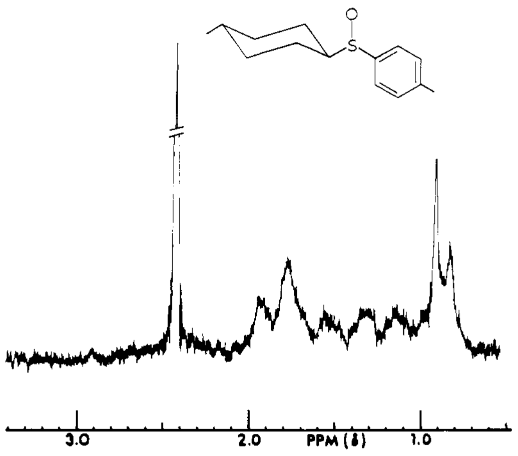

Figure 13.
trans-4-(*p*-Tolysulfonyl)-1-methylcyclohexane (*6*)

Studies have been made (*4, 5, 6*) which required preparation of a number of stereoisomeric 4-substituted-1-methylcyclohexanes. The NMR spectra of these compounds were determined routinely with a Varian A-60 spectrometer at ambient temperatures in chloroform-*d* containing tetramethylsilane internal standard. These spectra (Figures 1-13) provide additional corroboration of the general applicability of the useful stereochemical correlation originally suggested by the observations of Brownstein and Miller (*2*). Larger copies of the figures are available from ASIS.

LITERATURE CITED

(1) Armarego, W.L.F., *J. Chem. Soc.* **1967**, 337.
(2) Brownstein, S., Miller, R., *J. Org. Chem.* **24**, 1886 (1959).
(3) Gerig, J.T., Roberts, J.D., *J. Am. Chem. Soc.* **88**, 2791 (1966).
(4) Goldberg, S.I., Lam, F-L., *J. Org. Chem.* **31**, 2336 (1966).
(5) Goldberg, S.I., Lam, F-L., "Abstracts of Papers," p. P-31, 155th Meeting, ACS, San Francisco, Calif., April 1968.
(6) Goldberg, S.I., Sahli, M.S., *J. Org. Chem.* **32**, 2059 (1967).
(7) Jensen, F.A., Beck, B.H., *Tetrahedron Letters* **1966**, 4523.
(8) Musher, J., Richards, R.E., *Proc. Chem. Soc.* **1958**, 230.
(9) Riddell, F.G., Robinson, M.J.R., *Chem. Commun.* **1965**, 227.
(10) Smith, D.R., Maienthal, M., Lipton, J., *J. Org. Chem.* **17**, 294 (1952).

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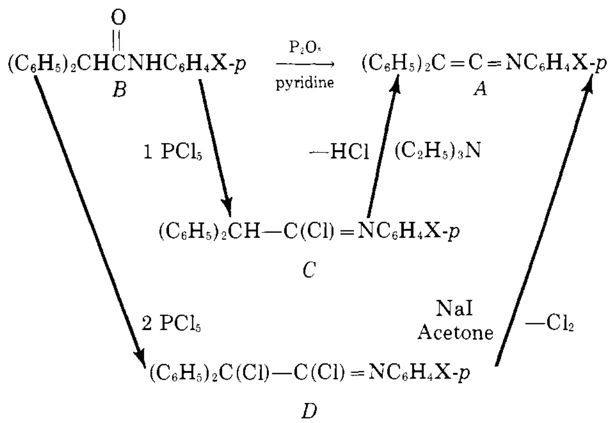
A Novel Method for the Preparation of Ketenes and Ketenimines

GOPAL H. SINGHAL and HERBERT Q. SMITH
Pennsalt Chemicals Corp. Technological Center, King of Prussia, Pa. 19406

A novel method of preparation of ketenes and ketenimines by the dechlorination of the corresponding α-chloroacid chlorides and α-chloroimino chlorides with copper powder is described.

