Photodecomposition of the Dianions of the Di-*p*-tosylhydrazones of Biacetyl and Benzil

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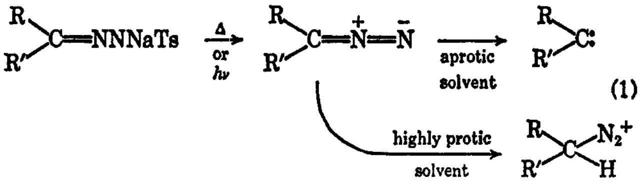
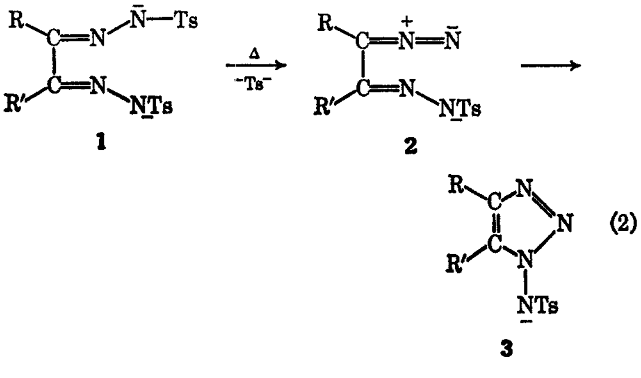
Received August 8, 1968

Irradiation of biacetyl di-*p*-tosylhydrazone dianion through Vycor gives 2-butyne as the only volatile product. The formation of 2-butyne is shown to arise *via* intermediate formation of the anion of 4,5-dimethyl-1-toluene-*p*-sulfonamido-1,2,3-triazole, which was isolable in the acid form in 81% yield when the irradiation was carried out employing a Corex filter. Irradiation of benzil di-*p*-tosylhydrazone dianion through Vycor gave a 74% yield of *cis*- and *trans*-α-methoxystilbene formed in the ratio 38:62. 4,5-Diphenyl-1-toluene-*p*-sulfonamido-1,2,3-triazole was isolated in 25% yield when the irradiation was carried out employing a Corex filter.

The course of the thermal decomposition of mono-*p*-tosylhydrazone salts has been well established.[1-6] *p*-Toluenesulfinate anion is eliminated in an initial step with resultant formation of a diazo compound. Depending on the choice of reaction conditions, the diazo compound may either be isolated[1b,3] or subsequently decomposed *in situ via* carbenoid or cationoid pathways.[1a,2,4,6] Dauben and Willey[7] have shown that the decomposition can also be effected photochemically. The evidence indicates that, in this case too, a fragmentation occurs first to give the diazo compound (reaction 1). Bamford and Stevens[5] discovered that the dianions of the di-*p*-tosylhydrazones of 1,2-diketones (**1**) decompose thermally to give derivatives of 1-toluene-*p*-sulfonamido-1,2,3-triazole anion (**3**). Apparently in this instance, the decomposition involves the loss of one toluenesulfinate anion thereby forming an intermediate α-diazotosylhydrazone anion (**2**) which then cyclizes to give **3** (reaction 2). Theoretical considerations which are presented below indicated to us that compounds with structure **1** might decompose photochemically by a different route from the one above to give alkynes instead of **3**. These considerations provided the necessary impetus for the investigation of the photochemistry of **1**.





A comparison of the molecular orbital nodal patterns in mono- and 1,2-ditosylhydrazone anions[8] suggests that the latter might decompose photolytically by way of a bis elimination process. The lowest energy electronic transition (ψ_5–ψ_6, Figure 1a) in a simple monotosylhydrazone anion should be accompanied by a decrease in the sulfur–nitrogen bond order. The initial fragmentation to give the diazo compound (reaction 1) is due to bond breaking at this position. Analogously, in the 1,2-ditosylhydrazone dianions, the bond order at both sulfur–nitrogen bonds is predicted to decrease on photoexcitation to the first excited state (ψ_{10}–ψ_{11}, Figure 1b). Possibly in this case, irradiation might effect the simultaneous elimination of two toluenesulfinate anions resulting in the formation of a didiazo compound (**4**, reaction 3). Regarding the fate of **4**, a consideration of molecular orbital nodal patterns[9] suggests that this type of compound might also decompose photolytically by way of a bis elimination process generating either a diradical or an alkyne depending on the spin multiplicity of the reactive intermediate. Possibly, the same species could result directly from **1** if cleavage at all four sites (*i.e.*, two S–N bonds and

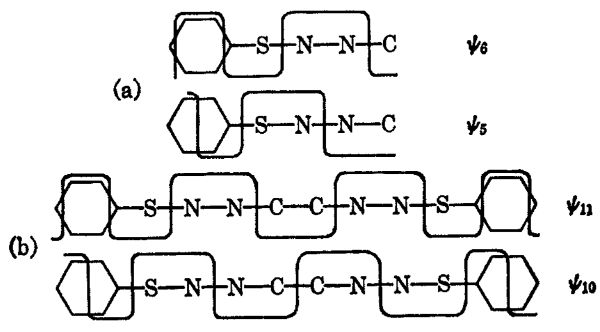


Figure 1.—Comparison of the nodal patterns in the highest energy bonding and lowest energy antibonding molecular orbitals for anions of (a) monotosylhydrazones and (b) 1,2-ditosylhydrazones.

