

Table IX. d-d Band Maximum (cm⁻¹) for Some Truly Square-Pyramidal Copper(II) Complexes

	d-d band max	chromo- phore	ref
[Cu(en) ₂ (NH ₃) ²⁻	17 400	CuN ₅	29
[Cu(Asp)bpy·H ₂ O]·3H ₂ O ^a	16 390	CuN ₃ O ₂	23b
[Cu(Ts-H ₁ gly)bpy·EtOH] ^a	16 400	CuN ₃ O ₂	30
[Cu(Asp)ImH]·2H ₂ O ^a	15 400	CuN ₂ O ₃	23a
K ₂ [Cu(Ts-H ₁ gly) ₂]	15 150	CuN ₂ O ₃	6
[Cu(Ts-H ₁ gly)(H ₂ O) ₃]	13 990	CuNO ₄	6
[Cu(Ts-α-H ₁ ala)(H ₂ O) ₂]·H ₂ O	13 650	CuNO ₄	this work

^a Asp²⁻ = aspartate dianion; Ts-H₁gly²⁻ = *N*-tosylglycinate dianion; bpy = 2,2'-bipyridine.

O(6)-H...O(4) 2.716 (5) Å is an intramolecular hydrogen bond. In the [PipdH₂]₂[Cu(Ts-α-H₁ala)₂]·H₂O complex (Figure 6) the piperidinium cation forms hydrogen bonds with coordinated and uncoordinated carboxylic oxygens. Possible hydrogen bonding and angles and contacts less than 3.5 Å, which complete the packing for all compounds are quoted in the supplementary material. In both structures no contacts between aromatic rings less than 3.6 Å were found.

Magnetic and Spectroscopic Results. The type 2 complexes (Table VIII) present room-temperature solid magnetic moments "normal" and typical of "magnetically dilute" complexes²⁵ and polycrystalline EPR spectra of axial type, suggesting an essentially d_{x²-y²} ground state, with g_{||} values consistent with the reported chromophores.²⁶⁻²⁸

The square-pyramidal [Cu(Ts-α-H₁ala)(H₂O)₂]·H₂O complex shows a d-d band maximum which correlates well with other CuN_xO_y (x + y = 5) chromophores^{6,23,29,30} Table IX), while the electronic spectra of the [Cu(Ts-α-H₁ala)₂]²⁻ complexes are typical of strictly square-planar compounds.⁶

In Table VIII are also reported the absorptions assigned to the most significant ligand functions of *N*-tosyl-α-alanine. By comparing these data with those of the type 1 complexes (Tables V

and VII) the main differences are observed in the NH and sulphonyl group spectral regions, as a consequence of the presence in type 2 complexes of a deprotonated nitrogen atom coordinated to the copper(II) ions.

Conclusions

The main conclusions to be drawn from this work are as follows: (1) The Cu²⁺-promoted amide deprotonation needs ligands containing a primary group. The carboxylic group of the *N*-protected amino acids, reported in ref 2-7, may act as primary ligating group only if the protecting group is a sulfonyl group in α position (*N*-tosyl-α-amino acids). For these ligands the amide hydrogen deprotonation in presence of Cu²⁺, occurs at pH ≥ 5, strongly anticipating their pK_A values (11-12)^{6,7}, with formation of a five-membered chelate ring involving in the metal ion coordination the carboxylate oxygen and the deprotonated sulfonamide nitrogen donor atoms.

(2) The similarity of the solid-state copper(II) complexes of *N*-tosylglycine⁶ and *N*-tosyl-α-alanine also suggests a parallelism in their solution behavior, supporting for the copper(II) ion-*N*-tosyl-α-alanine system in aqueous solution the statements of Sigel and Martin.²

(3) The shift of the carboxylic group in β-position, decreasing the acidity of the NH group (pK_A ~ 14), makes it ineffective in promoting amide deprotonation also in accordance with the lower stability of six-membered chelate ring compared to five-membered ones. This parallels the coordinative behavior of β-alaninamide with respect to that of glycineamide.²

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Registry No. I, 93923-32-1; II, 88764-97-0; III, 88390-92-5; Cu(Ts-α-ala)₂, 93923-28-5; Cu(Ts-β-ala)₂, 93923-29-6; K₂[Cu(Ts-α-H₁ala)₂], 93923-30-9; (MorfH₂)₂[Cu(Ts-α-H₁ala)₂], 93923-31-0; Cu(Ts-β-ala)₂·(MeImH)₂, 93942-83-7; Cu(Ts-β-ala)₂(PipdH)₂, 93923-33-2; Cu(Ts-β-ala)₂(MorfH)₂, 93923-34-3; Cu(Ts-α-ala)₂(ImH)₂, 88360-11-6; Cu(Ts-α-ala)₂(MeImH)₂, 93942-84-8.

