directly compared our oxidant with previous preparations, except in the case of the nitrogen compounds mentioned above, it remains for interested investigators to determine its suitability for various specific purposes.

Experimental Section

A.—A solution of 20 g of potassium permanganate in 250 ml of water contained in a 600-ml beaker was heated to the boiling point, removed from the source of heat, and treated portionwise over 5–7 min with 6.25 g of activated carbon.[7] The frothing was allowed to subside between additions. After complete addition of the carbon the mixture was boiled for 2–4 min until the purple color was completely discharged, allowed to stand at room temperature for 10–15 min and filtered on a Büchner funnel. The precipitate was washed four times with 50-ml portions of water and spread out to dry in the air. The air-dried material amounted to 22.2 g. After drying in an oven at 105–110° for 8–24 hr, the weight dropped to 18.7 g. After either air- or oven-drying, the oxidant was obtained as a fine powder which could be used directly without grinding.

B.—A solution of 20 g of potassium permanganate in 250 ml of water was stirred at room temperature with 10 g of activated carbon for 16 hr. Filtration and drying as in A gave 26.5 g of the air-dried or 22.2 g of the oven-dried oxidant.

Registry No.—Manganese dioxide, 1313-13-9; carbon 7440-44-0.

(7) Since it was on the shelf at the time this work was initiated, we have generally used activated carbon supplied by the J. T. Baker Co., Phillipsburg, N. J. Unfortunately this material, which proved to be the most active of all the carbon samples tested, was subsequently removed from the market. Some commercial samples of activated carbon were completely unreactive toward permanganate under the conditions studied. Of the various carbons tested to date, Nuchar C-190N appeared to give the best results, nearly comparable to those obtained with the J. T. Baker material. In general the "fluffy" carbons are effective whereas the dense ones are not. Effective, although yielding an oxidant less active than that obtained from J. T. Baker or Nuchar C-190N (possibly an advantage in the oxidation of some nitrogen compounds), were the following: Darco G-60 and Mallinckrodt USP. Ineffective were Fisher C-263 and Norit-neutral.
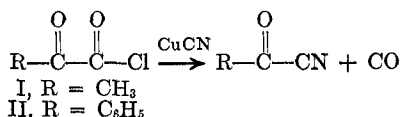

On the Thermal and Free-Radical Reactions of Pyruvyl Chloride and Benzoylformyl Chloride

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During the attempted synthesis of pyruvyl cyanide and benzoyl formyl cyanide from the reaction of the corresponding acyl chlorides (I and II) with cuprous cyanide, a reaction purported to be successful with other acid halides,[2a-c] it was found that only acetyl cyanide or benzoyl cyanide could be obtained. Since both benzoyl
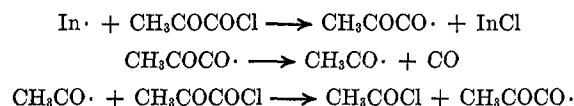
$$\underset{\substack{\text{I, R = CH}_3 \\ \text{II, R = C}_6\text{H}_5}}{R-\overset{\overset{\text{O}}{\|}}{C}-\overset{\overset{\text{O}}{\|}}{C}-Cl} \xrightarrow{\text{CuCN}} R-\overset{\overset{\text{O}}{\|}}{C}-CN + CO$$

* Author to whom correspondence should be addressed.
(1) Postdoctoral Fellow, University of Alberta, 1968–1969.
(2) (a) T. S. Oakwood and C. A. Weisgerber, "Organic Syntheses," Coll. Vol. III, Wiley, New York, N. Y., 1955, p 112; (b) H. Sutter, *Justus Liebigs Ann. Chem.*, **499**, 47 (1932); (c) L. Claisen, *Ber.*, **31**, 1023 (1898).

chloride and acetyl chloride will form acyl cyanides under these conditions,[2] the fragmentation of the corresponding keto acyl chlorides to form their acid chlorides was investigated.

Carbon tetrachloride solutions (0.2 M) of I were shown to undergo a free-radical chain fragmentation to yield acetyl chloride. The fragmentation could be initiated thermally (140°), or, under conditions where the keto acid chloride was stable, I could be converted to its acid chloride by photolysis (40°), by trace initiation with benzoyl peroxide (5%, 98°), or with AIBN (3%, 40°).

