Anal. Calcd for $C_{10}H_6N_6$: C, 57.13; H, 2.87; N, 39.98. Found: C, 56.93; H, 2.84; N, 39.85.

Similarly, **3,7-dimethylbis-*s*-triazolo[4,3-*a*:4,3-*c*]quinazoline** was purified by sublimation *in vacuo* [160° (0.1 mm)]: 1.9 g (80%); mp 315–316°; ir (KBr) 3125 (C–H), 1610 (C=N), 1525 (C=C) cm^{-1}; $\lambda_{max}^{CH_3OH}$ 240 nm; nmr ($CDCl_3$) τ 7.39 (s, 3, CH_3), 7.31 (s, 3, CH_3), 2.6–1.5 (m, 4, aromatic); mass spectrum M^+, *m/e* (rel intensity) 238 (100).

Anal. Calcd for $C_{12}H_{10}N_6$: C, 60.49; H, 4.23; N, 35.27. found: C, 60.25; H, 4.25; N, 35.24.

3,7-Diethylbis-*s*-triazolo[4,3-*a*:4,3-*c*]quinazoline was also purified by sublimation *in vacuo* [150° (0.1 mm)]: 1.7 g (65%); mp 258–259°; ir (KBr) 2980 (C–H), 1600 (C=N), 1580 (C=C) cm^{-1}; $\lambda_{max}^{CH_3OH}$ 240 nm; mass spectrum M^+, *m/e* (rel intensity) 266 (100).

Anal. Calcd for $C_{14}H_{14}N_6$: C, 63.14; H, 5.29; N, 31.56. Found: C, 63.22; H, 5.22; N, 31.74.

Reaction of Bis-*s*-triazolo[4,3-*a*:4,3-*c*]quinazoline with Dilute Acid.—Bis-*s*-triazolo[4,3-*a*:4,3-*c*]quinazoline (2.0 g, 0.008 mol) and 10% HCl (40 ml) were heated under reflux for 0.5 hr. The solvent was removed under reduced pressure. The residue crystallized from ethanol as fine, yellow needles. The product was identical in every respect with an authentic sample of 2,4-dihydrazinoquinazoline: 1.5 g (90%); mp 226–227° dec (lit.[15] mp 226–227° dec); ir 3450 (NH_2), 3050 (NH), 1650 (C=N), 1620 (NH), 1560 (C=C) cm^{-1}.

Sodium Borohydride Reduction of 2-Methyl-*s*-triazolo[1,5-*c*]quinazoline.—The quinazoline (1.0 g, 0.006 mol), methanol (50 ml), and excess sodium borohydride (1.6 g) were stirred at room temperature for 17 hr. The reaction mixture was evaporated to dryness under reduced pressure, and the crude residue was dissolved in water and the insoluble material filtered. The solution was then extracted with chloroform, dried (Na_2SO_4), and removed under reduced pressure. The crude product crystallized from benzene as fine, colorless needles: 0.6 g (60%); mp 150–151°; ir (KBr) 3200 (NH), 1640 (C=N), 1600 (NH), 1550 (C=C) cm^{-1}; $\lambda_{max}^{CH_3OH}$ 230 nm (log ϵ 3.19); nmr ($CDCl_3$) τ 7.58 (s, 3, 2-CH_3), 4.51 (s, 2, $-CH_2-$), 3.3–2.1 (m, 4, aromatic), 4.25 (b, 1, –NH); mass spectrum M^+, *m/e* (rel intensity) 186 (100).

Anal. Calcd for $C_{10}H_{10}N_4$: C, 64.50; H, 5.41; N, 30.09. Found: C, 64.28; H, 5.50; N, 29.87.

Registry No.—**2** (R[1] = H; R = H), 234-74-2; **2** (R[1] = Me; R = H), 25518-06-3; **2** (R[1] = Et; R = H), 25518-07-4; **2** (R[1] = H; R = Ph), 6506-59-8; **2** (R[1] = Et; R = Ph), 25518-09-6; **3** (R[1] = H; R = H), 234-74-2; **3** (R[1] = Me; R = H), 25518-11-0; **3** (R[1] = Et; R = H), 25518-12-1; **3** (R[1] = H; R = Ph), 25518-13-2; **5** (R[1] = R = H), 25518-14-3; **5** (R[1] = Me; R = H), 25568-69-8; **5** (R[1] = Ph; R = H), 25518-15-4; **6**, 25518-16-5; **6** (R = Me), 25518-17-6; **7**, 25518-18-7; **7** (R′ = R = Me), 25518-19-8; **7** (R[1] = R = Et), 25518-20-1; 5,6-dihydro-2-methyl-*s*-triazolo[1,5-*c*]quinazoline, 27111-63-3.

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Mesoionic Compounds. XI. Mesoionic Compounds of the 1,2,3-Triazole Series[1]

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Cyclization of ethyl N-methyl-N-arylazoaminoacetates with thionyl chloride gave anhydro-3-aryl-4-hydroxy-1-methyl-1,2,3-triazolium hydroxides. The corresponding N-methyl-N-arylazoaminoacetonitriles also underwent ready cyclization to anhydro-4-acetylimino-3-aryl-1-methyl-1,2,3-triazolium hydroxides with acetyl chloride, followed by treatment with base. Several cycloaddition reactions as well as chemical and spectral characteristics of this mesoionic system are described. In contrast to other mesoionic systems, protonation occurred readily at the exocyclic oxygen atom which was also the site of alkylation with triethyloxonium fluoroborate.

Since introduction of the original concept of mesoionic compounds,[2] comparatively few new systems have been described. As part of a general study of this interesting class of compounds, we have been investigating the synthesis of new types[3a] and now report our studies which have led to new mesoionic compounds of the 1,2,3-triazole series.[3b]

Cyclodehydration procedures have usually been used in the synthesis of mesoionic systems[4] and a variation of this approach was found to be effective in the 1,2,3-triazole system. Condensation of benzenediazonium chloride (**1**, R = Ph) with ethyl sarcosinate under carefully controlled conditions gave ethyl N-methyl-N-phenylazoaminoacetate (**2**, R = Ph) in 53% yield. Attempts to condense benzene–diazonium chloride with sarcosine itself under analogous conditions were unsuccessful, thus precluding the usual cyclodehydration of an appropriately substituted acid to the mesoionic system. Cyclization of the ester (**2**, R = Ph) with thionyl chloride–pyridine readily gave anhydro-4-hydroxy-3-phenyl-1-methyl-1,2,3-triazolium hydroxide (**4**, R = Ph) together with a small amount of a sulfur-containing product which has been identified as the sulfide (**6**). This sulfide was also obtained by the action of thionyl chloride–pyridine on the amide (**3**) as well as from the mesoionic system (**4**) and sulfur monochloride. Its structure was evident from analytical data which established the molecular formula as $C_{18}H_{16}N_6SO_2$ and from spectral data where the nmr spectrum was similar in all respects to that of **4** except that the 5-proton was absent. Use of *p*-toluenediazonium chloride in this reaction gave analogous products.