Supplementary Material Available: Listings of atomic coordinates and thermal parameters of hydrogen atoms, anisotropic thermal parameters, complete bond distances and angles, possible hydrogen bonding and angles, intermolecular contacts less than 3.5 Å, weighted least-squares planes, observed and calculated structure factors for the reflections used in the refinements, elemental analyses, and experimental and calculated corrected molar susceptibilities (54 pages). Ordering information is given on any current masthead page.

Capture of Electron-Deficient Species with Aryl Halides. New Syntheses of Hypervalent Iodonium Ylides

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Abstract: We have demonstrated the aryl iodide capture of β-diketocarbenes, generated from the diazo compound by using rhodium(II) acetate, under very mild conditions. This is a useful general preparative method for iodonium ylides under non-hydroxylic conditions. The thermal, catalytic, and photochemical decompositions of various azides in the presence of aryl iodides were carried out. With highly reactive nitrenes, intramolecular rearrangement takes precedence over capture. In the case of *p*-toluenesulfonyl azide, thermolysis in the presence of aryl iodides requires conditions under which the iminoiodane is itself decomposed. The capture of oxene by iodobenzene is discussed. The application of these capture processes is discussed as a synthetic route to hypervalent ylides as well as on the basis of mechanism.

Recently a number of examples have appeared in the literature in which an electron-deficient species X (nitrene,¹ carbene,² or

oxene³) is transferred from a hypervalent iodine precursor (ArI=NSO₂C₆H₄-*p*-CH₃, ArI=C(CO₂R)₂, and ArI=O) to an

Table I. Iodonium Ylides Formed in $\text{Rh}_2(\text{OAc})_4$ Catalyzed Decomposition of 2-Diazo-1,3-diketones

iodonium ylide	time, h	temp, °C	yield, %
1	0.5	40–44	37
2	0.5	55–60	54
3	0.5	40–44	71
4	1	65–70	49
5	1	40–44	52

acceptor.⁴ These reactions conform formally to the forward direction of the hypothetical scheme

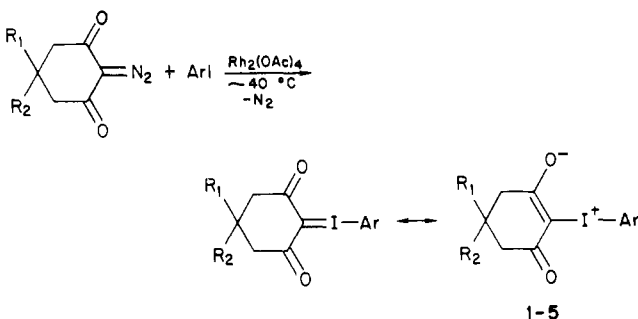


where A is an acceptor molecule for the electron-deficient species, ($\text{X}=\text{N}-\text{Ts}$, $\text{C}(\text{CO}_2\text{R})_2$, and O). Two cases may be delineated. In the first the electron-deficient species is transferred from $\text{ArI}=\text{X}$ directly to a substrate. An example of this is the oxidation of ketenes by $\text{C}_6\text{H}_5\text{I}=\text{O}$.⁴ In the second category, the electron-deficient species is transferred first to a metalloporphyrin or metal complex and subsequently to a second acceptor molecule. This is the case for $\text{C}_6\text{H}_5\text{I}=\text{O}^3$ and $\text{C}_6\text{H}_5-\text{I}=\text{NSO}_2\text{C}_6\text{H}_4-p-\text{CH}_3$.¹ For carbene transfer, the decomposition of iodonium ylides using copper catalysis may involve metalcarbenoid intermediates.²

We now report upon the *reverse of this process*, namely, the capture of electron-deficient species by aryl iodides.

The first examples are the aryl iodide capture of carbenes generated by the $\text{Rh}_2(\text{OAc})_4$ -catalyzed decomposition of various diazo- β -diketones.^{5,6} The diazo compound, either 2-diazo-cyclohexane-1,3-dione or 2-diazo-5,5-dimethylcyclohexane-1,3-dione, (1.5 mmol) is dissolved in the aryl iodide (24.5 mmol) and 5 mg of $\text{Rh}_2(\text{OAc})_4$ is added, and the reaction system is stirred at 40–44 °C for 0.5–1 h. After 20 min, during which time dinitrogen evolution occurs, iodonium ylides 1–5 crystallize out of solution (Table I).