On the basis of its initiation by light and by benzoyl peroxide or AIBN the fragmentation reaction can be postulated as a chain sequence[3] (Scheme I).

Scheme I

In· + CH₃COCOCl ⟶ CH₃COCO· + InCl

$$\text{In·} + \text{CH}_3\text{COCOCl} \longrightarrow \text{CH}_3\text{COCO·} + \text{InCl}$$

$$\text{CH}_3\text{COCO·} \longrightarrow \text{CH}_3\text{CO·} + \text{CO}$$

$$\text{CH}_3\text{CO·} + \text{CH}_3\text{COCOCl} \longrightarrow \text{CH}_3\text{COCl} + \text{CH}_3\text{COCO·}$$

In cyclohexane the reaction took a somewhat different course; not only was acetyl chloride produced but also a series of radical displacement reactions on I yielded as products cyclohexanecarboxylic acid chloride, cyclohexyl methyl ketone, and cyclohexyl chloride (see Table I). In addition to the products listed

Table I

Products from the Initiated Reaction of Pyruvyl Chloride (0.2 M) in Cyclohexane

Initiator	Temp, °C	CH₃-COCl	C₆H₁₁-COCH₃	C₆H₁₁-COCl	C₆H₁₁Cl
Benzoyl peroxide (5%)	98	50.3	10.0	39.5	3.0
Light	40	54.3	10.2	35.5	5.0
AIBN (8%)	40	75	3	17	Trace

in Table I, a significant quantity of gaseous material was produced during the reaction. These products could be fractionated by standard vacuum line procedures. Analysis of the gaseous products obtained from the photoinduced reaction of a solution of pyruvyl chloride (1.00 mmol) in cyclohexane (see Table I) showed hydrogen chloride (0.10 mmol), methane (0.41 mmol), and carbon monoxide (1.00 mmol). A combination of the yields of both the gaseous and nongaseous products constituted, within experimental limits, a quantitative material balance for the initial pyruvyl chloride.

On the basis of the products, the excellent material balance obtained, and the trace initiation observed, and by analogy to the reactions in cyclohexane of this system with those of oxalyl chloride[4] and biacetyl,[5] the following chain propagating steps are proposed to rationalize the observed reactions (see Scheme II). The inclusion in the mechanism of the propagation steps contained in Scheme I with those of Scheme II constitutes a plausible explanation for the initiated reactions of pyruvyl chloride in cyclohexane.

The competitive attack of the cyclohexyl radical on the carbonyl adjacent to the electron-donating methyl

(3) The possible inclusion of a chain transfer sequence with solvent has been suggested by the referee to account for the smooth conversion of I to acetyl chloride.
(4) M. S. Kharasch and H. C. Brown, *J. Amer. Chem. Soc.*, **64**, 329 (1942).
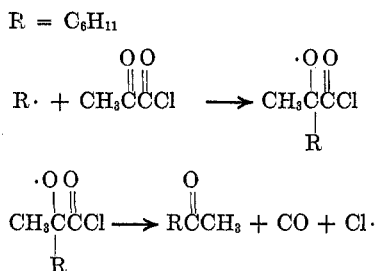(5) W. G. Bentrude and K. R. Darnall, *ibid.*, **90**, 3588 (1968).

Scheme II

Step a

R = C_6H_{11}

$$R\cdot + CH_3\overset{\overset{O}{\|}}{C}\overset{\overset{O}{\|}}{C}Cl \longrightarrow CH_3\overset{\overset{\cdot O}{\|}}{C}\overset{\overset{O}{\|}}{\underset{R}{C}}Cl$$

$$CH_3\overset{\overset{\cdot O}{|}}{\underset{R}{C}}\overset{\overset{O}{\|}}{C}Cl \longrightarrow R\overset{\overset{O}{\|}}{C}CH_3 + CO + Cl\cdot$$

Step b

$$R\cdot + CH_3\overset{\overset{O}{\|}}{C}\overset{\overset{O}{\|}}{C}Cl \longrightarrow CH_3\overset{\overset{O}{\|}}{C}\overset{\overset{O\cdot}{\|}}{\underset{R}{C}}Cl$$

$$CH_3\overset{\overset{O}{\|}}{C}\overset{\overset{O\cdot}{\|}}{\underset{R}{C}}Cl \longrightarrow R\overset{\overset{O}{\|}}{C}Cl + CH_3\overset{\overset{O}{\|}}{C}\cdot$$

