creasing solvent viscosity (Table X). We conclude from these results that cage disproportionation also occurs during the decomposition of NOON. Therefore, the amount of cage return calculated from our viscosity data on NOON is too high.[25]

Conclusion.—Thus we conclude that the viscosity test gives the "correct" answer for all the compounds which we have studied. However, for peroxides such as Bz_2O_2 which undergo a very small amount of cage return, the viscosity test may not always be capable of distinguishing one-bond from multi-bond scission.

Experimental Section

Hydrocarbons.—Technical grade alkanes from Phillips Petroleum Co. were purified as previously described.[5b]

Radical Scavengers.—Triply sublimed iodine from W. H. Curtin and Co. was used without further purification. Galvinoxyl was synthesized by the procedure of Kharasch and Joshi.[26] 4-Methyl-1-cyclohexene from Aldrich Chemical Co. was used without further purification. Styrene (Aldrich) was washed with 10% sodium hydroxide and water, dried, and distilled three times under reduced pressure.

Diaroyl Peroxide.—Benzoyl peroxide (Bz_2O_2) (Lucidol) was recrystallized several times from CCl_4 and methanol.

***tert*-Butyl Peroxy Esters.**—*tert*-Butyl peroxyacetate (TAc) and *tert*-butyl peroxyisobutyrate (TiBu), Lucidol, were distilled under reduced pressure at 25°. *tert*-Butyl peroxypropionate (TPr) was prepared by the method of Bartlett and Hiatt[19a] for TAc. A 75% solution of *tert*-butyl peroxypivalate (TPiv) in mineral spirits was purchased from Lucidol. The boiling points of the peroxy ester and the solvent were too close to allow separation by distillation. Chromatography, three passages, on Woelm neutral alumina grade 1, and with hexane as eluent, gave about 10% of 91% pure peroxy ester. The mineral spirits were eluted from the column very shortly before the peroxy ester. *tert*-Butyl peroxybenzoate (TBz), 98% pure (Lucidol), was used without further purification. Di-*tert*-butyl peroxyoxalate (TOx) was prepared by the method of Bartlett, Benzing, and Pincock.[27] The compound was recrystallized from pentane at −78°. (This compound is susceptible to detonation.) The peroxy esters TPr, TiBu, and TPiv were analyzed by iodometric titration.[28]

Dialkyl Peroxides.—*tert*-Butyl peroxide (TOOT), Lucidol, was used without further purification. *n*-Butyl peroxide (NOON) was prepared by the method of Mosher, *et al.*[29] *sec*-Butyl peroxide (SOOS) was synthesized by the method of Pryor and coworkers.[30]

Determination of CO_2 from Homolysis of Peroxy Esters.—Round-bottom ampoules (25 ml, Kontes) with two sealed tip side arms, 7 × 100 mm, were used as reaction vessels. The peroxy ester solution and a Teflon stir bar were introduced into the ampoule through its 10 × 70 mm neck, which was connected to a vacuum pump during the degassing procedure and thereafter was sealed off. The sealed ampoules were immersed in a constant-temperature bath and after complete reaction, the CO_2 was measured by absorption on Ascarite, KOH on asbestos (A. H. Thomas Co.) by the method of Shine and coworkers.[8b]

Procedure for Kinetic Runs.—We have used three methods for obtaining rate constants for homolysis of radical initiators: direct observance of initiator disappearance, first-order disappearance of scavenger, or zero-order disappearance of scavenger. These methods have been described previously,[5b] and the raw data were treated by a computer program to obtain a least squares fit of the data to the applicable rate law. Tables III, IV, and IX indicate the method used to find the rate constant for each peroxy compound. Our estimate of the accuracy of the rate constants is ±6% as determined from the probable error in each rate constant and the random variation in k_{obsd} with solvent viscosity for the multi-bond initiators in Table IV.

Registry No.—Benzoyl peroxide, 94-36-0; TAc, 107-71-1; TPr, 14206-05-4; TiBu, 109-13-7; TPiv, 927-07-1; TBz, 614-45-9; TOx, 1876-22-8; Ac_2O_2, 110-22-5; NOON, 3849-34-1; TOOT, 110-05-4; SOOS, 4715-28-0.

(25) (a) β Scission of the *n*-BuO· radical to formaldehyde and a propyl radical is considered negligible, since no β scission occurs for the *t*-BuO· radical, and both reactions have the same activation energy (13 kcal/mol) and preexponential (~10^{14} sec^{-1}) for β scission.[25b] The other decomposition mode of the *n*-BuO· radical to form a hydrogen atom and butyraldehyde will occur with even less probability.[25b] (b) P. Gray, R. Shaw, and J. C. J. Thynne in "Progress in Reaction Kinetics," Vol. 4, G. Porter, Ed., Pergamon Press, Oxford, 1967, pp 92–93.

(26) M. S. Kharasch and B. S. Joshi, *J. Org. Chem.*, **22**, 1435 (1957).

(27) P. D. Bartlett, E. P. Benzing, and R. E. Pincock, *J. Amer. Chem. Soc.*, **82**, 1762 (1960).

(28) L. S. Silbert and D. Swern, *Anal. Chem.*, **30**, 385 (1958).

(29) F. Welch, H. R. Williams, and H. S. Mosher, *J. Amer. Chem. Soc.*, **77**, 551 (1955).

(30) W. A. Pryor, D. M. Huston, T. R. Fiske, T. L. Pickering, and E. Ciuffarin, *ibid.*, **86**, 4237 (1964).