Rhodium(II) acetate is clearly the catalyst of choice for carbene capture by aryl iodides. Recent examples of the use of rhodium(II) acetate in carbenoid-type reactions are the deoxygenation of epoxides by $\text{N}_2\text{C}(\text{CO}_2\text{CH}_3)_2\text{Rh}_2(\text{OAc})_4$.^{7a} Traditional copper ca-



- 1 $\text{R}_1, \text{R}_2 = \text{CH}_3$, $\text{Ar} = \text{C}_6\text{H}_5$
 2 $\text{R}_1, \text{R}_2 = \text{CH}_3$, $\text{Ar} = p\text{-CH}_3\text{OC}_6\text{H}_4$
 3 $\text{R}_1, \text{R}_2 = \text{H}$, $\text{Ar} = \text{C}_6\text{H}_5$
 4 $\text{R}_1, \text{R}_2 = \text{CH}_3$, $\text{Ar} = p\text{-ClC}_6\text{H}_4$
 5 $\text{R}_1, \text{R}_2 = \text{CH}_3$, $\text{Ar} = o\text{-CH}_3\text{C}_6\text{H}_4$

(1) Breslow, R.; Gellman, S. H. *J. Chem. Soc., Chem. Commun.* **1982**, 1400. Recently the intramolecular analogue of this reaction: Breslow, R.; Gellman, S. H. *J. Am. Chem. Soc.* **1983**, 105, 6728.

(2) (a) Hayasi, Y.; Okada, T.; Kawanishi, M. *Bull. Chem. Soc. Jpn.* **1970**, 43, 2506. (b) Adamsone, B. Y.; Neiland, O. *J. Org. Chem. USSR (Engl. Transl.)* **1980**, 729.

(3) (a) Groves, J. T.; Nemo, T. E.; Meyer, R. S. *J. Am. Chem. Soc.* **1979**, 101, 1032. (b) Lichtenberger, F.; Nastainczyk, W.; Ullrich, V. *Biochem. Biophys. Res. Commun.* **1976**, 70, 939. (c) Groves, J. T.; Kruper, W. J.; Nemo, T. E.; Meyer, R. S. *J. Mol. Catal.* **1980**, 7, 169.

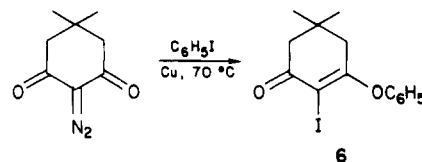
(4) Moriarty, R. M.; Gupta, S. C.; Hu, H.; Berenschot, D. R.; White, R. B. *J. Am. Chem. Soc.* **1981**, 103, 686.

(5) Doyle, M. P.; Tamblin, W. H.; Bagheri, V. *J. Org. Chem.* **1981**, 46, 5094. McKervey, M. A.; Ratanakul, P. *Tetrahedron Lett.* **1982**, 2509. Demonceau, A.; Noels, A. F.; Hubert, A. J.; Teyssie, P. *J. Chem. Soc., Chem. Commun.* **1981**, 688. Salzmann, T. N.; Ratcliffe, R. W.; Christensen, B. G.; Bouffard, F. A. *J. Am. Chem. Soc.* **1980**, 102, 6161.

(6) Anciaux, A. J.; Hubert, A. J.; Noels, A. F.; Petiniat, N.; Teyssie, P. *J. Org. Chem.* **1980**, 45, 695.

talysis (we tried copper bronze, $\text{Cu}(\text{acac})_2$, and CuCl_2)⁸ requires higher temperatures and longer reaction times, causing rearrangement of the initially formed iodonium ylide. Thus, 2-diazo-5,5-dimethylcyclohexane-1,3-dione \rightarrow 2-iodo-3-phenoxy-5,5-dimethyl-2-cyclohexenone (6).⁹

Carbene capture by alkyl and aryl halides has been studied in detail.^{10,11} For example, CH_2 triplet abstracts deuterium from CDCl_3 , but CH_2 singlet abstracts a chlorine atom possibly via a transitory ylide $\text{H}_2\text{C}^+-\text{Cl}^+-\text{CDCl}_2$.¹² In the case of a tritiated



analogue, CHT, the same type of behavior was observed for the singlet and triplet states.¹³ Olah et al. reported the generation of methylene methylbromonium ylides as reaction intermediates in the hydrogen–deuterium exchange of the corresponding dimethylhalonium ions in deuterated sulfuric acid.¹⁴

Sheppard and Webster isolated halonium ylides from the thermolysis of dicyanodiazimidazole in chloro-, bromo-, and iodobenzene.¹⁵ Janulis and Arduengo isolated bromonium and chloronium ylides from the photolysis of diazotetrakis(trifluoromethyl)cyclopentadiene in bromo- and chlorobenzene, respectively; however, the iodonium ylide was not isolated because of its photolability.¹⁶