IN RECENT years, three general methods for the synthesis of ketenimines have been introduced by Stevens and coworkers. These are the dechlorination of α-chloroimino chlorides with sodium iodide in acetone (*10*), the dehydrochlorination of imino chlorides with a tertiary amine (*11*), and the dehydration of amides with phosphorus pentoxide in combination with a tertiary amine (*12*). Basically, these methods involve the removal of a molecule of water from the amide (*B*) either directly or by converting the amide to an imino chloride (*C*) or an α-chloroimino chloride (*D*), followed by removal of a molecule of hydrogen chloride or chlorine, as illustrated.



These methods work very well when X is an electron-donating group—e.g., CH_3—, CH_3O—, etc. However, when X is a strong electron-withdrawing group, such as NO_2, these methods do not work well. Thus, the nitroketenimine (*A*, X = NO_2) could not be prepared by the dehydration of the corresponding amide (*12*). The amide (*B*, X = NO_2), on treatment with even 1 mole of phosphorus pentachloride, gives mainly the α-chloroimino chloride (*1*) (*D*, X = NO_2) and unreacted starting material, rendering the dehydrochlorination method via the imino chloride inapplicable. On the other hand, sodium iodide in acetone under the conditions described in the literature (*10*) for the preparation of *A* (X = CH_3), failed to dehalogenate *D* (X = NO_2). *D* (X = NO_2) could be obtained in excellent yield (*6, 9*) with these reagents in a sealed tube at 100° C., under strictly anhydrous conditions, or (*1*) in a moderate yield of 31% from sodium iodide in a higher-boiling ketone, 3-pentanone. However, the isolation procedure by this method is involved, tedious, and unsuitable for large scale preparations.

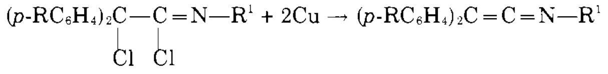
The authors were interested in the nitroketenimine, and the dechlorination route seemed to be the logical method of choice. Staudinger and Meyer (*8*) have reported that zinc failed to dechlorinate an α-chloroimino chloride to a ketenimine, even though this is a common method for the preparation of ketenes from α-haloacid halides (*3*).

Staudinger and Klever (*7*) also reported the preparation of ketene by debromination of bromoacetyl bromide with zinc in ether. This claim was later disputed by Hurd and coworkers (*4*), who attributed the failure of ketene formation to the catalytic effect of zinc bromide formed in the reaction. They also tried copper bronze, which gave a slower catalytic effect, but no ketene could be isolated.

In view of the extensive use of copper as a coupling agent in the Ullmann reaction (*2*) and allied transformations (*5*), it appeared to warrant investigation.

Copper powder dechlorinates α-chlorodiphenylacetyl chloride very smoothly in boiling benzene solution, to give diphenylketene in very high yield. In this experiment, no effort was made to isolate the ketene. The reaction mixture was filtered to remove excess copper powder and copper chloride, and the solution was treated with *p*-toluidine to give *N*-(*p*-tolyl)diphenylacetamide in 80% yield. This method has a practical advantage over the zinc method, since the inorganic material can be directly filtered off to give a solution of diphenylketene. In the zinc method, zinc chloride first has to be precipitated out by the addition of petroleum ether to the ether solution.

This method was also very successful for dechlorination of α-chloroimino chlorides to give ketenimines:



$$(p\text{-RC}_6\text{H}_4)_2\underset{\text{Cl}}{\text{C}}\text{—}\underset{\text{Cl}}{\text{C}}\text{=N—R}^1 + 2\text{Cu} \rightarrow (p\text{-RC}_6\text{H}_4)_2\text{C=C=N—R}^1$$