Analytical and spectral data clearly showed that ring closure to these mesoionic compounds had occurred. Particularly important in this respect were the ν_{CO} at 1650 cm^{-1} in the infrared spectra and a sharp singlet at

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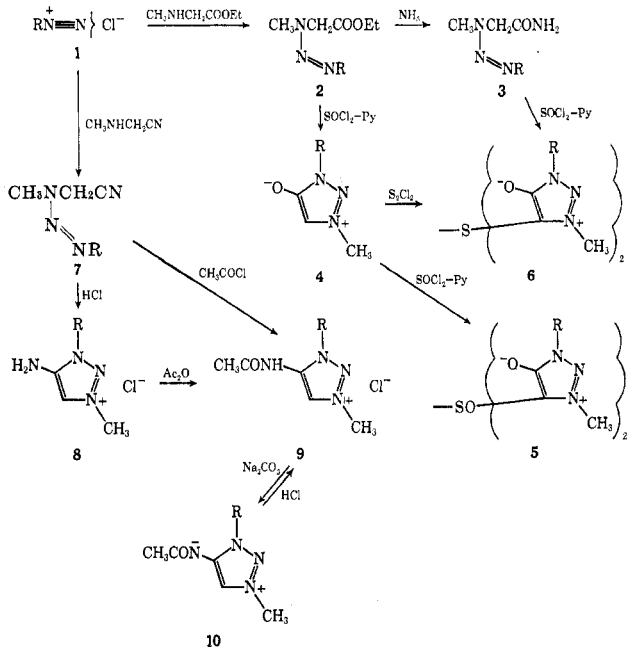
(2) F. L. Warren, *J. Chem. Soc.*, 1100 (1938); A. Schonberg, *ibid.*, 824 (1938); W. Baker and W. D. Ollis, *Quart. Rev. (London)*, **11**, 15 (1957).

(3) (a) *E.g.*, K. T. Potts and U. P. Singh, *Chem. Commun.*, 569 (1969); K. T. Potts, U. P. Singh, and E. Houghton, *ibid.*, 1128 (1969); K. T. Potts, E. Houghton, and U. P. Singh, *ibid.*, 1129 (1969); (b) anhydro-1,3-dimethyl-4-hydroxy-1,2,3-triazolium hydroxide has recently been obtained by methylation of 1-methyl-1,2,3-triazol-5-one [M. Begtrup and C. Pedersen, *Acta Chem. Scand.*, **20**, 1555 (1966); M. Begtrup and P. A. Kristensen, *ibid.*, **23**, 2733 (1969)].

(4) F. H. C. Stewart, *Chem. Rev.*, **64**, 129 (1964).

τ 3.34 attributable to the 5 proton in the nmr spectra, values consistent with those observed in other mesoionic systems.[3]

Condensation of benzenediazonium chloride with N-methylaminoacetonitrile gave N-methyl-N-phenylazoaminoacetonitrile (**7**, R = Ph). This nitrile, with dry hydrogen chloride, underwent cyclization to 4-amino-1-methyl-3-phenyl-1,2,3-triazolium chloride (**8**, R = Ph), a system analogous to the sydnone imines.[4] Like the latter, **8** could not be converted into the corresponding free base, but with acetic anhydride gave 4-acetamido-1-methyl-3-phenyl-1,2,3-triazolium chloride (**9**, R = Ph) which was also obtained directly from the nitrile (**7**) and acetyl chloride. Treatment of **9** with base gave the mesoionic compound anhydro-4-acetimino-1-methyl-3-phenyl-1,2,3-triazolium hydroxide (**10**, R = Ph) in which delocalization of the exocyclic negative charge over the acetimino group imparts stability to the system. An analogous series of products was obtained when *p*-toluenediazonium chloride was used in this reaction sequence. Analytical and spectral data established that ring closure of **7** to the salts **8** and **9** had occurred. In the infrared spectrum of **9**, the ν_{NH} at 3300–3200 cm^{-1} and ν_{CO} at 1650 cm^{-1} can be assigned to the exocyclic acetamido group and the disappearance of the –NH– absorption, together with a shift of ν_{CO} to 1600 cm^{-1}, provide excellent evidence for the assignment of structure **10** to the product obtained from **9** and base.



In contrast to other five-membered mesoionic systems with exocyclic oxygen atoms, anhydro-4-hydroxy-1-methyl-3-*p*-tolyl-1,2,3-triazolium hydroxide (**4**, R = *p*-$CH_3C_6H_4$) with dry hydrogen chloride in benzene protonates at the exocyclic oxygen atom giving 4-hydroxy-1-methyl-3-*p*-tolyl-1,2,3-triazolium chloride (**11**, R = *p*-$CH_3C_6H_4$). This conversion is quite apparent from the infrared spectra of the products, especially the disappearance of the ν_{CO} at 1650 cm^{-1} in **4** and the appearance of a very broad ν_{OH} at 2100 cm^{-1} in **11**. Similarly, a singlet at τ 2.02 in the nmr spectrum of **11** which exchanges with D_2O is indicative of an hydroxyl group, while the 5 proton in **11** occurs at τ 2.24 in contrast to τ 3.30 for the corresponding proton of **4**. In mesoionic compounds of the *s*-triazole series,[5] only those with an exocyclic sulfur atom are protonated under comparable conditions and it is only with six-membered mesoionic systems that protonation of the exocyclic oxygen has been observed.[6] On heating **11** *in vacuo* at 60°, it readily lost hydrogen chloride regenerating the mesoionic compound **4**, a behavior similar to that observed with the *s*-triazolium salts mentioned above.[5] No loss of methyl chloride occurred, as often has been observed on heating of heterocyclic quaternary salts,[7] and the regeneration of **4** would be expected to be assisted by its considerable resonance stabilization inherent in the mesoionic concept.[8] The elimination of hydrogen chloride also occurred with base and, indeed, the mesoionic compound itself is extremely stable to alkali, being recovered unchanged after refluxing with 10% sodium hydroxide solution for 24 hr. This ready salt formation and stability to alkali were extremely important in the procedure used for the isolation of the mesoionic compound (see below).

Attempts to methylate the exocyclic oxygen atom with methyl iodide were unsuccessful, results consistent with those reported for other five-membered mesoionic systems containing exocyclic oxygen atoms. However, reaction of **4** (R = *p*-$CH_3C_6H_4$) with triethyloxonium fluoroborate gave in good yield[9] 4-ethoxy-1-methyl-3-*p*-tolyl-1,2,3-triazolium fluoroborate (**12**, R = *p*-$CH_3C_6H_4$) which was quite stable and which was characterized as its picrate and iodide. This behavior is in direct contrast to that of anhydro-1,3-dimethyl-4-hydroxy-1,2,3-triazolium hydroxide[3b] which underwent ready reaction with methyl iodide.

Nmr data provided compelling evidence for structure **12**, with an ethyl group [τ 8.58 (t, 3, J = 7.0 Hz, $-CH_2-CH_3$; 5.49 (q, 2, J = 7.0 Hz, $-CH_2-CH_3$], an N–CH_3 group [τ 5.65 (s, 3)], a *p*-tolyl group [τ 7.58 (s, 3, C–CH_3), 2.53 (AB d, 2, J = 9.0 Hz); 2.30 (AB d, 2, J = 9.0 Hz], and a singlet proton at τ 1.28 (5-H). Both the N–CH_3 group and the 5 proton had undergone large downfield shifts (0.38 ppm and 2.02 ppm, respectively) owing to the conversion of the system into a 1,2,3-triazolium salt.