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(1) (a) J. H. Bayless, L. Friedman, F. B. Cook, and H. Shechter, *J. Amer. Chem. Soc.*, **90**, 531 (1968); (b) G. Kaufman, F. Cook, H. Shechter, J. Bayless, and L. Friedman, *ibid.*, **89**, 5736 (1967).

(2) R. H. Shapiro, J. H. Duncan, and J. C. Clopton, *ibid.*, **89**, 471, 1442 (1967).

(3) G. M. Kaufman, J. A. Smith, G. G. Vander Stouw, and H. Shechter, *ibid.*, **87**, 935 (1965).

(4) L. Friedman and H. Shechter, *ibid.*, **81**, 5512 (1959).

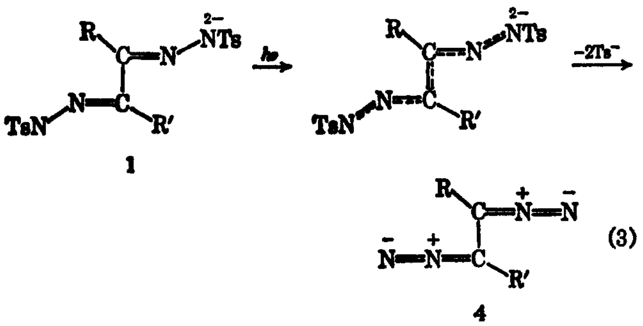
(5) W. R. Bamford and T. S. Stevens, *J. Chem. Soc.*, 4735 (1952).

(6) J. W. Powell and M. C. Whiting, *Tetrahedron*, **7**, 305 (1959).

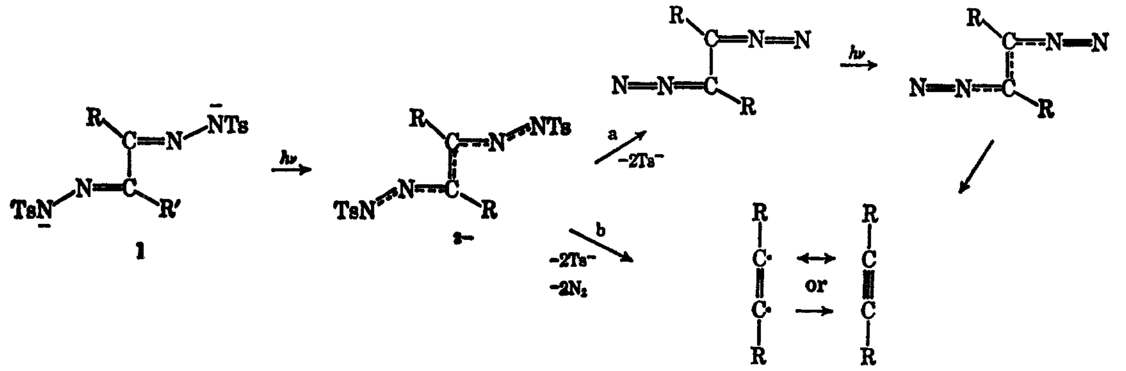
(7) W. G. Dauben and F. G. Willey, *J. Amer. Chem. Soc.*, **84**, 1497 (1962).

(8) The molecular orbital nodal patterns for mono- and 1,2-ditosylhydrazones shown in Figure 1 were adapted from the nodal patterns for 1-phenylbutadiene and 1,8-diphenyloctatetraene, respectively. See C. Coulson and A. Streitwieser, Jr., "Dictionary of π-Electron Calculations," W. H. Freeman and Co., San Francisco, Calif., 1965. Nodal positions in the corresponding species should be identical.

(9) The highest energy occupied molecular orbital ψ_4 in **4** is bonding at both C–N linkages and antibonding at C–C, while in the lowest energy unoccupied orbital, ψ_5, nodes occur at both C–N positions with bonding at the C–C linkage.