The Synthesis and Properties of Phosgene Phenylhydrazones

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Methods for the synthesis of phosgene phenylhydrazones, a new group of imidoyl chlorides, are described. Chlorination of various 2,3,4-pentanetrione 3-phenylhydrazones gave ring-substituted 1,1-dichloro-1-phenylazo-2-propanones that were readily hydrolyzed to the corresponding phosgene phenylhydrazones. Chlorination of glyoxylic acid 2-[(2,4,6-trichlorophenyl)hydrazone] (**19**) and formaldehyde (*p*-nitrophenyl) hydrazone (**23**) gave phosgene (2,4,6-trichlorophenyl)hydrazone (**10a**) and phosgene (2-chloro-4-nitrophenyl)hydrazone (**26**), respectively. Phosgene phenylhydrazones react relatively slowly with nucleophilic reagents with displacement of both acid chloride substituents; products formed by displacement of only one chlorine atom were not detected.

The chemistry of imidoyl halides has received considerable attention in the past and has recently been reviewed by Ulrich.[1] In the course of studies on the chlorination of phenylhydrazones we have discovered a new group of imidoyl chlorides, the phosgene phenylhydrazones (**2**); the preparation and properties of these compounds are detailed herein.

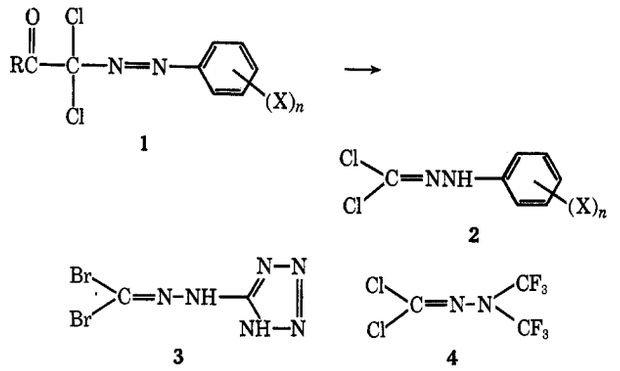
While synthesis of the carbonyl halide hydrazones **3**[2] and **4**[3] and preparation of a variety of carbonyl halide azines have been described,[2,4] no phosgene phenylhydrazone had been reported prior to our description of phosgene (2,4,6-trichloro-*m*-tolyl)hydrazone, which was prepared by refluxing ethyl dichloro[(2,4,6-tri-

(1) H. Ulrich, "The Chemistry of Imidoyl Halides," Plenum Press, New York, N. Y., 1968.

(2) J. Thiele, *Justus Liebigs Ann. Chem.*, **303**, 57 (1898).

(3) R. C. Dobbie and H. J. Emeleus, *J. Chem. Soc. A*, 933 (1966).

(4) (a) H. Reimlinger, *Chem. Ber.*, **97**, 3505 (1964); (b) R. A. Mitsch and P. H. Ogden, *J. Org. Chem.*, **31**, 3833 (1966); (c) F. L. Scott and D. A. Cronin, *Chem. Ind. (London)*, 1757 (1964); (d) F. L. Scott, J. Donovan, and J. K. O'Halloran, *Tetrahedron Lett.*, 4079 (1970).



chloro-*m*-tolyl)azo]acetate (general formula **1**, R = OC_2H_5) in acetic acid for 4 hr.[5] This reaction, a new example of the Japp–Klingemann reaction,[6] may alternately be effected at room temperature by treating the azo ester with 1 equiv of morpholine in methanol.

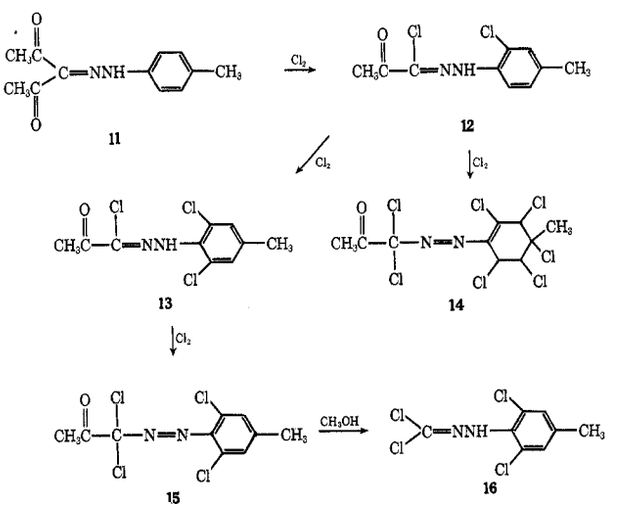
The most convenient synthesis of phosgene phenylhydrazones found to date is a modification of this method. The hitherto unreported azo ketones of structure **1** (R = CH_3), prepared by chlorination of 2,3,4-pentanetrione 3-phenylhydrazones, readily undergo Japp–Klingemann cleavage to phosgene phenylhydrazones when heated in methanol or when chromatographed on silica gel; azo esters of structure **1** are stable under these reaction conditions. Thus 2,3,4-pentanetrione 3-(*o*-tolylhydrazone) (**5**), prepared from 2,4-pentanedione and *o*-tolyldiazonium chloride, reacted in chloroform with 3 molar equiv of chlorine to give pyruvoyl chloride 1-[(4,6-dichloro-*o*-tolyl)hydrazone][7] (**6**) and with excess chlorine to give 1,1-dichloro-1-[(4,6-dichloro-*o*-tolyl)azo]-2-propanone (**7**). Compound **7**, an orange oil, decomposed with gas evolution on attempted distillation at reduced pressure; the structure of the crude product (>90% pure) was supported by nmr and ir spectra (no NH absorption, carbonyl band at 1735 cm^{-1}).[8] When **7** was heated in methanol, or treated with 1 equiv of morpholine in methanol, phosgene (4,6-dichloro-*o*-tolyl)hydrazone (**8**) was obtained (71% yield from **5**).

