to convert carbinol sulfonamides **6a, b** into water-soluble products under similar conditions.

Incidentally, the courses of the thermal reactions of carbinol sulfonamides **6a, b** and **2** differ, not only from each other, but also from that of carbinol carboxamides **8** which undergo thermal deamination to form lactone **10**.[5]

Experimental Section[6]

Metalations of 4a, b with *n*-Butyllithium to Form Dilithiosulfonamides 5a, b.—A solution of 0.020 mol of N-methyl- or N-phenyl-*o*-toluenesulfonamides (**4a** and **4b**, respectively) in 70 ml of tetrahydrofuran[7] in a dry flask under nitrogen was cooled to 0°, and 30 ml of (0.046 mol) of a solution of 1.6 *M* *n*-butyllithium in hexane[8] was added during 4–5 min. After stirring for 30 min at 0°, the clear, deep orange solution from **4a** and the clear, dark red solution from **4b** were considered to contain 0.020 mol of the dilithiosulfonamides **5a** and **5b**, respectively. These solutions were employed at 0° described below.

Condensations of Dilithiosulfonamides with Benzophenone to Form Carbinol Sulfonamides. A. Condensation of 5a to Form 6a.—To the stirred, cold solution of dilithiosulfonamide **5a** was added under nitrogen with stirring, during 4–5 min, a solution of 4.74 g (0.026 mol) of benzophenone in 30 ml of tetrahydrofuran,[7] and the stirring continued for 1 hr at 0°. To the resulting clear, yellow solution (at 0°) was added with stirring 30 ml of distilled water and then 35–40 ml of 5% hydrochloric acid. The two layers were separated. After saturation with sodium chloride, the aqueous layer was extracted three times with ether, and the extracts were combined with the organic layer. After washing twice with a saturated solution (30 ml) of sodium chloride and drying ($MgSO_4$), the solvent was removed under reduced pressure on the steam bath to give a slightly yellow, viscous liquid, which was stirred with a little methanol and then left to stand in a current of air under a hood for a few hours. The resulting crystals were collected, washed with a little cold methanol, and dried in air; more crystals were recovered from the filtrate to which the washings had been added. The combined crystals were recrystallized from methanol, giving 6.64 g (91%) of carbinol sulfonamide **6a** (prismatic crystals): mp 161–163°, and mp 163.5–164.5° after further recrystallization; ir 3495 (OH), 3315 (NH), 1295 (SO_2), 1145 (SO_2), 840, 780, 756, 740, and 695 cm^{-1}; nmr (acetone-d_6) δ 8.13–6.26 (m, 15.40, aromatic H and OH or NH), 5.04 (s, 0.7, NH or OH), 4.20 (s, 1.8, CH_2), and 2.55 ppm (d, 2.8, J = 5.3 cps, N–CH_3).

Anal. Calcd for $C_{21}H_{21}NSO_3$: C, 68.64; H, 5.76; N, 3.81. Found: C, 69.00; H, 5.51; N, 3.64.

B. Condensation of 5b to Form 6b.—This condensation was effected essentially as described above under A to give a clear, yellow-orange solution which, on work-up, afforded 7.06 g (82%) of carbinol sulfonamide **6b**, mp 149–151.5°. Recrystallization from methanol gave 5.73 g (67%) (large prismatic crystals, sample A): mp 152–153°; ir 3500, 3400 and 3265 (OH, broad), 3160 (NH), 1312 and/or 1290 (SO_2), 1150 and/or 1140 (SO_2), 934, 778, 757, 740, 690 cm^{-1}; nmr (acetone-d_6) δ 9.27 (s, 0.9, OH or NH), 8.67–6.42 (m, 19.4, aromatic H), 5.05 (s, 0.9, NH or OH), 4.21 ppm (s, 2.0, CH_2). After standing at room temperature for 3 months, the ir spectrum was unchanged; the nmr spectrum (acetone-d_6) showed δ 7.50–6.00 (m, 20.4, aromatic H and OH), 4.56 (broad, NH), and 3.73 ppm (s, 1.8, CH_2).

