2,3-Dichloro-4-hydroxy-6-methylacetophenone (XIII), recrystallized from methylene chloride–hexane, mp 107–108°, showed a strong unassociated hydroxyl absorption in the infrared at 3540 cm^{-1} (CCl_4). In the nmr ($CDCl_3$), it showed singlets at 2.20 (acetyl CH_3), 5.68 (phenolic OH), and 6.79 ppm (aromatic H) in the ratio of 3:3:1:1. The hydroxyl proton resonance was extremely broad (about 1 ppm).

Anal. Calcd for $C_9H_8Cl_2O_2$: C, 49.34; H, 3.68; Cl, 32.37. Found: C, 49.20; H, 4.25; Cl, 32.18.

X-Ray Structure Determination.[3]—A needle-shaped crystal of 1,2,3,3-tetrachlorocyclopropane-*cis*-1,2-diacetone was found to belong to the monoclinic space group $P2_1/c$, with lattice parameters a = 13.458 ±0.010 Å, b = 10.932 ±0.011 Å, c = 9.417 ±0.009 Å, β = 117.20 ±0.06°, Z = 4. Intensity data were collected on a Picker automatic diffractometer using Cu Kα radiation, and the structure was refined by full matrix least squares to a conventional reliability index of 6.5% for 1150 reflections above background.

Registry No.—VI, 21473-07-4; VIII, 21473-08-5; IX, 21473-09-6; X, 21472-85-5; XI, 21472-86-6; XII, 21473-10-9; XIII, 21472-87-7; VII, 21473-11-0; 1,2,3,3-tetrachlorocyclopropane-*cis*-1,2-diacetaldehyde, 19427-04-4; 1,2,3,3-tetrachlorocyclopropane-*cis*-1,2-diacetaldehyde bis(2,4-dinitrophenylhydrazone), 19427-06-6.

The Oxygenation of Enamines. Ketonization at the β Position to Give α-Amino Ketones

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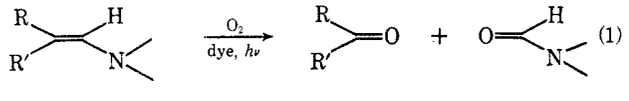
Within the last year, several communications have appeared concerning the reactions of enamines with oxygen. Foote and Huber[1] have reported the quantitative cleavage of the enamine double bond [eq 1



(1)

(both R and R′ alkyl or aryl groups)] in a dye-sensitized photooxygenation. The reaction of oxygen with enamines from α,β-unsaturated bicyclic ketones produces ene-diones in 65–85% yields.[2] More recently, the copper-catalyzed oxygenation of enamines has been reported to give cleavage of the double bond in a manner similar to the dye-sensitized process.[3] We have studied the oxygenation of enamines containing a vinyl hydrogen at the β position and have found α-amino ketones, products not previously reported in the oxidation of an enamine.

The reaction of 1-di-*n*-butylamino-1-butene (**1**) with oxygen in benzene at 25 or 80° gave a mixture of di-*n*-butylamine, N,N-di-*n*-butylformamide, and 1-N,N-di-*n*-butylamino-2-butanone (**2**). The latter two account

$(n\text{-Bu})_2NCH{=}CHCH_2CH_3$ (**1**) $(n\text{-Bu})_2NCH_2COCH_2CH_3$ (**2**)

for a *ca.* 55% yield. The products and yields as determined by gas–liquid chromatography are listed in Table I. Di-*n*-butylamine is generated very likely by hydrolysis of the enamine. The most probable source of the N,N-di-*n*-butylformamide is cleavage of the enamine double bond, the same type of process found in the sensitized photooxygenation[1] and the copper-catalyzed oxygenation.[3]

TABLE I

Product	Yield, % 25° (40.5 hr)[a]	Yield, % 80° (8 hr)[a]
Di-*n*-butylamine	10.1	7.2
N,N-Di-*n*-butylformamide	19.0	29.4
1-N,N-Di-*n*-butylamino-2-butanone (**2**)	34.3	26.0

[a] Reaction time.