The reactions reported in Table I are of synthetic interest in that they extend the scope of methods available for iodonium ylide formation. The most generally applicable extant methods are the condensation of an active methylene compound with AuIO or use of acetic anhydride, the β -diketone, and AuIO .^{2a}

Part of the reason for studying the carbene–iodobenzene reaction was our goal of obtaining monocarbonyl iodonium ylides in connection with the hypervalent iodine hydroxylation of ketones.^{4,17} A β -diketone such as cyclohexane-1,3-dione upon reaction with $\text{C}_6\text{H}_5\text{IO}/\text{CH}_3\text{OH}$ and KOH yields the iodonium ylide, e.g., 3. A monocarbonyl compound such as acetophenone, under these conditions, yields the α -hydroxydimethylacetal (10) presumably via an intermediate, 8, analogous to 7, as occurs in the ylide route $7 \rightarrow 3$.

Dehydration of intermediate 8 would yield ylide 11; however, in fact, C–I (III) bond cleavage takes precedence ($8 \rightarrow 9$).

(7) Also: (a) Martin, M. G.; Ganem, B. *Tetrahedron Lett.* **1984**, 251. The extremely mild decomposition of cyclic α -diazoketones has been described^{7b} (McKervey, M. A.; Tuladhar, S. M.; Fiona Twohig, M. *J. Chem. Soc., Chem. Commun.* **1984**, 129).

(8) Kirmse, W. "Carbene Chemistry", 2nd ed.; Academic Press: New York, 1971; p 116.

(9) Neilands, O.; Vanag, G. *Proc. Acad. Sci. USSR (Engl. Transl.)* **1960**, 130, 19. Neilands, O.; Vanag, G.; Gudrinietse, E. *J. Gen. Chem. USSR (Engl. Transl.)* **1958**, 28, 1256.

(10) For a discussion of halonium ylides in carbene reactions see: Marchand, A. P.; Mac Brockway, N. *Chem. Rev.* **1973**, 74, 431.

(11) (a) Bailey, R. J.; Shechter, H. *J. Am. Chem. Soc.* **1974**, 96, 8116. (b) Reference 8, pp 442–447. (c) Pirkle, W. H.; Koser, G. F. *Tetrahedron Lett.* **1968**, 3959. (d) Pirkle, W. H.; Koser, G. F. *J. Am. Chem. Soc.* **1968**, 90, 3598.

(12) Iwamura, H.; Imahashi, Y.; Oki, M.; Kushida, K.; Satoh, S. *Chem. Lett.* **1974**, 259.

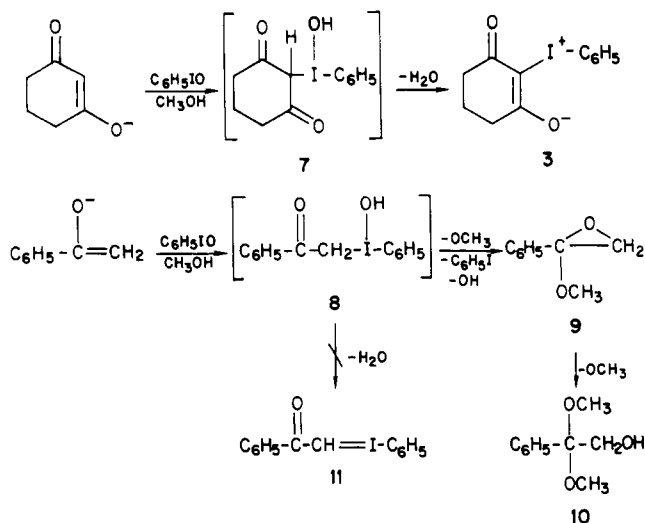
(13) Lee, P. S.-T.; Rowland, F. S. *J. Phys. Chem.* **1980**, 84, 3243.

(14) Olah, G. A.; Yamada, Y.; Spear, R. J. *J. Am. Chem. Soc.* **1975**, 97, 680. See also: Olah, G. A. "Halonium Ions", Wiley-Interscience: New York, 1975.

(15) Sheppard, W. A.; Webster, O. W. *J. Am. Chem. Soc.* **1973**, 95, 2695. In this paper these authors state erroneously that iodonium ylides have been prepared from diazoketones and aryl halides, giving as a reference the work of Hayasi et al.^{2a} Sheppard, W. A. U.S. Patent 3914247 (Cl. 260–309; CO7D), 21 Oct 1975; *Chem. Abstr.* **1976**, 84, 5955702.

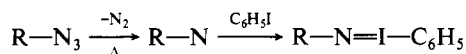
(16) Janulis, E. P., Jr.; Arduengo, A. J., III. *J. Am. Chem. Soc.* **1983**, 105, 3563.