Anal. Calcd for $C_{26}H_{23}NSO_3$: C, 72.70; H, 5.40; N, 3.26. Found: C, 72.81; H, 5.24; N, 3.17.

A 1-g sample of this compound was mixed well with 40 g of polyphosphoric acid. After standing at room temperature (25–30°) for 24 hr the mixture was poured, with stirring, onto 100 g of ice–water. The resulting solid was collected and recrystallized from methanol to give 0.96 g of recovered carbinol sulfonamide **6b** (fine crystals, sample B): mp 156–157.5°; with sample A, mmp 156–157°; ir 3500 (OH), 3265 (NH), 1315 and/or 1285 (SO_2), 1150 (SO_2), 918, 777, 753, 740, and 696 cm^{-1}; nmr (acetone-d_6) δ 8.00–6.33 (m, 21.4, aromatic H, OH and NH), and 4.17 ppm (s, 1.9, CH_2); nmr ($CDCl_3$) δ 8.03–6.80 (m, 18.7, aromatic H), 6.27 (broad, 0.9, NH), 4.05 (s, 2.2 CH_2), and 3.35 ppm (s, 1.0, OH). After standing at room temperature for 6 months, the ir spectrum was unchanged; the nmr spectrum (acetone-d_6) showed δ 7.50–6.00 (m, 20.0, aromatic H and OH), 4.50 (broad 0.6, NH), and 3.73 ppm (s, 2.1, CH_2).

Anal. Calcd for $C_{26}H_{23}NSO_3$: C, 72.70; H, 5.40; N, 3.26. Found: C, 72.90; H, 4.97; N, 3.15.

Dehydration of Carbinol Sulfonamides to Form *o*-Sulfamyltriphenyl ethylenes. A. Thermal Method.—A 1-g sample of carbinol sulfonamide **6a** was heated under a slow stream of nitrogen in a round-bottomed flask on a Wood's metal bath (220–230°) for 5 hr. The flask was removed from the bath, and the molten mass was allowed to come to room temperature. The resulting solid was recrystallized from methanol to give 0.77 g (81%) of **7a** (fine prismatic crystals): mp 107.5–109.5°; ir 3300 (NH), 1315 (SO_2), 1155 (SO_2), 843, 777, 764, 759, 744, and 695 cm^{-1}; nmr ($CDCl_3$) δ 8.17–6.88 (m, 14.2, aromatic H), 7.57 (s, 1.0, vinyl H), 4.53 (broad, 0.7, NH), and 2.57 ppm (d, 2.6, J = 5.1 cps, N–CH_3).

Anal. Calcd for $C_{21}H_{19}NSO_2$: C, 72.18; H, 5.48; N, 4.01. Found: C, 72.38; H, 5.37; N, 3.89.

Similarly, a 1-g sample of carbinol sulfonamide **6b** (sample A) was dehydrated at 235–245°. The resulting mass was recrystallized from methanol to give 0.92 g (96%) of **7b** (fine needles): mp 128.5–130°; ir 3240 (NH), 1315 (SO_2), 1150 (SO_2), 920, 829, 779, 757, 751, 738, 725, and 690 cm^{-1}; nmr ($CDCl_3$) δ 8.28–7.65 and 7.45–6.50 (m, 20.0, aromatic H and NH) and 7.25 ppm (s, 0.7, vinyl H).

Anal. Calcd for $C_{26}H_{21}NSO_2$: C, 75.88; H, 5.14; N, 3.40. Found: C, 75.76; H, 5.27; N, 3.45.