6, R = H, $R^1 = p\text{-}C_6H_4NO_2$	**1**, R = H, $R^1 = p\text{-}C_6H_4NO_2$
7, R = H, $R^1 = p\text{-}C_6H_4Cl$	**2**, R = H, $R^1 = p\text{-}C_6H_4Cl$
8, R = Cl, $R^1 = p\text{-}C_6H_4CH_3$	**3**, R = Cl, $R^1 = p\text{-}C_6H_4CH_3$
9, R = H, $R^1 = n\text{-}C_4H_9$	**4**, R = H, $R^1 = n\text{-}C_4H_9$
10, R = H, $R^1 = 4\text{-Cl-3-NO}_2\text{-}C_6H_3$	**5**, R = H, $R^1 = 4\text{-Cl-3-NO}_2\text{-}C_6H_3$

Thus, when a benzene solution of *N*-(*p*-nitrophenyl)-α-chlorodiphenylacetimino chloride (**6**) was refluxed for five hours with an excess of copper powder, a 91% yield of the nitroketenimine (**1**)was obtained. Under the same conditions, diphenylketen-*p*-chlorophenylimine (**2**) was obtained in 86% yield from the corresponding α-chloroimino chloride (**7**).

N-*p*-Tolyl-2-chloro-2,2-di-*p*-chlorophenylacetimino chloride (**8**), obtained as an oil from treatment of *N*-(*p*-tolyl)di-*p*-chlorophenylacetamide (**13**) with 2 moles of phosphorus pentachloride, could be smoothly dechlorinated with copper powder to give a 57% yield of the corresponding ketenimine (**3**) as a yellow crystalline solid.

The success of the method was not limited to *N*-phenyl-substituted ketenimines. Diphenylketen-*N*-butylimine (**4**) was obtained in 47% conversion from the corresponding α-chloroimino chloride (**9**)

Finally, *N*-(4-chloro-3-nitrophenyl)-2-chloro-2,2-diphenylacetimino chloride (**10**) was selected as a special example, since this compound contains an active chlorine atom (ortho to a nitro group). It was of interest to determine whether, under these reaction conditions, the Ullmann reaction would be competitive. Upon refluxing (**10**) with excess copper powder in toluene for three hours, diphenylketen-*N*-(4-chloro-3-nitrophenyl)imine (**5**) was the only product obtained in 71.5% recrystallized yield. An aliquot taken after 1.75 hours showed essentially complete reaction, as evidenced by the presence of a strong peak in the 5-micron region in the infrared (*10, 11*) and the absence of absorption in the 6.1-micron region, which is characteristic of the starting material.

EXPERIMENTAL

Preparation of Amides and α-Chloroimino Chlorides. The amides were prepared by the reaction of the corresponding acid chlorides with primary amines. The α-chloroimino chlorides were obtained by refluxing a mixture of amide and two equivalents of phosphorus pentachloride in benzene, followed by removal of volatiles under reduced pressure and azeotropic distillation of the last traces of phosphorus chlorides with benzene. The properties of the analyzed compounds are listed in Table I.

Also prepared were:

N-(*p*-Nitrophenyl)diphenylacetamide (**11**), m.p. 186–8° C., 74.7% yield; (*1*), m.p. 189–90° C.

N-(*n*-Butyl)diphenylacetamide (**14**), m.p. 96.5–98° C., 97.4% yield; (*11*), m.p. 96–7° C.

N-(*p*-Nitrophenyl) - α - chlorodiphenylacetimino chloride (**6**), m.p. 126–8° C., 83.2% yield; (*6*), m.p. 126–7° C.

N-(*p*-Tolyl)-α-chlorodi-*p*-chlorophenylacetimino chloride (**8**) could not be crystallized and was used without further purification.

N-(*n*-Butyl)-α-chlorodiphenylacetimino chloride (**9**), 90.6% yield, n_D^{27} 1.5735 on crude; (*11*), b.p. 160–3° C. (0.2 mm.), n_D^{25} 1.549. Attempted distillation led to extensive decomposition, in which some of the corresponding ketenimine was detected by the characteristic infrared peak around 5 microns.