A disadvantage of this synthetic method is that a pentanetrione phenylhydrazone may give on chlorination and subsequent Japp–Klingemann cleavage mixtures of ring-chlorinated azo ketones (**1**) and phosgene phenylhydrazones. For example, 2,3,4-pentanetrione 3-(phenylhydrazone) gave on chlorination a mixture of azo ketones that decomposed when chromatographed on silica gel to a separable mixture of phosgene (2,4,6-trichlorophenyl)hydrazone (**10a**), phosgene (2,4-dichlorophenyl)hydrazone (**10b**), and phosgene (*p*-chlorophenyl)hydrazone (**10c**).

A mixture of products was also obtained on chlorination of 2,3,4-pentanetrione 3-(*p*-tolyhydrazone) (**11**) and the yield of phosgene (2,6-dichloro-*p*-tolyl)hydrazone (**16**) was low (37%). A major by-product in the reaction was found to be **14** and, using limited amounts of chlorine, the reaction was shown to proceed according to Scheme I; formation of a perchlorinated product related to **14** during phenylhydrazone chlorination was recently reported.[5]

Pentanetrione phenylhydrazones may also be brominated to afford carbonyl bromide phenylhydrazones.

SCHEME I



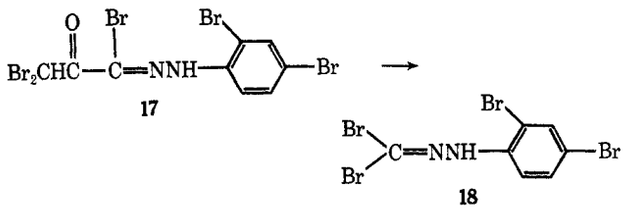
(5) M. W. Moon, *J. Org. Chem.*, **37**, 386 (1972); an alternate name for phosgene (2,4,6-trichloro-*m*-tolyl)hydrazone is (2,4,6-trichloro-*m*-toluidino)-imidocarbonyl chloride.

(6) R. R. Phillips, *Org. React.*, **10**, 143 (1959); azo compounds previously known to undergo the Japp–Klingemann reaction all have at least two unsaturated groups (*e.g.*, ketone, ester, or nitrile) attached to the α-carbon atom.

(7) Pyruvoyl chloride 1-phenylhydrazones have previously been obtained by chlorination of 2,3,4-pentanetrione 3-phenylhydrazones; see F. D. Chattaway and D. R. Ashworth, *J. Chem. Soc.*, 939 (1934).

(8) Related compounds have recently been shown to be azo compounds and not *N*-chloro compounds; see ref 5 and M. W. Moon, *J. Org. Chem.*, **37**, 383 (1972).

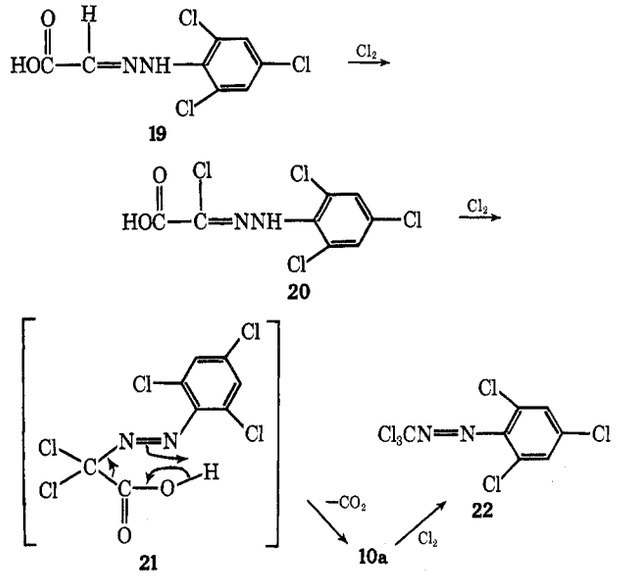
Thus **9** reacted with bromine to give dibromopyruvoyl bromide (2,4-dibromophenyl)hydrazone (**17**)[9] and this was treated with *N*-bromosuccinimide in methanol, giving carbonyl bromide (2,4-dibromophenyl)hydrazone (**18**).



17 **18**

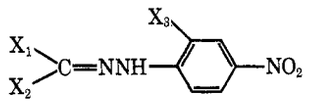
Phosgene phenylhydrazones may also be prepared by chlorination of glyoxylic acid phenylhydrazones and formaldehyde phenylhydrazones. These alternate syntheses have the disadvantage that chlorination gives the phosgene phenylhydrazones directly and these can react further with chlorine to give azo compounds, particularly when acetic acid is used as the reaction solvent.

Glyoxylic acid 2-[(2,4,6-trichlorophenyl)hydrazone] (**19**) reacted with chlorine in acetic acid to give chloroglyoxylic acid 2-[(2,4,6-trichlorophenyl)hydrazone] (**20**)[10] and this was further chlorinated to phosgene (2,4,6-trichlorophenyl)hydrazone (**10a**), presumably by formation and *in situ* decomposition of the unstable azo acid **21**.[11] Partial chlorination of **10a** gave 1′,1′,1′,2,4,6-hexachlorobenzeneazomethane (**22**) as a by-product.