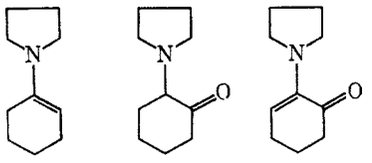
The di-*n*-butylamine and the formamide were identified by trapping each from the gas–liquid chromatogram and comparing their infrared spectra with those of authentic materials. Compound **2** was also isolated by trapping and it exhibited an infrared band at 1720 cm^{-1}. A mass spectrogram yielded a molecular ion at *m/e* 199 and a large peak at *m/e* 142 indicative of the cleavage shown in eq 2. This type of cleavage has

$$(n\text{-Bu})_2\overset{+}{N}CH_2COCH_2CH_3 \longrightarrow (n\text{-Bu})_2\overset{+}{N}{=}CH_2 + \cdot COCH_2CH_3 \quad (2)$$

m/e 142

been found for α-dimethylaminoacetone.[4] These data suggested structure **2** and the initial assignment was confirmed by comparison of the infrared spectrum with that of an authentic sample synthesized by the method of Bailey and Keller.[5]

The oxidation of 1-pyrrolidinocyclohexene (**3**) at 25° in benzene or ethyl acetate proceeded rapidly and with a mild exotherm to give α-pyrrolidinocyclohexanone (**4**) and 6-oxo-1-pyrrolidinocyclohexene (**5**) as the only identifiable products. However, some gum formation occurred which made isolation of **4** and **5** difficult. Early in the reaction, before any gum could be observed, a gas–liquid chromatogram revealed the presence of only **3**, **4**, **5**, and the hydrolysis products of **3**, pyrrolidine, and cyclohexanone. The products were isolated by trapping from the chromatogram and comparing their infrared spectra with authentic samples. Distillation of the crude dark product and analysis of the distillate by glpc indicated that the yield for **4** and **5** was 9.4 and 7.8%, respectively. A large dark pot residue remained. No products from cleavage of the enamine double bond could be detected in contrast to the cleav-



3 **4** **5**

(1) (a) C. S. Foote and J. Wei-Ping Lin, *Tetrahedron Lett.*, 3267 (1968); (b) J. E. Huber, *ibid.*, 3271 (1968).

(2) S. K. Malhotra, J. J. Hostynek, and A. F. Lundin, *J. Amer. Chem. Soc.*, **90**, 6565 (1968).

(3) V. Van Rheenen, *Chem. Commun.*, 314 (1969).

(4) F. R. Stermitz and K. D. McMurtrey, *J. Org. Chem.*, **33**, 1140 (1968). See also H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1967, p 11.

(5) P. S. Bailey and J. E. Keller, *J. Org. Chem.*, **33**, 2680 (1968).

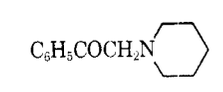
age of a similar cycloolefin enamine bond in the copper-catalyzed reaction.[3]

Compound **4** is not stable to the conditions of the oxidation and it rapidly absorbs oxygen to give **5**. Thus, the probable path of the reaction is **3** → **4** → **5**. Compound **5** has been isolated from the oxidation of **3** by nitrobenzenes containing electron withdrawing groups in *ca.* 25% yield.[6]

Compound **4** was synthesized by the reaction of α-hydroxycyclohexanone with pyrrolidine, a general type reaction for preparing pure α-amino ketones.[7] The nmr spectrum did not determine the position of the pyrrolidine group. However, the mass spectrogram, in addition to the molecular ion *m/e* 167, contained the base peak *m/e* 110 assignable to the $CH_2{=}CHCH{=}N^+C_4H_8$ ion, thus establishing the pyrrolidine group at the carbon α to the carbonyl group. A similar cleavage has been observed for α-dimethylaminocyclohexanone.[4]

An attempt to oxidize 1-morpholinocyclohexene (**6**) in benzene at 25° failed to give a reaction. A steroid morpholine enamine has been found also to be stable to oxygen.[1b] However, at 80°, reaction did take place to produce α-morpholinocyclohexanone (**7**) and some gum. The ease of oxidation of **3** compared to **6** is in agreement with the stronger base strength of pyrrolidine, pK_a = 11.27 (25°), compared to morpholine, pK_a = 8.39 (25°),[8] and also the ease with which **3** alkylates in relation to **6**.