Step c
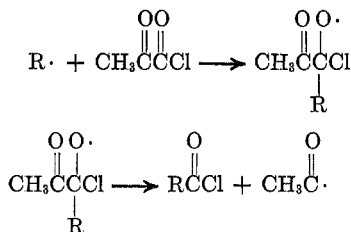
$$R\cdot + CH_3\overset{\overset{O}{\|}}{C}\overset{\overset{O}{\|}}{C}Cl \longrightarrow RCl + CH_3\overset{\overset{O}{\|}}{C}\overset{\overset{O}{\|}}{C}\cdot$$
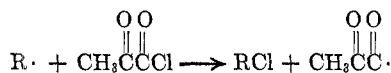
group or upon the one adjacent to the electron-withdrawing chlorine, is reflected, if one assumes that the addition of the cyclohexyl radical to either carbonyl is irreversible, in the ratio of carbonyl substituted cyclohexanes found. The preference for the addition of the alkyl radical to the electron deficient carbonyl is evident from the 1:3.8 ratio of cyclohexyl methyl ketone–cyclohexyl carboxylic acid chloride, the products obtained from the β-scisson of the corresponding radicals.[6]

Solutions of benzoylformyl chloride (0.2 *M*) in chlorobenzene at 120° were quantitatively converted to benzoyl chloride and carbon monoxide. This reaction could not be inhibited with iodine (5%), 1,3,5-trinitrobenzene (5%), or with molecular oxygen. Under conditions where the keto acid chloride (II) was found to be stable, 80°, in oxygen-free solutions of carbon tetrachloride or chlorobenzene, neither photolysis nor small amounts of benzoyl peroxide (5%) or AIBN (5%) initiated the fragmentation. In degassed solutions of cyclohexane, benzoylformyl chloride (0.2 *M*) could be initiated with 20% benzoyl peroxide to give low yields of cyclohexyl chloride (10%), cyclohexylcarbonyl chloride (5%), and benzoyl chloride (10–15%) as the only identifiable volatile products other than the unreacted keto acid chloride. Prolonged photolysis (5 days, 40°) of the same solutions yielded almost identical results.

Contrary to the results obtained with pyruvyl chloride, attempts to initiate the radical chain fragmentation of II either chemically or photochemically were unsuccessful, and the thermal fragmentation was not inhibited by several common inhibitors. These results suggest that the thermal fragmentation of II may not be a free-radical chain reaction but may be a molecular decomposition, although only negative evidence supports this proposal.

It was instructive to note that the initiated reactions of II in cyclohexane, although definitely not long-chain

processes, did produce cyclohexylcarbonyl chloride resulting, presumably, from attack of a cyclohexyl radical on II at the carbonyl adjacent to the electron-withdrawing chloride. This behavior is consistent with the observed preference for attack of the cyclohexyl radical at the more electron-deficient carbonyl group of I. The lack of product, cyclohexyl phenyl ketone, resulting from an attack of the radical on the carbonyl adjacent to the phenyl group is likewise in keeping with the absence of a similar type of radical addition β scission reported for the attempted initiated reaction of benzil with cyclohexane.[5]

Experimental Section

Materials.—Cyclohexane (Philips research grade) was used without further purification. Carbon tetrachloride, reagent grade, was distilled before use. All reagents were checked for purity by glpc using a 10 ft × 0.25 in. stainless steel column packed with 10% SE-30 on Chromosorb W. All of the analyses in this study were carried out with this column.

Pyruvyl Chloride (I).—To a cold, 0° mixture of anhydrous sodium carbonate (10.6 g, 0.1 mol), anhydrous dimethylformamide (0.1 ml), and pyruvic acid (17.6 g, 0.2 mol) in 125 ml of dry ether was slowly added (2 hr), a solution of oxalyl chloride (25.4 g, 0.2 mol) in 25 ml of dry ether. This reaction mixture was then allowed to warm to room temperature and was stirred for 24 hr. The reaction mixture was filtered and the filtrate was fractionated using a teflon annular spinning-band column. The fraction boiling at 75–80° (lit.[7] bp 75–80°) was pyruvyl chloride (5.30 g, 25%). The material was shown to be free of starting material and to be one compound by glpc analysis. The ir showed only two carbonyl absorptions at 5.60 and 5.70 μ.