19 **20** **21** **10a** **22**

Phosgene (2-chloro-4-nitrophenyl)hydrazone (**26**) was prepared by chlorination of formaldehyde (*p*-nitrophenyl)hydrazone (**23**) in chloroform. The chlorination proceeds sequentially *via* formyl chloride (*p*-nitrophenyl)hydrazone (**24**)[12] and formyl chloride (2-chloro-4-nitrophenyl)hydrazone (**25**). Formaldehyde phenylhydrazone, only recently characterized in its monomeric

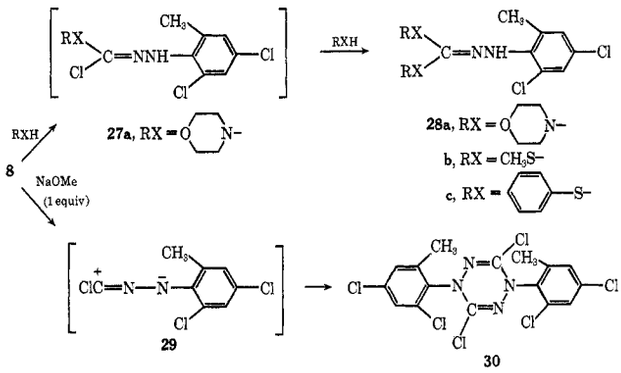


23, $X_1 = X_2 = X_3 = H$
24, $X_1 = Cl$; $X_2 = X_3 = H$
25, $X_1 = H$; $X_2 = X_3 = Cl$
26, $X_1 = X_2 = X_3 = Cl$

form,[13] reacted with 5 equiv of chlorine to give phosgene (2,4,6-trichlorophenyl)hydrazone (**10a**) (33%) and considerable amounts of unidentified tar.

The chemical properties of phosgene (4,6-dichloro-*o*-tolyl)hydrazone (**8**) are representative for the phosgene phenylhydrazones described in this report. This compound reacted slowly with morpholine at room temperature with formation of the bismorpholine derivative **28a**.[14] The monoadduct **27a** was not detected either when the reaction was carried out using limited amounts of morpholine, or using excess morpholine and a short reaction period. When **8** was treated with the sodium salts of thiophenol or methanethiol in methanol the products again were bisadducts, **28b** and **28c**, respectively. A complex mixture was obtained when a solution of **8** in tetrahydrofuran was treated with 1 equiv of sodium methoxide. From the highly colored reaction mixture **30** was isolated in low yield; this product can arise by elimination of hydrogen chloride from **8** followed by dimerization of the resulting dipolar intermediate **29** (Scheme II).

SCHEME II



29 **30**

The low reactivity of the phosgene phenylhydrazones contrasts with the properties of the related imidoyl chloride, *N*-phenyl imidocarbonyl chloride ($Cl_2C{=}N{-}C_6H_5$), which is highly reactive and readily reacts with nucleophiles with displacement of either one or both of the chlorine atoms.[15]

Experimental Section

Mass spectra were recorded at 70 eV on an Atlas CH4 spectrometer. Other analytical and chlorination procedures are as described in ref 8, Experimental Section.

Phosgene (2,4,6-Trichloro-*m*-tolyl)hydrazone.—Morpholine (0.87 g, 0.01 mol) was added to a solution of methyl dichloro[(2,4,6-trichloro-*m*-tolyl)azo]acetate (3.65 g, 0.01 mol) in methanol (20 ml). After 2 hr the solution was cooled to −10°

(9) F. D. Chattaway and R. G. Lye, *Proc. Roy. Soc., Ser. A*, **137**, 489 (1932).

(10) F. D. Chattaway and F. G. Daldy, *J. Chem. Soc.*, 2759 (1928).

(11) Related azo acids decompose spontaneously: see G. Favrel, *Bull. Soc. Chim. Fr.*, **41**, 1494 (1927).

(12) For an alternate synthesis of **24** see R. Huisgen and H. J. Koch, *Justus Liebigs Ann. Chem.*, **591**, 200 (1955).

(13) C. H. Schmidt, *Chem. Ber.*, **103**, 986 (1970).

(14) Products related to **28a** have been prepared by alternate routes. See (a) H. E. Neubauer, M. Seefelder, and H. Widinger, *Chem. Ber.*, **97**, 1232 (1964); (b) F. Runge, A. El-Hewehi, H. J. Renner, and E. Taeger, *J. Prakt. Chem.*, **11**, 284 (1960).

(15) W. R. Smith, *J. Amer. Chem. Soc.*, **16**, 372 (1894).

and the precipitate of phosgene (2,4,6-trichloro-*m*-tolyl)hydrazone (1.82 g, mp 35–37°) was filtered off; ir, nmr, and tlc of the product were identical with those of an authentic sample.[5]

2,3,4-Pentanetrione 3-(*o*-Tolylhydrazone) (5).—A solution of sodium nitrite (345 g, 5.0 mol) in water (800 ml) was added over 10 min to a stirred mixture of *o*-toluidine (535 g, 5.0 mol), concentrated hydrochloric acid (1.1 l., 11.0 mol), and water (1 l.) maintained at 0°. Sodium acetate trihydrate (680 g, 5.0 mol) in water (1.5 l.) was added to the reaction mixture. A cooled solution of 2,4-pentanedione (500 g, 5.0 mol) and sodium hydroxide (200 g, 5.0 mol) in 3 l. of 50% aqueous ethanol was then added rapidly to the reaction solution. After 10 min the precipitate that had formed was filtered off, washed well with water, washed further with methanol (4 l.), and air dried to give 784 g of 2,3,4-pentanetrione-3-(*o*-tolylhydrazone), mp 114–117°. Recrystallization of a sample from methanol and then ethyl acetate gave the analytical sample, mp 115–117°.