(3)

two C–N bonds) occurred simultaneously without intervention of 4 (reaction 4b).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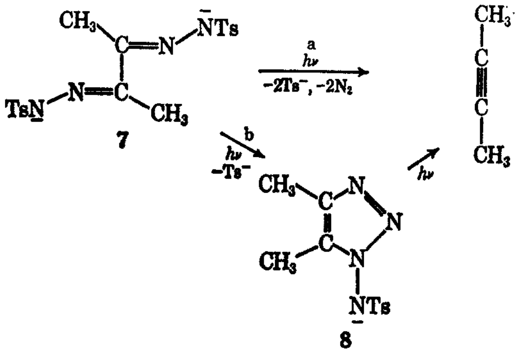
Results and Discussion

The photochemistry of biacetyl and benzil ditosylhydrazone dianions was investigated. These two species seemed especially appropriate in view of the fact that their behavior on thermal decomposition had previously been studied.[5] Biacetyl ditosylhydrazone dissolved in methanolic sodium methoxide solution giving lemon yellow solutions of the dianion **7**. Irradiation at room temperature with a 450-W Hanovia lamp, employing a Vycor filter, effected a smooth decomposition producing 2-butyne as the only volatile product. While this result is in line with our ideas based on molecular orbital nodal patterns, recent work of Willey[10] has shown that 4,5 dialkyl- and 4,5-diaryl-1-toluene-*p*-sulfonamido-1,2,3-triazole derivatives decompose photolytically in basic media giving alkynes, which raises the question as to whether 4,5-dimethyltoluene-*p*-sulfonamido-1,2,3-triazole anion (**8**) might be an intermediate in the photodecomposition of **7**. Indeed, when the irradiation was interrupted and recovered solid material analyzed by column chromatography, the triazole corresponding to **8** was isolated. A means of determining the relative importance of pathways a (bis elimination) and b (reaction *via* **8**) in reaction 5 was suggested on examination of the ultraviolet absorption curves for **7** and **8** (Figure 2). While the curve for **7** exhibits a prominent maximum at 307 mμ, the curve for **8** shows little absorption at wavelengths greater than 260 mμ. By employing an appropriate filter, it appeared that it might be possible to decompose **7** selectively without destroying **8**. When the irradiation was carried out employing a Corex filter, which transmits light of wavelength greater than 260 mμ, very little gas evolution was noted, and, after 2 hr, analysis of the reaction mixture revealed that nearly all of the dianion had been converted into **8** as indicated by the isolation of 4,5-dimethyl-1-toluene-*p*-sulfonamido-1,2,3-triazole in 81% yield. By far the most important source of 2-butyne, then, is **8** (reaction 5b). Instead of cleaving the dianion directly in a bis elimination process, the photoexcitation process seems to weaken only the sulfur–nitrogen bonds. Apparently, cleavage of a single sulfur–nitrogen bond is then followed by cyclization (reaction 2).[11]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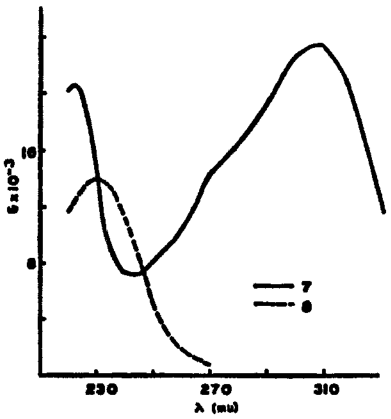

Figure 2.—Comparison of the ultraviolet absorption curves for the sodium salts of biacetyl ditosylhydrazone and 4,5-dimethyl-1-toluene-*p*-sulfonamide-1,2,3-triazole.

The behavior of benzil ditosylhydrazone dianon (**9**) on pyrolysis stands apart from the behavior of the ditosylhydrazone dianions derived from aliphatic 1,2-diketones. Bamford and Stevens[5] have reported that **9** gives a 73% yield of diphenylacetylene. No mention was made of the formation of any 4,5-diphenyl-1-

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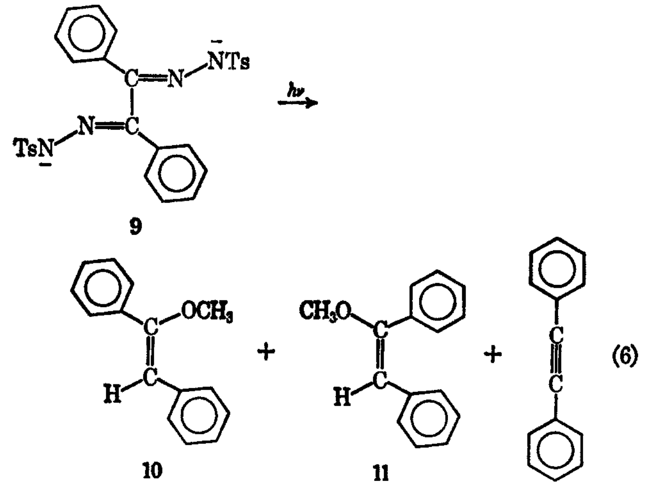
(10) F. Willey, *Angew. Chem. Intern. Ed. Engl.*, **3**, 138 (1964).

