

Polymeric Ligands. IV. Vinyltriacylmethanes

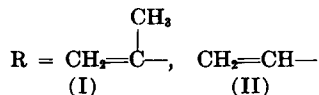
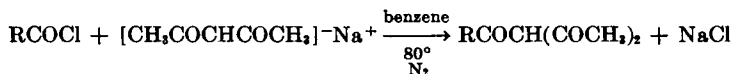
R. C. DEGEISO, L. G. DONARUMA, and E. A. TOMIC, *E. I. du Pont de Nemours & Company, Explosives Department, Experimental Station Laboratory, Wilmington, Delaware*

INTRODUCTION

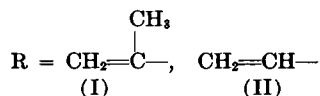
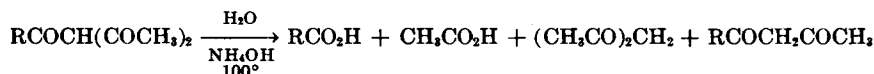
The first three papers of this series¹⁻³ described the preparation, characterization, and use of salicylic acid polymers and electron exchange reactions of polymeric chelates. Since then, we have sought to extend our knowledge and capabilities in the field of polymeric ligands. Therefore, we undertook investigations designed to achieve the synthesis of new types of triacylmethane derivatives, namely, vinyltriacylmethanes.

RESULTS AND DISCUSSION

Methacrylylacetylacetone (I) and acrylylacetylacetone (II) were readily prepared by the reaction of methacrylyl chloride and acrylyl chloride, respectively, with acetylacetone enolate salts:



The infrared spectra and elemental analyses were in accord with the postulated structures (I) and (II). Moreover, hydrolysis of the compounds gave the products which might be expected from the cleavage of triacylmethanes.⁴

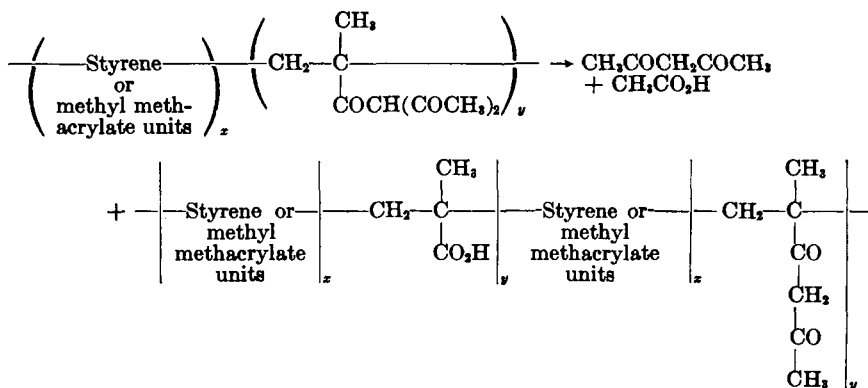


The near infrared spectra of (I) and (II) showed the presence of terminal methylene linkages,⁵ and ultraviolet spectra showed the maxima characteristic of α,β -unsaturated ketones.⁶ Both compounds gave the expected red colorations with Fe(III).⁷ The preparation of (II) yielded only C-

acylated product, but the preparation of (I) yielded small amounts of what is believed to be *O*-methacrylylacetylacetone, compound (III). This product had the same elemental analysis as compound (I) but a slightly different infrared spectrum. However, compound (III) did not form the colored iron chelate typical of (I) and (II).

Heating compound (I) with 0.1% benzoyl peroxide at 95–100° yielded a solid product softening at 105° which had the expected ultraviolet spectrum, infrared spectrum, and elemental analysis. Under similar conditions, compound (II) yielded polymeric oils.

Copolymerization of (I) with 10 parts styrene yielded a polymer with a softening point of 140° and a molecular weight of 356,000, according to light-scattering measurements in toluene. Copolymerization of (I) with 9 parts methyl methacrylate in the presence of 0.1% benzoyl peroxide at 100° yielded a copolymer softening at 293°. The molecular weight of this copolymer, by light-scattering measurements, was 2×10^6 in benzene, 2.5×10^6 in methyl ethyl ketone, and 2×10^6 in acetone. Elemental analyses and infrared spectra indicated that both comonomers were present in the copolymers. Hydrolysis of the copolymers with strong aqueous alkali confirmed the structures:



Also, the copolymers gave red or red-brown colorations when dissolved in dimethylformamide and treated with aqueous iron(III) solutions.