Anal. Calcd for $C_{12}H_{24}N_2O_2$: C, 66.03; H, 6.47; N, 12.84. Found: C, 65.92; H, 6.34; N, 13.03.

Pyruvoyl Chloride 1-[(4,6-Dichloro-*o*-tolyl)hydrazone] (6).—Chlorine (137 ml, 3.0 mol) was added over 10 min to a stirred solution of 2,3,4-pentanetrione 3-(*o*-tolylhydrazone) (218 g, 1.0 mol) in chloroform (1 l.) at −50°. The solution was allowed to warm to −20° during the addition and was then held at 15° for 30 min. Evaporation of the solvent under reduced pressure gave a solid that was recrystallized from methanol to give 188 g of **6**, mp 95–99°. A sample was recrystallized from methanol and finally ethyl acetate for analysis: mp 100–101.5°; ir (Nujol) 1685 cm^{-1} (C=O); nmr ($CDCl_3$) δ 2.43 (s, 3, CH_3), 2.50 (s, 3, CH_3), 7.12 (d, 1, J = 2 Hz, ArH), 7.23 (d, 1, J = 2 Hz, ArH), and 8.60 (s, 1, NH).

Anal. Calcd for $C_{10}H_9Cl_3N_2O$: C, 42.96; H, 3.24; Cl, 38.05; N, 10.02. Found: C, 43.17; H, 3.43; Cl, 38.19; N, 9.75.

1,1-Dichloro-1-[(4,6-dichloro-*o*-tolyl)azo]-2-propanone (7).—Chlorine (350 ml, 7.6 mol) was slowly added to a stirred, cooled solution of 2,3,4-pentanetrione 3-(*o*-tolylhydrazone) (279 g, 1.28 mol) in chloroform (1.25 l.). After addition of the chlorine was complete, the reaction solution was held at room temperature for 2 hr. The chloroform was then removed by evaporation to give **7** as an orange oil having the following properties: ir (film) 1735 cm^{-1} (C=O); nmr ($CDCl_3$) δ 2.30 (s, 3, CH_3), 2.50 (s, 3, CH_3), 7.13 (d, 1, J = 2 Hz), ArH) and 7.35 (d, 1, J = 2 Hz); λ_{max}^{hexane} 235 mμ (ϵ 7000), 295 (7950), and 418 (365).

Phosgene (4,6-Dichloro-*o*-tolyl)hydrazone (8). Method A.—The total product **7** from the above reaction was dissolved in methanol (500 ml) and was heated to 40° for 15 min. The solution was then cooled to −10° and the precipitate of **8** (157 g, mp 57–59°) was filtered off and washed with methanol. A further crop of **8** (65 g, mp 55–57°) formed when the methanolic mother liquors were allowed to stand at room temperature for 7 days. An aliquot was recrystallized twice from petroleum ether (bp 30–60°) to give the analytical sample: mp 57.5–59.5°; nmr ($CDCl_3$) δ 2.38 (s, 3, CH_3), 7.08 (d, 1, J = 2 Hz, ArH), 7.21 (d, 1, J = 2 Hz, ArH), and 7.66 (s, 1, NH).

Anal. Calcd for $C_8H_6Cl_4N_2$: C, 35.33; H, 2.22; Cl, 52.15; N, 10.30. Found: C, 35.60; H, 2.25; Cl, 51.99; N, 10.25.

Method B.—Morpholine (87 ml, 1.0 mol) was slowly added to a solution of compound **7** prepared as described earlier from 218 g of 2,3,4-pentanetrione 3-(*o*-tolylhydrazone) in methanol (1 l.). The temperature of the reaction solution rose to 50° during the addition. After cooling to 0°, 192 g (71%) of **8** was filtered off, mp 57–59°.

Chlorination of 2,3,4-Pentanetrione 3-(Phenylhydrazone) (9).—Chlorine (56 ml, 1.2 mol) was added to a cooled solution of 2,3,4-pentanetrione 3-phenylhydrazone[16] (40.8 g, 0.2 mol) in chloroform (400 ml). After 18 hr at room temperature the reaction solution was evaporated to an oil and hexane (100 ml) was added. The precipitate (18.6 g, a mixture of pyruvoyl chloride phenylhydrazones) that formed was filtered off and the hexane solution was chromatographed on silica gel (1500 g). Elution with hexane (4 l.) gave 8.2 g of phosgene (2,4-dichlorophenyl)hydrazone (**10b**). Two recrystallizations from petroleum ether gave the analytical sample: mp 59–60°; nmr ($CDCl_3$) δ 7.20 (m, 3, ArH) and 7.90 (s, 1, NH); mass spectrum m/e for ^{35}Cl (rel intensity, number of chlorine atoms in ion) 256 (71, 4), 160 (100, 2), 159 (71, 2), and 133 (71, 2).

Anal. Calcd for $C_7H_4Cl_4N_2$: C, 32.59; H, 1.56; N, 10.86. Found: C, 32.55; H, 1.60; N, 10.86.

Further elution with 2 l. of benzene–hexane (1:3) gave 4.1 g of phosgene (2,4,6-trichlorophenyl)hydrazone (**10a**). Recrystallization twice from petroleum ether gave the analytical sample: mp 29–30°; nmr ($CDCl_3$) δ 7.25 (s, 2, ArH) and 7.49 (s, 1, NH).

Anal. Calcd for $C_7H_3Cl_5N_2$: C, 28.75; H, 1.03; N, 9.58. Found: C, 28.88; H, 0.98; N, 9.64.

