COMMUNICATIONS TO THE EDITOR

THE MELTING POINT OF NEO-C_5F_{12}

Sir:

In a recent publication[1] the preparation and detection of neo-C_5F_{12} in a mixture of C_5F_{12} isomers was reported. The detection of the neo-C_5F_{12} was made with the aid of nuclear magnetic resonance analysis. When the mixture of C_5F_{12} isomers was being removed from the sample tube in which the analysis was performed, it was noted that near the very end of the transfer some solid crystals remained in the tube. The crystals were sealed off in the tube and a melting point was determined. The melting range was observed to be 72–76°. When another aliquot of the mixture of C_5F_{12} isomers was similarly treated, the crystalline residue was dissolved in pure CCl_4 and subjected to NMR analysis. The strong, single-peaked pattern obtained was interpreted as that which was characteristic of purified neo-C_5F_{12}.

More recently a larger sample of a mixture of C_5F_{12} isomers was prepared in this laboratory. The mixture had a b.p. of 28.5–29.5° and a mol. wt. of 287–288 and was prepared from the reaction between $(CF_3)_2SF_4$ and $CF_3CF{=}CF_2$ at 520°. Neo-C_5F_{12} enrichment was achieved by evaporation *in vacuo* at temperatures below 0°. Finally, a sample of material highly enriched in neo-C_5F_{12} was isolated. This residual material was a crystalline solid, reminiscent of CO_2, and it exerted a vapor pressure of 650 ± 2 mm at 26°. The solid sample amounted to one gram.

Aliquots of the sample were successively transferred *in vacuo* to heavy wall glass melting point tubes 2 mm. in diameter and 4 cm. long. These aliquots amounted to about 0.2 g. each and were sealed off, air-free, in their respective tubes. The melting points of the five aliquots were determined in a water-bath with a thermometer and a stirrer. The temperature gradient over the depth of the bath did not exceed 0.2° and the rate of change of the temperature in the bath during the determinations did not exceed 0.25°/min. and was maintained at 0.1°/min. near and at the melting points. The following short table shows the melting range of the five successively condensed aliquots.

Aliquot Order	Melting range in °C.
1	72.0–75.8
2	73.3–76.1
3	75.3–77.6
4	76.4–78.3
5	76.3–78.2

Accordingly, with the highest purity that could be obtained by the procedure outlined, the m.p. of neo-C_5F_{12}, under its own vapor pressure, was at least 78.3°.

Grateful acknowledgment is offered to Pvts. N. Muller and George Svatos for performing the NMR analyses, which were done at the Army Chemical Center, Md. Appreciation is expressed to Drs. F. W. Hoffman and T. C. Simmons of the Chemical and Radiological Laboratories of A.C.C. for making the NMR analyses possible. The work in this laboratory was supported by the Chemistry Branch of the Office of Naval Research under contract Nonr 580(03); 333-356.

Fluorine Research Laboratories
Department of Chemical Engineering
University of Florida R. D. Dresdner
Gainesville

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[1] Richard Dresdner, This Journal, **77**, 6633 (1955).

LIGHT CATALYZED ORGANIC REACTIONS. V.[1] THE ADDITION OF AROMATIC CARBONYL COMPOUNDS TO A DISUBSTITUTED ACETYLENE

Sir:

In a previous paper of this series[2] we have described a method for the synthesis of substituted trimethylene oxides by light initiated addition of carbonyl compounds to polysubstituted olefins. With the view of exploring this reaction in greater detail, a series of experiments involving substituted acetylenes was carried out. The conversions outlined below constitute a new kind of combination leading to α,β-unsaturated ketones containing the system

$$C_6H_5—\underset{\displaystyle R}{\underset{|}{C}}{=}\underset{\displaystyle R}{\underset{|}{C}}—CO—R.$$