Hot hydrobromic acid on **12** regenerated the mesoionic system **4**, showing that no skeletal rearrangement had occurred. Surprisingly, heating **12** above its melting point did not regenerate the mesoionic system though this procedure has been effective in similar conversions.

As has been found with the sydnones,[4] bromination of **4** readily gave anhydro-5-bromo-4-hydroxy-1-methyl-3-*p*-tolyl-1,2,3-triazolium hydroxide (**14**, R = *p*-$CH_3C_6H_4$), obtained initially as the salt **13** (R = *p*-$CH_3C_6H_4$). Furthermore, reaction with thionyl chloride gave the sulfoxide (**5**).

Attempts to use polyaza mesoionic systems as 1,3 dipoles in cycloaddition reactions have been relatively

(5) K. T. Potts, S. K. Roy, and D. P. Jones, *J. Org. Chem.*, **32**, 2245 (1967); *J. Heterocycl. Chem.*, **2**, 105 (1965).

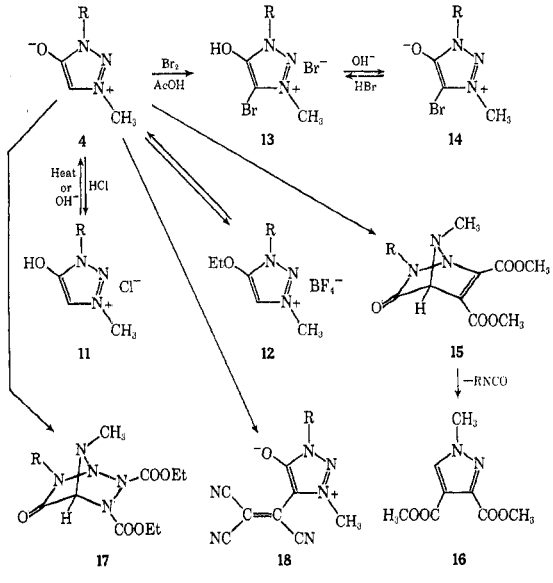
(6) S. A. Harris, T. J. Webb, and K. Folkers, *J. Amer. Chem. Soc.*, **62**, 3198 (1940); K. Mecklenborg and M. Orchin, *J. Org. Chem.*, **23**, 1591 (1958).

(7) *Heterocycl. Compounds*, **7**, 93 (1957).

(8) In the *s*-triazole series, 3,5-di(methylthio)-1,4-diphenyl-*s*-triazolium iodide, on treatment with pyridine, lost methyl iodide and gave the mesoionic anhydro-5-methylthio-3-mercapto-1,4-diphenyl-*s*-triazolium hydroxide (unpublished observations).

(9) D. E. Ames and B. Novitt, *J. Chem. Soc. C.*, 2355 (1969).

unsuccessful[10,11a] except in the case of the sydnones.[11] However, the 1,2,3-triazole system has now been found to undergo cycloaddition reactions with acetylenic and reactive olefinic-type dipolarophiles. Anhydro-4-hydroxy-1-methyl-3-*p*-tolyl-1,2,3-triazolium hydroxide (**4**, R = *p*-$CH_3C_6H_4$) on reflux with dimethyl acetylenedicarboxylate for 120 hr gave methyl 1-methylpyrazole-3,4-dicarboxylate (**16**), presumably *via* an intermediate such as **15**. The *p*-tolyl isocyanate eliminated during the reaction was identified as the corresponding urea. Reaction of the mesoionic compound **4** with ethyl azodicarboxylate in refluxing xylene for 1 hr gave a stable cycloadduct (**17**) from which *p*-tolyl isocyanate was not eliminated. This shows the importance of the double bond in the intermediate cycloadduct **15** in assisting aromatization. The structure of **17**, ethyl 7-methyl-



5-oxo-6-*p*-tolyl-1,2,3,6,7-pentaazabicyclo[2.2.1]heptane-2,3-dicarboxylate, was established from analytical and spectral data. The molecular formula $C_{16}H_{21}N_5O_5$ has to accommodate three carbonyl groups [ν_{CO} 1725 (b), 1670 cm^{-1}] two of which are present as nonequivalent ethyl ester groups from the nmr data [τ 8.83 (t, 3, J = 7.0 Hz), 8.77 (t, 3, J = 7.0 Hz), 5.91 (q, 2, J = 7.0 Hz), 5.76 (q, 2, J = 7.0 Hz)], a *p*-tolyl group [τ 7.63 (s, 3, C-CH_3), 2.76 (AB d, 2, J = 8.5 Hz) and 2.05 (AB d, 2, J = 8.5 Hz)], and an N-CH_3 group [τ 5.85 (s, 3)], together with a single aromatic-type proton (τ 0.18) which exchanged with D_2O under neutral conditions over a period of $\sim$ 72 hr. This bridgehead proton was broadened, probably by coupling with the bridge N-CH_3 group, a similar effect having been observed in the 1:1 cycloadduct of dimethylacetylene dicarboxylate and anhydro-4-hydroxy-2-methylcinnolinium hydroxide.[9] The above structural elements indicated by the nmr data are those present in the original reactants and are consistent with the formation of a 1:1 adduct.

Tetracyanoethylene underwent a ready reaction with the mesoionic compound. The dark red product obtained was found to have a molecular formula of $C_{15}H_{10}N_6O$ and, besides a strong -CN absorption at 2225 cm^{-1}, a strong carbonyl absorption at 1680 cm^{-1} was present in the infrared spectrum. Nmr data indicated the absence of the 5 proton of the original mesoionic compound and the structure of the product appears to be best represented as anhydro-4-hydroxy-1-methyl-3-*p*-tolyl-5-(1,2,2-tricyanoethyl)-1,2,3-triazolium hydroxide (**18**, R = *p*-$CH_3C_6H_4$). It is most likely that steric factors prevent cyclization in the 1,3-dipolar sense and that an "ene" type reaction product[12] that can readily lose hydrogen cyanide during the reaction to give **18** is formed. A similar type of product has also been observed in the reaction of andydro-5-hydroxy-3-methyl-2-phenylthiazolium hydroxide with tetracyanoethylene.[13]

Experimental Section[14]

Ethyl N-Methyl-N-phenylazoaminoacetate (2, R = Ph).—Aniline (9.3 g, 0.1 mol), dissolved in concentrated hydrochloric acid (20 ml) and water (20 ml) at −10°, was treated with a solution of sodium nitrite (7.2 g) in water (50 ml). After diazotization was complete, sodium acetate (20 g) in water (100 ml) was added, followed by the addition with stirring of ethyl sarcosinate hydrochloride (15.0 g, 0.1 mol) in water (50 ml) keeping the temperature below 0°. After 1 additional hr the yellow oil which separated was extracted with ether, the ether extract was washed twice with 10% sodium carbonate solution (10 ml each) and dried (Na_2SO_4). After removal of the ether, the residual oil was distilled under reduced pressure resulting in a pale yellow mobile oil: 12.0 g (53%); bp 122–123° (0.5 mm); ir (liq film) 3000, 2950, 2900 (m) (CH), 1750 (s) (CO), 1600 (w) (N=N) cm^{-1}; uv max (CH_3OH) 308 sh nm (log ϵ 4.07), 283 (4.12), 224(3.95), 218 sh (3.92); nmr ($CDCl_3$) τ 8.74 (t, 3, J = 7.5 Hz, CH_3 of ethyl), 6.58 (s, 3, N—CH_3), 5.78 (qt, 2, J = 7.5 Hz, -CH_2 of ethyl), 5.55 (s, 2, -N—CH_2), 2.62 (m, 5, aromatic); mass spectrum (70 eV) *m/e* (rel intensity) 221 (8), 105 (43), 78 (16), 77 (100), 51 (12), 44 (23), 43 (21).

