mono-halo derivatives of the indenone and a monobromo indanone of unknown structure.

Two new compounds of possible value as phytotoxic or insecticidal agents, β,β-bis-(3,4-dimethoxyphenyl)-acrylic acid and β,β-bis-(3,4-dimethoxyphenyl)-propionic acid, have also been prepared.

BETHLEHEM, PENNA. RECEIVED JUNE 29, 1949

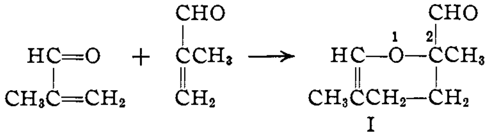
---

[CONTRIBUTION FROM BATTELLE MEMORIAL INSTITUTE]

# Methacrylaldehyde Dimer. Derivatives Obtained through the Cannizzaro Reaction[1]

BY GEORGE G. STONER[2] AND JUSTIN S. MCNULTY

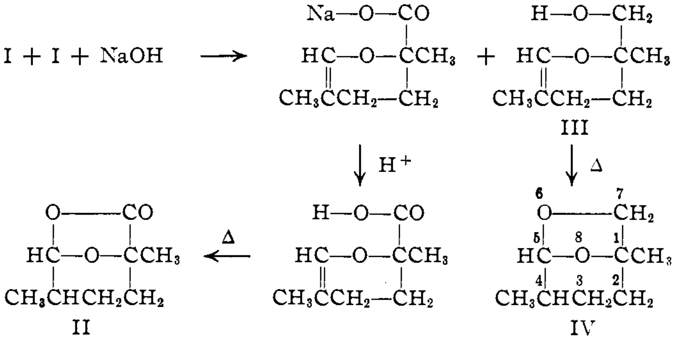
In common with other α,β-unsaturated aldehydes[3a,b,c] and ketones,[3b,d,e] methacrylaldehyde (methylpropenal, methacrolein) undergoes a Diels–Alder type[4] of reaction with itself to produce a dimer[5] (I), 3,4-dihydro-2,5-dimethyl-1,2H-pyran-2-carboxaldehyde.

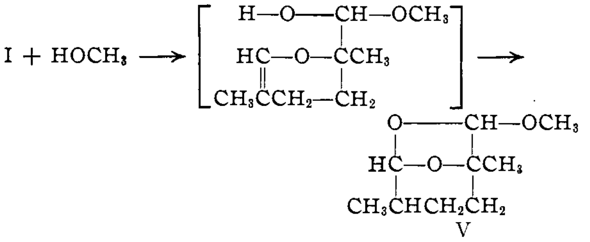


In storage, methacrylaldehyde containing hydroquinone dimerized 29% in one year at 26–27°. After freshly distilled methacrylaldehyde had been refluxed (68–72°) for two days with 1% of its weight of hydroquinone, the conversion into dimer was about 10%. Under autogenous pressure at 140–150°, 89% of the methacrylaldehyde dimerized in forty-four hours. The dimer had a tendency to retard macropolymerization, possibly because of allylically activated hydrogen atoms in the 4-position and in the 5-methyl group, thus terminating chains. Practically no tendency was shown by the dimer to form a trimer of methacrylaldehyde by participating as a "dienophile" (more strictly, as an enalophile). Substitution in the 5-position presumably suppressed such a tendency. (Acrolein dimer readily reacted with acrolein to form a series of low polymers.[3a,c]) Furthermore, dimerization of methacrylaldehyde probably was enhanced by a favorable polarizing influence of its methyl group.[6]

Methacrylaldehyde dimer is an aldehyde which has no α-hydrogen. Accordingly, the Cannizzaro reaction was clean-cut.[5b] The expected unsaturated acid[5b] and alcohol[5a,b] (III) isomerized readily into a saturated lactone (II) and acetal (IV), respectively. Such reactions are characteristic of substituted vinyl-type ethers such as 3,4-dihydro-1,2H-pyrans.

A saturated methyl acetal (V), stable to hot, 20% sodium hydroxide solution, was formed at room temperature from a solution of the dimer, methanol and calcium chloride. It did not represent reaction solely of the aldehyde function, nor solely of the vinyl-type ether grouping (as did acetals formed in the presence of more acidic catalysts from dihydropyran[7] and from butenone dimer).[3d] Moreover, it was not the simple combination of both of these types (see data in Table I), although both functional groups were involved. Probably the intermediate was an unsaturated hemiacetal.





