(**16a**).[23a] These epimeric alcohols are not separated under our gas chromatographic conditions.

The Ionization Constants of the Bicyclic Acids.—The ionization constants of bicyclo[2.2.1]hept-2-ene-*syn*-7-carboxylic acid (**22**),[42] bicyclo[2.2.1]hept-2-ene-*anti*-7-carboxylic acid (**23**),[42] and bicyclo[2.2.1]heptane-7-carboxylic acid (**24**)[42] were determined by potentiometric titration according to the procedure of Albert and Serjeant.[48] Standard aqueous solutions of the carboxylic acids ($\sim$0.01 M in acid) were titrated with 0.1 N standard sodium hydroxide using a glass *vs.* a standard calomel electrode in conjunction with a Beckman Model G pH Meter. The pK_a values are recorded in Table VII. They represent averages of 20–30 readings and two to four determinations each.

Acknowledgment.—It is a pleasure to acknowledge the financial support given this work by the Petroleum Research Fund of the American Chemical Society, Grant No. 911-A4.

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[48] A. Albert and E. P. Serjeant, "Ionization Constants of Acids and Bases," John Wiley and Sons, Inc., New York, N. Y., 1962, p 16 ff.

The Reactions of Phosphorus Compounds. XII.[1] A New Synthesis of 1,2,3-Triazoles and Diazo Esters from Phosphorus Ylids and Azides

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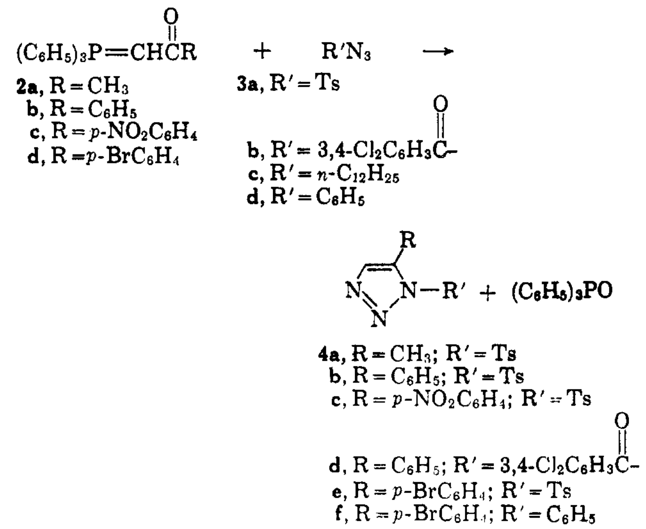
Acylmethylenetriphenylphosphoranes react with organic azides to furnish either 1,5-disubstituted 1,2,3-triazoles or α-diazocarbonyl compounds in high yield. The course of the reaction depends upon the nature of the carbonyl group of the ylid. The mechanism and scope of the reaction are discussed. The 1-tosyltriazoles produced from tosyl azide solvolyze readily in hot ethanol to generate 5-substituted triazoles and ethyl tosylate.

The reaction of phosphorus ylids with organic azides would be expected to parallel the reactions of phosphines,[2] Grignard reagents,[3] and carbanions[4] with azides. In these three cases nucleophilic attack occurs on the azide terminus to give initially a triazo intermediate **1** which is either stable[3] or decomposes to other products.[2,4] Indeed, adducts from acyl ylids and organic azides fall within this latter group and their mode of decomposition depends upon the electrophilicity of the carbonyl group of the ylid. When the carbonyl moiety of the ylid is a ketone the triazo intermediate [**1**, Y = $(C_6H_5)_3P^+\overset{-}{C}HC(=O)R$] decomposes to a vicinal triazole. If the carbonyl group of this intermediate is an ester or amide, collapse to a diazo compound occurs. This paper discusses these two new reactions in terms of the common triazo intermediate.

$$Y^- + N_3R \longrightarrow \underset{\mathbf{1}}{Y\text{-}N{=}N\text{-}\bar{N}\text{-}R} \longrightarrow \text{products}$$

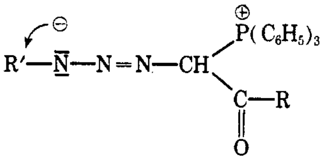
Acylmethylenetriphenylphosphoranes **2** react with acyl and aryl azides **3** at ambient temperatures to furnish 1,5-disubstituted *v*-triazoles (**4**) in high yield. The products are tabulated in Chart I.