N-(4-Chloro-3-nitrophenyl)diphenylacetimino chloride (**10**), 87% yield, m.p. 146–7° C., used without analysis; the infrared spectrum was consistent with the structure.

Preparation of Ketenimines. The preparation of diphenylketen-*N*-(*p*-nitrophenyl)imine (**1**) is given as a representative example. Other examples are given in Table II.

Diphenylketen-*N*-(*p*-nitrophenyl)imine (**1**). A stirred mixture of 35.0 grams (0.091 mole) of *N*-(*p*-nitrophenyl)-2-chlorodiphenylacetimino chloride (**6**), 31.0 grams of copper powder (Natural copper 44F, United States Bronze Powders Inc., Flemington, N.J.), and 450 ml. of anhydrous benzene was refluxed for five hours. The reaction mixture was filtered and the solid was washed with benzene (3 × 50 ml.). Benzene was removed from the combined washings and filtrate under reduced pressure. To the residual oil was added 200 ml.

Table I. Properties of Amides and α-Chloroimino Chlorides

Compound	M.P., ° C.	Yield, %	Analysis, % Calcd. C	H	N	Found C	H	N
N-(*p*-Chlorophenyl)diphenylacetamide (**12**)	198–199	60.5	74.65	4.98	4.35	74.74	5.25	4.12
N-(*p*-Tolyl)di-*p*-chlorophenylacetamide (**13**)	217–218	91.	67.65	4.86	3.81	68.10	4.91	3.78
N-(4-Chloro-3-nitrophenyl)-diphenylacetamide (**15**)	172–173	70.8	65.47	4.00	7.64	65.44	4.58	7.53
N-(*p*-Chlorophenyl)-α-chloro-diphenylacetimino chloride[a] (**7**)	109–110	94.8	63.98	4.01		64.07	3.74	

[a] Also Found: Cl, 28.55. Calcd., 28.44.

Table II. Ketenimines

Compound	M.P., °C.	Yield, %	Analysis, % Calcd. C	H	N	Found C	H	N
Diphenylketen-(*N*-*p*-chlorophenyl)imine (2)	69.5–71	86.4	79.09	4.61	4.61	79.04	4.84	4.92
Di-*p*-chlorophenylketen-*N*-(*p*-tolyl)imine[a] (3)	82–84	57.4	71.60	4.26	3.98	71.22	4.56	4.19
Diphenylketen-*N*-(4-chloro-3-nitrophenyl)imine[b] (5)	72–73	71.4	68.86	3.73	8.03	68.66	4.06	8.08

[a] Prepared from the crude α-chloroimino chloride. [b] Toluene used instead of benzene as solvent.

of petroleum ether and sufficient ethyl ether to give a solution. It was filtered to remove traces of impurities, and the filtrate was allowed to stand, to give 19.1 grams of the product, m.p. 85–7° C.; (*1*) m.p. 74–5° C.; (*6*), m.p. 85–7° C. Another 7 grams of product, m.p. 82–4° C., was obtained from the filtrate after concentration and cooling. The combined yield was 26.1 grams (91.4%).

Diphenylketen-*N*-(*n*-butyl)imine (4). The compound was similarly prepared, 47.3% yield from the crude α-chloroimino chloride, n_D^{25} 1.6030; (*11*), b.p. 154–8° C. (0.15 mm.), n_D^{25} 1.6026, 1.6006.