Continued elution with the same solvent gave 1.1 g of phosgene (*p*-chlorophenyl)hydrazone (**10c**). Recrystallization from Skellysolve B gave the analytical sample: mp 50–54°; nmr ($CDCl_3$) δ 6.96 (d, 2, J = 9 Hz, ArH), 7.27 (d, 2, J = 9 Hz, ArH), and 7.48 (s, 1, NH); mass spectrum m/e for ^{35}Cl (rel intensity, number of chlorine atoms in ion) 222 (13, 3), 187 (3, 2), 152 (7, 1), 126 (80, 1), and 125 (100, 1).

Anal. Calcd for $C_7H_5Cl_3N_2$: C, 37.61; H, 2.26; N, 12.54. Found: C, 37.99; H, 2.44; N, 12.37.

Pyruvoyl Chloride 1-[(2-Chloro-*p*-tolyl)hydrazone] (12).—To a stirred solution of 2,3,4-pentanetrione 3-(*p*-tolylhydrazone)[17] (55.5 g, 0.25 mol) in chloroform at −40° was added chlorine (28 ml, 0.55 mol). After 15 min at −40° the solvent was removed under reduced pressure and the residual oil was crystallized from hexane (200 ml) to give 38.5 g (63%) of **12**, mp 100–102°. Recrystallization from hexane gave the analytical sample: mp 102–104°; ir (Nujol) 1690 cm^{-1} (C=O).

Anal. Calcd for $C_{10}H_{10}Cl_2N_2O$: C, 49.00; H, 4.11; Cl, 28.93; N, 11.43. Found: C, 49.10; H, 4.04; Cl, 28.81; N, 11.22.

Pyruvoyl Chloride 1-[(2,6-Dichloro-*p*-tolyl)hydrazone] (13).—Chlorine (50 ml, 1.1 mol) was added to a solution of 2,3,4-pentanetrione 3-(*p*-tolylhydrazone)[17] (43.6 g, 0.2 mol) in methylene chloride (250 ml). The solution was held at −30° for 1 hr and the methylene chloride was then removed. The residual oil was crystallized from 120 ml of hexane–ethyl acetate (5:1) to give 15.1 g of pyruvoyl chloride 1-[(2,6-dichloro-*p*-tolyl)hydrazone]. Two recrystallizations from hexane–ether gave the analytical sample: mp 93–95°; nmr ($CDCl_3$) δ 2.30 (s, 3, CH_3), 2.48 (s, 3, CH_3), 7.20 (s, 2, ArH), and 8.44 (s, 1, NH).

Anal. Calcd for $C_{10}H_9Cl_3N_2O$: C, 42.96; H, 3.24; Cl, 38.04; N, 10.08. Found: C, 42.64; H, 3.18; Cl, 38.69; N, 9.81.

The mother liquor from the original crystallization was evaporated to an oil and this was dissolved in benzene–hexane (1:1) and chromatographed on silica gel (800 g). The column was eluted with 6 l. of benzene–hexane (1:1), the eluate being discarded. Continued elution with the same solvent mixture gave 9 g of **14**. The compound was recrystallized several times from hexane to give the analytical sample: mp 114–117°; ir (Nujol) 1710 cm^{-1} (C=O); λ_{max}^{hexane} 239 mμ (ϵ 17,500) and 265 (inflection, 3400); nmr δ 2.10 (s, 3, CH_3) and 2.69 (s, 3, CH_3) with cyclohexene ring protons at 4.85 (d, 1, J = 7 Hz), 5.04 (d, 1, J = 7 Hz), and 5.42 (s, 1).

Anal. Calcd for $C_{10}H_9Cl_7N_2O$: C, 28.50; H, 2.15; Cl, 58.90; N, 6.65. Found: C, 28.52; H, 2.32; Cl, 59.46; N, 6.99.

Phosgene (2,6-Dichloro-*p*-tolyl)hydrazone (16).—Chlorine (100 ml, 2.2 mol) was passed into a solution of 2,3,4-pentanetrione 3-(*p*-tolylhydrazone) (30 g, 0.14 mol) in chloroform (300 ml). After 24 hr excess chlorine and the chloroform were removed by evaporation and the residual oil was chromatographed on silica gel. Elution with benzene–hexane (1:9) gave 13.9 g of phosgene (2,6-dichloro-*p*-tolyl)hydrazone. The crystalline product was recrystallized from methanol and finally from hexane to give the analytical sample: mp 52–54°; nmr ($CDCl_3$) δ 2.25 (s, 3, CH_3), 7.12 (s, 2, ArH), and 7.47 (s, 1, NH).

Anal. Calcd for $C_8H_6Cl_4N_2$: C, 35.33; H, 2.22; Cl, 52.15; N, 10.30. Found: C, 35.46; H, 2.31; Cl, 51.89; N, 10.26.

Chlorination of Pyruvoyl Chloride (2,6-Dichloro-*p*-tolyl)-hydrazone (13).—Chlorine (10 ml, 0.22 mol) was added to a stirred solution of **13** (5 g, 0.018 mol) in chloroform (50 ml). The resulting solution was stirred at room temperature for 2 hr and the chloroform was then evaporated. The product was identified as **15** from its nmr spectrum: nmr ($CDCl_3$) δ 2.33 (s, 3, CH_3), 2.47 (s, 3, CH_3), and 7.18 (s, 2, ArH). The compound decomposed when heated in methanol to give phosgene (2,6-dichloro-*p*-tolylhydrazone) as the sole product.