Chart I



Qualitative observations of reactivity, as determined by the time required for complete reaction (see Table I), suggest nucleophilic attack of the ylid on the terminus of the azide.[2–4] The order of reactivity is dependent upon the electron-donating character of the R group in **2** ($CH_3 > C_6H_5 > p\text{-}NO_2C_6H_4$).[5] This is easily seen from the first three reaction times recorded in Table I. The *p*-nitrophenacyl ylid **2c** required 10 hr (infrared monitor) with tosyl azide to obtain the triazole **4c**; the acetonyl ylid **2a** required only 15 min for complete conversion to triazole **4a**. These observations are in accord with the reported basicities of the ylids.[5]

Chart II



5

The adduct from tosyl azide (**5**, $R' = p\text{-}CH_3C_6H_4SO_2\text{–}$; see Chart II) can delocalize the electron pair *via* p–d overlap with the sulfonyl group thus diminishing the reversibility of the reaction. Similar resonance stabilization is possible in the adduct from benzoyl azide. However, when R′ is alkyl, *e.g.*, **3c**, or aryl, **3d**, no such

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[1] Paper XI: A. J. Speziale and K. W. Ratts, *J. Am. Chem. Soc.*, **87**, 5603 (1965).

[2] (a) H. Staudinger and J. Meyer, *Helv. Chim. Acta*, **2**, 635 (1919); (b) J. E. Franz and C. Osuch, *Tetrahedron Letters*, **13**, 841 (1963).

[3] O. Dimroth, *Chem. Ber.*, **38**, 670 (1905).

[4] A. M. van Leusen, P. M. Smid, and J. Strating, *Tetrahedron Letters*, **6**, 337 (1965).

[5] For discussions of ylid basicities, see (a) A. J. Speziale and K. W. Ratts, *J. Am. Chem. Soc.*, **85**, 2790 (1963); (b) S. Fliszar, R. F. Hudson, and G. Salvadori, *Helv. Chim. Acta*, **46**, 1580 (1963).

TABLE I

1,2,3-TRIAZOLES

Triazole	Yield, %	Mp, °C	Reaction time, hr[a]	Recrystn solvent	Formula	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N
4a	98	119.5–121	0.25	Aq alcohol	$C_{10}H_{11}N_3SO_2$	50.70	4.64	17.73	50.82	4.71	17.94
4b	98	114–115	1	Aq alcohol	$C_{15}H_{13}N_3SO_2$	60.18	4.38	14.03	60.06	4.51	14.08
4c	87	172–173	10	Ethyl acetate	$C_{15}H_{12}N_4SO_4$	52.30	3.52	16.28	52.11	3.51	16.38
4d	97	134–135	18	Chloroform–hexane	$C_{15}H_9N_3Cl_2CO$	56.60	2.85	13.20	56.53	2.68	13.13
4e	80	139.5 dec	5	Chloroform–hexane	$C_{15}H_{12}N_3SO_2Br$[b]	47.70	3.18	Br, 21.07	47.80	3.38	Br, 21.07
4f[c]	24	61–62.5	80[d]	Hexane	C_9H_9N						
7a	62	198–199		Chloroform–hexane	$C_8H_6N_4O_2$	50.50	3.18		50.09	3.30	
7b	71	185–187		Chloroform–hexane	$C_8H_6N_3Br$	42.89	2.70		42.80	2.84	

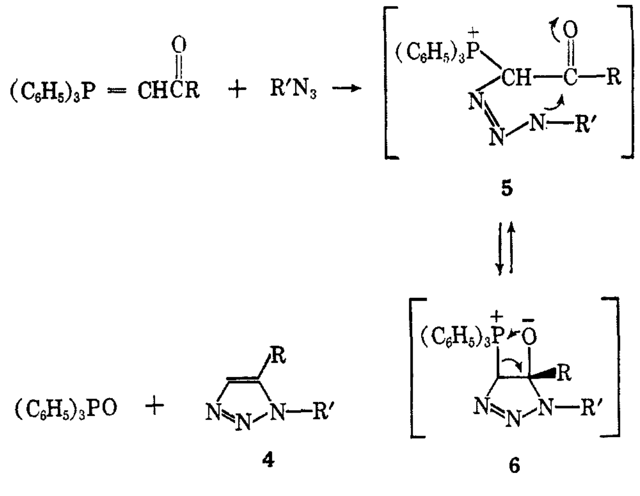
[a] Methylene chloride solvent; monitored by infrared. [b] O. Dimroth, *Chem. Ber.*, **35**, 1033 (1902). [c] *Anal.* Calcd: Br, 21.07. Found: Br, 21.07. [d] At reflux.

stabilization of the adduct **5** is possible. In fact, no reaction was observed between **2d** and *n*-dodecyl azide even after prolonged heating in chloroform. The reaction of phenyl azide **3d** was only 24% complete with the reactive acetonyl ylid **2a** after 80 hr of reflux (Table I).