When the dye-sensitized oxidation was carried out with an enamine containing a β hydrogen, *e.g.*, β-piperidinostyrene, the yield of double bond cleavage products was reduced to about 50% and unidentified nonvolatile products were produced.[1a] The available low-temperature chemical and spectroscopic evidence supports formation of a cyclic peroxide containing a carbon–oxygen bond β to the nitrogen.[1a] In the case of the β-piperidinostyrene, this peroxide may have decomposed thermally to give some α-piperidinoacetophenone (**9**) and thus reduce the yield of cleaved products. The products we isolated in the nonsensitized oxygenation may be formed through the intermediacy of **10** which can close to the peroxide **11** or undergo proton transfer to the enol hydroperoxide **12**. A radical chain process has already been suggested to form an intermediate similar to **10** for a vinylogous enamine.[2] Compound **12** could undergo homolytic oxygen–oxygen cleavage, followed by hydrogen abstraction to give the enol of **2**. Our identification of N,N-di-*n*-butylformamide may indicate that double bond cleavage of enamines by oxygen is relatively insensitive to the oxygen multiplicity.



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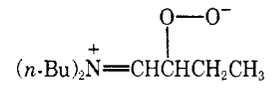

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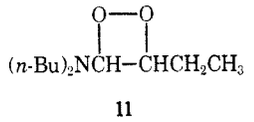

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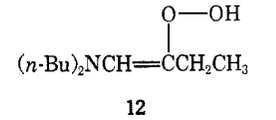

12

(6) S. Danishefsky and R. Cavanaugh, *Chem. Ind.* (London), 2171 (1967).

(7) R. A. Jerussi, manuscript in preparation. See also P. Klemmensen, G. Schroll, and S. Lawesson, *Ark. Kemi*, **28**, 405 (1968).

(8) D. D. Perrin, "Dissociation Constants of Organic Bases in Aqueous Solution," Buttersworth & Co., Ltd., London, 1965, pp 135, 196.

Experimental Section[9]

Oxidation of 1-Di-*n*-butylamino-1-butene (1) at 25°.—1-Di-*n*-butylamino-1-butene (3.80 g, 0.0208 mol) was dissolved in 60 ml of dry benzene in a 100-ml three-neck flask. Oxygen was passed through the solution at 0.1 ft³/hr after 5 g of anhydrous magnesium sulfate had been added. The reaction was terminated by discontinuing the oxygen flow after 40.5 hr. A vapor phase chromatogram of the reaction solution (60° start; 10°/min program) indicated major peaks at 7.2 min (X16 peak height), 9 min (X16), 9.5 min (X16), and 10.5 min (X32-64). The 4.2-, 9- and 9.5-min peaks were trapped and their infrared spectra when compared with those of authentic materials indicated that they were di-*n*-butylamine, starting enamine, and N,N-di-*n*-butylformamide. The 10.5-min product was trapped also. Its infrared spectrum contained a strong band at 1720 cm^{-1} and a mass spectrogram indicated an *m/e* peak at 199 (molecular ion) with major peaks at *m/e* 142, 100 (base peak), 86, and 57. The mixture was filtered to remove the drying agent and the solvent removed under reduced pressure. The dark oil remaining was distilled in a bulb-to-bulb apparatus; 3.40 g of a yellow oil was obtained, bath temperature 100–150° (0.05 mm). A vapor phase chromatogram indicated the same peaks as listed above, but with a greatly reduced enamine peak. Integration of the chromatogram gave the reaction yields listed in Table I.