## Experimental Details

**Methacrylaldehyde Dimer (I).**—The following conditions were the best found in a series of such dimerizations

---

[1] This work was sponsored by the Minnesota Mining & Manufacturing Company, St. Paul 6, Minn.

[2] Mailing address: 129 Grant Street, Easton, Pa.

[3] (a) K. Alder and E. Rüden, *Ber.*, **74B**, 920–926 (1941); (b) K. Alder, H. Offermanns and E. Rüden, *ibid.*, **74B**, 926–929 (1941); (c) S. M. Sherlin, A. Ya. Berlin, T. A. Serebrennikova and F. E. Rabinovich, *J. Gen. Chem.* (*U. S. S. R.*), **8**, 22–34 (1938); (d) K. Alder, H. Offermanns and E. Rüden, *Ber.*, **74B**, 905–920 (1941); and (e) C. Mannich, *ibid.*, **74B**, 554–570 (1941).

[4] (a) J. A. Norton, *Chem. Revs.*, **31**, 494 (1942); and (b) compare E. C. Coyner and W. S. Hillman, THIS JOURNAL, **71**, 324–326 (1949).

[5] (a) N. M. Bortnick, U. S. Patent 2,473,497 (1949); (b) R. R. Whetstone, U. S. Patent 2,479,283 (1949); and (c) also compare R. R. Whetstone, U. S. Patent 2,479,284 (1949).

[6] For instance, T. L. Gresham and T. R. Steadman, THIS JOURNAL, **71**, 737–738 (1949), reported that 2-methyl-1,3-pentadiene underwent a Diels–Alder type of reaction with formaldehyde, whereas 1,3-butadiene did not react in that way with formaldehyde.

[7] G. F. Woods and D. N. Kramer, *ibid.*, **69**, 2246 (1947).

TABLE I

METHACRYLALDEHYDE DIMER AND RELATED COMPOUNDS

| Compound[a] | Formula | Carbon, % | | Hydrogen, % | | $d^{20}_4$ | $n^{20}\text{D}$ | $MR_D$[b] | | B. p. (uncor.) | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Calcd. | Found | Calcd. | Found | | | Found | Calcd. | °C. | Mm. |
| (I) Methacrylaldehyde dimer | $C_8H_{12}O_2$ | 68.54 | 68.4 | 8.63 | 8.3 | 0.992 | 1.454 | 38.2 | 38.13 | 166 | 750[c] |
| | | | | | | | | | | 104 | 100[d] |
| (II) Saturated lactone | $C_8H_{12}O_3$ | 61.51 | 60.7 | 7.75 | 7.3 | 1.108 | 1.449 | 37.8 | 38.08 | 209 | 750 |
| (III) Unsaturated alcohol | $C_8H_{14}O_2$ | 67.57 | 66.8 | 9.92 | 9.2 | 1.016 | 1.475 | 39.5 | 39.64 | 199 | 750 |
| | | | | | | | | | | 124 | 100 |
| (IV) Saturated acetal | $C_8H_{14}O_2$ | 67.57 | 66.7 | 9.92 | 9.7 | 1.010 | 1.447 | 37.7 | 38.07 | 166 | 750 |
| (V) Methyl acetal | $C_9H_{16}O_3$ | 62.77 | 62.2 | 9.36 | 9.0 | 1.025 | 1.445 | 44.7 | 44.33 | 125 | 100 |