Hoffmann has reported[6] the only other case of the reaction of an ylid with an azide; benzylidenetriphenylphosphorane with phenyl azide gave N-phenyltriphenylphosphinimine and benzaniline. These products were explained by initial nucleophilic attack of the ylid on the terminal nitrogen of the azide followed by loss of nitrogen from the triazo intermediate. In the present case of an acyl ylid the intermediate, **5**, has alternate pathways for collapse to a stable compound, *i.e.*, attack at the carbonyl carbon.

With the forementioned information a mechanistic pathway to 1,2,3-triazoles can be postulated which satisfies the empirical observations (Chart III). The ring closure of **5** to the betaine **6** is feasible only when the carbonyl group is electrophilic as in a ketone. When R is an alkoxy or amino radical, ring closure occurs at phosphorus. Furthermore, this ring closure should be reversible in analogy with Wittig reaction[7] and other carbonyl addition intermediates. The elimination of phosphine oxide from **6** drives the reaction to completion. One would expect that a transition state resembling a bicyclo[3.2.0]heptene would have a sufficiently high energy barrier so as to preclude reaction. To account for the facility of the reaction it can be assumed that there is considerable bond breaking in the transition state derived from **6** and that it closely resembles products.

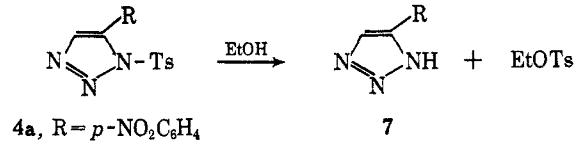
CHART III



The new triazoles reported here are crystalline solids (**4c** and **4e** crystallize directly from the reaction mixture) with decomposition points 1 to 2° above their melting points (gas evolution). They exhibit characteristic[8] absorption spectra maxima at *ca.* 230 mμ in the ultraviolet and at 8.5 μ in the infrared. The nmr spectra have triazole ring-proton signals at δ 7.5–8.5 indicating the aromatic ring current. The assignments are tabulated in Table II.

A remarkable solvolysis of the 1-tosyl triazoles in ethanol was observed to furnish the detosylated heterocycle and ethyl tosylate.[9] The solvolysis proceeded in good yield although optimization was not attempted (Chart IV). A similar sulfonamide cleavage was observed by Morgan and Godden[10] on a naphthotriazole.

CHART IV



4a, R = p-$NO_2C_6H_4$
b, R = p-BrC_6H_4

7

The sulfonamide cleavage reaction broadens the scope of this synthesis from 1,5-disubstituted to 5-substituted triazoles and makes it the method of choice in most cases. The triazole yields are the highest reported for this heterocyclic system.[7a,11]

When the carbonyl moiety of the ylid is weakly electrophilic as in an ester or amide, the reaction with tosyl azide takes a different course and leads to α-diazo

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[6] H. Hoffmann, *Chem. Ber.*, **95**, 2563 (1962).

[7] A. J. Speziale and D. E. Bissing, *J. Am. Chem. Soc.*, **85**, 3878 (1963).

[8] (a) J. H. Boyer, "Heterocyclic Compounds," Vol. 7, R. C. Elderfield, Ed., John Wiley and Sons, Inc., New York, N. Y., 1957, p 422; (b) L. W. Hartzel and F. R. Benson, *J. Am. Chem. Soc.*, **76**, 667 (1954); (c) C. S. Rondestvedt, Jr., and P. K. Chang, *ibid.*, **77**, 6532 (1955).

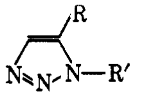
[9] A good review of attempts to cleave sulfonamides is found in E. Negishi and A. R. Day, *J. Org. Chem.*, **30**, 43 (1965).

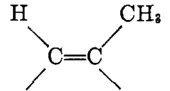
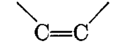
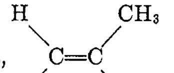
[10] G. T. Morgan and W. Godden, *J. Chem. Soc.*, **97**, 1702 (1910).

[11] J. A. Durden, Jr., H. A. Stansbury, and W. A. Catlette, *J. Chem. Eng. Data*, **9**, 228 (1964).