Oxidation of 1-Di-*n*-butylamino-1-butene (1) at 80°.—1-Di-*n*-butylamino-1-butene (5.90 g, 0.0322 mol) was dissolved in 60 ml of benzene in a dry three-neck 100-ml flask attached to a Dean–Stark trap. The solution was heated at reflux while oxygen was passed in at 0.075 cm ft/hr. After 1.5 hr, a vapor phase chromatogram indicated that appreciable reaction had occurred: peaks at 9 min (X32 peak height), starting enamine; 10 min (X16), N,N-di-*n*-butylformamide; and 10.8 min (X32), 1-di-*n*-butylamino-2-butanone. The reaction was terminated after 8 hr by cooling and stopping the oxygen flow. Some water had collected in the trap. The solvent was removed under reduced pressure and the residue was distilled in a bulb-to-bulb apparatus using a free flame and a pressure of 0.05 mm. An amber distillate, 4.82 g, was collected whose vapor phase chromatogram contained major peaks at 4.5 min, 9.5 min, and 10.5 min (60° start; 10°/min program). These peaks were trapped and identified by their infrared spectra as di-*n*-butylamine, N,N-di-*n*-butylformamide, and 1-di-*n*-butylamino-2-butanone, respectively. Integration of the chromatogram gave the reaction yields listed in Table I.

Preparation of 1-Di-*n*-butylamino-1-butene (1).—This compound was prepared according to the method of Henbest and Stratford.[10] The product was isolated by distillation: bp 48°; (0.25 mm); ir (neat) 1650 and 930 cm^{-1} (lit.[10] bp 62° (0.5 mm); ir 1640 and 930 cm^{-1}).

Preparation of 1-Di-*n*-butylamino-2-butanone (2).—The title compound was prepared according to the method of Bailey and Keller.[5] The crude product was distilled: bp 99–100° (7.5 mm); $n^{25}D$ 1.4352 (lit.[5] bp 92° (5 mm); $n^{25}D$ 1.4355); ir (neat) 1720 cm^{-1} (C=O). The infrared spectrum was essentially identical with that of the infrared spectrum of the 10.5–10.8-min retention time material in the oxidation of **1**.

Oxidation of 1-Pyrrolinocyclohexene (3).—1-Pyrrolidinocyclohexene (1.960 g, 0.013 mol) was injected through a rubber septum into a flask containing 70 ml of dry ethyl acetate. The flask was suspended in a water bath at ambient temperature and was attached to oxygen burets. Oxygen uptake began immediately and in 20 min 293 ml had been absorbed (theory, 317 ml). The reaction was terminated by evacuating the system several times and refilling with nitrogen each time. The reaction solution gradually became amber and turbid during the oxygen uptake period. Toward the end of the reaction, some insoluble gum settled out. Magnesium sulfate was added and the turbidity disappeared. A glpc (60° start; 10°/min program) of the clear orange supernatant liquid indicated the following: several peaks with retention times less than 1 min, a peak at 3.3 min (peak height X32), 10.5 min (X8), and 12.4 min (X8). Cyclohexanone, α-pyrrolidinocyclohexanone (**4**), and 6-oxo-1-pyrrolidinocyclohexene (**5**) had the same retention times, respectively. There was

(9) Infrared spectra were take on a Perkin–Elmer Model 337 instrument. The gas–liquid chromatographic analyses were carried out using an F & M Model 700 instrument with 4 ft × 0.25 in. 10% SE-30 silicone gum rubber on 60–80 mesh Diatoport S packing. Mass spectra were obtained on a General Electric Monopole 600 spectrometer.

(10) H. B. Henbest and M. J. W. Stratford, *J. Chem. Soc.*, 711 (1964).

no unreacted enamine **3**. The 10.5- and 12.4-min peaks were trapped and their infrared spectra were essentially identical with authentic **4** and **5**, respectively. The drying agent was removed by filtration in a nitrogen drybox and the filtrate was concentrated under vacuum (20 mm). The resultant oil was distilled in a bulb-to-bulb apparatus with a free flame at 0.5 mm. Some water came over and then a reddish oil was collected, 0.657 g. A glpc of this oil indicated that compounds **4** and **5** were still the major constituents (*ca.* 51%), but a number of other peaks were present which were not present at the end of the reaction. Integration gave the following reaction yields: **4**, 9.4%, and **5**, 7.8%.