B. Acetic–Sulfuric Acid Method.—A solution of a 1-g sample of carbinol sulfonamide **6a** in 30 ml of glacial acetic acid containing 0.015 ml of concentrated sulfuric acid was refluxed for 24 hr and then cooled to room temperature. The clear, colorless solution was poured onto 100 ml of ice–water. The mixture was made basic with sodium carbonate. The resulting white solid was collected and dissolved in hot methanol. After separation of insoluble material (0.14 g), the filtrate was evaporated to give 0.69 g (73%) of **7a** (fine prismatic crystals): mp 106.5–108°; mixture melting point with **7a** obtained under A, 106–108°; the ir spectra of the two samples were identical.

C. *p*-Toluenesulfonic Acid Method.—A solution of 0.60 g of carbinol sulfonamide **6b** (sample B) in 30 ml of benzene containing 0.03 g of *p*-toluenesulfonic acid (hydrate) was refluxed for 10 hr, during which a Dean–Stark water trap was used to remove water as an azeotrope of benzene–water. The hot, colorless, clear solution was allowed to evaporate in a current of air under a hood. The resulting sticky liquid was scratched to solidify. The solid was washed with dilute sodium carbonate solution and water, and then recrystallized from methanol to give 0.56 g (89%) of **7b** (fine needles): mp 128.5–130°; mixture melting point with **7b** obtained under A, 128.5–130°; ir spectra of the two samples were identical.

Registry No.—*n*-Butyllithium, 109-72-8; benzophenone, 119-61-9; **6a**, 17510-55-3; **6b**, 17510-56-4; **7a**, 17510-57-5; **7b**, 17510-58-6.

(5) R. L. Vaulx, W. H. Puterbaugh, and C. R. Hauser, *J. Org. Chem.*, **29**, 3514 (1964).

(6) Melting points are uncorrected. Elemental analyses were performed by M-H-W Laboratories, Garden City, Mich. Ir spectra (KBr method) were produced on Perkin-Elmer Infracord Model 137 and Model 237. Nmr spectra were obtained with a Varian A-60 spectrometer using tetramethylsilane (δ 0 ppm) as an internal standard.

(7) Freshly distilled from lithium aluminum hydride.

(8) Foote Mineral Co., Exton, Pa.

Fluorination of Methyl Isobutyrate with Perchloryl Fluoride[1]

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Enolates react with perchloryl fluoride to give α-fluoro carbonyl derivatives. This kind of fluorination

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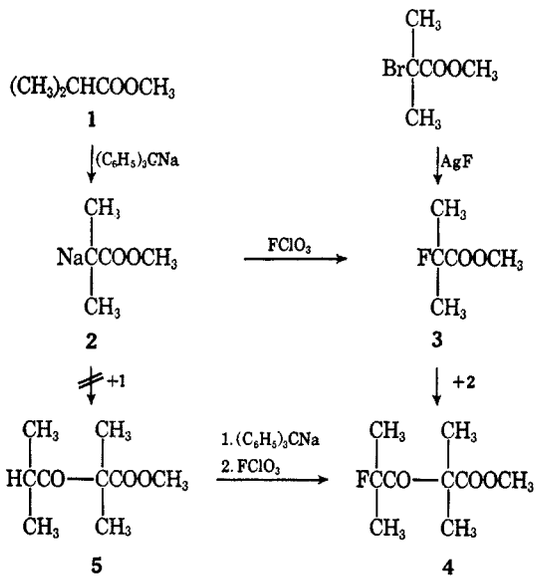
generally makes use of 1,3-dicarbonyl compounds, so that the position undergoing substitution is activated by two groups.[2] We wish to report evidence for fluorination at a position activated by only a single carbonyl group.

