of the simple olefins the amount of "reverse" addition was negligible in comparison to the amount of "normal" addition. From butadiene the following mixture of nitriles was obtained in 60% conversion (80% yield) in the relative amounts indicated: 2-methyl-3-butenenitrile (8%), 3-pentenenitrile (60%), 4-pentenenitrile (7%), 2,3-dimethylsuccinonitrile (5%) and 2-methylglutaronitrile (20%). Isoprene gave about 40% conversion to a mixture of the two possible 1,4-adducts, 3-methyl-3-pentenenitrile (33%) and 4-methyl-3-pentenenitrile (67%).

The Diels–Alder adducts of cyclopentadiene with itself (dicyclopentadiene), with acrylonitrile, and with maleic anhydride all added hydrogen cyanide using dicobalt octacarbonyl at 130° in sealed vessels. Mixtures of geometric and/or position isomers were obtained.

In general, the reaction was run under autogenous pressure at 130° using 5 mole per cent. of dicobalt octacarbonyl based on the hydrogen cyanide used. With ethylene and propylene it was found that increased pressure improved the conversion of hydrogen cyanide to propionitrile and isobutyronitrile, respectively, but the reaction became violent if not carefully controlled. Hydrocyanation was effected at temperatures from 70–160°, but best conversions were usually obtained around 130°. In most cases, solvents were not used. However, with polymerizable unsaturated compounds such as styrene and butadiene, it was advantageous to use benzene as an inert solvent along with a polymerization inhibitor such as hydroquinone or picric acid. Ethanol and diethyl ether were found to retard hydrocyanation.

Dicobalt octacarbonyl was not recovered from the hydrocyanation reactions. It reacted with hydrogen cyanide to form blue solids. Some of these blue solids, prepared separately by reaction of hy-

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(2) C. R. Harris and W. W. DeAtley, U. S. Patent 2,455,995, December 14, 1948.

(3) T. G. O'Neill and F. W. Kirkbride, British Patent 687,014, February 4, 1953.

(4) W. A. Schulze and J. A. Mahan, U. S. Patent 2,422,859, June 24, 1947; U. S. Patent 2,447,600, August 24, 1948; U. S. Patent 2,464,723, March 15, 1949.

(5) D. D. Coffman, L. F. Salisbury and S. L. Scott, U. S. Patent 2,509,859, May 30, 1950.

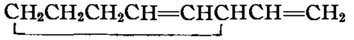
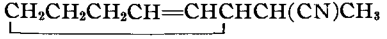
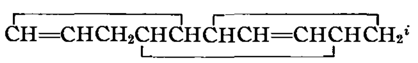
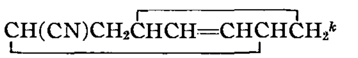
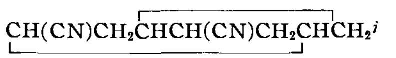
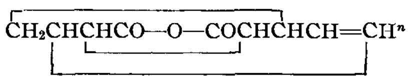
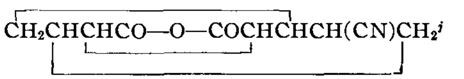
(6) P. Arthur and B. C. Pratt, U. S. Patent 2,571,099, October 16, 1951.

(7) D. D. Coffman and L. F. Salisbury, U. S. Patent 2,402,873, June 25, 1946.

(8) P. Arthur, Jr., and B. C. Pratt, U. S. Patents 2,666,748 and 2,666,780, January 19, 1954.

TABLE I

HYDROCYANATION OF UNSATURATED COMPOUNDS[a]