Oxidation of α-Pyrrolidinocyclohexanone (4).—α-Pyrrolidinocyclohexanone (4.09 g, 0.0244 mol) was injected into a mixture of 70 ml of ethyl acetate and 5 g of magnesium sulfate contained in a flask attached to an oxygen buret. Oxygen uptake commenced immediately and 353 ml (61%) had been absorbed in 18 min. After 117 min, 463 ml (78%) had been taken up. A glpc indicated three peaks: 4.5 min (X4 peak height), 10.5 min (X32), and 12.5 min (X4). The latter two had the same retention times as those of the starting ketone **4** and 6-oxo-1-pyrrolidinocyclohexene (**5**). The 12.5-min peak was trapped and its infrared spectrum was identical with that of authentic **5**. The reaction was allowed to proceed for an additional 18.5 hr during which an additional 310 ml of oxygen was absorbed (total uptake 773 ml or 1.3 molar equiv). A glpc indicated peaks at 4.5 min (X8), 10.5 min (X8), and 12.5 min (X4). There were now several minor peaks at longer retention times.

Preparation of α-Pyrrolidinocyclohexanone (4).—α-Hydroxycyclohexanone (11.41 g, 0.10 mol), pyrrolidine (8.35 ml, 0.10 mol), and benzene (50 ml) were placed in a flask connected to a Dean–Stark trap. The system was flushed with nitrogen and heated at reflux for 3 hr at which time 0.10 mol of water had collected in the trap. The benzene was removed under vacuum (20 mm) and the residue distilled to give 14.26 g (89%) of title compound: bp 91–93° (4.5 mm); $n^{20}D$ 1.4893; ir (neat) 1720 cm^{-1} (C=O); nmr (C_6H_6) δ 2.8–1.9 (m, 7), 1.9–1.2 (m, 10); mass spectrum (50 eV) *m/e* (rel intensity) 167 (23), 139 (53), 110 (284), 97 (38), 96 (101).

Anal. Calcd for $C_{10}H_{17}NO$: C, 71.81; H, 10.25; N, 8.37. Found: C, 71.7; H, 10.4; N, 8.2.

Preparation of 6-Oxo-1-pyrrolidinocyclohexene (5).—Cyclohexa-1,2-dione (10.20 g, 0.091 mol) and pyrrolidine (6.47 g, 0.091 mol) were dissolved in 40 ml of benzene and heated at reflux for 4 hr. A total of 1.5 ml of water collected in a Dean–Stark trap (theory, 1.64). The benzene was removed at 20 mm and the dark oil remaining was distilled. A fraction was collected: 9.0 g; bp 70–71° (0.2 mm); ir (neat) 1680 and 1600 cm^{-1} [lit.[6] bp 70–72° (0.07 mm); ir 1681 and 1605 cm^{-1}].

Oxidation of 1-Morpholinocyclohexene (6) at 80°.—1-Morpholinocyclohexene (28.75 g, 0.172 mol) was dissolved in 150 ml of anhydrous benzene in an apparatus containing a Dean–Stark trap. The solution was heated at reflux while oxygen was bubbled through at 0.05 ft^3/hr. After 22 hr, no water had collected, the solution was red, and a dark film adhered to the reactor walls. A glpc (70° start, 10°/min program) indicated a number of peaks, among which the major peaks were at 3 min, 10.5 min, and 11.5 min. The latter two peaks were trapped and their infrared spectra were essentially identical with 1-morpholinocyclohexene **6** and α-morpholinocyclohexanone **7**, respectively.

Registry No.—**1**, 15431-00-2; **3**, 1125-99-1; **4**, 22003-63-0; **6**, 670-80-4.