[a] Systematic names: (I) 3,4-dihydro-2,5-dimethyl-1,2H-pyran-2-carboxaldehyde; (II) 1,4-dimethyl-6,8-dioxabicylo[3.2.1]octan-7-one, or 6-hydroxy-2,5-dimethyltetrahydropyran-2-carboxylic acid lactone; (III) 3,4-dihydro-2,5-dimethyl-1,2H-pyran-2-methanol; (IV) 1,4-dimethyl-6,8-dioxabicyclo[3.2.1]octane; (V) 7-methoxy-1,4-dimethyl-6,8-dioxabicyclo[3.2.1]octane. [b] Molar refraction (found) = $[(n^2 - 1)/(n^2 + 2)]M/d$. Atomic and constitutive refractions (ml./mole, sodium D light; latest values in Landolt–Börnstein–Roth–Scheel, "Physikalisch-chemische Tabellen," Julius Springer, Berlin): C, 2.418; H, 1.100; O (in hydroxyl), 1.525; O (between carbon atoms), 1.643; O (in carbonyl), 2.211; N (in aliphatic oxime), 3.901; ethylenic bond, 1.733; and 5-atom ring, 0.04. [c] Bortnick[5a] reported 171–172°. [d] Whetstone[5b] reported 101.0–101.4° at 90 mm.; $n^{20}\text{D}$ 1.4537.

in which variations were made in temperature, time, atmosphere and added materials. Hydroquinone (0.175 g.) was dissolved in 17.5 g. of freshly distilled methacrylaldehyde[8] and the solution was sealed in a Pyrex tube having a capacity of about 50 ml. The sample was water-clear after having been forty-four hours at 140–150°. Fractional distillation revealed 1.2 g. (7%) of methacrylaldehyde, 15.6 g. (89%) of dimer and 0.7 g. (4%) of less volatile liquid.

Methacrylaldehyde dimer distilled at 63° at 20 mm., and remained liquid at −75°. It had a pleasant odor, and was practically insoluble in water. It readily gave positive tests with Tollens and Schiff reagents. Assuming only one ethylenic bond, bromine absorption showed its molecular weight to be 145 (calcd., 140.2). A trace of boron fluoride caused immediate polymerization into a colorless, brittle resin. Boron fluoride ethyl etherate rapidly converted it into a tar. Less rapid resinification was effected by ferric and stannic chlorides and by iodine. Benzoyl peroxide (5%) was ineffective in bringing about macropolymerization within fifty hours at 80°.

The extent to which the dimer functioned as a retarder of macropolymerization was revealed by the following experiments. In each of three test-tubes was placed 10 ml. of freshly distilled methacrylaldehyde. Then 0.0, 0.1 and 1.0 ml., respectively, of dimer was added, and the tubes were corked and kept in the dark at room temperature.[8] The control (blank) was one-tenth solid after one day, and completely solid within four days. The sample containing 0.1 ml. of dimer was water-clear until the third day, one-tenth solid by the fifth day and completely solid by the seventeenth day. The solution containing 1 ml. of dimer remained water-clear for a longer period. In another experiment, freshly distilled methacrylaldehyde (15 g.) was subjected to partial distillation at 5° and 50 mm. from a Pyrex tube until only 7.7 g. of inhibitor-free and air-free methacrylaldehyde remained. The tube was sealed during distillation, leaving its capacity at approximately 25 ml. It was promptly heated to 108–118° and maintained within that range of temperature for forty-five hours. As shown by distillation, 13% was methacrylaldehyde, 73% was dimer and 14% was a colorless, glass-like resin. Presumably, a sufficiently large concentration of dimer had been built up during the initial part of the heating period to repress extensive macropolymerization.

**Oxime** (of I).—Its synthesis was patterned after that of Sherlin, *et al.*,[3a] and the yield was 75%. Methacrylaldehyde dimer oxime was a practically odorless, water-clear liquid, distilling at 92–95° at 3 mm., $d^{20}$ 1.055 g. per ml., $n^{20}\text{D}$ 1.489, $MR_D$ 42.47 ml. (found), 42.45 ml. (predicted).

*Anal.* Calcd. for $C_8H_{13}NO_2$: N, 9.03. Found: N, 9.0.

**Cannizzaro Reaction.**—A mole (140 g.) of the dimer was stirred in a flask cooled in a bath of ice-water while 110 g. of 20% solution (0.55 mole) of sodium hydroxide was added dropwise. The temperature rose from 5 to 22° during the period of sixty-eight minutes which was required. After the solution had remained sixteen hours at room temperature, it was heated for thirty minutes at 94°. The solution was cooled to 10° and extracted by eight 40-ml. portions of ethyl ether. It was processed as follows.