TABLE II

SPECTROSCOPIC DATA OF 1,2,3-TRIAZOLES

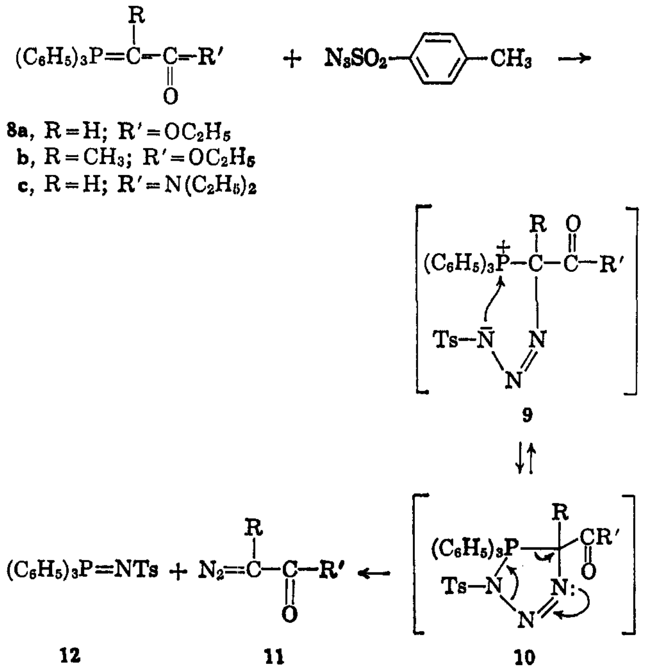


Triazole	R	R′	Infrared, cm^{-1}	Ultraviolet, λ_{max}, mμ (ε)	Nmr, δ
4a	CH_3	Ts	1389 (SO_2)[a] 1183 (triazole)	231 (20,000)	2.30 (3H singlet, CH_3Ar) 2.48 (3H doublet, ) 7.50 (4H aromatic quartet) 7.20 (1H quartet, )
4b	C_6H_5[b]	Ts	1383 (SO_2) 1183 (triazole)	237 (24,600)	7.0–7.6 (10H multiplet, phenyl and triazole ring)
4c	p-$NO_2C_6H_4$	Ts	1517, 1342 (NO_2)	274 (10,000)	(in CF_3COOH) 9.76 (1H singlet, triazole ring)
4d	C_6H_5	3,4-$Cl_2C_6H_3C(=O)$-	724 (N-C(=O)Ar)	225 (17,000) 300 (17,000)	7.0–8.2 (aromatic multiplet)
4e	p-BrC_6H_4	Ts	1393 (SO_2) 1178 (triazole)	232 (20,000)	7.0–7.7 (9H aromatic multiplet)
4f	CH_3[c]	C_6H_5	1212 (triazole)	222 (15,400)	2.21 (3H doublet, ) 7.30 (6H spike, phenyl and triazole ring)

[a] Ref 9. [b] Ref 12. [c] J. H. Boyer, C. H. Mack, N. Goebel, and L. R. Morgan, Jr., *J. Org. Chem.* **23**, 1051 (1958). These authors report this triazole but no spectral evidence is presented. Furthermore, they found that the triazole crystallizes from aqueous alcohol as a monohydrate, mp 171°. We have been unable to form this hydrate.

esters or amides and N-tosyltriphenylphosphinimine. The initial step in this sequence must also be nucleophilic attack of the ylid carbanion on the azide to form a triazo intermediate **9**. But due to the decreased electrophilicity of the ester carbonyl as compared to ketones, the ring closure preferentially takes place at the electrophilic phosphorus atom. Collapse of the intermediate **10** leads directly to the products (Chart V). The success of the reaction depends upon the phosphinimine **12** being unreactive toward the diazo compound **11**. An N-alkyl phosphinimine would react with the diazo group. The reaction is remarkably fast and is complete 10 min after mixing the reactants at 0° in methylene chloride. The diazo compound is obtained by triturating the concentrated reaction mixture with ether to allow **12** to crystallize. The diazo compound remaining in solution may then be isolated. The isolated yields of diazo compounds were 60–80%. They were characterized by their infrared[12] and nmr spectra and by comparison with published physical data.

CHART V



8a, R=H; R′=OC_2H_5
b, R=CH_3; R′=OC_2H_5
c, R=H; R′=$N(C_2H_5)_2$

9

12 **11** **10**

The two new reactions of Wittig reagents reported here are indicative of the broad reaction spectrum of which ylids are capable in addition to the usual olefin-forming reactions.[13] The diazo ester synthesis has extensive utility because of the facility of the reaction; it proceeds at low temperatures and employs readily available starting materials. It has further advantage that it is conducted in aprotic solvents—a feature not shared by other syntheses of diazo compounds.