Anal. Calcd for $C_{11}H_{15}N_3O_2$: C, 59.73; H, 6.78; N, 19.00. Found: C, 59.60; H, 6.95; N, 19.15.

Similarly, **ethyl N-methyl-N-*p*-tolylazoaminoacetate** (**2**, R = *p*-$CH_3C_6H_4$) was obtained from *p*-toluenediazonium chloride in 85% yield as a pale yellow oil: bp 126° (0.5 mm), solidifing on cooling and crystallizing from petroleum ether as colorless, irregular prisms: mp 31–32°; ir (liq film) 2990, 2925 (m) (CH), 1750 (s) (CO), 1590 (w) (N=N) cm^{-1}.; uv max (CH_3OH) 313 nm (log ϵ 4.10), 285 (4.14), 227 (3.96), 222 sh (3.93); nmr ($CDCl_3$) τ 8.71 (t, 3, J = 7.5 Hz, CH_3 of ethyl), 7.65 (s, 3, C—CH_3), 6.6 (s, 3, N—CH_3), 5.78 (qt, 2, J = 7.5 Hz, CH_2 of ethyl), 5.56 (s, 2, -N—CH_2), 2.86 (AB d, 2, J = 9.0 Hz, aromatic), 2.64 (AB d, 2, J = 9.0 Hz, aromatic); mass spectrum (70 eV) *m/e* (rel intensity) 235 (8), 120 (13), 119 (22), 92 (11), 91 (100), 65 (16), 44 (19), 43 (9), 42 (44).

Anal. Calcd for $C_{12}H_{17}N_3O_2$: C, 61.28; H, 7.23; N, 17.86. Found: C, 61.39; H, 7.37; N, 17.70.

N-Methyl-N-phenylazoaminoacetamide (3, R = Ph).—The ester (2; R = Ph) (2.0 g) was stirred overnight with concentrated ammonium hydroxide (50 ml). The colorless product which had separated was recrystallized from benzene forming colorless plates: 1.2 g (70%); mp 132–133°; ir (KBr) 3325, 3175 (s) (NH_2), 2960, 2910 (m) (CH), 1650 (s) (CO), 1590 (w) (N=N) cm^{-1}; uv max (CH_3OH) 304 nm (log ϵ 4.09), 284 (4.12), 224 (3.94), 218 sh (3.92); mass spectrum (70 eV) *m/e* (rel intensity) 192 (9), 106 (4), 105 (46), 78 (9), 77 (100), 51 (13), 50 (3), 44 (15), 43 (6).

(10) K. T. Potts and D. N. Roy, *Chem. Commun.*, 1061 (1968); unpublished observations.

(11) (a) R. Huisgen, H. Gotthardt, and R. Grashey, *Chem. Ber.*, **101**, 536 (1968); (b) H. Gotthardt and R. Huisgen, *ibid.*, 552; (c) H. Gotthardt, R. Huisgen, and R. Knorr, *ibid.*, 1056; (d) R. Huisgen, R. Grashey, and H. Gotthardt, *ibid.*, 829; (e) H. Kato, S. Sato, and M. Ohta, *Tetrahedron Lett.*, 4261 (1967).

(12) H. M. R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 556 (1969); A. H. Lautzenheiser and P. W. Le Quesne, *Tetrahedron Lett.*, 207 (1969).

(13) Unpublished observations.

(14) Spectral characterization of products was carried out on the following instrumentation: ir, Perkin-Elmer Model 337 spectrophotometer; uv, Cary Model 14 spectrophotometer; nmr, Varian A-60 spectrometer using TMS as internal standard; mass spectra, Hitachi Perkin-Elmer RMU 6E spectrometer, using the direct inlet probe at ~150°. All evaporations were done under reduced pressure using a Rotavap apparatus and melting points were taken in capillaries. Microanalyses were by Galbraith Laboratories Inc., Knoxville, Tenn., and Instranal Laboratories, Rensselaer, N. Y.

Anal. Calcd for $C_9H_{12}N_4O$: C, 56.25; H, 6.25; N, 29.16. Found: C, 56.31; H, 6.32; N, 29.02.

Similarly, **N-methyl-N-p-tolylazoaminoacetamide** (**3**, R = *p*-$CH_3C_6H_4$) crystallized from benzene as colorless needles: 1.5 g (76%); mp 143–144°; uv max (CH_3OH) 313 nm (log ϵ 4.11), 287 (4.15), 227 (3.95), 222 sh (3.94); mass spectrum (70 eV) *m/e* (rel intensity) 206 (11), 120 (4), 119 (32), 92 (10), 91 (100), 65 (18), 44 (8).

Anal. Calcd for $C_{10}H_{14}N_4O$: C, 58.23; H, 6.84; N, 27.17. Found: C, 58.05; H, 6.71; N, 27.27.

N-Methyl-N-phenylazoaminoacetonitrile (**7**, **R = Ph**).—Aniline (9.3 g, 0.1 mol), dissolved in concentrated hydrochloric acid (20 ml) and water (20 ml), was cooled to −10° and a solution of sodium nitrite (7.2 g) in water (50 ml) was added dropwise with stirring. After the addition was completed, cooling and stirring were continued for 1 hr, and a solution of sodium acetate (20 g) in water (100 ml) added bringing the pH to 7. N-Methylaminoacetonitrile hydrochloride (10.6 g, 0.1 mol) in water (20 ml) was added; cooling and stirring were continued for 1 additional hr during which solid separated. The reaction mixture was extracted with ether; the ether extract was washed with 10% sodium carbonate solution (twice, 10 ml each) and dried (Na_2SO_4). The residue on removal of the ether was recrystallized from benzene–petroleum ether (bp 60–80°) affording colorless needles of the nitrile: 6.0 g (35%); mp 31–33°; ir (KBr) 3060, 2975, 2950 (m) (CH), 2250 (m) (CN), 1600 (m) (N=N) cm^{-1}; uv max (CH_3OH) 283 nm (log ϵ 4.15), 224 (4.01), 218 sh (3.97); nmr ($CDCl_3$) τ 6.69 (s, 3, N—CH_3), 5.51 (s, 2, -N—CH_2), 2.62 (m, 5, aromatic); mass spectrum (70 eV) *m/e* (rel intensity) 174 (12), 105 (28), 78 (18), 77 (100), 51 (17), 42 (12).

Anal. Calcd for $C_9H_{10}N_4$: C, 61.87; H, 5.74; N, 32.19. Found: C, 62.05; H, 5.73; N, 31.92.