N-(*p*-Tolyl)diphenylacetamide via diphenylketene. Into a flame-dried, one-liter three-necked flask carrying a mechanical stirrer and a reflux condenser carrying a calcium chloride drying tube were placed 13.25 grams (0.0500 mole) of α-chlorodiphenylacetyl chloride (*11*), 14 grams of copper powder and 300 ml. of anhydrous benzene. The mixture was refluxed with stirring for 2.5 hours, while an atmosphere of nitrogen was maintained over the mixture. The mixture was chilled, filtered, and the residue was washed with anhydrous benzene (2 x 50 ml.). To the combined filtrate and washings was added a solution of 5.37 grams (0.050 mole) of recrystallized *p*-toluidine in 100 ml. of benzene. After the reaction had subsided, the mixture was concentrated to dryness under reduced pressure, and the residual solid was recrystallized from aqueous acetone to give 11.8 grams (78.4%) of *N*-(*p*-tolyl)diphenylacetamide, m.p. 179–81° C. A mixture melting point with an authentic sample prepared by the reaction of diphenylacetyl chloride and *p*-toluidine was not depressed.

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LITERATURE CITED

(1) De Young, J.J., Ph.D. thesis, Wayne State University, Detroit, Mich., 1957.
(2) Fanta, P.E., *Chem. Rev.* **38**, 139 (1946).
(3) Hanford, W.E., Souer, J.C., *Org. Reactions* **III**, 123, 138 (1946).
(4) Hurd, C.D., Cashion, F.W., Perletz, P., *J. Org. Chem.* **8**, 367 (1943).
(5) Rabjohn, N., *Org. Synthesis*, Coll. Vol. 4, 878, 914 (1963).
(6) Singhal, G.H., Ph.D. thesis, Wayne State University, Detroit, Mich., 1962.
(7) Staudinger, H., Klever, H.W., *Ber.* **41**, 595 (1908).
(8) Staudinger, H., Meyer, J., *Ibid.*, **53**, 72 (1920).
(9) Stevens, C.L., Chua, J., Niethammer, K., Wayne State University, Detroit, Mich., unpublished results, 1961.
(10) Stevens, C.L., French, J.C., *J. Am. Chem. Soc.* **75**, 657 (1953).
(11) *Ibid.*, **76**, 4398 (1954).
(12) Stevens, C.L., Singhal, G.H., *J. Org. Chem.* **29**, 34 (1964).

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Fluorodinitroethyl Esters of Dicarboxylic Acids

MARION E. HILL, DONALD L. ROSS, CLIFFORD L. COON, and LEONARD O. ROSS
Organic and Polymer Chemistry Division, Stanford Research Institute, Menlo Park, Calif. 94025

The fluorodinitroethyl esters of fumaric, maleic, itaconic, and malonic acids were synthesized, using known procedures; the physical properties of the esters are given. Attempts to prepare bis(fluorodinitroethyl) methylenemalonate from bis(fluorodinitroethyl) malonate by two different procedures led to some unexpected products.

UNSATURATED dicarboxylic acid esters of fluoronitro alcohols have been of interest as comonomers in ester polymerization. Recently, the synthesis of esters of 2,2-difluoro-2-nitroethanol (*3*) was described. Completion of this work formed part of a series of unsaturated esters of negatively substituted alcohols consisting of 2,2,2-trifluoroethanol and 2,2,2-trinitroethanol. The authors now report the preparation of the analogous 2-fluoro-2,2-dinitroethyl esters of fumaric, maleic, itaconic, and malonic acids. Attempts to prepare bis(2-fluoro-2,2-dinitroethyl) methylenemalonate led to some unexpected derivatives of bis(2-fluoro-2,2-dinitroethyl) malonate.

Several standard methods of esterification were used for 2-fluoro-2,2-dinitroethanol, but no single method was useful for each ester, and the efficacy of each procedure depended upon the reactivity of the acid or acyl chloride. The esters and their properties are summarized in Table I.

Fumaric acid could not be esterified by the usual azeotropic distillation method. However, when fuming sulfuric acid was used as solvent (*1*), the half ester, 2-fluoro-2,2-dinitroethyl fumarate, I, formed preferentially at moderate temperatures; the bis ester, bis(2-fluoro-2,2-dinitroethyl) fumarate, II, could be obtained only after prolonged heating at 60° C. In contrast, II was prepared in 84%