EXPERIMENTAL

Preparation and Characterization of Methacrylylacetylacetone (I)

A 46 g. sample of sodium sand (2.0 moles) was suspended in 1 l. of dry benzene containing 0.1% of hydroquinone under an atmosphere of nitrogen. To the rapidly stirred suspension was added 200 g. (2.0 moles) of acetylacetone, dropwise, at such a rate that the rate of reflux did not exceed the capacity of the condenser. When the addition was complete, the mixture was stirred until no further hydrogen was evolved. The benzene was then heated to reflux and 200 g. (1.92 moles) of methacrylyl chloride added

dropwise to the mixture while the benzene was refluxing. When the addition was complete, the temperature was maintained at the reflux for 2 hrs. or until the pH of the reaction mixture registered 5 on a piece of moist pH paper. The benzene was then almost totally removed under vacuum and the residue thoroughly triturated with water and extracted with ether. The extract was dried and the solvents removed under vacuum. The residue was distilled at 0.3 mm. in the presence of 0.5 g. of hydroquinone yielding the following cuts:

Cut	B.p., °C.
1	25-90
2	90-110
3	110-120
4	120-drop

Cut 1 was redistilled at 0.3 mm.

1-1	51-70
2-1	70-80

Cuts 2, 3, and 4, and 2-1 were redistilled at 0.25 mm.

Cut	B.p., °C.	Wt., g.	n_D^{25}
1-2	30-50	42.3	1.4840
2-2	50-68	49.2	1.4731
3-2	68-74	92.7	1.4808
4-2	74-78	97.6	1.4932
5-2	78-80	16.8	1.4975

} Yield calculated
from these cuts
was 76%

Cuts 4-2 and 5-2 redistilled at 0.25 mm.

Cut	B.p., °C.	Wt., g.	n_D^{25}
1-3	50-68	4.1	1.4898
2-3	68-70	3.3	1.4939
3-3	70-73	39.1	1.4955
4-3	73°-drop	22.9	1.4970

} Pure methacrylyl-
acetyl acetone
($n_D^{24} = 1.4967$)

All cuts of n_D^{25} below 1.4900 were redistilled at 0.25 mm. The cuts boiling in the range 45-50° of $n_D^{25} = 1.4700$ or better were *O*-methacrylylacetylacetone ($n_D^{25} = 1.4700-1.4720$). The yield was 12 g.

C-methacrylylacetylacetone analysis. Calcd. for $C_9H_{12}O_3$: C 64.2%, H 7.17%. Found: C 64.33, H 7.60.

O-Methacrylylacetylacetone analysis. Calcd. for $C_9H_{12}O_3$: C 64.2%, H 7.17%. Found: C, 64.09%, 64.14; H 7.10%, 7.26.

Both products gave the correct combustion analysis for carbon and hydrogen. The near infrared spectra of both products showed terminal

methylene groups. The ultraviolet and infrared spectra of both products were consistent with the postulated structures. The structure proof of the C-methacrylylacetylacetone was completed by basic hydrolysis of the compound to yield acetylacetone, acetic acid, methacrylic acid, and methacrylylacetylacetone.