Run	Formula	g.	Time, hr.	Pressure, atm.	Product Formula	Product g.	Conversion, %[b]	B.p. °C.	B.p. Mm.	n^{25}D
1	$CH_2{=}CH_2$	Excess[c]	7	200	CH_3CH_2CN	35	63.6	96.8[d] [1]		1.3682
2	$CH_2{=}CHCH_3$	150	15	110	$CH_3CH(CN)CH_3$	45	65	100–107[d] [2]		1.3756
3	$CH_2{=}CHCH_3$	150[e]	14.5	100[f]	$CH_3CH(CN)CH_3$	52	75			
4	$CH_2{=}CHCH_2CH_3$	56[g]	8	40	$CH_3CH(CN)CH_2CH_3$	29	67.5	126–127[d] [3]		1.3882
5	$CH_3CH{=}CHCH_3$	56[g]	8	32	$CH_3CH(CN)CH_2CH_3$	4	9.3			
6	$CH_3CH{=}CHCH_3$	56[e,g]	8	39	$CH_3CH(CN)CH_2CH_3$	17.8	43			
7	$CH_2{=}CH(CH_2)_5CH_3$	56	8	46	$CH_3CH(CN)(CH_2)_5CH_3$	3.7	5.3	208		1.4181
8	$CH_2{=}CH(CH_2)_5CH_3$	56[e]	8	43	$CH_3CH(CN)(CH_2)_5CH_3$	16.5	23.7			
9	$CH_2{=}CH(CH_2)_3CN$	19	8	...	$CH_3CH(CN)(CH_2)_3CN$	8.7	35.6	125	2	1.4348
10	$CH_2{=}CH(CH_2)_3COOCH_3$	22	8	28	$CH_3CH(CN)(CH_2)_3COOCH_3$	4.9	18.6	148	40	
11	$CH_2CH{=}CHCH_2CN$	40.5	14.5	..	$CH_3CH(CN)CH_2CH_2CN$	3.9	7.2	115	7	1.4340
12	$CH_3CH{=}CHCH_2CN$	40.5[e]	8	..	$CH_3CH(CN)CH_2CH_2CN$	8.3	15.4			
13	 $CH_2CH_2CH_2CH{=}CHCHCH{=}CH_2$	54	19.5	47	 $CH_2CH_2CH_2CH{=}CHCHCH(CN)CH_3$	9.5	14	134	58	1.4707
14	$C_6H_5CH{=}CH_2$	104[h]	8	25	$C_6H_5CH(CN)CH_3$	68.5	52	101	10	1.5098
15	 $CH{=}CHCH_2CHCHCHCH{=}CHCHCH_2$[i]	60[e]	15.5	44	 $CH{=}CHCH_2CHCHCHCH_2CH(CN)CHCH_2$[j]	17.4	24	136	14	1.5169
16	 $CH(CN)CH_2CHCH{=}CHCHCH_2$[k]	167[l]	8	..	 $CH(CN)CH_2CHCH(CN)CH_2CHCH_2$[j]	126	62[m]	159	2	
17	 $CH_2CHCHCO{-}O{-}COCHCHCH{=}CH$[n]	164[p]	8	..	 $CH_2CHCHCO{-}O{-}COCHCHCH(CN)CH_2$[j]	44	28	210–235	4	

[a] Each run was carried out at 130° with 17 g. of dicobalt octacarbonyl and 27 g. of hydrogen cyanide unless specified otherwise. [b] Based on limiting reactant. [c] Ethylene pressured into reactor, see text. [d] V. Migrdichian, "The Chemistry of Organic Cyanogen Compounds," Reinhold Publ. Corp., N. Y., 1947, pp. 19–20.[1] Propionitrile, b.p. 97.08°,[2] isobutyronitrile, b.p. 107–108° and *n*-butyronitrile, b.p. 117.4°,[3] isovaleronitrile, b.p. 129.3–129.5° at 764.3 mm. and *n*-valeronitrile, b.p. 140.4° at 739.3 mm. [e] 8.5 g. of triphenylphosphine added. [f] At 70° the reaction flashed to 183° and 300 atm. This may be due to acceleration of the reaction by triphenylphosphine since otherwise the reaction was run in the same manner as run 2. [g] 14 g. of hydrogen cyanide used. [h] 2 g. of hydroquinone added. [i] Dicyclopentadiene. [j] Position of the nitrile group is unknown and may be on adjacent carbon. [k] Cyclopentadiene–acrylonitrile adduct. [l] 51 g. of dicobalt octacarbonyl, 54 g. of hydrogen cyanide and 25 g. of triphenylphosphine used. [m] 70% yield allowing for recovered unsaturate. [n] Cyclopentadiene–maleic anhydride adduct. [p] 68 g. of dicobalt octacarbonyl, 54 g. of hydrogen cyanide, 20 g. of triphenylphosphine and 200 ml. of benzene used.