In a similar fashion **N-methyl-N-*p*-tolylazoaminoacetonitrile** (**7**, **R** = *p*-$CH_3C_6H_4$) was obtained from *p*-toluenediazonium chloride in 35% yield. It crystallized from benzene–petroleum ether as colorless needles: mp 56–57°; ir (KBr) 3020, 2910 (m) (CH), 2250 (w) (CN), 1590 (m) (N=N) cm^{-1}; uv max (CH_3OH) 284 nm (log ϵ 4.14), 227 (4.01), 222 (4.00); nmr ($CDCl_3$) τ 7.66 (s, 3, C—CH_3), 6.66 (s, 3, N—CH_3), 5.50 (s, 2, N—CH_2), 2.8 (AB d, 2, J = 9.0 Hz, aromatic), 2.59 (AB d, 2, J = 9.0 Hz, aromatic); mass spectrum (70 eV) *m/e* (rel intensity) 188 (11), 119 (24), 91 (100), 77 (5), 65 (20), 42 (8).

Anal. Calcd for $C_{10}H_{12}N_4$: C, 63.83; H, 6.38; N, 29.79. Found: C, 63.96; H, 6.50; N, 29.92.

Anhydro-4-hydroxy-1-methyl-3-phenyl-1,2,3-triazolium Hydroxide (**4**, **R = Ph**).—Ethyl N-methyl-N-phenylazoaminoacetate (**2**, R = Ph) (2.0 g) in pyridine (3 ml) at 5° was treated dropwise with redistilled thionyl chloride (1.3 g) with stirring. After 10 hr at room temperature the reaction mixture was poured into ice water and extracted with chloroform. The chloroform was distilled and the residue triturated with small portions of acetone whence the product solidified. It crystallized from benzene as colorless plates of the sulfide **6** (R = Ph): 30 mg; mp 236–237°; ir (KBr) 3075–2990 (w) (CH), 1675 (s) (sh), 1650 (s) (CO), 1585 (m) (N=N) cm^{-1}; uv max (CH_3OH) 303 nm (log ϵ 4.15), 228 (4.32); nmr ($CDCl_3$) τ 5.62 (s, 3, N—CH_3), 2.58–2.08 (m, 5, aromatic); mass spectrum (70 eV) *m/e* (rel intensity) 380 (48), 218 (11), 206 (18), 188 (44), 105 (28), 78 (26), 77 (100).

Anal. Calcd for $C_{18}H_{16}N_6O_2S$: C, 56.74; H, 4.21; N, 22.10; S, 8.42. Found: C, 56.67; H, 4.12; N, 22.11; S, 8.69.

The above aqueous phase was concentrated on a rotatory evaporator, basified with ammonium hydroxide, and extracted with chloroform. After removal of the chloroform the residue was dissolved in benzene and chromatographed on neutral alumina. The colorless crystalline product obtained on elution with chloroform crystallized from benzene giving the mesoionic compound **4** (R = Ph) as colorless needles: 150 mg; mp 94–96°; ir (KBr) 3425 (m) (OH), 3150 (m) (CH), 1650 (s) (CO), 1590 (m) (N=N) cm^{-1}; uv max (CH_3OH) 298 nm (log ϵ 3.82), 237 (3.62), 203 (3.88); nmr ($CDCl_3$) τ 6.08 (s, 3, N—CH_3), 3.34 (s, 1, 5-H), 2.6–2.05 (m, 5, aromatic); mass spectrum (70 eV) *m/e* (rel intensity) 175 (100), 105 (32), 78 (14), 77 (62), 51 (38).

Anal. Calcd for $C_9H_9N_3O \cdot 0.5\ H_2O$: C, 58.69; H, 5.43; N, 22.82. Found: C, 58.84; H, 5.41; N, 22.81.

Similarly, **anhydro-4-hydroxy-1-methyl-3-*p*-tolyl-1,2,3-triazolium hydroxide** (**4**, **R** = *p*-$CH_3C_6H_4$) crystallized from benzene–petroleum ether as colorless needles: 400 mg (28%); mp 141–143°; ir (KBr) 3080 (m) (CH), 1660 (s) (CO), 1520 (m) (N=N) cm^{-1}; uv max (CH_3OH) 298 nm (log ϵ 3.98), 241 (3.90); nmr ($CDCl_3$) τ 7.62, (s, 3, C—CH_3), 6.03 (s, 3, N—CH_3), 3.3 (s, 1, 5-H), 2.72 (AB d, 2, J = 8.5 Hz, aromatic), 2.1 (AB d, 2, J = 8.5 Hz, aromatic); mass spectrum (70 eV) *m/e* (rel intensity), 189 (70), 119 (9), 91 (100), 65 (23), 42 (33).

Anal. Calcd for $C_{10}H_{11}N_3O$: C, 63.48; H, 5.86; N, 22.21. Found: C, 63.61; H, 5.91; N, 22.07.

Associated with this mesoionic compound was the sulfide **6** (R = *p*-$CH_3C_6H_4$) which crystallized from benzene as colorless needles: mp 268°; ir (KBr) 3040–2920 (w) (CH), 1650 (s) (CO), 1505 (m) (N=N) cm^{-1}; uv max (CH_3OH) 322 nm (log ϵ 4.28), 215 (4.33); nmr ($CDCl_3$) τ 7.73 (s, 3, C—CH_3), 5.7 (s, 3, N—CH_3), 3.07 (AB d, 2, J = 9.0 Hz aromatic), 2.33 (AB d, 2, J = 9.0 Hz, aromatic); mass spectrum (70 eV) *m/e* (rel intensity) 408 (8), 232 (6), 220 (9), 202 (17), 119 (13), 91 (100), 65 (21).

Anal. Calcd for $C_{20}H_{20}N_6O_2S$: C, 58.80; H, 4.94; N, 20.58; S, 7.84. Found: C, 59.18; H, 4.70; N, 20.37; S, 7.40.

Reaction of Thionyl Chloride with N-Methyl-N-*p*-tolylazoaminoacetamide (**3**, **R** = *p*-$CH_3C_6H_4$).—The above amide (2.0 g) in pyridine (2 g) at ~0° was treated with thionyl chloride (1.1 g). After several hours the reaction mixture was poured into water and the yellow solid which separated recrystallized from benzene. It formed colorless needles of the sulfide **6** (R = *p*-$CH_3C_6H_4$): 40 mg, mp 267–268°. The mixture melting point with the sulfide **6** (R = *p*-$CH_3C_6H_4$) prepared above was not depressed and the two products had identical infrared spectra. Reaction of the mesoionic compound (**4**) with sulfur monochloride in methylene chloride gave the same product.

Reaction of Thionyl Chloride with Anhydro-4-hydroxy-1-methyl-3-*p*-tolyl-1,2,3-triazolium Hydroxide (**4**, **R** = *p*-$CH_3C_6H_4$).—The mesoionic compound (200 mg) in pyridine (2 ml) at 5° was treated with thionyl chloride (150 mg). A colorless product separated within 20 min and stirring was continued for 2 hr at room temperature. The reaction mixture was poured into water and the solid which separated recrystallized from chloroform–petroleum ether, forming colorless, irregular prisms of the sulfoxide **5** (R = *p*-$CH_3C_6H_4$): mp 250–255° dec; ir (KBr) 3050 (w) (CH), 1655 (s) (CO), 1510 (m) (N=N) cm^{-1}; uv max (CH_3OH) 327 nm (log ϵ 4.20), 217 (4.31), 203 (4.35); nmr ($CDCl_3$) τ 7.65 (s, 3, C—CH_3), 5.58 (s, 3, N—CH_3), 2.76 (AB d, 2, J = 9.0 Hz, aromatic), 2.2 (AB d, 2, J = 9.0 Hz, aromatic); mass spectrum (70 eV) *m/e* (rel intensity) 408 (9), 232 (3), 220 (38), 202 (15), 119 (28), 92 (16), 91 (100), 65 (30), 43 (46), 41 (28), 39 (30).