A 21 g. (0.125 mole) quantity of methacrylylacetylacetone (C-acylated derivative) was mixed with 75 ml. of water, 16 g. of ammonium chloride, and 5 ml. of concentrated ammonium hydroxide. This mixture was heated for 15 min. on a steam bath with good agitation. The mixture was cooled and extracted with ether. The aqueous layer was made acid and again extracted with ether. The combined ether extracts were dried and the solvent was removed under vacuum. The residue was distilled at 0.15 mm. to yield 17.6 g. of recovered methacrylylacetylacetone. The contents of the cold trap weighed 1.1 g. Analysis of this mixture by gas chromatography showed the presence of 0.621 g. of acetylacetone, 0.063 g. of acetic acid, 0.098 g. of methacrylic acid, and 0.342 g. of methacrylylacetylacetone.⁸

Isolation of Methacrylylacetylacetone from Methacrylylacetylacetone (I)

Methacrylylacetylacetone (21 g., 0.125 mole) was mixed with 75 ml. of water, 16 g. of ammonium chloride, and 5 ml. of concentrated ammonium hydroxide. This mixture was heated for 15 min. on a steam bath with agitation. The mixture was cooled and extracted with ether. The aqueous layer was made acid and again extracted with ether. The combined extracts were dried and the solvent was removed under vacuum. The residue was distilled at 0.15 mm. to yield 17.6 g. of recovered methacrylylacetylacetone. The contents of the cold trap weighed 1.3 g. and had a volume of 1.8 ml. It was dissolved in twice its volume of alcohol and added to an excess of copper acetate solution. A blue-gray precipitate appeared which was removed by filtration. The filtrate was extracted with benzene and the benzene removed under vacuum to leave a bluish-gray solid. By fractional crystallization of the combined solids from hexane, 0.44 g. of the Cu(II) chelate of methacrylylacetylacetone was obtained. The infrared spectrum of this product was identical with the infrared spectrum of an authentic sample of the copper complex of methacrylylacetylacetone.⁸

Preparation and Characterization of Acrylylacetylacetone (II)

A 23 g. (1.0 mole) amount of sodium sand was dispersed in 500 ml. of dry benzene containing 0.1% hydroquinone under a blanket of nitrogen. Acetylacetone, 100 g. (1.0 mole), was added dropwise at such a rate that the rate of reflux did not exceed the capacity of the condenser. After stirring overnight, the mixture was heated to reflux and 50 g. of acryly chloride (0.55 mole) was added slowly to the mixture. The mixture was heated at reflux during the addition and for 2 hrs. afterwards, or until the pH of the reaction mixture on a piece of moist pH paper read 5. The ben-

zene was partially removed under vacuum and the residue triturated well with water. The mixture was extracted with ether and the ether extract dried. The solvent was removed under vacuum and the residue distilled at 0.15–0.2 mm. in the presence of hydroquinone, yielding the following cuts:

Cut	B.p., °C.	Wt., g.
1	40–48	Trace
2	48–49	
3	52–66	
4	66–80	25 (30%)
5	80–drop	

Cuts 4 and 5 were redistilled at 0.15–0.2 mm. to yield the following cuts:

Cut	B.p., °C.	n_D^{25}
1-1	71–77	1.4990
2-1	77–80	1.5035
3-1	80–88	1.5044
4-1	88–91	1.5028

Cut 3-1 was redistilled for analysis under the same conditions. The boiling range at 0.15 mm. was 78–82°, $n_D^{25} = 1.5063$.

In this reaction only a single product was obtained and *O*-acrylylacetylacetone was not isolated from the reaction mixture. The product gave the correct carbon-hydrogen analysis and a red coloration with Fe(III).⁷ The infrared spectrum showed the bands characteristic of the postulated structure and the near infrared spectrum showed the presence of a terminal methylene group. The ultraviolet spectrum showed a maximum typical of α,β -unsaturated ketones.⁶

ANAL. Calcd. for $C_8H_{10}O_3$: C 62.3%, H 6.49%. Found: C 62.10%, 62.03; H 6.85%, 6.78.

When the compound was heated at 95–100° with benzoyl peroxide for 16 hrs. a hexane-insoluble oil was formed which was probably polymeric.

Hydrolysis of the product with aqueous ammonia by the procedure described in the preceding series of experiments yielded acetic acid and acetylacetone. No acrylic acid was isolated. However, an unidentified component was present in the gas chromatogram which may have been acrylylacetylacetone. The preparation of acrylylacetylacetone has not been reported in the literature to date. Attempts have been made to synthesize the compound, but only polymers were isolated.⁸

Polymers and Copolymers of Methacrylylacetylacetone (I)

Homopolymerization of Methacrylylacetylacetone (I)

Heating of 5 g. of methacrylylacetylacetone containing 5 mg. of benzoyl peroxide at 95–100° for 48 hrs. followed by precipitation of the crude poly-

mer from benzene with hexane yielded a solid product softening at 105° and having an infrared spectrum which might be considered reasonable for the structure polymethacrylylacetylacetone.