drogen cyanide with dicobalt octacarbonyl, brought about conversion of olefins and hydrogen cyanide to nitriles. The mercury salt of cobalt carbonyl hydride was just as effective as dicobalt octacarbonyl for hydrocyanation. Improved yields of nitriles were obtained in some reactions by adding triphenylphosphine. They are recorded in Table I.

Experimental

Hydrogen Cyanide.—This material was purchased in cylinders from the American Cyanamid Co. It was reported to contain as stabilizers against explosive polymerization, small amounts of phosphoric acid, sulfuric acid and sulfur dioxide, in addition to 2.5% water. Superior results were obtained by purifying this material by distillation from phosphorus pentoxide before use. Unstabilized hydrogen cyanide was frozen in Pyrex brand bottles at Dry Ice temperature for storage.

Dicobalt Octacarbonyl.—This compound was prepared[9] in high conversion from pelleted, reduced cobalt oxide at 170° and 700–1000 atm. carbon monoxide pressure without a solvent. A stationary tube equipped with a special brass sieve and liner was used. The reduced oxide was contained in the sieve, suspended at the top of the tube. As the molten carbonyl formed, it dripped into the removable liner of the tube. After cooling and venting, the solid carbonyl was chipped out and immediately stored under nitrogen at Dry Ice temperature, where it could be kept indefinitely.

Reaction Method.—Reactions were conducted in stainless steel or silver-lined agitated vessels of about 400-ml. capacity. After they had been flushed with dry nitrogen and cooled in a Dry Ice–acetone-bath, the solid and liquid reactants were added under nitrogen. If a gaseous reactant was to be added, the sealed vessel usually was evacuated and the gas condensed as a liquid into the cooled vessel. Reactions generally were run at 130° for 7–15 hours, although many were probably complete within 1 hr. At the end of the reaction period the vessels were cooled, the pressure released slowly and the product rinsed out with benzene or ether. The inorganic solid was filtered off and the filtrate distilled to isolate the products. Details of the runs made are summarized in Table I and below.

Hydrocyanations. Ethylene.—At 30-atm. pressure, ethylene and hydrogen cyanide gave about 10% conversion to propionitrile. Increased ethylene pressure gave higher conversions to propionitrile, but caution was necessary to prevent violent reactions which blew out the rupture disc of the tube. The result given in Table I, run 1, was obtained by running at 70° for 1 hr., raising the temperature 10° per hour until 100° was reached, and continuing the reaction at this temperature for 7 hr.

Propylene.—As in the case of ethylene, the reaction temperature was approached slowly to prevent "flash" reactions. The use of the reaction product of hydrogen cyanide with dicobalt octacarbonyl to catalyze the hydrogenation of propylene is illustrated below. Dicobalt octacarbonyl (17 g.) reacted with hydrogen cyanide (27 g.) in benzene (100 ml.) at 130° under autogenous pressure. The resulting blue solid was kept moist with benzene and used as catalyst for the reaction of propylene (150 g.) with hydrogen cyanide (27 g.). Isobutyronitrile (29 g., 42% conversion of hydrogen cyanide) was obtained.

When an equimolar amount (27 g.) of the mercury salt of cobalt carbonyl hydride was used in place of dicobalt octacarbonyl with 1.7 moles of hydrogen cyanide, there was obtained 79 g. (63% conversion) of isobutyronitrile.

1-Butene.—Solvent and temperature variables for hydrocyanation of 1-butene were examined briefly, and the results served as a basis for choosing conditions for other hydrocyanations. The effect of temperature on conversion of hydrogen cyanide to isovaleronitrile is shown by the following series of runs made under conditions otherwise the same: at 70°, 12% conversion; 100°, 52%; 130°, 67%; and 160°, 40%. The highest temperature gave more higher-boiling residue. Conversions at the lowest temperature could be increased by increasing the time of reaction (28% in 15 hr. compared to 12% in 8 hr.). The presence of ether or ethanol decreased conversion to isovaleronitrile; benzene was an inert solvent.