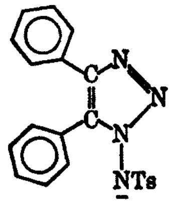
(11) This assumes that the *p*-toluenesulfinate anion(s) is (are) lost from an excited state in the *s-trans* conformation. A second consideration is that it is not inconceivable that the excited state actually loses two toluenesulfinate anions, cyclization occurs, and one toluenesulfinate ion is reincorporated to yield triazole anion **8**.

toluene-p-sulfonamido-1,2,3-triazole.[12] Rather unexpected behavior was also shown on irradiation (Vycor). Instead of producing diphenylacetylene as the major product, photodecomposition of benzil ditosylhydrazone in methanolic sodium methoxide gave a 74% yield of the two isomeric α-methoxystilbenes **10** and **11** formed in the ratio 62:38 (reaction 6). The gross structure of these compounds was established by their facile hydrolysis to deoxybenzoin. The stereochemical assignment was complicated by the difficulty encountered in obtaining one of the isomers free from contaminating diphenylacetylene (formed in 20% yield). The infrared and ultraviolet spectra of the two isomers were quite similar; however, a choice can be made by consideration of the nmr spectra. Assuming an angle of twist out of the plane of the double bond of 40° for the phenyl groups of both isomers[13] and using the data of Johnson and Bovey,[14] it can be calculated that the olefinic hydrogen of the *trans* isomer should be deshielded to a greater extent than that of the *cis* isomer, while the methoxyl of the *cis* derivative should be deshielded to a greater extent than that of the *trans*. On this basis, the predominant stilbene component (=CH, τ 3.92; OCH_3, 6.42) was assigned the *trans*-α-methoxystilbene structure and the minor component (=CH, τ 4.20; OCH_3 6.26) the *cis* structure. Isomeric α-methoxystilbenes **10** and **11** were shown to be primary reaction products rather than secondary products formed by the photoaddition of methanol to diphenylacetylene. When diphenylacetylene was irradiated under the conditions of the original experiment, a nearly quantitative yield of unchanged starting material was recovered from the reaction.



9 10 11 (6)

The behavior of **9** on irradiation is similar to **7** in that a toluenesulfonamidotriazole anion (**12**) is formed as an intermediate in the reaction. Irradiation through Corex, however, resulted in a smaller yield (25% maximum) of **12**. The phenyl substituents in **12** extend the length of conjugation so that this anion shows considerable ultraviolet absorption at wavelengths greater than 260 mμ (Figure 3). Photodecomposition of **12** as well as of **9** is then to be expected under these conditions.



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The fact that most of **9** undergoes reaction to form **10** and **11**, whereas no detectable amount of similar products could be found in the case of **7**, is strongly reminiscent of the contrasting chemistry of dialkyl- and diarylcarbenes.[15] Dialkycarbenes usually react by intramolecular routes of insertion, hydrogen migration, and rearrangement, whereas intermolecular reactions, such as abstraction, are common for diarylcarbene intermediates.[16] Therefore, it appears tempting to rationalize the present case tentatively on the basis that the photodecomposition of **12** results in the generation of a triplet-state intermediate, whereas in the case of **8** product is formed by way of a singlet-state intermediate. Additional experimentation designed to elucidate the details of the photodecompositions of the triazole anions **8** and **12** is presently underway.

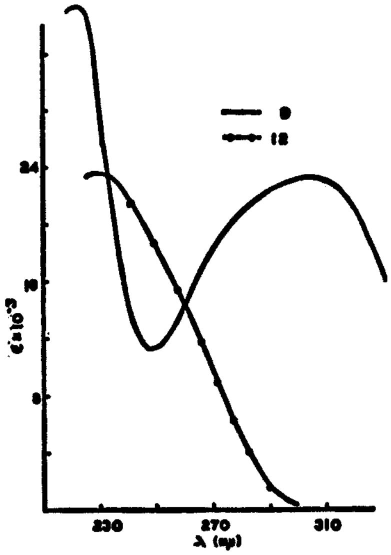

Figure 3.—Comparison of the ultraviolet absorption curves for the sodium salts of benzil ditosylhydrazone and 4,5-diphenyl-1-toluene-p-sulfonamido-1,2,3-triazole.

In summary, the photodecomposition of **7**, the ditosylhydrazone dianion of a representative aliphatic 1,2-diketone, has been shown to give 2-butyne as the sole volatile reaction product. This product arises, nevertheless, *via* the intermediate formation of **8** rather than by way of a bis elimination process involving the loss of two toluenesulfinate anions and two molecules of nitrogen. The direct photochemical generation of an alkyne from the ditosylhydrazone of a 1,2-diketone represents a potentially useful synthetic route to

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(12) Willey[10] indicates, however, that the 4,5-diphenyl-1-toluene-p-sulfonamido-1,2,3-triazole is available by way of the Bamford and Stevens method.

(13) See H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley & Sons, Inc., New York, N. Y., 1962, p 424.

(14) C. E. Johnson, Jr. and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).

(15) W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964, Chapters 3 and 5.