The Reaction of Hexafluoroacetone with Olefins

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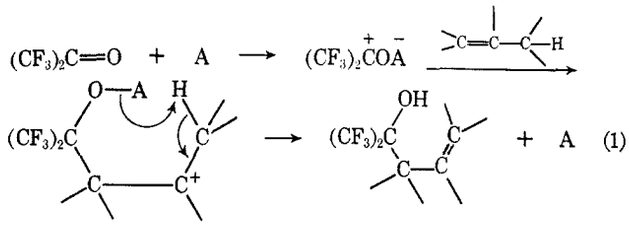
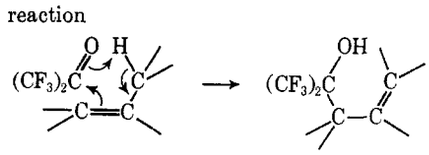
Several papers have recently discussed the reactions of hexafluoroacetone or fluoral with olefins.[1] These reactions may be carried out in good yield either by heating olefin and hexafluoroacetone or by treating them with a Lewis acid catalyst at low (−10°) temperature in hydrocarbon solvent. Both methods are reported to yield a single product, 1,1-bis(trifluoromethyl)-3-alken-1-ol. Mechanisms proposed to account for the single product and the double bond position are shown below.

catalyzed reaction



(1)

thermal reaction



(2)

In connection with other studies, we have recently had occasion to apply the $AlCl_3$-catalyzed reaction of hexafluoroacetone to a complex olefin system. In view of the intractable mixture of products obtained, the simpler alkenes propylene and 1-butene were reexamined.

A cold (−30°) mixture of olefin, hexafluoroacetone, and $AlCl_3$ catalyst in pentane was allowed to warm slowly. At *ca.* −15° there was an exothermic reaction, after which the mixture was stirred at 0° for 2 hr. The product mixture from either propylene or 1-butene was primarily *cis*- and *trans*-1,1-bis(trifluoromethyl)-2-alken-1-ols, with lesser amounts of the reported[1] 3-alken-1-ols. These products were isolated by preparative scale glpc methods and characterized by elemental analysis as well as nmr and infrared spectroscopy.

The thermal reaction of hexafluoroacetone with these olefins was carried out for comparison; and in these cases, as reported,[1] the only materials isolated were the isomeric 1,1-bis(trifluoromethyl)-3-alken-1-ols.

Products and yields for these reactions are shown in Table I.

In order to determine if the spectrum of compounds obtained from the $AlCl_3$-catalyzed reaction represents primary products or a secondarily rearranged mixture, each of the available isomers was treated with the catalyst in pentane solution. Treatment of **1**, *trans*-**3**, and *trans*-**4** yielded only the unchanged starting material, while *trans*-**2** was converted to 1,1-bis(trifluoromethyl)-4-methyltetrahydrofuran. From the absence of double-bond isomerization, it must be concluded that the observed products are formed in a primary reaction.

These results indicate that, while the cyclic concerted process (eq 2) is probably appropriate for the thermal reaction, the $AlCl_3$-catalyzed process is better thought of in terms of a Friedel–Crafts type of reaction involving

(1) (a) N. P. Gambaryan, El. M. Rokhlina, and Yu. V. Zeifman, *Bull. Acad. Sci. USSR, Div. Chem. Sci.* (Engl. Transl.), **8**, 1425 (1965); (b) H. R. Davis, Abstracts, 140th National Meeting of the American Chemical Society, Chicago, Ill., 1961, p 25M; (c) I. L. Knunyants and B. L. Lyatkin, *Bull. Acad. Sci. USSR, Div. Chem. Sci.* (Engl. Transl.), **2**, 329 (1962); (d) R. L. Adelman, *J. Org. Chem.*, **33**, 1400 (1968); (e) R. Poutral, J. Marteau, and R. Cheritat, *Bull. Soc. Chim. Fr.*, 1182 (1968).