1-Octene.—Hydrogen cyanide was treated with 1-octene (runs 7 and 8) to give 2-methylcapronitrile, b.p. 209° (lit.[10] 85.4° at 10 mm.), identified by conversion to 2-methylcaproamide, m.p. 78–80° (lit.[10] 80.8°).

5-Hexenenitrile (run 9) reacted with hydrogen cyanide to give a dinitrile presumably 2-methyladiponitrile.

Anal. Calcd. for $C_7H_{10}N_2$: N, 22.9. Found: N, 22.7.

Methyl 5-hexenoate (run 10) added hydrogen cyanide in 18% conversion (44% yield allowing for recovered starting material) to give a mononitrile believed to be methyl 5-cyanocaproate.

Anal. Calcd. for $C_8H_{13}O_2N$: C, 61.9; H, 8.4; N, 9.0. Found: C, 61.8; H, 8.7; N, 8.8.

4-Vinylcyclohexene (run 13).—The hydrocyanation product was hydrogenated over 10% palladium-on-charcoal in methanol at room temperature. Filtration and removal of solvent gave a crude product which was hydrolyzed to an acid, m.p. 55–57°, which was not depressed on admixture with a sample of 2-cyclohexylpropionic acid,[11] m.p. 61–62°. This established the structure of the hydrogen cyanide adduct as 2-(3-cyclohexenyl)-propionitrile, assuming no migration of the double bond in the ring.

Anal. Calcd. for $C_9H_{13}N$: C, 80.0; H, 9.7; N, 10.4. Found: C, 79.5; H, 9.9; N, 10.4.

Styrene (Run 14).—The hydrocyanation product was identified as 2-phenylpropionitrile by hydrolysis with potassium hydroxide in diethylene glycol solution to 2-phenylpropionic acid, b.p. 177° (44 mm.), which was converted to its anilide, m.p. 134–135° (lit.[12] 133–134°) and amide, m.p. 93–94° (lit.[13] 91–92°).

Butadiene (162 g.), hydrogen cyanide (108 g.), dicobalt octacarbonyl (51 g.) and benzene (300 ml.) were heated at 130° for 14.5 hr. There were obtained on distillation 97 g. (40%) of a mononitrile fraction, 30 g. (18.5%) of a dinitrile fraction and 17.5 g. of residue. Composite crude samples of mono- and dinitriles were fractionally distilled to obtain the following products (approximate average percentage conversions based on butadiene charged are given in parentheses): impure vinylcyclohexene (5%), b.p. 100–126°; 2-methyl-3-butenenitrile (5%), b.p. 126–129°, $n^{25}\text{D}$ 1.4095, identified by hydrogenation over palladium-on-charcoal in methanol followed by hydrolysis to 2-methylbutyric acid, anilide m.p. 105–7° (lit.[14] 110–111°); 3-pentenenitrile (36%) and 4-pentenenitrile (4%), b.p. 138–143°, $n^{25}\text{D}$ 1.4170–1.4242, relative amounts estimated by infrared analysis, identified by hydrogenation and hydrolysis to valeric acid, anilide m.p. 62–63° (lit.[15] 63°); 2,3-dimethylsuccinonitrile (3%), b.p. 73–84° (5 mm.), $n^{25}\text{D}$ 1.4570, characterized by hydrolysis to 2,3-dimethylsuccinic acid, m.p. 193–195° dec. (lit.[16] 196° dec.); 2-methylglutaronitrile (12%), b.p. 114–115° (7 mm.), $n^{25}\text{D}$ 1.4338, hydrolyzed to 2-methylglutaric acid, m.p. 76–77° (lit.[17] 76°), and polymer (10%). By hydrocyanation of 2-methyl-3-butenenitrile in a separate run it was possible to isolate in low yield a more nearly pure sample of 2,3-dimethylsuccinonitrile, b.p. 167° (100 mm.), m.p. 51–52°.