A 3:1 mixture of benzaldehyde and 5-decyne was irradiated with a mercury resonance arc at 40° for 96 hours. Starting materials were removed by distillation, b.p. 40–60° (6 mm.) and V (13% yield) isolated by chromatography of the residue. 6-Benzylidene-5-decanone (V) had b.p. 108–111° (0.1 mm.), infrared max. 605, 6.24 μ; 2,4-DNP m.p. 116–117°; *Anal.* Calcd. for $C_{23}H_{28}N_4O_4$: C, 65.07; H, 6.65; N, 13.20. Found: C, 64.87; H, 6.71; N, 13.26. Catalytic reduction of V over $Pd/CaCO_3$ catalyst in ethanol solution produced a homogeneous dihydro derivative (VII), infrared max. 5.85 μ; *Anal.* Calcd. for $C_{17}H_{26}O$: C, 82.87; H, 10.64. Found: C, 82.69; H, 10.36. The structure of V was firmly established by unequivocal synthesis: α-Butylcinnamoyl chloride, b.p. 85° (0.35 mm.) secured from *trans*-α-butylcinnamic acid[3] and thionyl chloride was condensed with dibutylcadmium to give V, b.p. 110° (0.06 mm.); λ_{max} 279 mμ, (log ε 4.2); *anal.* Calcd. for $C_{17}H_{24}O$: C, 83.55; H, 9.90. Found: C, 83.47; H, 9.72. The infrared spectra of this sample and the one obtained in the photochemical reaction were nearly identical. Further confirmation of identity was obtained by infrared and mixed melting point

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[1] Part of a program of research supported by a grant from the Godfrey L. Cabot Fund, Publication No. 62, M.I.T. Solar Energy Conversion Project.

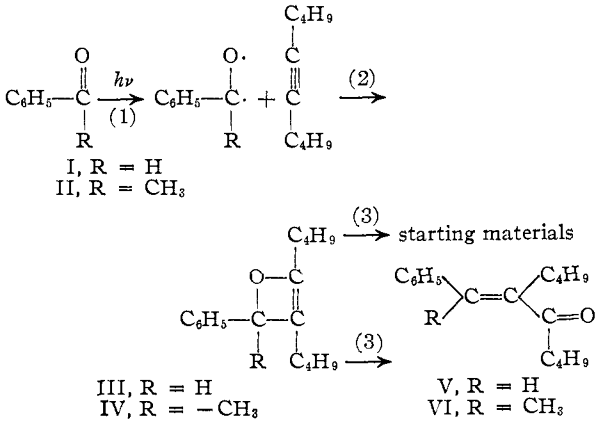
[2] G. Büchi, C. G. Inman and E. S. Lipinsky, This Journal, **76**, 4327 (1954); E. Paterno and G. Chieffi, *Gazz. chim. ital.*, **39**, 341 (1909).

[3] A. Michael, *Chem. Ber.*, **34**, 918 (1901); M. Metayer, *Rec. trav. chim.*, **71**, 158 (1952).

comparison of the 2,4-DNP's as well as infrared comparison of the homogeneous saturated ketones (VII).

A 1:1 mixture of acetophenone and 5-decyne was irradiated for 84 hours and the reaction product, 2-phenyl-3-*n*-butyl-2-octene-4-one (VI), isolated by distillation followed by chromatography of the fraction b.p. 110–125° (0.35 mm.). The structural assignment for VI rests on the following data: (1) b.p. 120–125° (0.35 mm.); infrared max. 5.95 μ; λ_{max} 248 mμ (log ϵ 3.77); (2) catalytic reduction of VI over Pd/$CaCO_3$ catalyst resulted in the formation of VIII ($C_{18}H_{28}O$), infrared max. 5.85 μ; (3) reduction of VI with sodium borohydride gave the corresponding unsaturated alcohol IX characterized by its 3,5-dinitrobenzoate m.p. 109–110° (*Anal.* Calcd. for $C_{25}H_{30}N_2O_6$: C, 66.06; H, 6.65. Found: C, 66.27; H, 6.54) and (4) synthesis of VI by an unambiguous route. Reformatsky condensation of ethyl α-bromocaproate with acetophenone gave X, infrared max. 2.95, 5.88 μ (*Anal.* Calcd. for $C_{16}H_{24}O_3$: C, 72.69; H, 9.15. Found: C, 72.83; H, 9.28) which was converted to the unsaturated ester XI, (infrared max. 5.82μ; λ_{max} 237 mμ (log ϵ 3.95); *anal.* Calcd. for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 78.13; H, 9.09) by dehydration with iodine. α-*n*-Butyl-β-methylcinnamic acid (XII) obtained by base hydrolysis of XI (characterized by its amide m.p. 164–164.5°, *anal.* Calcd. for $C_{14}H_{19}NO$: C, 77.38; H, 8.81; N, 6.45. Found: C, 77.27; H, 8.67; N, 6.38; λ_{max} 229 mμ (log ϵ 3.95)) was converted to the acid chloride and condensed with dibutylcadmium to give (VI), b.p. 112–114° (0.15 mm.); infrared max. 5.95μ; λ_{max} 245 mμ (log ϵ 3.83); *anal.* Calcd. for $C_{18}H_{26}O$: C, 83.66; H, 10.14. Found: C, 83.93; H, 9.95. Identity with the product (VI) described above was established by spectral comparison and mixed m.p. determination of the 3,5-dinitrobenzoate of the corresponding secondary alcohol. The unsaturated ketones (V and VI) produced in the photochemical process appear to be a mixture of *cis* and *trans* isomers but we have so far been unable to achieve complete separation. The fact that the infrared spectra of the synthetic ketones, of known *trans* configuration, are nearly the same before and after prolonged irradiation indicates that the photochemical equilibrium mixture contains mainly *trans* isomer. Attempts to add aldehydes to monosubstituted acetylenes (benzaldehyde to phenylacetylene, butyraldehyde to 1-hexyne and benzaldehyde to 1-hexyne) resulted in the formation of the symmetrical acyloins rather than the expected 1:1 adducts.