Anal. Calcd for $C_{20}H_{20}N_6O_3S$: C, 55.60; H, 4.75; N, 19.80. Found: C, 56.07; H, 4.54; N, 19.34.

4-Hydroxy-1-methyl-3-*p*-tolyl-1,2,3-triazolium Chloride (**11**, **R** = *p*-$CH_3C_6H_4$).—A solution of the mesoionic compound **4** (R = *p*-$CH_3C_6H_4$) (1.0 g) in benzene (20 ml) was saturated with dry hydrogen chloride at about 0°. The product which separated was recrystallized from ethanol–ether, forming colorless, irregular prisms: 1.1 g (100%); mp 195–198°; ir (KBr) 3080 (m) (CH), 2100 (broad, m) (OH), 1600 (s) (N=N), 1575 (s) (C=C) cm^{-1}; nmr (DMSO-d_6) τ 7.62 (s, 3, C—CH_3), 5.85 (s, 3, N—CH_3), 2.63 (AB d, 2, J = 8.0 Hz, aromatic), 2.27 (AB d, 2, J = 8.0 Hz, aromatic), 2.24 (s, 1, 5-H), 2.02 (s, 1, 4-OH, exchanged with D_2O).

Anal. Calcd for $C_{10}H_{12}ClN_3O$: C, 53.21; H, 5.32; N, 18.62. Found: C, 53.40; H, 5.36; N, 18.87.

When the above chloride was heated *in vacuo* for 6 hr, or passed through a column of neutral alumina and the product eluted with methanol, the mesoionic compound **4** (R = *p*-$CH_3C_6H_4$) was obtained.

4-Ethoxy-1-methyl-3-*p*-tolyl-1,2,3-triazolium Fluoroborate (**12**, **R** = *p*-$CH_3C_6H_4$).—The mesoionic compound **4** (R = *p*-$CH_3C_6H_4$) (1.0 g) in dichloromethane (10 ml) and triethyloxonium fluoroborate[15] (1.0 g) in dichloromethane (20 ml) were kept overnight at room temperature and the reaction mixture then diluted with dry ether (200 ml). The colorless product which separated on cooling crystallized from absolute ethanol–ether as colorless rhombs: 1.5 g (95%); mp 81–83°; ir (KBr) 3150, 3000 (m) (CH), 1620 (s) (N=N), 1060 (broad, s) (COC) cm^{-1}; uv max (CH_3OH) 252 nm (log ϵ 4.00).

Anal. Calcd for $C_{12}H_{16}BF_4N_3O$: C, 47.21; H, 5.24; N, 13.77. Found: C, 47.07; H, 5.27; N, 13.67.

The picrate, prepared in ethanol, crystallized from ethanol as yellow needles, mp 165°.

Anal. Calcd for $C_{18}H_{19}N_6O_8$: C, 48.31; H, 4.28; N, 18.78. Found: C, 48.29; H, 4.13; N, 18.83.

(15) H. Meerwein, *Org. Syn.*, **46**, 113 (1966).

When the above fluoroborate (400 mg) was refluxed with HBr (15 ml of 48%) for 2 hr, the red reaction mixture basified with 10% sodium hydroxide solution and the alkaline solution extracted with chloroform, the product obtained was shown to be anhydro-4-hydroxy-1-methyl-3-*p*-tolyl-1,2,3-triazolium hydroxide.

Anhydro-5-bromo-4-hydroxy-1-methyl-3-*p*-tolyl-1,2,3-triazolium Hydroxide (14, R = *p*-$CH_3C_6H_4$).—The mesoionic compound **4** (R = *p*-$CH_3C_6H_4$) (100 mg) in acetic acid (5 ml) was cooled and bromine (200 mg) in acetic acid (2 ml) added dropwise with stirring. After 2 hr at room temperature the excess acid was removed on a rotatory evaporator, water and a solution of sodium carbonate added, and the solution extracted with chloroform. The residue left after removal of the chloroform was dissolved in benzene, chromatographed on neutral alumina and eluted with a chloroform–methanol mixture (97:3). It crystallized from benzene–petroleum ether as colorless needles: 90 mg (68%); mp 135°; ir (KBr) 1650 (s) (CO), 1505 (m) (N=N) cm^{-1}; uv max (CH_3OH) 310 nm (log ϵ 4.26), 248 (4.03), 202 (4.34); nmr ($CDCl_3$) τ 7.60 (s, 3, C—CH_3), 5.98 (s, 3, N—CH_3), 2.7 (AB d, 2, J = 8.5 Hz, aromatic), 2.08 (AB d, 2, J = 8.5 Hz, aromatic); mass spectrum (70 eV) *m/e* (rel intensity) 270 (2.5), 269 (22), 268 (2.5), 267 (22), 119 (11), 91 (100), 65 (13).

Anal. Calcd for $C_{10}H_{10}BrN_3O$: C, 44.78; H, 3.73; N, 15.67. Found: C, 44.92; H, 3.81; N, 15.54.

Reaction of 4 with Dimethyl Acetylenedicarboxylate.—The mesoionic compound **4** (R = *p*-$CH_3C_6H_4$) (200 mg) and dimethyl acetylenedicarboxylate (140 mg) in benzene (5 ml) were heated under reflux for 120 hr. The reaction mixture was poured into water and next morning evaporated to dryness on a rotatory evaporator. The residue was leached with benzene and the small amount of undissolved material was identified as di-*p*-tolylurea, mp 267°, not depressed on admixture with an authentic specimen.

The benzene solution was evaporated and the residue recrystallized from benzene–petroleum ether affording colorless needles of methyl 1-methylpyrazole-3,4-dicarboxylate: 150 mg (75%), mp 68–69°. This product was identical in all respects with an authentic sample of the pyrazole.[16]

Reaction of 4 with Ethyl Azodicarboxylate.—The mesoionic compound **4** (R = *p*-$CH_3C_6H_4$) (100 mg) and ethyl azodicarboxylate (100 mg) in xylene (5 ml) were refluxed for 1 hr. Removal of the xylene on a rotatory evaporator and recrystallization of the residue from benzene–petroleum ether afforded the cycloadduct ethyl 7-methyl-5-oxo-6-*p*-tolyl-1,2,3,6,7-pentaazabicyclo[2.2.1]heptane-2,3-dicarboxylate (**17**, R = *p*-$CH_3C_6H_4$) as colorless needles: 130 mg (72%); mp 172–173°; ir (KBr) 3175, 3000 (m) (CH), 1725 (s) (CO), 1670 (s) (CO) cm^{-1}; uv max (CH_3OH) 304 nm (log ϵ 4.03), 245 (3.58), 201 (4.30); nmr ($CDCl_3$) τ 8.83 (t, 3, J = 7.0 Hz, CH_2—**CH_3**), 8.77 (t, 3, J = 7.0 Hz, CH_2—**CH_3**), 7.63 (s, 3, C—CH_3), 5.85 (s, 3, N—CH_3), 5.91 (q, 2, J = 7.0 Hz, **CH_2**—CH_3), 5.76 (q, 2, J = 7.0 Hz, **CH_2**—CH_3), 2.76 (AB d, 2, J = 8.5 Hz, aromatic), 2.05 (AB d, 2, J = 8.5 Hz, aromatic), ~0.18 (s, 1, CH); mass spectrum (70 eV) *m/e* (rel intensity) 363 (15), 290 (19), 245 (8), 230 (12), 218 (33), 203 (7), 189 (27), 133 (10), 119 (15), 104 (8), 92 (12), 91 (100), 78 (17), 77 (9), 65 (15), 57 (13).