Anal. Calcd. for $C_6H_8N_2$: N, 25.9. Found: N, 25.5.

Isoprene (68 g.), hydrogen cyanide (27 g.), dicobalt octacarbonyl (17 g.) and 100 ml. of benzene heated to 130° for 18.5 hr. gave 48 g. (50%) of product, b.p. 135–165°, and 13.2 g. of residue. The conversion was 40% when run for only 8 hr. under the same conditions, and only 26% when the benzene was omitted. Fractional distillation of a composite sample of the product indicated the presence of two fractions: about 1 part of I, b.p. 160°, $n^{25}\text{D}$ 1.4460, and 2 parts of II, b.p. 165°, $n^{25}\text{D}$ 1.4430.

Fraction I was shown to be a mixture of about two parts of a hydrocarbon, presumably dipentene, and one part of a mononitrile which on hydrogenation and hydrolysis gave 3-methylvaleric acid, identified by conversion to its amide,

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(9) Unpublished results of Dr. W. W. Prichard of this Laboratory.

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m.p. 122–123°, and anilide, m.p. 80–82° (lit.[18] 125 and 88°, respectively). The latter did not depress the melting point of the anilide prepared from an authentic sample of the acid.[19]

3-Methylvaleric acid could only be derived from 3-methyl-3-pentenenitrile (a 1,4-adduct) or 3-methyl-4-pentenenitrile (a reverse 1,2-adduct). The infrared bands at 10.0 and 10.8 μ characteristic of the unsaturation in 4-pentenenitrile were not present in the infrared spectrum of fraction I; therefore, the unsaturated nitrile present was 3-methyl-3-pentenenitrile, resulting from a 1,4-addition of hydrogen cyanide to isoprene. Fraction II was shown by analysis to be a monoadduct.

Anal. Calcd. for C_6H_9N: C, 75.7; H, 9.5; N, 14.7. Found: Fraction II, 3, 75.5; H, 9.5; N, 14.3.

Hydrogenation and hydrolysis gave 4-methylvaleric acid, amide m.p. 118–119° (lit.[20] 119°), anilide m.p. 108–109° (lit.[21] 111°). The latter did not depress the melting point of the anilide prepared from an authentic sample of the acid.[22] This acid could only be derived from 4-methyl-3-pentenenitrile (a 1,4-adduct) or 4-methyl-4-pentanenitrile (a reverse 1,2-adduct). The nitrile showed no infrared adsorption at 3.25, 10.1, 10.4 or 11.3 μ, characteristic of terminal unsaturation. Hence, it must be 4-methyl-3-pentenenitrile, resulting from 1,4-addition of hydrogen cyanide to isoprene. The two products, 3-methyl-3-pentenenitrile and 4-methyl-3-pentenenitrile, were obtained in the ratio of about 1:3.

Dicyclopentadiene (run 15) reacted with hydrogen cyanide to give a mononitrile, but the location of the nitrile group was not established.

Anal. Calcd. for $C_{11}H_{13}N$; N, 8.8. Found: N, 8.5.

Bicyclo[2.2.1]-5-heptene-2-carbonitrile, prepared by the Diels–Alder addition of cyclopentadiene to acrylonitrile,[23] reacted with hydrogen cyanide (run 16) to give a semi-solid product at room temperature which was probably a mixture of geometric and/or position isomers. Filtration at room temperature gave an oil and a white solid.

Anal. Calcd. for $C_9H_{10}N_2$: C, 74.0; H, 6.9; N, 19.2; mol. wt., 146. Found: (solid) C, 74.4; H, 6.9; N, 18.7; mol. wt., 125, 130. Found: (oil) C, 74.3; H, 6.7; N, 18.2; mol. wt., 151, 145.

The dinitriles were hydrogenated over a cobalt catalyst in ammonia at 125–130° and 250 atm. to obtain a diamine in 90% yield, b.p. 100–101° (1 mm.), n^{25}D 1.5082, neut. equiv. 77.5 (calcd. for $C_9H_{14}(NH_2)_2$: neut. equiv., 77.1).