Experimental Section[14-16]

Synthesis of the Ylids.—Ylids **2a**, **2b**, **2d**, and **2f** were prepared from the appropriate halide and triphenylphosphine followed by treatment of the salt with aqueous potassium carbonate according to the directions of Ramirez.[17] The physical constants

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[12] P. Yates, B. L. Shapiro, N. Yoda, and J. Fugger, *J. Am. Chem. Soc.*, **79**, 5756 (1957).

[13] S. Trippett, *Quart. Rev.* (London), **17**, 406 (1963).

[14] All melting points are uncorrected. The infrared spectra were determined in chloroform, unless specified otherwise, with a Beckman IR-5A recording spectrophotometer. The ultraviolet spectra were determined in absolute ethanol with a Beckman DK-2A recording spectrophotometer.

[15] Unless specified otherwise, the nmr spectra were determined in deuteriochloroform with a Varian A-60 spectrometer. The data are reported in parts per million downfield from tetramethylsilane.

[16] The microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn.

[17] F. Ramirez and S. Dershowitz, *J. Org. Chem.*, **22**, 41 (1957).

and spectra were in agreement with those reported. Ylids **2c** and **2e** were similarly prepared by the directions of Prevost[18] and agreed with the reported physical data.

General Procedure for 1,2,3-Triazoles (4).—To 0.02 mole of the ylid, **2**, in 50 ml of methylene chloride was added in one portion 0.02 mole of the azide, **3**, in 20 ml of solvent. When the reaction was complete (Table I) the solution was concentrated and recrystallized from the appropriate solvent. The crystals were filtered and air dried before melting point and spectral determinations were made. Consult Tables I and II for experimental details and spectroscopic data.

The mother liquors from the recrystallization were concentrated and the residue recrystallized from hexane to obtain 0.02 mole of triphenylphosphine oxide. The melting point and mixture melting point (155–156°), infrared, and nmr spectra were identical with those of an authentic sample.

***p*-Toluenesulfonyl Azide.**—This azide was prepared by the method of Doering and DePuy.[19] The spectra were in agreement with those reported.

3,4-Dichlorobenzoyl Azide (3b).—To 50 g (0.24 mole) of 3,4-dichlorobenzoyl chloride in 50 ml of acetone at 0° was added 16 g (0.24 mole) of sodium azide in 25 ml of water. The mixture was stirred for 0.25 hr, diluted with water, and filtered to obtain 60 g (100%) of the azide having mp 58–59° dec. *Anal.* Calcd. for $C_7H_3Cl_2N_3O$: C, 38.90; H, 1.40. Found: C, 39.05; H, 1.59.

Phenyl Azide.—This azide was prepared by the method of Lindsay and Allen.[20] The physical constants were in agreement with those reported.

5-(*p*-Bromophenyl)-1,2,3-triazole (7b).—Triazole **4e** (11.7 g, 0.031 mole) was refluxed in 50 ml of 90% ethanol for 1 hr, diluted with water to 200 ml, and cooled to furnish 11.7 g of white flakes, mp 180°. Recrystallization from chloroform–hexane gave 5.0 g (71%) of **7b** having mp 185–187°; infrared absorption (Nujol) at 1220 cm^{-1} (triazole); nmr signals (CF_3COOH) at 7.55 (4H doublet of phenyl ring, J = 2 cps) and 8.35 ppm (1H singlet, triazole).

From the mother liquors of the above recrystallizations was isolated by evaporative distillation 5.1 g (83%) of ethyl tosylate having mp 33–34° (lit.[21] mp 33–34°). The nmr spectrum exhibited the expected signals at 1.2 (3H triplet) and 4.0 (2H quartet), 2.35 (3H singlet) and δ 7.4 (4H quartet).

5-(*p*-Nitrophenyl)-1,2,3-triazole (7a).—Compound **4c** (2 g) was refluxed for 1 hr in 50 ml of 90% ethanol, diluted with water to 200 ml, and cooled. The powdery precipitate was collected and dried to obtain 0.6 g (62%) of **7a**: mp 198–199°; nmr signals (CF_3COOH) at 8.0 and 8.4 (4H quartet, *p*-nitrophenyl ring, J = 5 cps), and 8.8 ppm (1H singlet, triazole).