**Saturated Lactone** (II).—The aqueous raffinate was acidified by 105 ml. (0.63 mole) of 6 *N* hydrochloric acid. The oil was separated, washed, shaken with sodium sulfate and then with calcium chloride.[9] Upon fractional distillation at 30 mm., the lactone was collected at 108–110°: 65.6 g., a yield of 84%. It remained liquid at 5°, had a camphoraceous odor, and was practically insoluble in water. A 0.4155-g. portion, dissolved in 200 ml. of 50% aqueous ethanol, was essentially neutral initially to phenolphthalein. During a period of six days, a total of 10.3 ml. of 0.253 *N* sodium hydroxide was used to keep it neutral as it stood at room temperature. After that, no further acidity developed; saponification equivalent: found, 159; calcd., 156.2. Using potassium hydroxide in diethylene glycol,[10] a value of 158 was found for the saponification equivalent. The lactone was saturated with respect to Wijs reagent.

**Unsaturated Alcohol** (III).—The combined ethyl ether extracts of the solution resulting from the Cannizzaro reaction were washed by a saturated solution of sodium bisulfite, dried by anhydrous sodium sulfate, and distilled at atmospheric pressure. The product, collected at 195–203°, weighed 56.7 g., an 80% yield of 3,4-dihydro-2,5-dimethyl-1,2H-pyran-2-methanol. Upon redistillation at 57 mm., it was collected at 113°. This primary alcohol, which reacted readily with sodium, had an odor milder than that of methacrylaldehyde dimer. Its reaction with Wijs reagent indicated one double bond, but after this compound had stood at room temperature for twenty days, unsaturation was only 85% of the theoretical value. During that time, $n^{20}\text{D}$ decreased from 1.475 to 1.473, indicative of partial isomerization.[11]

---

[8] Ordinarily, freshly distilled methacrylaldehyde, whether in the presence of air or not, developed a milkiness within about one hour when stored at room temperature without added macropolymerization inhibitor. Within three to four days it was entirely polymerized into a hard, chalky resin.

[9] Crystallization of 3,4-dihydro-2,5-dimethyl-1,2H-pyran-2-carboxylic acid, m. p. 61.0–62.5°, has been described.[5b]

[10] Shriner and Fuson, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., second edition, 1940, p. 117.

[11] Bortnick[5a] reported $n^{20}\text{D}$ 1.4710 and b. p. 101–103° at 23 mm.; Whetstone[5b] reported $n^{20}\text{D}$ 1.4733 and b. p. 75.8–79.6° at 7–8 mm. for the unsaturated alcohol (III).

**Saturated Acetal** (IV).—A 14.2-g. portion of the unsaturated alcohol (III) was refluxed until the temperature of the boiling liquid had decreased to a constant value (171°). This required ninety minutes, and the weight remained constant within 1%. The isomer was distilled at atmospheric pressure, the recovery being 12.3 g. (86%) of 1,4-dimethyl-6,8-dioxabicyclo[3.2.1]octane, a water-clear liquid having a camphoraceous odor. It was saturated with respect to Wijs reagent.

**Methyl Acetal** (V).—Anhydrous calcium chloride (4.5 g., 0.04 mole) was dissolved in 16 g. (0.5 mole) of methanol, and 28.0 g. (0.2 mole) of methacrylaldehyde dimer was added. The solution was kept one day at room temperature. The resulting mixture was washed free of calcium chloride by cold water, and extracted by cold, dilute potassium carbonate solution. The washed liquid was dried by potassium carbonate and fractionally distilled at 100 mm. At 124–126°, 17.2 g. (50% of the theoretical yield) of 7-methoxy-1,4-dimethyl-6,8-dioxabicyclo[3.2.1]octane was collected. This water-clear liquid had a camphoraceous odor. It was saturated, and it was recovered unchanged after having been stirred for thirty minutes with 20% aqueous sodium hydroxide at 70°. Furthermore, it was not polymerized by boron fluoride or the ethyl etherate, nor did it react with sodium at 100°.

**Acknowledgment.**—Thanks are due Dr. H. N. Stephens, Director of Research, Minnesota Mining & Manufacturing Company, for permission to publish these results. The authors are pleased to express appreciation also to Dr. W. E. Sohl of the Minnesota Mining & Manufacturing Company; to Dr. M. M. Baldwin of Battelle Memorial Institute; and to Dr. R. S. Shutt and Dr. Fred E. Sheibley, both formerly of Battelle Memorial Institute.