(17) Moriarty, R. M.; Hu, H. *Tetrahedron Lett.* **1981**, 22, 2747. Moriarty, R. M.; Hu, H.; Gupta, S. C. *Tetrahedron Lett.* **1981**, 22, 1283. Moriarty, R. M.; John, L. S.; Du, P. C. *J. Chem. Soc., Chem. Commun.* **1981**, 641. Moriarty, R. M.; Hou, K.-C. *Tetrahedron Lett.* **1984**, 25, 691. Moriarty, R. M.; Prakash, O.; Freeman, W. A. *J. Chem. Soc., Chem. Commun.* **1984**, 927.

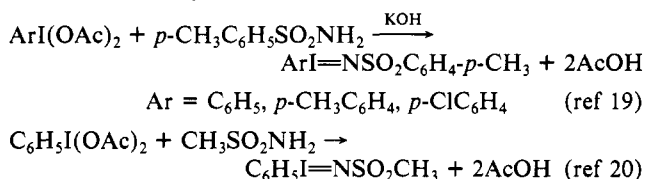


Thermolysis of diazoacetophenone in iodobenzene in the presence of $\text{Rh}_2(\text{OAc})_4$ and 3 equiv of CH_3OH did not yield **11** but only methyl phenylacetate. Presumably, intramolecular Wolff rearrangement is faster than bimolecular carbene capture. Similarly, thermolysis of $\text{C}_6\text{H}_5\text{COCN}_2\text{C}_6\text{H}_5$ in iodobenzene in the presence of $\text{Rh}_2(\text{OAc})_4$ yielded diphenylketene.

Next we investigated the possible reaction of a nitrene with iodobenzene to yield an iminoiodane



Some evidence exists in the literature for interaction between a nitrene and an appropriately situated halogen atom. For example the thermal decomposition of *o*-iodobenzoyl azide was found to be anomalous relative to other ortho-substituted derivatives.¹⁸ The possibility of bonding by the nitrene to the adjacent iodine atom was considered, but the authors note that the product probably decomposes at the temperature of the azide decomposition. These workers obtained *o*-iodobenzenesulfonamide from chromatography of thermolysate from *o*-iodobenzenesulfonyl azide. Hydrolysis of the intramolecular iminoiodane would yield this product. The only examples of isolable ylides of this type reported in the literature are sulfonyliminoiodanes.^{19,20}



Accordingly, we carried out the thermolysis of *p*-toluenesulfonyl azide in the presence of iodobenzene. This process occurs at 120 °C over a 15-h period. Under these conditions $p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{N}=\text{IC}_6\text{H}_5$ decomposes.²¹ In contrast to diazo thermolysis, no catalyst comparable to $\text{Rh}_2(\text{OAc})_4$ was found for azide decomposition. Thus, copper,²² copper bronze,²² $\text{Mo}(\text{CO})_6$, $\text{Ru}_3(\text{CO})_{12}$, PtCl_2 , CoCl_2 , $\text{Cr}(\text{CO})_6$, and CrCl_2 ²³ required elevated temperatures at which the iminoiodane itself decomposed to yield iodobenzene and *p*-toluenesulfonamide. The low temperature catalytic decomposition of sulfonyl azides remains an unsolved problem.

Azides which undergo thermolytic loss of dinitrogen at lower temperatures, in the presence of $\text{C}_6\text{H}_5\text{I}$, do so without attack on the aryl iodide ($p\text{-XC}_6\text{H}_4\text{CON}_3 \rightarrow p\text{-XC}_6\text{H}_4\text{N}=\text{C}=\text{O}$ ($\text{X} = \text{NO}_2$,

H , or CH_3O , 70 °C). Similar behavior was noted with other acyl azides. We would expect a low thermal stability for (acylimino)iodoarenes, and their intermediacy is indicated but not established in these experiments. The Hofmann rearrangement of amides to amines has been effected by using bis(trifluoroacetoxy)iodobenzene^{24a-c} as well as with iodosobenzene.^{24d} An (acylimino)iodobenzene would appear to be reasonable reaction intermediate in these transformations. Recently an attempt to synthesize (cyanoimino)iodobenzene in the reaction $\text{C}_6\text{H}_5\text{I}(\text{OAc})_2 + \text{NH}_2\text{CN} + 2\text{KOH} \rightarrow \text{NCN}=\text{IC}_6\text{H}_5$ failed presumably because of the instability of this product.²⁵ The iminoiodanes are less thermally stable than the corresponding ylides formed in the capture of sulfonylnitrenes by diaryl sulfides,²⁶ dialkyl sulfoxides,²⁷ triarylsulfines,²⁸ and triphenylphosphine.²⁹