(16) A somewhat analogous case to that presently under consideration is found in the photodecomposition of 1,4-bis(α-diazobenzyl)benzene, which has been shown to yield a triplet-state dicarbenoid intermediate: R. Murray and A. Trozzolo, *J. Org. Chem.*, **26**, 3109 (1961); A. Trozzolo, R. Murray, G. Smolinsky, W. Yager, and E. Wasserman, *J. Amer. Chem. Soc.*, **85**, 2526 (1963).

alkynes, eliminating the necessity of preparing the triazole intermediate in a separate step. Dianion **9** exhibits the same general behavior undergoing photocyclization to **12**, but the subsequent photodecomposition of **12** differs significantly from that of **8**, in that it leads to an incorporation of a molecule of solvent, producing methoxystilbenes as the major product fraction.

Experimental Section

All melting and boiling points were uncorrected. Microanalyses were performed by Alfred Bernhardt, Mikroanalytisches Laboratorium, Max Planck Institut fur Kohlenforschung, Mülheim (Ruhr), Germany, or Galbraith Microanalytical Laboratories, Knoxville, Tenn. Infrared spectra were recorded on a Perkin-Elmer Model 137 spectrometer. Spectral absorptions are reported in wavenumbers (cm^{-1}) and are subject to the following general reading errors: $\Delta\nu$ >3000, 10 cm^{-1}; 2200–3000, 5–9 cm^{-1}; 1200–2200, 2–4 cm^{-1}. The intensities of the absorption bands are denoted by the code s (strong), m (medium), and w (weak). Nmr spectra were measured on a Varian Associates A-60 spectrometer using carbon tetrachloride as solvent and tetramethylsilane as an internal standard. Vapor phase chromatographic analyses were performed on an Aerograph A-90-P gas chromatograph equipped with a thermal conductivity detector. Two columns were employed: column A, a 15 ft × 0.25 in. aluminum column containing 15% Carbowax 20M on 70–80 Anakrom A-S; column B, a 7.5 ft × 0.25 in. aluminum column containing 10% Carbowax 20M on 70–80 Chromosorb G. Ultraviolet spectra were obtained using a Cary Model 14 recording spectrometer.

Biacetyl Di-*p*-tosylhydrazone.—*p*-Tosylhydrazine[17] (50.0 g, 0.259 mol) was dissolved in 135 ml of methanol contained in a 500-ml three-necked flask equipped with a dropping funnel, mechanical stirrer, and a thermometer. The solution was maintained at 45–50° while a solution of 11.6 g (0.135 mol) of freshly distilled biacetyl [bp 87° (690 mm)] in 85 ml of methanol was added with stirring over a period of 2.5 hr. After addition was complete, stirring was continued at the same temperature for three additional hours. The solid was removed by filtration, washed with methanol, and air dried. The yield of biacetyl di-*p*-tosylhydrazone was 48.4 g (85%), mp 190° dec (lit.[5] mp 204° from acetic acid). The infrared spectrum (Nujol mull) of this material showed absorptions at 3295 m (N–H), 1595 with shoulder at 1585 w (overlap of aromatic C=C with C=N) 1490 w, 1336 s (SO_2–N, asymmetric), 1293 m, 1184 m, 1166 s (SO_2–N, symmetric), 1096 w, 1068 m, 1017 w, 936 m, 811 m, and 708 cm^{-1} w.

Anal. Calcd for $C_{18}H_{22}O_4N_4S_2$: C, 51.17; H, 5.25. Found: C, 51.30; H, 5.25.

In variations of procedure in which the reagents were mixed all at once in methanol or aqueous N-hydrochloric acid,[5] the product was contaminated with monotosylhydrazone (infrared, weak conjugated carbonyl absorption at 1690 cm^{-1}).

Benzil Di-*p*-tosylhydrazone.—The procedure of Bamford and Stevens[5] was used employing 22.4 g (0.108 mol) of benzil, 40.1 g (0.216 mol) of *p*-tosylhydrazine, and 250 ml of 1% ethanolic hydrochloric acid. The yield of benzil di-*p*-tosylhydrazone was 43.5 g (74%). Recrystallization of the crude product from aqueous acetonitrile gave material melting at 176–178° dec (lit.[3] mp 184° dec from isoamyl alcohol); the infrared spectrum (Nujol mull) showed absorption bands at 3225 m (N–H), 1593 m (aromatic C=C), 1493 m, 1353 s, 1341 s (SO_2–N, asymmetric), 1300 m, 1253 w, 1184 s, 1162 s (SO_2–N, symmetric), 1118 m, 1090 s, 1064 s, 1035 m, 1009 s with shoulder 1018 m, 998 w, 981 w, 955 w, 914 m, 850 w, 835 w, 811 s with shoulder 815 m, 779 w, 766 m, 745 s, and 688 cm^{-1} s.

Irradiations.—Irradiations were conducted in a specially designed immersion reactor (capacity, 200 and 425 ml) which consisted of an interchangeable three-necked cylindrical Pyrex flask; within its standard taper 60/50 center neck was a water-jacketed quartz probe housing a Hanovia 450-W Type L high pressure mercury arc lamp. Vycor and Corex filters were used as specified. All irradiations were carried out in anhydrous methanol prepared by distillation from magnesium metal turnings.[18] Sodium methoxide solutions were prepared by the dissolution of freshly cut sodium metal in anhydrous methanol.