Carbonyl Bromide (2,4-Dibromophenyl)hydrazone (18).—A mixture of dibromopyruvoyl bromide (2,4-dibromophenyl)-

(16) C. Beyer and L. Claisen, *Chem. Ber.*, **21**, 1697 (1888).

(17) G. Bülow and W. Spengler, *ibid.*, **58**, 1375 (1928).

hydrazone[8] (53 g, 0.1 mol), *N*-bromosuccinimide (50 g, 0.28 mol), chloroform (250 ml), and methanol (250 ml) was stirred at room temperature for 30 min. The solvents were then evaporated and the residue was extracted with hexane. The hexane-soluble fraction was chromatographed on silica gel. Elution with hexane gave 6.9 g of carbonyl bromide (2,4-dibromophenyl)hydrazone as a crystalline solid. Recrystallization from ethyl acetate and finally from hexane gave the analytical sample: mp 89–91°; nmr ($CDCl_3$) δ 7.26 (m, 2, ArH), 7.53 (d, 1, J = 2 Hz, ArH), and 8.08 (s, 1, NH).

Anal. Calcd for $C_7H_4Br_4N_2$: C, 19.29; H, 0.92; Br, 73.35; N, 6.43. Found: C, 19.38; H, 0.91; Br, 73.06; N, 6.38.

Chlorination of Chloroglyoxylic Acid 2-[(2,4,6-Trichlorophenyl)hydrazone] (20).—To a stirred suspension of chloroglyoxylic acid 2-[(2,4,6-trichlorophenyl)hydrazone] (15.0 g, 0.05 mol) in acetic acid (100 ml) was added chlorine (5 ml, 0.11 mol). The solid dissolved after 4 hr; after 6 hr the acetic acid was removed by evaporation at reduced pressure. The residual oil was dissolved in Skellysolve B and was chromatographed on silica gel. Elution of the column with Skellysolve B gave 3.2 g of 1′,1′,1′,2,4,6-hexachlorobenzeneazomethane (**22**) as the first fraction. The product, an orange oil, was analyzed after evaporation at 100° (10 mm): nmr ($CDCl_3$) singlet absorption at δ 7.45; mass spectrum m/e for ^{35}Cl (rel intensity, number of chlorine atoms in ion) 289 (16, 5), 207 (66, 3), and 179 (100, 3).

Anal. Calcd for $C_7H_2Cl_6N_2$: C, 25.72; H, 0.62; N, 8.57. Found: C, 26.44; H, 1.04; N, 8.43.

Continued elution of the column gave 7.5 g of phosgene (2,4,6-trichlorophenyl)hydrazone identical with the sample of **10a** prepared earlier.

Chlorination of Formaldehyde Phenylhydrazone.—To a stirred solution of formaldehyde phenylhydrazone (5.5 g, 0.05 mol) in chloroform (100 ml) at −40° was added chlorine (11.5 ml, 0.25 mol) over a period of 10 min. The violet-colored reaction solution was allowed to warm to room temperature and, after an additional 30 min, was evaporated. The product was chromatographed on silica gel to give 4.4 g (33%) of phosgene (2,4,6-trichlorophenyl)hydrazone identical with the sample previously prepared by nmr, ir, and tlc analysis.

Formyl Chloride (*p*-Nitrophenyl)hydrazone (24)—*tert*-Butyl hypochlorite (9.0 ml, 0.075 mol) was added to a stirred suspension of formaldehyde (*p*-nitrophenyl)hydrazone[18] (8.2 g, 0.05 mol) in chloroform (200 ml). The temperature of the solution rose to about 45° and a homogeneous solution was obtained within 5 min. The solution was then evaporated and the solid product was recrystallized from benzene–hexane to give 4.5 g of formyl chloride (*p*-nitrophenyl)hydrazone, mp 135–138°. Recrystallization from methanol and finally benzene–hexane gave the analytical sample: mp 140–143°; nmr ($CDCl_3$) δ 6.96 (s, 1, N=CHCl), 7.13 (d, 2, J = 9 Hz, ArH), 8.18 (d, 2, J = 9 Hz, ArH), and 8.45 (s, 1, NH).

Anal. Calcd for $C_7H_6ClN_3O_2$: C, 42.12; H, 3.03; Cl, 21.05; N, 17.77. Found: C, 42.38; H, 3.00; Cl, 20.94; N, 17.85.

Formyl Chloride (2-Chloro-4-nitrophenyl)hydrazone (25).—Chlorine (10 ml, 0.22 mol) was slowly added to a stirred suspension of formaldehyde (*p*-nitrophenyl)hydrazone (16.5 g, 0.1 mol) in chloroform (200 ml) at −40°. The solution was allowed to warm to room temperature. After 1 hr the reaction mixture was filtered to remove insoluble tars and the chloroform was evaporated. The residue was crystallized from methanol to give **25**, mp 122–125°. The product was recrystallized from ethyl acetate to afford 7.8 g of product: mp 124–126°; nmr ($CDCl_3$) δ 7.10 (s, 1, N=CHCl), 7.50 (d, 1, J = 8.5 Hz, ArH), 8.13 (d of d, 1, J = 2 and 8.5 Hz, ArH), 8.26 (d, 1, J = 2 Hz, ArH), and 8.75 (s, 1, NH).

Anal. Calcd for $C_7H_5Cl_2N_3O_2$: C, 35.92; H, 2.15; Cl, 30.30; N, 17.95. Found: C, 35.99; H, 2.39; Cl, 30.39; N, 17.67.