When perchloryl fluoride was bubbled into an ethereal solution of the sodioenolate 2 of methyl isobutyrate, methyl 4-fluoro-3-oxo-2,2,4-trimethylpentanoate (4)



was isolated as the only pure product. The assigned structure of 4 is consistent with the presence of two carbonyl absorption maxima in its infrared absorption spectrum and of three kinds of proton signals in its nmr spectrum. Product 4 could arise either from condensation of the first-formed fluorination product 3 with a second mole of sodio derivative 2, or it could arise by fluorination of the Claisen condensation product 5 from methyl isobutyrate. The fact that methyl α-fluoroisobutyrate (3)[3] condensed smoothly with methyl sodioisobutyrate (2) to give methyl 4-fluoro-3-oxo-2,2,4-trimethylpentanoate (4) makes the 2 → 3 → 4 sequence admissable in the perchloryl fluoride action. Fluorination of the sodio derivative of methyl 3-oxo-2,2,4-trimethylpentanoate (5)[4] also gave methyl 4-fluoro-3-oxo-2,2,4-trimethylpentanoate (4), so that on this basis the alternate 2 → 5 → 4 sequence could not be excluded. However, failure to isolate Claisen product 5 from reactions designed to furnish 5 suggested that it could not be an intermediate and thereby speaks against the latter sequence.

Whether fluorinations on singly activated positions will be successful only with tertiary H's as in methyl isobutyrate (1) or methyl 3-oxo-2,2,4-trimethylpentanoate (5) remains to be seen.

Experimental Section

General.—Boiling points are uncorrected. Ultraviolet spectra were taken with a Beckman DK spectrophotometer; infrared spectra were taken with Perkin-Elmer Infracords. Nmr spectra were determined on a Varian 60-MHZ instrument;[5] the chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane. Gas–liquid partition chromatographic analysis made use of an ionization detector and a column with diethylene glycol succinate or neopentyl glycol succinate as stationary phases. Analyses for elements were reported by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., and Galbraith Laboratories, Inc., Knoxville, Tenn.

Methyl 4-Fluoro-3-oxo-2,2,4-trimethylpentanoate (4) from the Sodio Derivative 2 of Methyl Isobutyrate and Perchloryl Fluoride.—Methyl isobutyrate (1, 0.89 g or 8.7 mmol) was added to 8 mmol of triphenylmethylsodium[6] as a 0.13 *M* solution in ether at 0°. Enough additional triphenylmethylsodium was introduced to produce a persistent red color (total reagent, 9.0 mmol). Perchloryl fluoride[7] was passed through a tube packed with anhydrous calcium sulfate and then into the cold reaction mixture. The gas flow was adjusted to be rapid at first and then slow. The red color disappeared within 1 min; a precipitate was evident after 5 min. After 20 min, a drop of the mixture on wet pH paper showed pH 5. Dry nitrogen was then bubbled through the solution for about 20 min to remove excess perchloryl fluoride. The solids were separated and washed with ether. The combined ether filtrate and washings were concentrated, and the residue was distilled to give 0.25 g (30%) of water-white methyl 4-fluoro-3-oxo-2,2,4-trimethylpentanoate (4), bp 80° (15 mm). This product was homogeneous to the extent of 97% according to glpc.

Anal. Calcd for $C_9H_{15}FO_3$: C, 56.83; H, 7.95; F, 9.99. Found: C, 57.01; H, 8.01; F, 10.17.

As a 2.5×10^{-3} *M* solution in absolute ethanol, the product 4 showed λ_{max} 214 mμ (ε 420) and 273.5 (104). The ir absorption spectrum taken with neat material showed carbonyl peaks at 1720 (ketone) and 1760 cm^{-1} (ester) but no hydroxyl or carboxyl absorption above 3000 cm^{-1}. The liquid tended to become yellow on standing.

Methyl α-Fluoroisobutyrate (3).—Methyl α-bromoisobutyrate, bp 31–32° (0.4 mm),[8] was obtained in 80% yield by allowing a solution of α-bromoisobutyryl bromide in anhydrous methanol to stand for 5 hr. The nmr spectrum of the bromo ester in deuteriochloroform showed peaks at 1.89 [6 H, s, $BrC(CH_3)_2$] and 3.71 ppm (3 H, s, OCH_3). A stirred mixture of bromo ester (21.0 g or 0.116 mol) and dry powdered silver fluoride (30.0 g or 0.236 mol; gray, used as received) was held for 3 hr in a bath at 140–145° under a reflux condenser. The cooled reaction mixture, diluted with 30 ml of ether, was filtered, and the solids were washed with ether. The ether solutions were washed with water, dried, and passed through an 80-g column of silica gel. Another 25 ml of ether was passed through the column. After removal of solvent from the combined ether solutions, fractionation of the residue through a 16-in. spinning-band column gave 2.8 g (20%) of methyl α-fluoroisobutyrate (3), bp 43–45° (75 mm), and 2.0 g of liquid, bp 35–39° (1 mm), identical with methyl α-bromoisobutyrate according to glpc and ir absorption comparisons.