Bicyclo[2.2.1]-5-heptene-2,3-dicarboxylic anhydride, prepared by Diels–Alder addition of cyclopentadiene to maleic anhydride,[24] reacted with hydrogen cyanide (run 17). Recrystallization of the product from toluene–xylene mixture gave 31 g. of white crystals, m.p. 155–167°, probably a mixture of isomers.

Anal. Calcd. for $C_{10}H_9O_3N$: C, 62.8; H, 4.7; N, 7.3. Found: C, 63.2; H, 5.0; N, 7.8.

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WILMINGTON, DELAWARE

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON]

The Photolysis of Diazomethyl *t*-Butyl Ketone

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The photolysis of diazomethyl *t*-butyl ketone has been investigated, and the structures of the products obtained have been determined. The major product was found to be α,γ-di-*t*-butyl-$\Delta^{\beta\gamma}$-butenolide, and the principal by-product was 2,2,6,6-tetramethyl-4-heptenone-3. The results of the photolysis of diazoacetone and diazoacetophenone suggest that the formation of the butenolide is not a general synthetic method.

The photolysis of diazoketones with ultraviolet light has been investigated in order to determine whether this might be a convenient alternate method for effecting the Wolff rearrangement.[1] The advantages of such a method would be that steric hindrance should not affect this reaction and that diazoketones derived from optically active secondary acids might not be racemized under these conditions.[2] The ketene which is presumed to be an intermediate[3] in the Wolff rearrangement might also be isolated. The results obtained by the irradiation of the pure liquid diazoketones are reported herein, whereas the results obtained in various solvents will be described in a later communication.

The first diazoketone investigated was diazomethyl *t*-butyl ketone (I). Irradiation of I with ultraviolet light led to nitrogen evolution with an accompanying decrease in the characteristic 4.81 μ band of the diazoketone.[4] The material obtained was distilled giving two compounds. The first (II) was a liquid with an empirical formula $C_{11}H_{20}O$ and the second was a colorless low-melting solid III having the formula $C_{12}H_{20}O_2$ and was obtained in 62% of the theoretical amount.

The solid III was found to react with potassium permanganate and with bromine, but it did not react with carbonyl reagents. The product of the reaction with bromine was found to have been formed by the addition of two atoms of bromine. The reduction of III with hydrogen and palladium-on-barium sulfate gave a saturated compound V with the absorption of one mole of hydrogen. The ultraviolet spectrum (λ_{max} 224 mμ, ϵ_{max} 2,450) indicated the absence of conjugate unsaturation, as is suggested also by the infrared spectrum. The 5.55 μ band in the infrared is suggestive of a strained ring carbonyl.

Treatment of III with base gave an isomer IV which had a conjugated double bond as indicated by the spectra (λ_{max} 212 mμ, ϵ_{max} 11,300; I.R. car-

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[1] The Wolff rearrangement has been effected by treatment with ultraviolet light in the case of a few aromatic diazoketones (*cf.* L. Horner, E. Spietschka and A. Gross, *Ann.*, **573**, 17 (1951)).

[2] J. F. Lane, J. Willenz, A. Weissberger and E. S. Wallis, *J. Org. Chem.*, **5**, 276 (1940), reported that the rearrangement of diazomethyl 1-phenyl-2-propyl ketone gave largely racemization. This was attributed to enolization on the catalyst surface (J. F. Lane and E. S. Wallis, *ibid.*, **6**, 443 (1941)).

[3] L. Wolff, *Ann.*, **394**, 23 (1912); F. Arndt and B. Eistert, *Ber.*, **68**, 200 (1935).

[4] A. K. Bose and P. Yates, THIS JOURNAL, **74**, 4703 (1952) reported that diazoketones have a characteristic N=N band at 4.83 μ and that the carbonyl band is shifted to about 6.2 μ. The infra-red spectra of six diazoketones taken in this Laboratory showed a strong diazo band at 4.80–4.82 μ and a strong carbonyl band at 6.1–6.2 μ.