ANAL. Calcd. for $C_9H_{12}O_3$: C 64.2%, H 7.17%. Found: C 63.71%, H 7.26%.

Copolymerization of Methacrylylacetylacetone (I) with Styrene

A mixture of 1 g. of methacrylylacetylacetone and 10 g. of styrene was heated 8 hrs. at 100° in a sealed tube in the presence of 0.5 g. of benzoyl peroxide. The product was a hard transparent material which dissolved in benzene and precipitated readily on the addition of methanol to yield a white solid (9.2 g.). The product softened at 105° and had an infrared spectrum consistent with the expected structure.

ANAL. Calcd. for $C_{13}H_{14}O_3$: C 89.7%, H 7.64%. Found: C 90.96%, H 7.65%.

Repetition of this experiment with 0.1% benzoyl peroxide at 100° for 12 hrs. yielded 4.6 g. of solid, softening at 140° and having a reasonable infrared spectrum. The molecular weight of this material by light-scattering measurements in toluene was 356,000.

ANAL. Calcd. for $C_{25}H_{28}O_3$: C 89.7%, H 7.64%. Found: C 89.3%, H 7.8%.

Copolymerization of Methyl Methacrylate with Methacrylylacetylacetone (I)

A 1 g. quantity of methacrylylacetylacetone and 9 g. of methyl methacrylate were copolymerized in bulk, in a sealed tube, in the presence of 0.1% benzoyl peroxide, at 100° for 12 hrs. Dissolution of the product in benzene followed by precipitation with methanol yielded 8.2 g. of product softening at 293°. The infrared spectrum of this product was consistent with the expected structure.

ANAL. Calcd. for $C_9H_8O_2$: C 60.00%, H 8.00%. Calcd. for $C_{25}H_{18}O_{3.8}$: C 59.95%, H 7.82%. Found: 59.36%, H 8.14%.

The molecular weight of this polymer by light-scattering measurements in acetone was shown to be 2,000,000. In methyl ethyl ketone a value of 2,500,000 was obtained. In benzene a value of 2,000,000 was obtained.

Characterization of Homopolymers and Copolymers

All of the polymers whose preparation has been previously described, showed, in addition to correct analyses and reasonable infrared spectra, red or red-brown colorations when placed in contact with Fe(III). This phenomenon is characteristic of β -dicarbonyl compounds. In addition, after reflux for 2 to 3 days in hot concentrated alkali, followed by acidification, ether extraction, removal of the solvent from the ether extract, and gas chromatography of the residue, the chromatogram showed that acetic acid and acetylacetone were present in the hydrolysis products of both copolymers.

References

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Synopsis

Methacrylylacetylaceton and acrylylacetylaceton were prepared by acylation of acetylaceton enolate salts with methacrylyl chloride and acrylyl chloride, respectively. Both monomers yielded poor homopolymers. Methacrylylacetylaceton formed copolymers with styrene and methyl methacrylate without difficulty.

Résumé

On a préparé la méthacrylylacétyl-acéto-ne et l'acrylylacétyl-acéto-ne par acylation de l'enolate d'acétylacéto-ne avec respectivement les chlorure de méthacrylyle et d'acrylyle. Ces deux monomères polymérisent difficilement. La méthacrylylacétylacéto-ne forme sans difficulté des copolymères avec le styrène et le méthacrylate de méthyle.

Zusammenfassung

Methacrylylacetylaceton und Acrylylacetylaceton wurden durch Acylierung von Acetylacetonenolatsalzen mit Methacrylylchlorid bzw. Acrylylchlorid dargestellt. Beide Monomere lieferten schlechte Homopolymere. Methacrylylacetylaceton bildete ohne Schwierigkeit Copolymere mit Styrol und Methylmethacrylat.

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