The desired methyl α-fluoroisobutyrate (3) showed ir absorption peaks at 1753 (carbonyl) and 1145 cm^{-1} (C–F). In deuteriochloroform, the material gave nmr signals at 1.52 (6 H, d, J = 21.5 Hz, CH_3 groups) and 3.70 ppm (3 H, s, OCH_3).

Anal. Calcd for $C_5H_9FO_2$: C, 50.00; H, 7.49; F, 15.83. Found: C, 50.30; H, 7.68; F, 16.10.

(2) C. E. Inman, E. A. Tyczkowski, R. E. Oesterling, and F. L. Scott, *Experientia*, **14**, 355 (1958); C. E. Inman, R. E. Oesterling, E. A. Tyczkowski, *J. Amer. Chem. Soc.*, **80**, 6533 (1958); H. M. Kissman, A. M. Small, M. J. Weiss, *ibid.*, **82**, 2312 (1960); H. M. Kissman, A. S. Hoffman, and M. J. Weiss, *J. Org. Chem.*, **26**, 973 (1966); A. H. Nathan, J. C. Babcock, and J. A. Hogg, *ibid.*, **24**, 1395 (1959); A. H. Nathan, B. J. Magerlein, and J. A. Hogg, *ibid.*, **24**, 1517 (1959); S. A. Fuqua and R. M. Silverstein, *ibid.*, **29**, 395 (1964); J. Edwards and H. J. Ringold, *J. Amer. Chem. Soc.*, **81**, 5262 (1959); A. S. Kende, *Tetrahedron Lett.*, No. 14, 13 (1959); C. H. Robinson, N. F. Bruce, E. P. Oliveto, S. Tolksdorf, M. Steinberg, and P. L. Perlman, *J. Amer. Chem. Soc.*, **82**, 5256 (1960); and S. Nakanishi, K. Morita, E. V. Jensen, *ibid.*, **81**, 5259 (1959). The last article has an example of an attack on an α position activated by one carbonyl and two fluorine groups. If the carbonyl compound is a ketone, α fluorination may be effected indirectly *via* the enamine, the enol ether, or the enol acetate. [*Cf.* J. W. Chamberlin, "Steroid Reactions," C. Djerassi, Ed., Holden-Day, Inc., San Francisco, Calif., 1963, p 164.]

(3) *Cf.* B. C. Saunders and G. J. Stacey, *J. Chem. Soc.*, 1773 (1948).

(4) *Cf.* R. Levine and C. R. Hauser, *J. Amer. Chem. Soc.*, **66**, 1768 (1944).

(5) We wish to acknowledge the help of National Science Foundation in providing funds for the purchase of a Varian A-60 nmr spectrometer (Research Equipment Grant GP 3618).

(6) W. B. Renfrow, Jr., and C. R. Hauser, "Organic Syntheses," Coll. Vol. II, John Wiley & Sons, Inc., New York, N. Y., 1943, p 607.

(7) The information on perchloryl fluoride provided by the manufacturer, Pennsalt Chemicals Corp., Philadelphia, Pa., in its booklet DC-1819 should be carefully noted.

(8) *Cf.*, C. C. Price and E. C. Coyner, *J. Amer. Chem. Soc.*, **62**, 1306 (1940).

An earlier preparation according to this method[3] gave impure fluoro ester, bp 24–30° (24 mm), in unspecified yield.