## Summary

A study was made of several reactions of methacrylaldehyde dimer, 3,4-dihydro-2,5-dimethyl-1,2H-pyran-2-carboxaldehyde, characteristic of it as a vinyl-type ether and an aldehyde without α-hydrogen. The products of the Cannizzaro reaction isomerized readily into bicyclic compounds. The isomer of the alcohol was a saturated acetal, 1,4-dimethyl-6,8-dioxabicyclo[3.2.1]octane. The isomer of the acid was a lactone which was the 7-oxo derivative of the acetal. Moreover, the 7-methoxy derivative of the acetal was obtained directly from the dimer by a mild reaction with methanol in the presence of calcium chloride.

COLUMBUS 1, OHIO RECEIVED SEPTEMBER 1, 1949

---

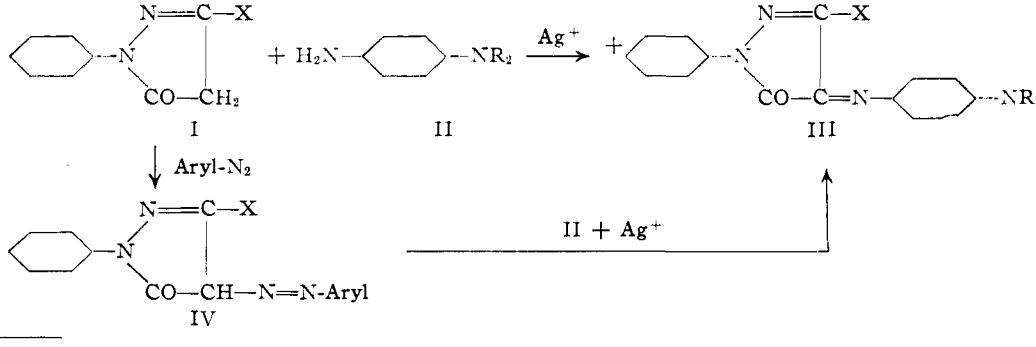
[COMMUNICATION NO. 1289 FROM THE KODAK RESEARCH LABORATORIES]

# The Formation of Azomethine Dyes from 4-Arylazo-5-pyrazolones

BY PAUL W. VITTUM, GEORGE W. SAWDEY, REBECCA A. HERDLE[1] AND MARY K. SCHOLL

Pyrazolone derivatives (I, where X may be alkyl,[2] $-NH_2$[3] or –NH acyl,[3] for example) readily undergo oxidative condensation (coupling) with N,N-disubstituted-*p*-phenylenediamines (II) to form azomethine dyes (III). This dye-forming reaction, which is of importance for the production of magenta dye images in various color photographic processes,[4] is closely analogous, and probably very similar in mechanism, to that involved in the formation of an indoaniline dye from II and a phenol derivative.[5]

It has recently been found[6] that the 4-arylazo derivatives of these pyrazolone couplers (IV) can also be condensed with II under oxidizing conditions to produce azomethine dyes, the process apparently taking place by replacement of the azo group by the *p*-phenylenediamine residue. This interesting conversion of an azo dye to an azomethine, which has been found to have valuable applications in color photography,[7] appears not to have been observed previously. Accordingly, the work described in this paper was undertaken to gain a more complete understanding of the nature of the reaction.



---

[1] Present address: 315 Colebrook Drive, Rochester, New York.

[2] Seymour, U. S. Patent 1,969,479 (1934).

[3] Weissberger and Porter, THIS JOURNAL, **64**, 2133 (1942).

[4] Mees, "The Theory of the Photographic Process," The Macmillan Co., New York, N. Y., 1942, p. 393.

[5] Vittum and Brown, THIS JOURNAL, **68**, 2235 (1946).

[6] Glass, Vittum and Weissberger, U. S. Patent 2,455,170 (1948).

[7] Hanson and Vittum, *PSA Journal*, **13**, 94 (1947); Hanson, U. S. Patent 2,449,966 (1948)· Hanson, *J. Opt. Soc. Am.*, in press.