Irradiation of the Dianion of Biacetyl Di-*p*-tosylhydrazone.—Biacetyl di-*p*-tosylhydrazone (42.0 g, 0.100 mol) was dissolved in a sodium methoxide–methanol solution (425 ml) prepared using 4.8 g (0.21 g-atom) of sodium metal. The solution was placed in the immersion reactor (see above) provided with an outlet through a Dry Ice–isopropyl alcohol cold trap to a wet test meter. Irradiation through Vycor for 9 hr resulted in the evolution of 75% of the theoretical volume of gas. The cold trap contained a liquid (0.5 g) whose nmr spectrum displayed signals due to methanol and a sharp singlet at τ 8.28, which corresponded exactly with the methyl singlet in the spectrum of an authentic sample of 2-butyne. Vpc analysis on column A at 35° revealed the presence of only one product component; its retention time was the same as that of authentic 2-butyne. Additional 2-butyne (0.64 g) was recovered from the reaction mixture as a 25% solution in methanol by warming under a stream of nitrogen directed to a cold trap. Vpc analysis of the reaction mixture employing pentane as an internal standard revealed the presence of 1.26 g of residual 2-butyne. The over-all yield of 2-butyne was 2.00 g (50% based on starting material decomposed) which represents a lower limit for the actual amount of this elusive hydrocarbon formed in the reaction. The reaction mixture was diluted with four volumes of water and extracted with three 300-ml portions of ether which after drying and concentration left a liquid residue. Vpc analysis (column A at 70°) showed the presence of toluene, ether, and methanol but no other aliphatic products.

Incomplete Photodecomposition of the Dianion of Biacetyl Di-*p*-tosylhydrazone. Isolation of 4,5-Dimethyl-1-toluene-*p*-sulfonamido-1,2,3-triazole.—Biacetyl di-*p*-tosylhydrazone (22.75 g, 0.0539 mol) was dissolved in a solution of methanolic sodium methoxide (200 ml) prepared using 2.5 g (0.108 g-atom) of sodium metal. The solution was irradiated in the manner described previously except that irradiation was discontinued after 1.08 hr (29% of the theoretical volume of gas). The reaction mixture was treated with 52 ml of 2 *N* hydrochloric acid and the precipitated solid removed by filtration. The dry solid was identified as starting material (2.63 g, 12%) by a comparison of infrared spectra. Concentration of the filtrate by use of a rotary evaporator left an aqueous residue containing a separated yellow oil. The oil was taken up in ether (two extractions). Removal of the ether gave back the oil which was dissolved in chloroform and placed on a chromatographic column containing 120 g of acidic alumina (pH 4) previously moistened with 7.2 ml of water to achieve a Brockman activity grade of III. The column was successively eluted with the following solvents and solvent mixtures, with the eluent collected in 50-ml fractions: chloroform, four fractions; 25% ethyl acetate–75% chloroform, three fractions; ethyl acetate, three fractions; 25% methanol–75% ethyl acetate, four fractions; and 50% methanol–ethyl acetate, three fractions. Residues, either oils or solids, remained on evaporation of solvent from all of the collected fractions. The solid obtained from fraction 10 (mp 137.5–142.0°) did not depress the melting point of authentic 4,5-dimethyl-1-toluene-*p*-sulfonamido-1,2,3-triazole[5] in a mixture melting point determination; infrared spectra of the two materials were virtually identical. The quantity of the triazole obtained from fractions 6–13 was 1.49 g 12% based on unrecovered starting material).

Irradiation of the Dianion of Biacetyl Di-*p*-tosylhydrazone Using a Corex Filter.—The initial procedure was the same as described above, employing 20.0 g (0.0474 mol) of ditosylhydrazone, 2.3 g (0.10 g-atom) of sodium metal, and 200 ml of methanol. The solution was irradiated through Corex for 2 hr during which period nitrogen evolution was very slow (total volume of liberated gas, 175 ml). The reaction mixture was diluted with four volumes of water and treated with 50 ml of 2 *N* hydrochloric acid. The precipitated solid was removed by filtration and dried giving 8.20 g of material melting 150–170°. On standing, the filtrate deposited two crops of white crystals (4.02 g) which did not depress the melting point of authentic 4,5-dimethyl-1-toluene-*p*-sulfonamido-1,2,3-triazole. The solid which initially precipitated on acidification of the reaction mixture was stirred with 150 ml of methanol. Insoluble material was removed by filtration and shown to be starting material by comparison of infrared spectra (3.38 g). Concentration of the filtrate gave an oil which

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[17] L. Friedman, R. Little, and W. Reichle, *Org. Syn.*, **40**, 63 (1960).