Methyl 4-Fluoro-3-oxo-2,2,4-trimethylpentanoate (4) from the Claisen Condensation of Methyl Sodioisobutyrate (2) and Methyl α-Fluoroisobutyrate (3).—Ethereal triphenylmethylsodium (100 ml, 9.7 mmol) was added slowly and with stirring to 0.80 g (7.8 mmol) of methyl isobutyrate (1) freshly distilled from calcium hydride. A stream of pure nitrogen was passed through the flask before and during the reaction. The red color was quickly discharged; only at the end of the addition did a persistent (15 min) red develop. To this enolate (2) solution, 0.90 g (7.5 mmol) of methyl α-fluoroisobutyrate (3) was added over a period of 5 min, and the mixtue was stirred at room temperature for 24 hr. A solution of acetic acid (1 ml) plus water (15 ml) was added; the aqueous layer was discarded; and the ether layer was first shaken with 10% aqueous sodium carbonate solution and then dried. Removal of solvent left a residue which on distillation afforded 0.73 g (51%) of water-white methyl 4-fluoro-3-oxo-2,2,4-trimethylpentanoate (4), bp 77–79° (14 mm). The ir absorption curve for this material and that for the same material described above, both taken with neat liquids, were identical. The condensation product dissolved in deuteriochloroform showed nmr signals at 1.35 (6 H, s, 2,2-dimethyl), 1.48 [6 H, d, J = 21.5 Hz, $FC(CH_3)_2$], and 3.67 ppm (3 H, s, OCH_3).

Attempted Self-Condensation of Methyl Isobutyrate (1) with Methyl 3-Oxo-2,2,4-trimethylpentanoate (5). A. With Sodium Hydride.—A mixture of dry, freshly distilled methyl isobutyrate (46.3 g or 0.45 mol) and commercial sodium hydride (5.84 g or 0.24 mol) was boiled in an atmosphere of nitrogen for 4 hr. Hydrogen was evolved during the early stages of the reaction. The cooled mixture was poured over a mixture of concentrated sulfuric acid (20 ml) and crushed ice (100 g). The mixture was extracted with ether, and the ether solution was washed free of acid, dried, and warmed to remove solvent. Fractional distillation afforded 16 ml of unchanged starting material followed by about 11 ml of liquid, bp 80–110° (110–120 mm). Glpc revealed the presence of eight components. This product was not examined more closely.

B. **With Triphenylmethylsodium.**—Methyl isobutyrate (0.80 g or 7.8 mmol) was converted into its sodio derivative 2 exactly as described above in the condensation with methyl α-fluoroisobutyrate. Then, instead of the fluoro ester, 0.80 g of methyl isobutyrate (1) was added. The same treatment as before produced 1.3 g (81%) of unchanged starting material, bp 85–89°. The ir and the nmr spectra of the recovered material were the same as those from pure methyl isobutyrate.[9]

Other attempts at forming methyl 3-oxo-2,2,4-trimethylpentanoate (5) by Claisen condensation of methyl isobutyrate also failed.

Methyl 3-Oxo-2,2,4-trimethylpentanoate (5).—Diisopropyl ketone (10 ml of 0.091 mol) that had been distilled from calcium hydride was treated with 555 ml of a 0.138 M ethereal solution of triphenylmethylsodium (0.076 mol) until the red color persisted. The solution was poured over 50 g of solid carbon dioxode. The ether layer, rinsed with water and dried, was treated with excess ethereal diazomethane. Removal of solvent followed by two distillations of the residue gave 7.3 g (47%) of methyl 3-oxo-2,2,4-trimethylpentanoate (5), bp 93–94° (25 mm). By glpc this material contained less than 2% impurities.

Anal. Calcd for $C_9H_{16}O_3$: C, 62.76; H, 9.37. Found: C, 63.08; H, 9.35.

The neat liquid showed ir absorption peaks at 1720 and 1748 cm^{-1}.