Phosgene (2-Chloro-4-nitrophenyl)hydrazone (26).—Chlorine (5 ml, 0.11 mol) was added to a stirred solution of formyl chloride (2-chloro-4-nitrophenyl)hydrazone (**25**, 5.3 g, 0.023 mol) in chloroform (100 ml) at 0°. After 3 hr the chloroform was removed, and the residue was dissolved in methanol and cooled to −10° to give 2.7 g of phosgene (2-chloro-4-nitrophenyl)-hydrazone, mp 96–102°. Recrystallization twice from hexane and finally from methanol gave the analytical sample: mp 102–104°; nmr ($CDCl_3$) δ 7.43 (d, 1, J = 8 Hz, ArH), 8.08 (d of d, 1, J = 2 and 8 Hz, ArH), 8.17 (d, 1, J = 2 Hz, ArH), and 8.30 (s, 1, NH).

Anal. Calcd for $C_7H_4Cl_3N_3O_2$: C, 31.31; H, 1.50; Cl, 39.62; N, 15.62. Found: C, 31.54; H, 1.66; Cl, 40.08; N, 15.63.

4,4′-Carbonyldimorpholine (4,6-Dichloro-*o*-tolyl)hydrazone (28a).—A mixture of phosgene (4,6-dichloro-*o*-tolyl)hydrazone (9 g, 0.03 mol) and morpholine (20 ml) in chloroform (50 ml) was allowed to stand at room temperature for 2 days. The chloroform solution was then washed well with water, dried over sodium sulfate, and evaporated. Skellysolve B was added to the residual oil and the crystalline product (10.1 g, mp 115–120°) was filtered off. It was recrystallized from ethyl acetate to give 6.9 g of **28a**, mp 128–131°. Recrystallization from methanol gave the analytical sample, mp 130–132°.

Anal. Calcd for $C_{16}H_{22}Cl_2N_4O_2$: C, 51.48; H, 5.94; Cl, 19.00; N, 15.01. Found: C, 51.70; H, 6.04; Cl, 19.09; N, 15.50.

Diphenyl (4,6-Dichloro-*o*-toluidino)dithioimidocarbonate (28c).—A solution of thiophenol (7.3 g, 0.066 mol) in 2 *N* sodium methoxide (33 ml) was added to a stirred solution of phosgene (4,6-dichloro-*o*-tolyl)hydrazone (9 g, 0.03 mol) in methanol. An oily layer separrated and this was extracted into benzene. The benzene extract was washed well with water, dried over sodium sulfate, and evaporated. The residual oil was dissolved in Skellysolve B and, after cooling to −10°, 7.6 g of **28c**, mp 33–35°, was filtered off. Recrystallization from Skellysolve B and finally petroleum ether gave the analytical sample, mp 35–37°.

Anal. Calcd for $C_{20}H_{16}Cl_2N_2S_2$: C, 57.27; H, 3.85; Cl, 16.90; N, 6.68; S, 15.28. Found: C, 57.42; H, 3.84; Cl, 16.68; N, 6.65; S, 15.30.

Dimethyl (4,6-Dichloro-*o*-toluidino)dithioimidocarbonate (28b).—A solution of phosgene (4,6-dichloro-*o*-tolyl)hydrazone (6.1 g, 0.02 mol) in chloroform (10 ml) was slowly added with stirring to 50 ml of a solution of sodium thiomethylate (18%) in methanol. The precipitate that formed was filtered off and dried to give 5.8 g of **28c**, mp 63–66°. Recrystallization from petroleum ether and finally from methanol gave the analytical sample, mp 65–67°.

Anal. Calcd for $C_{10}H_{12}Cl_2N_2S_2$: C, 40.68; H, 4.10; Cl, 24.02; N, 9.49; S, 21.72. Found: C, 40.51; H, 3.94; Cl, 23.97; N, 9.48; S, 21.37.

Preparation of 30.—To a stirred solution of phosgene (4,6-dichloro-*o*-tolyl)hydrazone (18 g, 0.066 mol) in a mixture of tetrahydrofuran (50 ml) and methanol (25 ml) was added 66 ml of 2 *N* sodium methoxide in methanol. After 15 min the dark reaction solution was evaporated, water was added, and the resulting solution was extracted into benzene. The benzene extract was dried, concentrated, and chromatographed on silica gel. Elution with benzene gave in the early fractions 1.3 g of **30**, mp 235–240°. Two recrystallizations from ethyl acetate gave the analytical sample: mp 245–248°; mass spectrum m/e for ^{35}Cl (rel intensity, number of chlorine atoms in ion) 468 (54, 6), 433 (5, 5), and 398 (10, 4).

Anal. Calcd for $C_{16}H_{10}Cl_6N_4$: C, 40.80; H, 2.14; N, 11.90. Found: C, 40.67; H, 2.26; N, 11.50.

Registry No.—**5,** 24756-03-4; **6,** 34387-69-4; **7,** 34387-70-7; **8,** 34387-71-8; **10a,** 34387-72-9; **10b,** 34402-62-5; **10c,** 34387-73-0; **12,** 34387-74-1; **13,** 34387-75-2; **14,** 34387-76-3; **15,** 34387-77-4; **16,** 34387-78-5; **18,** 34387-79-6; **22,** 34387-80-9; **24,** 34387-81-0; **25,** 34387-82-1; **26,** 34387-83-2; **28a,** 34387-84-3; **28b,** 34387-85-4; **28c,** 34387-86-5; **30,** 34387-87-6; phosgene (2,4,6-trichloro-*m*-tolyl)hydrazone, 32974-73-5.

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(18) E. Bamberger, *Chem. Ber.*, **32**, 1807 (1899).