Anal. Calcd for $C_{16}H_{21}N_5O_5$: C, 52.88; H, 5.83; N, 19.28. Found: C, 52.95; H, 5.92; N, 19.18.

Reaction of 4 with Tetracyanoethylene.—The mesoionic compound **4** (R = *p*-$CH_3C_6H_4$) (200 mg) and tetracyanoethylene (140 mg) in xylene (5 ml) were heated under reflux for 6 hr. The dark red solid which separated on cooling was recrystallized from chloroform–petroleum ether giving deep red plates of anhydro-4-hydroxy-1-methyl-5-(1,2,2-tricyanoethyl)-3-*p*-tolyl-1,2,3-triazonium hydroxide **18** (R = *p*-$CH_3C_6H_4$): 205 mg (55%); mp 210–211°; ir (KBr) 2225 (m) (CN), 1690 (s) (CO), 1530 (s) (N=N) cm^{-1}; uv max(CH_3OH) 362 nm (log ϵ 4.00), 243 (3.91), 203 (4.01); nmr (DMSO-d_6) τ 7.58 (s, 3, C—CH_3), 5.62 (s, 3, N—CH_3), 2.55 (AB d, 2, J = 8.5 Hz, aromatic), 2.20 (AB d, 2, J = 8.5 Hz, aromatic); mass spectrum (70 eV) *m/e* (rel intensity) 290 (33), 119 (8), 92 (8), 91 (100), 65 (19).

Anal. Calcd for $C_{15}H_{10}N_6O$: C, 62.06; H, 3.47; N, 28.95. Found: C, 61.79; H, 3.50; N, 28.42.

4-Amino-1-methyl-3-phenyl-1,2,3-triazolium Chloride (8, R = Ph).—Dry hydrogen chloride was passed into a solution of N-methyl-N-phenylazoaminoacetonitrile (2.0 g) in anhydrous ether (20 ml) for 20 min during which a colorless product separated. It crystallized from ethanol–ether as colorless, irregular prisms and was extremely hygroscopic. It was characterized as the picrate which crystallized from methanol as yellow needles, mp 176–177°.

Anal. Calcd for $C_{15}H_{13}N_7O_7$: C, 44.67; H, 3.22; N, 24.31. Found: C, 44.84; H, 3.26; N, 24.47.

4-Amino-1-methyl-5-*p*-tolyl-1,2,3-triazolium chloride (8, R = *p*-$CH_3C_6H_4$) was likewise extremely hygroscopic and was also characterized as the picrate which crystallized from methanol as yellow needles, mp 190–191°.

Anal. Calcd for $C_{16}H_{15}N_7O_7$: C, 46.05; H, 3.59; N, 23.51. Found: C, 46.10; H, 3.64; N, 23.45.

Anhydro-4-acetimino-1-methyl-3-phenyl-1,2,3-triazolium Hydroxide (10, R = Ph). A. From 7 (R = Ph) and Acetyl Chloride.—The nitrile (2.5 g) in benzene (50 ml) was treated dropwise at room temperature with acetyl chloride (1.5 g) and, after ~1 hr, a brown solid had separated. After warming the reaction mixture gently for an additional hour, the brown product was collected and recrystallized several times from ethanol–ether, forming colorless irregular prisms which darken on standing and have a wide melting point range: ir (KBr) 3300–3200, (s) (NH), 3140, 3050 (s) (CH), 1650 (s) (CO), 1600 (s) (N=N) cm^{-1}. This product was assigned the structure 4-acetamido-1-methyl-3-phenyl-1,2,3-triazolium chloride (**9**, R = Ph) and was characterized as the picrate which separated from methanol as yellow needles: mp 194–195°.

Anal. Calcd for $C_{17}H_{15}N_7O_8$: C, 45.83; H, 3.37; N, 22.02. Found: C, 46.01; H, 3.49; N, 21.90.

The above chloride was dissolved in water and the solution basified with ammonium hydroxide. The solution was extracted with chloroform, the chloroform extract was dried (Na_2SO_4) and, after removal of the chloroform, the residue was recrystallized from benzene (charcoal) forming colorless needles of **10** (R = Ph): 0.6 g (20%); mp 177–178; ir (KBr) 3175 (m) (CH), 1600 (s) (CO), 1550 (s) (N=N) cm^{-1}; uv max (CH_3OH) 303 nm (log ϵ 3.91), 228 (4.08); nmr ($CDCl_3$) τ 7.83 (s, 3, -CO-CH_3), 5.84 (s, 3, N—CH_3), 2.47–1.94 (m, 5, aromatic), 1.37 (s, 1, 5-H); mass spectrum (70 eV) *m/e* (rel intensity) 216 (28), 202 (11), 201 (100), 188 (5), 123 (6), 92 (5), 77 (15), 51 (6), 43 (15).

Anal. Calcd for $C_{11}H_{12}N_4O$: C, 61.10; H, 5.55; N, 25.92. Found: C, 60.99; H, 5.60; N, 25.76.

B. From 8 and Acetic Anhydride.—The chloride **8** (R = Ph) (1.0 g) and acetic anhydride (5.0 ml) were heated on the water bath for 2 hr and, on cooling, a brown product separated. Excess acetic anhydride was removed under reduced pressure on the steam bath and the residue dissolved in a small volume of water and basified with ammonium hydroxide. After work-up as above, colorless needles of **10** (R = Ph), mp 177–178°, were obtained.

In the above fashion **anhydro-4-acetimino-1-methyl-3-*p*-tolyl-1,2,3-triazolium hydroxide (10, R = *p*-$CH_3C_6H_4$)** was obtained as colorless needles from methanol–benzene (charcoal): 30%, mp 214–215°; ir (KBr) 3175, 2925 (m) (CH), 1600 (s) (CO), 1550 (N=N) cm^{-1}; uv max (CH_3OH) 303 nm (log ϵ 3.94), 245 (4.11); nmr ($CDCl_3$) τ 7.85 (s, 3, -$COCH_3$), 7.6 (s, 3, C—CH_3), 5.85 (s, 3, N—CH_3), 2.67 (AB d, 2, J = 9.0 Hz, aromatic), 2.1 (AB d, 2, J = 9.0 Hz, aromatic), 1.43 (s, 1, 5-H); mass spectrum (70 eV) *m/e* (rel intensity) 230 (25), 216 (12), 215 (100), 123 (25), 119 (4), 91 (40), 65 (24), 43 (55), 42 (13).

Anal. Calcd for $C_{12}H_{14}N_4O$: C, 62.62; H, 6.08; N, 24.35. Found: C, 62.48; H, 6.16; N, 24.19.

The corresponding salt, 4-acetamido-1-methyl-3-*p*-tolyl-1,2,3-triazolium chloride, obtained from **7** (R = *p*-$CH_3C_6H_4$) and acetyl chloride was hygroscopic and could not be purified satisfactorily. It was characterized as the picrate which crystallized from methanol as yellow needles: mp 178–179°.