Levine and Hauser, who employed the same method, but with sodium amide in place of triphenylmethylsodium, reported bp 93° (27 mm).[4]

Perchloryl Fluoride Fluorination of Methyl 3-Oxo-2,2,4-trimethyl pentanoate (5).—Methyl 3-oxo-2,2,4-trimethylpentanoate (5, 7.0 ml of 0.039 mol) was added in an atmosphere of nitrogen to 350 ml of a 0.10 M ethereal solution of triphenylmethylsodium (0.035 mol). The red color persisted for 10 min. An additional quantity of reagent was admitted (0.004 mol), and the mixture was allowed to stand for 30 min. Dry perchloryl fluoride was then bubbled through the orange solution. After 45 min, a drop of the reaction mixture in contact with water showed pH 5. Further treatment similar to that in the fluorination starting with methyl isobutyrate afforded 1.5 ml of distillate, bp 71° (6 mm), which by glpc contained at least 70% of methyl 4-fluoro-3-oxo-2,2,4-trimethylpentanoate (4). The fluorine content of the mixture was low (7.84 instead of 9.99%) and the carbon content was high (58.76 instead of 56.83%). The ir absorption curve of this material was practically identical with that obtained before for 4.

Registry No.—1, 547-63-7; 3, 338-76-1; 4, 17555-86-1; 5, 918-71-8; perchloryl fluoride, 7616-94-6.

(9) Interestingly, Claisen condensation does occur when *ethyl* isobutyrate is treated with triphenylmethylsodium. *Cf.* C. R. Hauser and W. B. Renfrow, Jr., *ibid.*, **59**, 1824 (1937). Also *cf.* M. Hamell and R. Levine, *J. Org. Chem.*, **15**, 162 (1950).

Cyclization and Rearrangement of Substituted Glyoxal Aldoxime Semicarbazones to 6-Substituted *as*-Triazine-3,5(2H,4H)-diones

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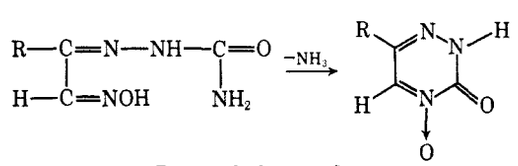
Cyclization of benzil monoxime guanylhydrazone nitrate to 2-imino-5,6-diphenyl-*as*-triazine 4-oxide, according to Scott and Reilly,[1] and the synthesis of 2-aminopyrazine 1-oxides by condensation of aminonitriles with substituted glyoxal aldoximes[2] are examples of the preparation of N-oxides from hydroximino compounds.

As a result of our attempts to prepare *as*-triazine derivatives (azapyrimidines) of pharmacological interest, it has been found that pyruvaldehyde aldoxime semicarbazone and arylglyoxal aldoxime semicarbazones undergo cyclization with loss of ammonia in boiling aqueous alkaline solutions.

From simple structural considerations the expected product would be 6-methyl- (or aryl-) *as*-triazine-3(2H)-one 4-oxide according to eq 1.



(1)

R = methyl or aryl

Physical properties and chemical reactions showed, however, that the compounds obtained are in fact the *as*-triazine-3,5(2H,4H)-diones identical with samples prepared by other methods.[3-5] Small amounts of nitriles (5–10%) and acids (10–20%) related to the starting materials were found as by-product. Thus benzonitrile was separated by steam distillation of the reaction mixture, and benzoic acid was extracted from the crude 6-phenyl-*as*-triazine-3,5(2H,4H)-dione.

(1) F. L. Scott and J. Reilly, *Chem. Ind.* (London), 907 (1952).
(2) W. Sharp and F. S. Spring, *J. Chem. Soc.*, 932 (1951).
(3) J. Thiele and J. Bailey, *Ann.*, **303**, 75 (1898).
(4) S. Rossi, *Gazz. Chim. Ital.*, **83**, 133 (1953).
(5) J. Bougault, *Compt. Rend.*, **159**, 83 (1914).