Benzoylformyl Chloride.—Benzoylformic acid (15.0 g, 0.1 mol) and oxalyl chloride (51.0 g, 0.4 mol) were heated to reflux for 6 hr. The excess oxalyl chloride was removed by distillation at atmospheric pressure and the benzoylformyl chloride was distilled under reduced pressure, 90–92° (10 mm) [lit.[4] bp 91° (9.5 mm)], yield 12.8 g (75%).

The product was shown to be free of starting materials by glpc analysis and showed only one peak on its glpc chromatogram. The ir showed only two carbonyl absorptions at 5.65 and 5.90 μ.

Reactions of Pyruvyl Chloride (I).—Solutions of I (0.2 *M*) and chlorobenzene (0.2 *M*) in carbon tetrachloride or cyclohexane were sealed in degassed Pyrex ampoules or break-seals with the desired initiator or inhibitor and the reaction mixtures were subjected to the appropriate reaction conditions.

The fragmentation reactions carried out in carbon tetrachloride could be followed by the disappearance of the carbonyl absorptions of I at 5.60 and 5.70 μ, and the appearance of the spectrum of acetyl chloride (C=O, 5.50 μ). The reactions could also be monitored by glpc analysis. Both methods were consistent within experimental error.

The decompositions carried out in solvent cyclohexane were monitored and quantitated by glpc analysis. The liquid products were identified by a comparison of their glpc retention times and ir spectra with those of authentic samples.

In order to analyze the gaseous products, the reactions were carried out in break-seals (0.02 *M*, 5 ml). After the completion of the reactions, the break-seals were opened to a vacuum line and the gases were distilled through a −80° trap to collect the hydrogen chloride gas. The methane and carbon monoxide were collected and measured using a Toepler pump. The HCl was absorbed in standard aqueous base and determined by back titrating. Methane and carbon monoxide were found by glpc retention time (6 ft-column of molecular sieve 5A) to be the only two noncondensable gases. The ratio of methane and carbon monoxide was determined by quantitative mass spectrometry (AEI, Model MS-9 spectrometer).

Reactions of Benzoylformyl Chloride (II).—The reactions of II (0.2 *M*) in chlorobenzene or cyclohexane were carried out and monitored as were those of I. The ir method of analysis utilized the ability to follow the disappearance of the carbonyl absorption frequencies of II (C=O, 5.90, 5.65) and the appearance of

(6) An investigation is now in progress on the electronic effects operative in similar carbonyl addition reactions: private communication from Professor W. G. Bentrude.

(7) Pierre-Carré and P. Jullien, *C. R. Acad. Sci., Ser. C*, **202**, 1521 (1936).

the spectrum of benzoyl chloride (C=O, 5.60). The decomposition products of II were analyzed and characterized as were those of I.
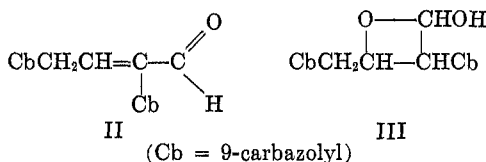
The Alumina-Catalyzed Condensation of 9-Carbazolylacetaldehyde[1]

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The literature contains few examples of the condensation of aldehydes or ketones catalyzed by alumina.[3] During a study of the decarbonylation of 9-carbazolylacetaldehyde[4] (I), we found that, when this aldehyde is passed through a chromatographic column prepared with neutral alumina (activity grade I), it undergoes facile conversion to 2,4-dicarbazol-9-yl-2-butenal (II) (20%) and to an alcohol III (7%), which was assigned the novel structure III, along with considerable polymeric solid.

$$CbCH_2CH=C-C{\overset{O}{\underset{Cb}{\diagup}}}{\overset{}{\underset{H}{\diagdown}}} \qquad CbCH_2\overset{O-CHOH}{\underset{CH-CHCb}{|}}$$

II   III

(Cb = 9-carbazolyl)

Structure II was assigned on the basis of information obtained from its mass, infrared, and nmr spectra and by conversion to derivatives which were characterized by similar techniques (see Table I). Reduction of II with sodium borohydride in 80% aqueous dioxane gave an alcohol IV (76%) which when treated with pyridine-acetic anhydride gave the monoacetate V (76%).