A final point regards the use of "heavy atom" solvents such as ArI as promoters for intersystem crossing of nitrenes from the singlet-to-triplet state. Formation of an intermediary iminoiodane has not been discussed for this process and the present results point to the need to consider this possibility.^{30a,b}

The capture of oxene by aryl halides is somewhat more obscure than the analogous reaction with carbenes mainly because it is difficult to produce kinetically free oxene. Many of the oxidative routes to iodosobenzene could involve oxene. One good candidate for this description is the production of iodosobenzene in the ozonation of iodobenzene.³¹ In this case iodobenzene formally accepts an oxene atom with the production of iodosobenzene and dioxygen. A final relevant observation is that activated cytochrome P-450 oxidizes iodobenzene to iodosylbenzene.³² This represents the reverse of the anaerobic activation of cytochrome P-450 by iodosylbenzene.

Experimental Section

Melting points were determined with a Thomas-Hoover capillary melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 727B spectrometer. NMR spectra were recorded on a Varian A-60 or Varian EM-360 spectrometer. Microanalyses were performed by Microtech Labs, Skokie, IL.

p-Iodoanisole, *p*-chloriodobenzene, *o*-iodotoluene, and iodobenzene diacetate were obtained from Aldrich. Rhodium diacetate was obtained from Alfa.

Procedure for the Synthesis of 2-Diazocyclohexane-1,3-dione and 2-Diazo-5,5-dimethylcyclohexane-1,3-dione. To a cooled (3–5 °C) solution or suspension of 0.050–0.0515 mol of diketone in 30 mL of anhydrous methylene chloride was added with stirring 0.050 mol of triethylamine: 3–5 min later a solution of tosyl azide in 5–10 mL was added in one portion, and stirring was continued until completion of the reaction as monitored by TLC. The now heterogeneous reaction mixture (due to precipitated tosylamide) was transferred to a separatory funnel and extracted with two 100-mL portions of aqueous potassium hydroxide. The organic layer was separated and dried (MgSO_4), and solvent and triethylamine were removed in vacuo. The 2-diazo-1,3-diketone was fractionated at 0.08–0.15 min to yield pure product.

2-Diazocyclohexane-1,3-dione: reaction time 0.35–0.5 h, yield 60%, mp 52–53 °C (lit.³³ mp 47–48 °C).

(24) (a) Radhakrishna, A. S.; Parham, M. E.; Riggs, R. M.; Loudon, G. M. *J. Org. Chem.* **1979**, *44*, 1746. (b) Loudon, G. M.; Radhakrishna, A. S.; Almond, M. R.; Blodgett, J. K.; Boutin, R. H. *J. Org. Chem.* **1984**, *49*, 4272. (c) Boutin, R. H.; Loudon, G. M. *J. Org. Chem.* **1984**, *49*, 4277. (d) Radhakrishna, A. S.; Rao, C.; Varma, R. K.; Singh, B. B.; Bhatnager, S. P. *Synthesis* **1983**, 538.

(25) Kemp, J. E. G.; Ellis, D.; Closier, M. D. *Tetrahedron Lett.* **1979**, 3781.

(26) Ohashi, T.; Matsunga, K.; Okahara, M.; Komari, S. *Synthesis* **1971**, 2, 96. Okahara, M.; Swern, D. *Tetrahedron Lett.* **1969**, 3301.

(27) Horner, L.; Christmann, A. *Chem. Ber.* **1963**, *96*, 388.

(28) Cadogan, J. I. G.; Gosney, I. J. *Chem. Soc., Perkin Trans. 1* **1974**, 460.

(29) Staudinger, H.; Hauser, E. *Helv. Chim. Acta* **1921**, *4*, 861; Kabachnik, M. I.; Gilyarov, V. A. *Izvest. Akad. Nauk SSSR Otdel. Khim. Nauk* **1956**, 790; *Chem. Abstr.* **1957**, *51*, 1823.

(30) (a) McGlynn, S. P.; Azumi, T.; Kinoshita, M. "Molecular Spectroscopy of the Triplet State"; Prentice-Hall: Englewood Cliffs, NJ, 1969; Chapter 7. (b) For a discussion see: Iddon, B.; Meth-Cohn, O.; Scriven, E. F. V.; Suschitzky, H.; Gallagher, P. T. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 900.

(31) Harries, C. *Ber.* **1903**, 2996.

(32) Macdonald, T. L.; Narashimhan, N.; Burka, L. T. *J. Am. Chem. Soc.* **1980**, *102*, 7760.

(33) Stetter, H.; Kiehs, K. *Chem. Ber.* **1965**, *98*, 1184.