[18] L. Fieser, "Experiments in Organic Chemistry," 3rd ed, D. C. Heath and Co., Boston, Mass., 1957, p 289.

yielded a yellowish solid (4.47 g) on trituration with water. The infrared spectrum of this material was virtually identical with that of authentic triazole. The combined yield of the triazole was 8.49 g (80.7% based on unrecovered starting material).

Irradiation of the Dianion of Benzil Di-*p*-tosylhydrazone.—Benzil di-*p*-tosylhydrazone (34.9 g, 0.0639 mol) was stirred into a solution of methanolic sodium methoxide prepared using 4.4 g (0.191 g-atom) of sodium metal and 4.25 ml of methanol. The resulting suspension of the salt[19] was irradiated through Vycor until gas evolution retarded (*ca.* 5.5 hr, 72% of the theoretical quantity of gas). The final red-orange solution was diluted with three volumes of water and extracted with four 150-ml portions of petroleum ether (bp 30–60°). Removal of petroleum ether using a steam bath left a residual oil (11.6 g) whose nmr spectrum showed absorption bands due to aromatic hydrogens, a pair of olefinic hydrogens (τ 3.92 and 4.20), and a pair of methoxyl resonances (τ 6.26 and 6.42). After removal of an additional quantity of petroleum ether (2.63 g) by distillation at atmospheric pressure, the residual liquid was distilled under reduced pressure giving the following fractions: 90.5–94.0° (0.02–0.03 mm), 0.68 g; 94.0–97.5° (0.02–0.03 mm), 2.49 g; and 93–96° (0.04 mm), 2.94 g, leaving a residue (1.50 g). The nmr spectra of the fractions showed the features of the undistilled material. Vpc analysis (column B at 200–220°) showed two major peaks of varying area ratio. Material corresponding to the two peaks, here designated as isomer 1 and isomer 2 in order of increasing vpc retention time, were subsequently identified as *cis*- and *trans*-α-methoxystilbene, respectively, on the basis of the spectral and chemical evidence presented below.

Analysis of Isomer 1, *cis*-α-Methoxystilbene.—Samples of this isomer obtained by vpc were always contaminated with the *trans* isomer (10–20%) and another impurity (35–50%) with retention time identical with the *cis* isomer, but exhibiting only aromatic hydrogens; the impurity is identified as diphenylacetylene. The following spectra were obtained: infrared ($CDCl_3$) 3090 s, 2945 m, 2820 w, 1870 w, 1800 w, 1747 w, 1642 s (C=C conjugated with aromatic ring), 1600 s, 1573 m (C=C aromatic, indicative of conjugation with olefinic bond), 1497 s, 1460 m, 1440 s, 1375 m, 1307 w, 1282 w, 1237, 1200 s (either band assignable to =COC, asymmetric), 1188 w, 1156 w, 1121 s (=COC, symmetric), 1073 m, 1038 m, 1000 w, 960 m, 876 m, 842 w, 814 m, and 776 cm^{-1} s. The four bands which are assigned above with the exception of the band at 1573 cm^{-1} are completely absent from the spectrum of diphenylacetylene in $CDCl_3$. The band at 1573 cm^{-1} has only a weak counterpart in the latter spectrum. The nmr spectrum ($CDCl_3$) showed signals at τ 2.30–3.10 (multiplet, aromatic, 20.5 H) 4.20 (singlet, olefinic, 1.0 H), 6.26 (singlet, OCH_3, 3.0 H) and 6.42 (singlet, OCH_3 due to the *trans* isomer, 0.6 H). The spectrum is consistent with a mixture of 10% *trans*-α-methoxystilbene, 49% *cis*-α-methoxystilbene, and 41% diphenylacetylene. The ultraviolet spectrum (methanol) showed considerable fine structure in the form of four rather sharp maxima at 264 mμ (ϵ ~19,000), 278.5 (~27,000) with a shoulder at 272.5 (~21,000), 287 (~20,000), and 295.5 (~23,000). The values for the extinction coefficients, which are uncorrected for the presence of impurities, are included in order to give a rough measure of absorption intensity.

Analysis of Isomer 2, *trans*-α-Methoxystilbene.—A sample of this compound obtained by vpc was a solid melting 45–50°, containing less than 8% *cis* isomer. The infrared spectrum showed absorption bands at 3030 s, 2935 m, 2825 m, 1950 w, 1875 w, 1800 w, 1720 w, 1635 s (C=C conjugated with aromatic ring), 1600 s (C=C, aromatic), 1570 m (C=C aromatic, indicative of conjugation with olefinic bond), 1492 s (C=C, aromatic), 1445 s, 1340 s, 1280 m, 1255 m, 1200 s (=COC, asymmetric) 1178 w, 1153 w, 1120 w, 1062 s (=COC, symmetric), 1026 s, 1000 m, 980 s, 856 m, and 770 cm^{-1} s. The nmr spectrum displayed signals at τ 2.12–3.06 (multiplet, aromatic, 10.0 H), 3.92 (singlet, olefinic, 0.9 H), and 6.42 (singlet, OCH_3, 2.9 H). The ultraviolet spectrum (methanol) showed structureless maxima at 220 mμ (ϵ 12,250) and 292 (21,000).