Attempted Reaction of *n*-Dodecyl Azide with 2e.—*n*-Dodecyl azide[22] (19.6 g, 0.093 mole) and ylid **2e** (4.1 g, 0.093 mole) were refluxed for 48 hr in chloroform. Infrared monitoring showed no change at any time in the azide or ylid concentration. The solution was cooled and 0.093 mole of tosyl azide was added. Within 5 hr there was collected an 80% yield of 1-tosyl-5-(*p*-bromophenyl)-1,2,3-triazole (**4e**).

Ethyl Diazoacetate (11a).—To 5.7 g (0.029 mole) of tosyl azide in 30 ml of methylene chloride cooled to 0° was added slowly 10 g (0.029 mole) of carbethoxymethylenetriphenylphosphorane (Aldrich Chemical Co.) in 30 ml of the same solvent. After 0.5 hr, the solution was concentrated and the gummy residue triturated with ether to obtain 10 g (80%) of N-tosyltriphenylphosphinimine. After recrystallization from benzene–pentane the white flakes had only mp 182–183° (lit.[23] mp 187°); the product was identical (infrared, nmr, and melting point) with a sample prepared by reacting tosyl azide with triphenylphosphine.[2b]

The mother liquors were concentrated to a light yellow oil, 2.3 g (70%). The infrared spectrum of this oil was superimposable on that of authentic ethyl diazoacetate (Aldrich Chemical Co.).

Ethyl 2-Methyldiazoacetate (11b).—To 18.1 g (0.092 mole) of tosyl azide in 100 ml of methylene chloride cooled to 0° was added 33.3 g (0.092 mole) of carbethoxymethylmethylenetriphenylphosphorane[24] in 50 ml of the same solvent. After 3 hr at 0° the solution was concentrated and distilled, bp 50° (0.2 mm), into a Dry Ice trap. The colorless oil, 7.3 g (62%), had n^{24}_D 1.4474 (lit.[25] n^{20}_D 1.4472); infrared absorption at 2105 and 1727 cm^{-1}; nmr signals at 1.3 and 4.2 (5H ethyl septet) and 1.55 ppm (3H singlet, $\overset{+}{N}_2\text{–}\overset{-}{C}{<}^{CH_3}$.

N,N-Diethylcarbamoylmethylenetriphenylphosphorane (8c).—This ylid was prepared by the procedure of Ramirez[17] from N,N-diethylchloroacetamide and triphenylphosphine. The analytical sample had mp 151–153°. *Anal.* Calcd for $C_{24}H_{26}NOP$· C, 76.77; H, 6.98; N, 3.73. Found: C, 77.18; H, 7.52; N, 3.71.

α-Diazo-N,N-diethylacetamide (11c).—To 19.6 g (0.10 mole) of tosyl azide in 100 ml of methylene chloride at 0° was added 37.5 g (0.10 mole) of ylid **8c** in 100 ml of the same solvent. After 2 hr at 0° the solution was concentrated and the residue triturated with ether several times. The ether extracts were concentrated to a red oil having infrared absorption at 2128 (doublet, $N_2^+\text{–}CH\text{–}$ and 1626 cm^{-1} (amide); nmr signals at 1.1 and 3.15 (10H ethyl septet, J = 7 cps) and 2.40 ppm (1H singlet, $N_2^+\text{–}CH\text{–}$). The oil decomposed on attempted distillation even at 35°.

Acknowledgment.—The author expresses his gratitude to Dr. K. W. Ratts for the many suggestions and critical discussions concerning this work.

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[18] H. Strzelecka, M. Sumalty-Siematycki, and C. Prevost, *Compt. Rend.*, **254**, 696 (1962).

[19] W. von E. Doering and C. H. DePuy, *J. Am. Chem. Soc.*, **75**, 5995 (1953).

[20] R. O. Lindsay and C. F. H. Allen, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p 710.

[21] I. Heilbron, Ed., "Dictionary of Organic Compounds," Vol. IV, Oxford University Press, New York, N. Y., 1953, p 518.

[22] K. Henkel and F. Weygand, *Chem. Ber.*, **76**, 812 (1943).

[23] F. G. Mann and E. J. Chaplin, *J. Chem. Soc.*, 527 (1937).

[24] H. Saikachi, Y. Tamguchi, and H. Ogawa, *Yakugaku Zasshi*, **82**, 1262 (1962); *Chem. Abstr.*, **58**, 13887*d* (1963).

[25] H. Müller, *Chem. Ber.*, **37**, 1270 (1904).