(18) Leffler, J. E.; Tsuno, Y. *J. Org. Chem.* **1963**, *28*, 902.

(19) Yamada, Y.; Yamamoto, T.; Okwara, M. *Chem. Letts.* **1975**, 361.

(20) Abramovitch, R. A.; Bailey, T. D.; Takaye, T.; Uma, V. *J. Org. Chem.* **1974**, *39*, 340.

(21) Similar behavior was noted by Abramovitch et al. (ref 20).

(22) Kwart, H.; Kahn, A. A. *J. Am. Chem. Soc.* **1967**, *87*, 1950. Kwart, H.; Kahn, A. A. *Ibid.* **1967**, *89*, 1951.

(23) Kaufmann, E. J.; Thompson, R. C. *J. Am. Chem. Soc.* **1977**, *99*, 1824.

2-Diazo-5,5-dimethylcyclohexane-1,3-dione: reaction time, 2.5–3 h, yield 90%, mp 107–108 °C (lit.³⁴ mp 106–108 °C).

Iodosylbenzene. This compound was prepared either by aqueous sodium hydroxide hydrolysis of iodobenzene diacetate or iodobenzene dichloride. Iodobenzene dichloride was synthesized according to the method of Lucas and Kennedy.³⁵ **Iodosyl-*p*-anisole.** This compound was made by aqueous sodium hydroxide hydrolysis of iodoanisole dichloride, which, in turn, was made from iodoanisole by the method of Lucas and Kennedy.³⁵ **Iodosyl-*o*-toluene.** This compound was synthesized by aqueous sodium hydroxide hydrolysis of *o*-iodotoluene dichloride, which, in turn, was synthesized from *o*-iodotoluene by the method of Lucas and Kennedy.³⁵ **Iodosyl-*p*-chlorobenzene.** This compound was obtained by aqueous sodium hydroxide hydrolysis of *p*-chloriodobenzene dichloride, which, in turn, was synthesized from *p*-chloriodobenzene by the method of Lucas and Kennedy.³⁵

Procedure for Synthesis of Iodonium Ylides via Condensation Reaction.

A stirred solution of 0.01 mol of the arylidioso compound and 0.01 mol of the 1,3-diketone in 10 mL of chloroform was allowed to react at room temperature for 30 min. Then ether was added, and the iodonium ylides were precipitated and collected. The ylides were purified by precipitation from chloroform with petroleum ether or recrystallized from ethanol. **1:** mp 133–134 °C (lit.³⁶ mp 132–133 °C); ¹H NMR (CDCl₃) δ 1.05 (s, 6 H, CH₃), 2.42 (s, 4 H, CH₂), 7.4–7.8 (m, 5 H, aromatic). **2:** mp 155–159 °C (lit.^{37,38} mp 155 °C); ¹H NMR (CDCl₃) δ 1.05 (s, 6 H, CH₃), 2.45 (s, 4 H, CH₂), 3.78 (s, 3 H, CH₃O), 6.8–7.9 (m, 4 H, aromatic). **3:** mp 128–132 °C (lit. mp 109–110 °C); ¹H NMR (CDCl₃) δ 1.95 (q, 2 H, CH₂), 2.6 (t, 4 H, CH₂), 7.2–7.8 (m, 5 H, aromatic). **4:** mp 131–133 °C; ¹H NMR (CDCl₃) δ 1.05 (s, 6 H, CH₃), 2.48 (s, 4 H, CH₂), 7.15–7.8 (m, 4 H, aromatic). **5:** mp 100–102 °C; ¹H NMR (CDCl₃) δ 1.05 (s, 6 H, CH₃), 2.48 (s, 4 H, CH₂), 2.68 (s, 3 H, CH₃), 7.15–7.95 (m, 4 H, aromatic).

General Procedure for Decomposition of 2-Diazo-1,3-diketones with Rhodium(II) Acetate in the Presence of Aryl Iodides. A mixture of the 2-diazo-1,3-diketone (1.5 mmol), aryl iodide (24.5 mmol), and rhodium acetate (5 mg) was heated in a oil bath (40–70 °C) for 0.5–1 h. When nitrogen evolution ceased, the mixture was cooled, and the thus precipitated white solid was dissolved in chloroform. Rhodium acetate was removed by filtration, and the ylide was precipitated by addition of petroleum ether: **1** (37%), **2** (54%), **3** (71%) **4** (49%), and **5** (52%).