The peroxide induced addition of aliphatic aldehydes to acetylenes to give 1,4-diketones by combination of two molecules of aldehyde with one molecule of acetylene has recently been reported.[4] To rationalize their results the authors have adopted a radical-chain mechanism initiated by $R\dot{C}{=}O$ which had been postulated previously[5] for the photochemical addition of aliphatic aldehydes to terminal olefins. It is known[5] that aromatic aldehydes undergo such additions with considerable difficulty and it does not seem possible to construct a mechanism directly related to this one which would be capable of accomodating the changes outlined above. The most reasonable scheme to rationalize the formation of α,β-unsaturated ketones seems to be



(1) Conversion of the aromatic carbonyl compound to the biradical triplet state (I, II) by absorption of light, followed by (2) formation of the corresponding oxetenes (III, IV) and (3) decomposition of these intermediates to either products (V, VI) or starting materials. An attempt has been made to isolate III but no evidence for its presence in the products of the reaction could be obtained.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE, MASSACHUSETTS

G. BÜCHI
JAMES T. KOFRON
E. KOLLER
DAVID ROSENTHAL

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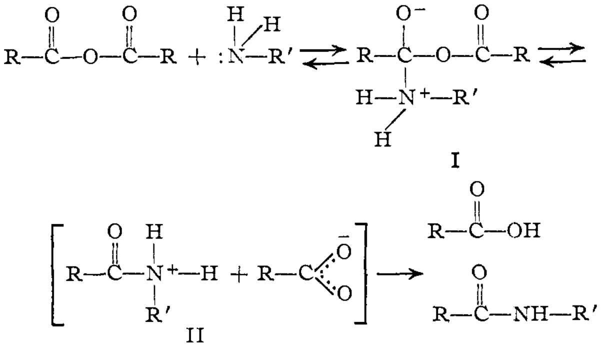
CONCERNING THE MECHANISM OF THE REACTION OF ANHYDRIDES WITH AMINES

Sir:

Data from several sources[1,2,3] can be used to formulate the following general scheme for reactions of anhydrides with amines and other nucleophiles.



We wish to report data which throw considerable

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[4] H. H. Schlubach, V. Franzen and E. Dahl, *Ann.*, **587**, 124 (1954).

[5] M. S. Kharasch, W. H. Urry and B. M. Kuderna, *J. Org. Chem.*, **14**, 248 (1949).

[1] E. Berliner and L. Altschul, THIS JOURNAL, **74**, 4110 (1952).

[2] V. Gold, J. Hilton and E. Jefferson, *J. Chem. Soc.*, 2756 (1954).

[3] C. Bunton, T. Lewis and D. Llewellyn, *Chem. and Ind.*, 1154 (1954).