Anal. Calcd for $C_{18}H_{17}N_7O_8$: C, 47.07; H, 3.70; N, 21.35. Found: C, 47.27; H, 3.73; N, 21.19.

Registry No.—**2** (R = Ph), 21600-46-4; **2** (R = *p*-$CH_3C_6H_4$), 25677-19-4; **3** (R = Ph), 25725-99-9; **3** (R = *p*-$CH_3C_6H_4$), 25677-20-7; **4** (R = Ph), 15284-64-7; **4** (R = *p*-$CH_3C_6H_4$), 25677-22-9; **5** (R = *p*-$CH_3C_6H_4$), 25677-23-0; **6** (R = Ph), 25677-24-1; **6** (R = *p*-$CH_3C_6H_4$), 25677-25-2; **7** (R = Ph), 25677-26-3;

(16) K. T. Potts and U. P. Singh, *Chem. Commun.*, 66 (1969).

7 (R = *p*-$CH_3C_6H_4$), 25677-27-4; **8** (R = Ph), 25726-00-5; **8** [R = *p*-$CH_3C_6H_4$ (picrate)], 25677-28-5; **9** [R = Ph (picrate)], 25677-29-6; **10** (R = Ph), 25677-30-9; **10** (R = *p*-$CH_3C_6H_4$), 25677-31-0; **10** [R = *p*-$CH_3C_6H_4$ (picrate)], 25677-32-1; **11** (R = *p*-$CH_3C_6H_4$), 25677-33-2; **12** (R = *p*-$CH_3C_6H_4$), 25676-99-7; **12** [R = *p*-$CH_3C_6H_4$ (picrate)], 25677-34-3; **14** (R = *p*-$CH_3C_6H_4$), 25677-35-4; **17** (R = *p*-$CH_3C_6H_4$), 25677-36-5; **18** (R = *p*-$CH_3C_6H_4$), 25677-37-6.

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An Intramolecular Facilitated Acylation of a Tertiary Hydroxyl Group in a Perhydrobenzo[*b*]quinolizinetetrol[1,2]

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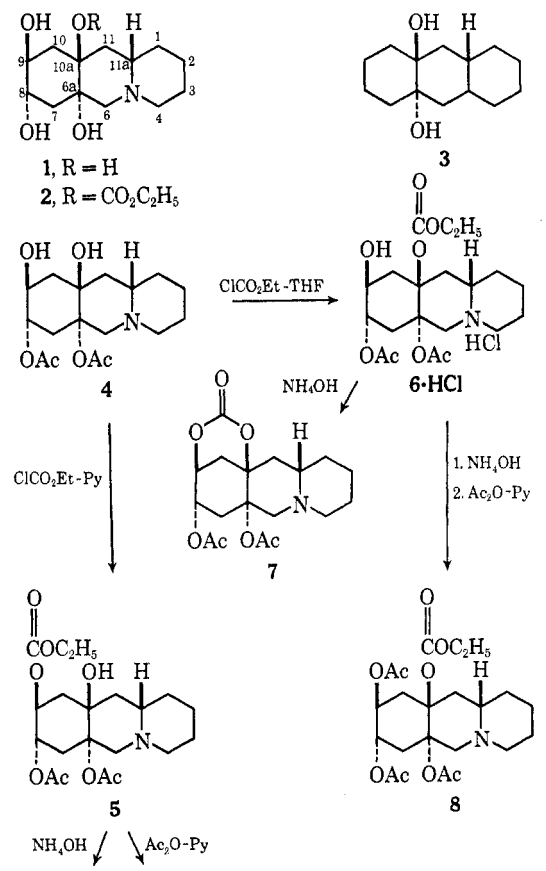
During the structure elucidation of 1,3,4,6,6a,7,8,9,10,10a,11,11a-dodecahydro-2H-benzo[*b*]quinolizine-6a,8,9-10a-tetrol (**1**), a selective acylation of the tertiary 10a-hydroxyl was observed. This reaction has been examined in more detail on the 6a,8-diacetate derivative **4**. It has been found that the acylation is solvent dependent. In pyridine, the secondary 9-hydroxyl is acylated with difficulty. In chloroform and tetrahydrofuran, the 10a-ethyl carbonate is obtained. Evidence is given for postulating that the acylation occurs directly by attack on the tertiary 10a-hydroxyl with an assist by the secondary *cis*-9-hydroxyl and by what appears to be a long-range field effect of the ring nitrogen.

In an earlier paper,[3] the novel facile acylation of a tertiary hydroxyl group bearing a 1,3-diaxial juxtaposition to both a secondary hydroxyl and a nitrogen lone pair of electrons was reported. The compound under investigation was 1,3,4,6,6a,7,8,9,10,10a,11,11a-dodecahydro-2H-benzo[*b*]quinolizine-6a,8,9,10a-tetrol (**1**), and the tertiary hydroxyl was located at position 6a.[4] During the stereochemical elucidation of the all-axial tetrol **1**, it was decided that one approach would be to form bridged structures of the two pairs of *cis*-1,3-diaxial hydroxyl groups. One method is to form a carbonate bridge using ethyl chloroformate.[5]

Treatment of tetrol **1** in tetrahydrofuran (THF) yielded the 10a-ethyl carbonate **2**.[3] Fieser has reported on the use of ethyl chloroformate as an alcohol protecting group. He called the reaction cathylation and the products cathylates. He also noted that no carbonates (cathylates) would form if the hydroxyl group was axial.[6] Thus here is ethyl chloroformate acylating an axial tertiary hydroxyl group. Because of the unusual nature of this acylation, it was decided to investigate this reaction further.

In studying the properties of this reaction in more detail, two items of information became apparent: (1) the C-9 secondary hydroxyl is necessary and (2) the reaction is solvent dependent. There was no reaction when diol **3** was the starting material.[3] Use of pyridine gave a mixture of products when **1** was the starting material, presumably owing to partial acylation of any of the four possible hydroxyls and in any combination. In order to eliminate two of the four possible hydroxyls, it was decided to use the known 6a,8-diacetate[3] (**4**) as the starting material.



Acylation of the 6a,8-diacetate (**4**) in tetrahydrofuran yielded the 6a,8-diacetate tertiary 10a-ethyl carbonate (**6**) in low yield. It was not possible to isolate

(1) This work was presented before the Medicinal Chemistry Section of the Academy of Pharmaceutical Sciences at the annual meeting of the American Pharmaceutical Association, Montreal, Quebec, May 1969, Abstracts, p 88.

(2) Financial support by the General Research Fund of the Oregon State University Graduate School is gratefully acknowledged.

(3) S. M. Kupchan, J. H. Block, and A. C. Isenberg, *J. Amer. Chem. Soc.* **89**, 1189 (1967).

(4) All asymmetric synthetic products described are racemic mixtures. Only one optical antipode for each is drawn for convenience of representation and discussion. In the representation of the quinolizidine derivatives the electron pair on nitrogen is understood to project downward, and a heavy bond to the 11a hydrogen indicates the *trans*-quinolizidine configuration.

(5) L. Hough, J. E. Priddle, and R. S. Theobold, *Advan. Carbohyd. Chem.*, **15**, 91 (1960).

(6) L. Fieser and M. Fieser, "Steroids," Reinhold, New York, N. Y. 1959, pp 192, 217–219, 221, 241, 836.