Thermal Isomerization of 2-Diazo-5,5-dimethyl-1,3-cyclohexanedione to 2-Iodo-3-phenoxy-5,5-dimethyl-2-cyclohexanone (6). A mixture of 2-diazo-5,5-dimethyl-1,3-cyclohexanedione, 0.25 g, iodobenzene, 5 g, and copper powder, 100 mg, was heated at 70 °C for 16 h. Then excess

iodobenzene was removed in vacuo and the solid was washed with hot chloroform. The chloroform was concentrated to dryness to yield a brown gum which was crystallized by trituration with ether to yield 200 mg: mp 165–166 °C (lit.⁹ mp 165–166 °C); ¹H NMR (CDCl₃) δ 1.03 (s, 6 H, CH₃), 2.26 (s, 2 H, CH₂), 2.43 (s, 2 H, CH₂) 6.8–7.5 (m, 5 H, aromatic).

Thermal Decomposition of Tosyl Azide under Various Conditions. The lowest temperature at which we could observe thermal loss of molecular dinitrogen from tosyl azide in various aryl iodide solutions was 120 °C. This was not significantly lowered by addition of various potential catalysts. In a typical experiment using 2.0 g of tosyl azide, 10 mL of iodobenzene and 100 mg of freshly reduced copper powder and heating at 120 °C for 12 h, only 1.1 g of iodobenzene and 510 mg of tosylamide could be isolated from a tarry crude reaction product.

Thermolysis of Tosyliminoiodane in the Presence of Copper Bronze. To 1.0 g of tosyliminoiodane in 10 mL of iodobenzene was added 1.0 g copper bronze. The reaction was heated under nitrogen for 1 h at 120 °C. Removal of iodobenzene yielded a black tar. No starting material appeared to be present by TLC or infrared analysis. No characterizable product was isolated by chromatography.

Thermolysis of Tosyl Azide in the Presence of Various Catalysts. The decomposition of tosyl azide in iodobenzene was not catalyzed below 60 °C using CoCl₂, PtCl₂, Ru₃(CO)₁₂, Mo(CO)₆, Cr(CO)₆, or Cu. In all cases unchanged starting material was obtained.

Attempts to Synthesize Monocarbonyl Ylide. Four grams of phenylbenzoyldiazomethane was dissolved in 20 mL of iodobenzene, and 5 mg of rhodium diacetate was added to it. The solution was heated at 60 °C for 2 h. The solution was cooled and filtered. Iodobenzene was removed in vacuo. Distillation yielded 3.1 g of diphenylketene.

Two grams of diazoacetophenone was dissolved in 20 mL of iodobenzene, and 5 mL of CH₃OH and 10 mg of rhodium diacetate were heated at 60 °C for 3 h. The solution was cooled and filtered.

The NMR of the resulting solution indicated the presence of iodobenzene and methylphenyl acetate. This was confirmed by GC and HPLC by using known samples.

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Registry No. **1**, 35024-12-5; **2**, 23383-02-0; **3**, 86396-02-3; **4**, 94569-93-4; **5**, 59577-80-9; **6**, 94569-94-5; iodobenzene diacetate, 94569-95-6; iodosylanisole, 87539-52-4; iodoanisole dichloride, 31599-50-5; iodosyl-*o*-toluene, 64297-59-2; *o*-iodotoluene dichloride, 31599-49-2; iodosyl-*p*-chlorobenzene, 52207-56-4; tosyliminoiodane, 55962-05-5; methyl phenylacetate, 101-41-7; iodobenzene, 591-50-4; *p*-iodoanisole, 696-62-8; 1-chloro-4-iodobenzene, 637-87-6; *o*-iodotoluene, 615-37-2; 1,3-cyclohexanedione, 504-02-9; 5,5-dimethyl-1,3-cyclohexanedione, 126-81-8; 2-diazo-1,3-cyclohexanedione, 1460-08-8; 2-diazo-5,5-dimethyl-1,3-cyclohexanedione, 1807-68-7; iodosylbenzene, 536-80-1; iodobenzene dichloride, 932-72-9; *p*-chloriodobenzene dichloride, 10304-75-3; rhodium diacetate, 5503-41-3; tosyl azide, 941-55-9; phenylbenzoyldiazomethane, 3469-17-8; diphenylketene, 525-06-4; diazoacetophenone, 3282-32-4.

(34) Verschambre, H.; Vocelle, D. *Can. J. Chem.* **1969**, *47*, 1981.

(35) Lucas, H. J.; Kennedy, E. R. "Organic Synthesis"; Wiley: New York, 1955; Collect. Vol. III, pp 482–483.

(36) Karele, F.; Neiland, O. *Zh. Org. Khim.* **1968**, *4*, 1818.

(37) Gayasum, U.; Okada, T.; Kawanisi, M. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 2506.

(38) Gudrinietse, E.; Neilands, O.; Vanag, G. *J. Gen. Chem. USSR (Engl. Transl.)* **1957**, *27*, 2777.