$$CbCH_2CH=C-CH_2OR$$
$$\underset{Cb}{|}$$

IV, R = H
V, R = Ac
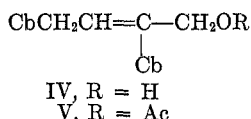
The elucidation of the structure of III was difficult owing to its very low solubility in conventional solvents. Its structure is based in part on spectroscopic data and the properties of its derivatives given in Table I. Purified III gave one spot by tlc, a correct analysis for $C_{28}H_{22}N_2O_2$, and an ir spectrum which is consistent with the proposed structure. In addition, mass spectroscopy gave a molecular weight of 418 and a fragmentation pattern similar to that of the dehydrated form II. The reaction of III with base yielded, on neutralization, car-

bazole (27%), a small amount of II, and considerable amorphous solid. The isolation of II from these hydrolyses confirms the conclusions reached from the mass spectral data and establishes the presence of the carbon skeleton of II as part of structure III. Evidently, the reaction of III with base causes the oxetane ring to open with the simultaneous formation of an aldehyde group which activates the carbazole bearing 2 position toward nucleophilic attack.

This possibility was supported when the hydrolysis of III was carried out under reducing conditions with sodium borohydride. Under these conditions the aldehyde group was reduced as it formed yielding the diol VI (90%) which gave a negative periodic acid test as expected. The diacetate VII was prepared as usual with pyridine and acetic anhydride.

$$CbCH_2\overset{OR}{\underset{Cb}{CH-CH-CH_2OR}}$$

VI, R = H
VII, R = Ac
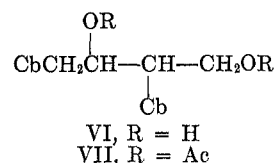
The amorphous solid obtained in the column reaction could not be separated into components by either chromatography, sublimation, or attempted recrystallization. Its infrared spectrum was identical with that of the polymeric material obtained by the acid-catalyzed condensation of I.

When III was acetylated, an acetate (VIII) formed (67%) which had a saponification equivalent consistent with the monoacetate of III and showed a single acetate carbonyl peak in the ir spectrum and one acetate peak in the nmr spectrum. The saponification yielded the same products as did the treatment of III with base.

The mass spectrum of VIII had a fragmentation pattern very similar to that of III except for the parent peak of III at m/e 418 and a peak at m/e 669 (8.1%). We have not yet identified the latter peak but it seems reasonable to assume that it is due to some decomposition product which could have formed at the near decomposition temperature (about 300°) required to vaporize this sample.[5]

In an effort to obtain further confirmation of the molecular weight of III, cryoscopic and ebullioscopic molecular weight determinations were attempted. Unfortunately, these attempts were not successful due to the low solubility of III and its low stability. In hot solvent (about 90°) nmr showed extensive decomposition in a matter of minutes; at room temperature under dry nitrogen, degradation became apparent by elemental analysis after a few weeks.

The mechanism of this reaction appears to be an acid-catalyzed aldol condensation which must occur in this system because of high attraction of the carbazole nucleus for the activated alumina surface[6] and the increased stability of the enol form of the aldehyde due to its conjugation with the heteroaromatic ring system. In strongly acidic solutions the condensation proceeds rapidly to produce an insoluble material even at temper-

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(1) Presented in part at the Northeast Regional Meeting of the American Chemical Society, Boston, Mass., Oct 14, 1968.

(2) American Hoechst Fellow, 1967–1968.

(3) For room temperature reactions, see A. M. Kuliev, A. M. Levshina, and A. G. Zul'fugarova, *Azerb. Khim. Zh.*, No. 5, 29 (1959); *Chem. Abstr.*, **59**, 2638a (1963); also, K. Tanabe and Y. Morisowa, *Chem. Pharm. Bull.*, **11**, 536 (1963).

(4) Synthesis reported in B. M. Vittimberga and M. L. Herz, *J. Org. Chem.*, **35**, 3694 (1970).

(5) We had also considered the dimer of structure III as a possibility for III, but this seems unlikely because of the absence of a complicated fragmentation pattern above m/e 400.

(6) E. Funakubo, T. Nagai, and J. Moritani, *Kogyo Kaguku Zasshi*, **65**, 782 (1962); *Chem. Abstr.*, **59**, 1445g (1963). Also, E. Funakubo, T. Nagai, and G. Kon, *Kogyo Kagaku Zasshi*, **66**, 33 (1963); *Chem. Abstr.*, **59**, 12145f (1963).