Anal. Calcd for $C_{15}H_{14}O$: C, 85.68; H, 6.71. Found: C, 85.50; H, 6.85.

The yield of products was *ca.* 8.0 g (93% based on a 72% conversion of starting material). The product mixture was composed of approximately 80% isomeric α-methoxystilbenes (62% *trans* and 38% *cis*) calculated on the basis of nmr.

Hydrolysis of *cis*- and *trans*-α-Methoxystilbene to Deoxybenzoin.—A sample (0.5–1 g) containing approximately equal amounts of the two isomers was added to 50 ml of aqueous 6 *N* sulfuric acid containing dioxane to increase the solubility of the organic material. The mixture was heated for 4 hr on a steam bath and then extracted with three portions of chloroform. The combined extracts were washed with three portions of water and with 10% sodium bicarbonate solution. The chloroform was removed by distillation using a steam bath leaving a residual oil. Vpc showed the absence of peaks due to the two isomeric α-methoxystilbenes and in their place a new peak. The material corresponding to the new peak, separated by vpc, was a solid melting at 54.8–55.8°. Its infrared spectrum was essentially identical with one of an authentic sample of desoxybenzoin.

Irradiation of the Dianion of Benzil Di-*p*-tosylhydrazone Using a Corex Filter.—The initial procedure was the same as that described above, employing 17.0 g (0.0311 mol) of benzil di-*p*-tosylhydrazone, 1.55 g (0.0674 g-atom) of sodium metal and 200 ml of methanol. The intensely yellow solution of the ditosylhydrazone dianion was irradiated through Corex for a period of 55 min, during which period 670 ml of gas was evolved (39% of the theoretical volume). The reaction mixture was diluted with two volumes of water and extracted with four 80-ml portions of cyclohexane. The extracted reaction mixture was treated with 34 ml of 2 *N* hydrochloric acid and the yellowish precipitate was removed by filtration and dried giving 8.43 g. The solid was stirred with 150 ml of absolute ethanol and the insoluble material collected by filtration (6.22 g). The ethanol was evaporated leaving 1.94 g of solid residue which was recrystallized from aqueous ethanol which afforded 0.22 g of purified material. The material was identified as 4,5-diphenyl-1-toluene-*p*-sulfonamido-1,2,3-triazole. The infrared spectrum (Nujol mull) showed absorptions at 1597 w, 1302 w, 1288 w, 1272 w, 1260 w, 1184 w, 1167 s, (SO_2–N, symmetric), 1155 m, 1140 w, 1087 w, 1040 w, 1019 w, 981 w, 925 w, 865 w, 831 w, 814 m, 779 w, 761 m, 730 w, and 693 cm^{-1} m. This spectrum was identical with one of a material melting at 226° dec obtained in larger amounts (3.18 g) when a 20.0-g quantity of crude ditosylhydrazone in 250 ml of sodium methoxide solution in methanol was irradiated in a 500-ml quartz flask, using a Vycor filter. The maximum yield of the triazole based on 1.94 g of crude material and 10.78 g of unrecovered starting material is 25%.

Anal. Calcd for $C_{21}H_{18}N_4O_2S$: C, 64.60; H, 4.65. Found: C, 64.43; H, 4.65.

The combined cyclohexane extracts (above) after drying were stripped of solvent by distillation employing a steam bath yielding 5.11 g of residual liquid. An nmr spectrum of this material indicated the presence of the isomeric methoxystilbenes, only in the ratio 62:38 *cis*:*trans*.

Irradiation of Diphenylacetylene in Methanol.—Diphenylacetylene (8.95 g, 0.0503 mol) was dissolved in 200 ml of methanolic sodium methoxide solution prepared using 1.5 g (0.0652 g-atom) of sodium metal. The solution was irradiated for 3.75 hr. Work-up in the usual manner employing petroleum ether (bp 30–60°) as extracting solvent afforded a green oil from which crystals readily deposited. An nmr spectrum of the mother liquor revealed the absence of both olefinic and methoxyl hydrogens as did a spectrum of the crystalline solid which showed only aromatic hydrogens. The identity of the solid was confirmed as starting material by a mixture melting point determination. The recovery of diphenylacetylene was 8.26 g (92%).

Registry No.—**7**, 19185-60-5; **8**, 19185-61-6; **9**, 19185-62-7; **10**, 19202-54-1; **11**, 19191-03-8; **12**, 19185-63-8.

Acknowledgment.—We wish to express our thanks to the National Institute of General Medical Sciences division of the National Institutes of Health for their generous support of this work in the form of a predoctoral fellowship for R. C. J. (1-F1-GM-33,506-01).

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[19] The concentration of excess sodium methoxide (*ca.* 0.14 *M*) is sufficient to cause precipitation of the salt in this instance.